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Discussions

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Development of a photochemical source for the production and calibration of acyl peroxynitrate compounds

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Abstract

A dynamic system for the calibration of acyl peroxynitrate compounds (APNs) has been developed in the laboratory to reduce the difficulty, required time, and stability of laboratory produced standards for difficult to synthesize APN species. In this work we present a photochemical source for the generation of APN standards: acetyl peroxynitrate (PAN), propionyl peroxynitrate (PPN), acryloyl peroxynitrate (APAN), methacryloyl peroxynitrate (MPAN) and crotonyl peroxynitrate (CPAN). APNs are generated via photolysis of a mixture of acyl chloride (RC(O)Cl) and ketone (RC(=O)R) precursor compounds in the presence of O_2 and NO_2. Subsequent separation by a prep-scale gas chromatograph and detection with a total NO_y instrument serves to quantify the output of the APN source. Validation of the APN products was performed using iodide ion chemical ionization mass spectroscopy (I^- CIMS). This method of standard production is an efficient and accurate technique for the calibration of instrumentation used to measure PAN, PPN, APAN, MPAN, and CPAN.

1 Introduction

Peroxycarboxylic nitric anhydrides or acyl peroxynitrates (APANs) have long been considered important atmospheric constituents (Roberts and Koppmann, 2007; Roberts, 1990; Stephens, 1987). Often the most abundant odd nitrogen species, e.g. NO_y ($NO + NO_2 + NO_3 + 2N_2O_5 + HNO_3 +$ $HONO + HO_2NO_2 +$ APNs + organic nitrates + …) in the atmosphere, APNs play an integral part of ozone photochemistry in remote regions (Singh et al., 1992; Roberts, 1990; Roberts and Koppmann, 2007) as byproducts of the reaction of NO_x ($NO + NO_2$) and volatile organic compounds (VOC). Thermal decomposition of APNs, on a timescale of hours to months, is often the most dominant atmospheric sink and results in release of NO_x. APNs, as a NO_x reservoir, therefore serve as an important pathway for transport of NO_x to remote regions (Moxim et al., 1996; Horowitz and Jacob, 1999).

The most atmospherically abundant and well understood of the APNs is acetyl peroxynitrate (PAN, $CH_3C(O)O_2NO_2$) formed from the oxidation of VOC (Roberts and Koppmann, 2007; Fischer et al., 2014; Singh et al., 1992; LaFranchi et al., 2009; Moxim et al., 1996; Phillips et al., 2013; Roberts et al., 2004, 2007; Williams et al., 1997). Recent research has become increasingly focused on less well-studied APNs due to their involvement in several key atmospheric processes. Of these, interest has been generated for acryloyl peroxynitrate (APAN, $CH_2CHC(O)O_2NO_2$), a product of acrolein oxidation, where the dominant atmospheric source is understood to be from aged biomass burning emissions (Yokelson et al., 2009). Methacryloyl peroxynitrate (MPAN, $CH_2C(CH_3)C(O)O_2NO_2$) has received recent attention due to its involvement as an intermediate in secondary organic aerosol formation from isoprene (Surratt et al., 2010). PPN, formed from precursors such as propanal, 1-butene, and alkanes (Williams et al., 1997; Roberts et al., 2001), is understood to be a tracer for anthropogenic photochemistry, as biogenic precursors are expected to be a negligible source.

A multitude of techniques have been employed for routine measurement of atmospheric APNs since the middle of the 20th century. The oldest and most widely used of these techniques is gas chromatography (GC) coupled to a detection method such as (I) electron capture (Darley et al., 1963; Williams et al., 2000; Flocke et al., 2005; Schrimpf et al., 1995; Roberts et al., 2006; Roberts, 1990), (II) chemiluminescence (Gaffney et al., 1998), or (III) mass spectrometry (Tanimoto et al., 1999). Liquid chromatography has also been used for the measurement of PAN with limited results (Grosjean et al., 1991). Optical techniques such as FTIR (Tuazon et al., 1978) and thermal dissociation-laser induced fluorescence (TD-LIF) (Wooldridge et al., 2010) have been employed with more recent developments, such as cavity ring down spectroscopy (Paul et al., 2009), showing promise as fast-response measurement techniques.

Among the newer methods gaining traction are mass spectrometric techniques, such as chemical ionization mass spectrometry, CIMS (Hastie et al., 2010; Hansel and Wisthaler, 2000; Huey, 2007). An increasingly popular method is thermal dissociation chemical ionization mass spectrometry (TD-CIMS) for the measurement of APNs

(Slusher et al., 2004; Phillips et al., 2013; Zheng et al., 2011). Comparisons of the TD-CIMS method with other techniques, such as GC and TD-LIF, show reasonably good agreement (Wooldridge et al., 2010; Tyndall et al., 2005). However, there exists the potential for various interferences, such as peroxy acetic acid and carboxylic acids that requires additional consideration (Phillips et al., 2013).

Detection sensitivity is not inherently deducible from the TD-CIMS method; rather it is a function of the thermal-dissociation efficiency, ion transmission, and inlet losses therefore calibration is a necessary requirement in order to perform accurate, quantitative measurements. A multitude of APN calibrations procedures have been developed over the years, with the earliest examples focused exclusively on the synthesis and calibration to PAN with later methods expanded to include additional APN species. Currently there exist two widely used synthesis methods, wet chemical synthesis (Kravetz et al., 1980; Nielsen et al., 1982) followed by purification (Gaffney et al., 1984; Holdren and Spicer, 1984; Ciccioli et al., 1992) and online photo-production (Furgeson et al., 2011; Grosjean et al., 1984; Warneck and Zerbach, 1992a; Joos et al., 1986; Grosjean and Harrison, 1985). While both methods are effective, the amount of time, difficulty and hazards involved in the wet chemical handling, storage, and disposal make it a less desirable approach. Online photo-production of APNs, however, offers a more rapid alternative with significantly reduced complexity in comparison to wet chemical synthesis methods.

In this work, we present a new, dynamic photochemical source for the production of PAN, PPN, APAN, MPAN, and CPAN in the laboratory. The method developed here relies on the photolysis of acyl chloride (RC(O)Cl) compounds or ketones (RC(=O)R) in the presence of O_2 and NO_2 resulting in the formation of various APNs. Results will be shown validating the production of APAN, MPAN, and CPAN from acyl chloride precursors through the use of preparatory scale GC and subsequent detection with both a NO_y detector and a TD-CIMS using I^- primary ions (I^- CIMS). Production of PAN and PPN, via photolysis of acetone and 3-pentanone respectively (Furgeson et al., 2011; Warneck and Zerbach, 1992a; Volz-Thomas et al., 2002), will also be shown.

A brief discussion on APN sensitivity as a function of inlet dissociation temperature will also be provided.

2 Methods

Figure 1 shows a simplified schematic of the photolysis source used in this work. This photolysis source is similar to that used in previous photo-based PAN calibration methods (Furgeson et al., 2011). In fact, the production of PAN and PPN used here has been described previously using the respective precursors compounds acetone and 3-pentanone (Furgeson et al., 2011; Warneck and Zerbach, 1992a; Volz-Thomas et al., 2002). In this work we show a new method for the online synthesis of APAN, MPAN, and CPAN using acryloyl chloride, methacryloyl chloride, and crotonyl chloride precursor compounds, respectively. Precursor compounds are diluted with tridecane, in the ratios reported in Table 1 according to their volatility, and placed into a glass diffusion cell with a headspace flow of 20 sccm zero air. The outflow of the diffusion cell is mixed with approximately 5 sccm of a 5 ppmv $\mathrm{NO_2}$ mixture. The mixture is photolyzed using a 254 nm Pen-Ray® lamp in a fused silica cell, with a residence time of approximately 6 min. Photolysis of acyl chloride precursors in the presence of $\mathrm{O_2}$ and $\mathrm{NO_2}$ proceed via the following reactions:

$$\mathrm{RC(O)Cl} \xrightarrow{\Delta} \mathrm{RC(O)^{\bullet}} + \mathrm{Cl^{\bullet}} \tag{R1}$$

$$\mathrm{RC(O)^{\bullet}} = \mathrm{O_2} \longrightarrow \mathrm{RC(O)O_2^{\bullet}} \tag{R2}$$

$$\mathrm{RC(O)O_2^{\bullet}} + \mathrm{NO_2} \longrightarrow \mathrm{RC(O)O_2NO_2} \tag{R3}$$

Resulting APN products are subsequently separated using a prep-scale GC similar to that described by Flocke et al. (2005). Flow from the photolysis cell is injected onto an Rtx-200 gas chromatography column (15 m, 0.53 mm I.D., 1.5 µm) and held at a temperature of 30 °C with a helium carrier gas flow of 10 sccm. The column effluent is analyzed using both a $\mathrm{NO_y}$ analyzer and $\mathrm{I^-}$ CIMS.

$\mathrm{NO_y}$ was quantified using a laboratory built analyzer that converts PAN to NO on a molybdenum tube followed by chemiluminescence detection (Ridley and Howlett, 1974; Fehsenfeld et al., 1987). The conversion efficiency of the $\mathrm{NO_y}$ instrument used in this study was approximately 96 % with a sensitivity of $4.07 \pm 0.08\,\mathrm{Hz\,pptv^{-1}}$.

A detailed description of the $\mathrm{I^-}$ CIMS is presented elsewhere (Slusher et al., 2004). Briefly, APNs are dissociated in a heated inlet, subsequently react with iodide ions ($\mathrm{I^-}$), and are detected as carboxylate anions using a quadrupole mass analyzer:

$$\mathrm{RC(O)O_2NO_2} \xrightarrow{\Delta} \mathrm{RC(O)O_2} + \mathrm{NO_2} \tag{R4}$$

$$\mathrm{RC(O)O_2} + \mathrm{I^-} \longrightarrow \mathrm{RC(O)O^-} + \mathrm{IO} \tag{R5}$$

Iodide ions are generated via the electron attachment reaction of $\mathrm{CH_3I}$ in a $^{210}\mathrm{Po}$ ionizer. A critical orifice was used to maintain an inlet flow of 2.2 slpm at a flow tube pressure of 50 mbar. A switchable inlet was used for sampling through a heated dissociator to allow detection of APNs via Reactions (R4) and (R5), or a “cold” (30 °C) inlet, to serve as an instrumental background. Unless otherwise stated, the inlet dissociator temperature was set to 150 °C for the experiments presented in this work. In response to a well known dependence of PAN detection on the water concentration in the flow tube (Slusher et al., 2004), a 100 % RH, 10 sccm $\mathrm{N_2}$ flow was added directly to the flow tube. The instrument was tuned to minimize the detection of cluster ions such that the observed $\mathrm{I^{\bullet}H_2O^-}$ to $\mathrm{I^-}$ ratio was 0.002.

3 Results

3.1 Acyl Peroxynitrate (APNs) synthesis and calibration

Precursor compounds were individually diluted with tridecane in the ratios reported in Table 1 and placed into glass diffusion cells. As discussed in Sect. 2, flow from the diffusion cell is mixed with NO_2, photo-reacted, GC separated, and sampled with the NO_y instrument and I^- CIMS. An example chromatogram, detected using I^- CIMS, is shown in the bottom four panels of Fig. 2 for each single component mixture. The data are displayed as m/z observed with respect to retention time.

In all four single precursor mixtures, PAN production was also observed as a product. Two possible explanations exist for the observation of PAN formation. First, acetone is applied as a rinsing and drying reagent for the glass diffusion cells of which there is likely a residual amount in the cell after cleaning. This residual acetone will react with NO_2 in the presence of oxygen to form PAN when irradiated by a UV light source (Warneck and Zerbach, 1992b; Volz-Thomas et al., 2002). Additionally, PAN is an expected byproduct of the photolysis of ketones, as illustrated below for the synthesis of PPN:

$$CH_3CH_2C(O)CH_2CH_3 \xrightarrow{\lambda} CH_3CH_2C(O) + CH_2CH_3 \tag{R6}$$

$$CH_3CH_2C(O) \xrightarrow{+O_2,NO_2} CH_3CH_2C(O)O_2NO_2 \tag{R7}$$

$$CH_2CH_3 \longrightarrow \mathrm{PAN} \tag{R8}$$

According to the expected I^- CIMS ion chemistry, PAN (m/z 59), APAN (m/z 71), and PPN (m/z 73) are detected at unique m/z ratios. MPAN (m/z 85) and CPAN (m/z 85), however, yield isobaric products and are therefore inseparable using I^- CIMS. Aside from the previously discussed PAN production, photo-production of

PPN, APAN, and MPAN all yield a single product ion as expected. However, in the case of the CPAN source, via crotonoyl chloride, two peaks are observed at m/z 85 eluding at different retention times ($t_r \sim 9$ and 14 min). It is our belief that these peaks represent the cis-CPAN (m/z 85, $t_r = 9$ min) and trans-CPAN (m/z 85, $t_r = 14$ min) isomers. Considering the NO_y observations, Fig. 2 (bottom panel), the CPAN mixture appears to be racemic in the cis and trans isomers as the measured NO_y concentrations for both peaks are nearly identical.

It is important to note that direct sampling of the photolysis source output is not recommended as the reaction produces a large number of undesired byproducts, such as $ClNO_2$ and Cl_2. Furthermore, recent work suggests that synthesis of APN standards using acyl chloride compounds should be avoided for reasons of impurities (Tokarek et al., 2014), however, the use of a GC pre-separation step eliminates any possibility of unwanted measurement interferences.

After validation of the photochemistry using single component mixtures, a multicomponent mixture was prepared containing all five precursor compounds in the volumetric mixing ratios reported in Table 1. In the top panel of Fig. 2, a chromatogram of the products from the multicomponent mixture, measured on both the CIMS and NO_y instruments, is shown. It is clear from these results that mixing the precursor compounds prior to reaction produces no additional, unexpected products. After this initial analysis, the precursor mixture was stored in a laboratory freezer for several months and reanalyzed. While, the mixture was observed to yellow over time, no additional reaction products were observed as a result of the long-term storage of the solution. It is noteworthy that the same yellowing was not observed for the long-term storage of individual component mixtures.

The data contained in the top panel of Fig. 2 can be used to determine the sensitivity of I^- CIMS to APN detection. The area of each observed peak, measured using CIMS and NO_y, was determined by applying an exponentially modified Gaussian peak fitting routiene. After accounting for dilution, the I^- CIMS sensitivity ($\mathrm{Hz\,ppbv^{-1}}$) was determined as the ratio of the CIMS measured signal to the NO_y concentration for each corresponding peak. Normalized (10^6 cps I$^-$, m/z 127) calibration factors calculated in this manner are reported in Table 1 for each of the APN products observed. Also included in Table 1 are calibration factors reported relative to the measured PAN sensitivity and instrumental detection limits (3σ).

3.2 Thermo-dissociation of APNs

In order to probe the sensitivity of the iodide CIMS to the various APN species as a function of dissociation temperature, a series of measurements were made at various inlet dissociator temperatures ranging from 70–200 °C. In these experiments, the APN mixture (PAN, APAN, MPAN, PPN, CPAN) was photo-reacted, injected onto the GC column, and subsequently analyzed via I$^-$ CIMS at various inlet dissociator temperatures. The total inlet flow was 2.2 slpm yielding an inlet residence time of 0.25 s in the heated region. Unfortunately the gas temperature in the dissociator is not monitored, which would serve as a better metric for the amount of energy in the dissociator than the external temperature reported here.

Eluting peak areas at a given inlet dissociation temperature for each m/z were calculated (Fig. 3a for PAN, m/z 59), normalized to the maximum observed signal throughout the temperature range, and plotted versus inlet dissociator temperature (Fig. 3b). Full thermal dissociation profiles for the various APN species measured are shown in Fig. 3b. This dependence of TD-CIMS sensitivity on the inlet dissociator temperature has been previously reported in multiple studies (Mielke and Osthoff, 2012; Furgeson et al., 2011; Zheng et al., 2011). The sensitivity dependence reported in this work is specific to this particular inlet design and largely controlled by a combination of the residence time, temperature, and pressure field in the inlet dissociator and are system specific. These experiments should be repeated on each individual instrument to better understand the effect of inlet dissociator conditions on measurement sensitivity.

The information in Fig. 3b serves as an aid for determining optimal inlet dissociation temperatures for various applications. In this system, the most efficient detection

of PAN, PPN and APAN corresponds to an inlet temperature of 150 °C. However, for measurement of MPAN and CPAN an inlet dissociation temperature of 130 °C would result in improved sensitivity. It is an interesting result that the cis and trans isomers of CPAN show a marginally different temperature optimum. These results are consistent with the relative calibrations factors measured, Table 1, where at a thermal dissociation temperature of 150 °C the detection of trans-CPAN is more sensitive than cis-CPAN. Similarly, from the temperature profiles in Fig. 3, one would expect PAN, APAN, and PPN to be detected with similar efficiencies at 150 °C, while detection of MPAN should be significantly reduced in comparison. This is clearly reflected in the measured calibration factors displayed in Table 1.

Unfortunately, MPAN is detected at the same product ion as CPAN (m/z 85) preventing the attribution of that mass to either species unambiguously. It may however be possible to utilize the inlet dissociation temperature as a method of discrimination between these species. At the concentrations used in this study, operation at an inlet dissociator temperature of 180 °C would reduce the sensitivity of MPAN to levels below the detection limit while allowing for detection of trans-CPAN. It is therefore possible that periodically modulating the inlet temperature during measurement to 180 °C could be used as a method of zeroing the MPAN and cis-CPAN contributions to m/z 85. Using this method, and assuming a racemic CPAN mixture in the atmospheric, one could potentially determine both MPAN and CPAN (the sum of the cis and trans isomer) concentrations during ambient measurement. Optimization of the inlet dissociator geometry and operating conditions could potentially improve the thermal separation in the relative sensitivities further aiding in the separation of MPAN and CPAN.

4 Conclusions

In this work we have detailed a new method for the production and calibration of APNs. This method provides a simplified alternative to liquid based synthesis of some of the less well-studied APN species, e.g. APAN, MPAN, and CPAN. Due to the ease of APN production, it may be possible to improve on the methodology presented here to develop a field deployable calibration system. Unfortunately, due to impurities formed in the photolysis of acyl chloride compounds this method necessitates the use of a prep-scale GC, which may be limiting. However, this ease of operation and ability to generate simultaneous APN calibrations makes this technique ideal for a laboratory setting. Although not shown here, this method should be compatible with GC/ECD systems provided that pre-separation is used to prevent exposure of the ECD system to any chlorinated starting materials and associated photoproducts.

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Table 1. Summary of calibration factors (CF, Hz pptv $^{-1}$) relative to PAN using results from the calibration mixture. The mix ratio represents the volumetric mixing ratio of precursor compound to tridecane used and is held constant for both single component mixtures and multicomponent mixtures.

Analyte	Precursor	Mix	$\mathrm{CF}^{\mathrm{a}}_{\mathrm{norm}}$	$\mathrm{CF}^{\mathrm{b}}_{\mathrm{rel}}$	DL, pptv[c]
PAN	Acetone		13.3 ± 0.4	1	2.8
APAN	Acryloyl Chloride	1 : 45	12.8 ± 1.4	0.97 ± 0.08	2.8
PPN	3-Pentanone	1 : 11	13.1 ± 2.3	0.95 ± 0.15	1.9
MPAN	Methacryloyl Chloride	1 : 11	1.3 ± 0.1	0.10 ± 0.01	21
cis-CPAN	Crotonyl Chloride	1 : 11	3.9 ± 0.6	0.29 ± 0.04	7.0
trans-CPAN	Crotonyl Chloride	1 : 11	7.1 ± 0.4	0.53 ± 0.04	3.8

[a] Normalized CF is reported relative to a primary ion count rate of 10^6 I^- (m/z 127). [b] The relative CF is defined as the instrumental sensitivity of each APN relative to the PAN sensitivity. [a] Detection limits determined from the standard deviation in the instrument background are reported at the 3σ level.

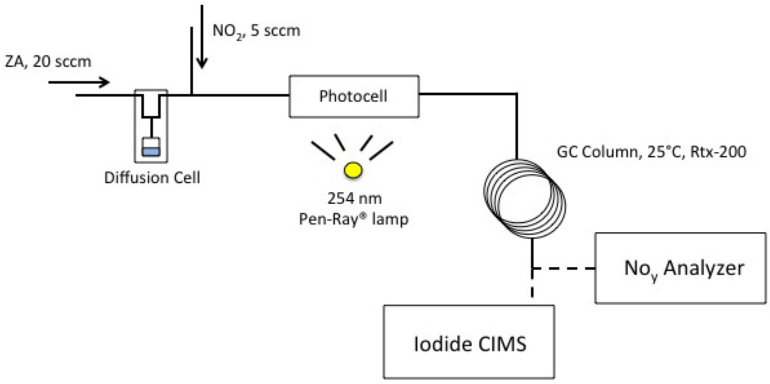

Figure 1. Shown is a schematic of the photochemical calibration system used in this work for the production of APNs with subsequent detection using a total NO_y detector and an iodide ion TD-CIMS.

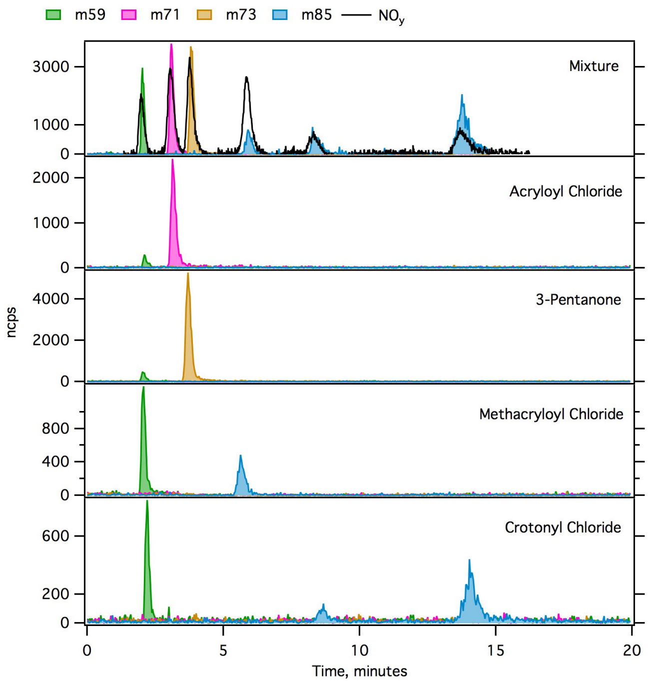

Figure 2. I$^-$ CIMS and baseline corrected NO$_y$ measurements are shown for a single GC chromatogram of a calibration mixture containing all four precursor compounds (top panel). I$^-$ CIMS measurements of individual calibration mixtures for each of the precursor compounds included in Table 1 (bottom four panels).

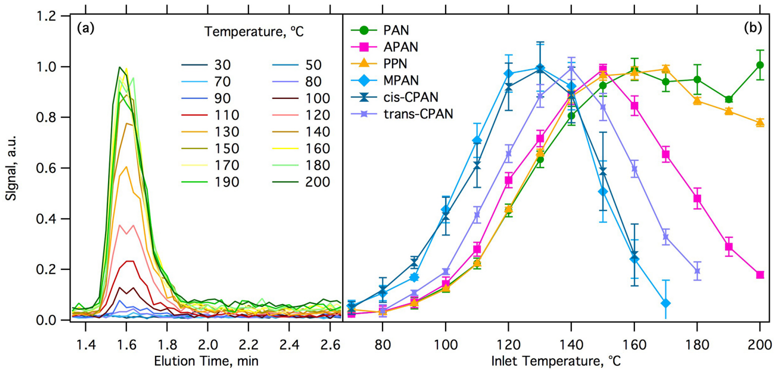

Figure 3. Panel **(a)** shows the signal observed at m/z 59 (PAN) across a range of inlet dissociator temperatures. Fitting the peak areas for each APN produced and plotting the result versus the inlet dissociation temperature yields the figure shown in panel **(b)**. Thermograms for all of the APNs measured in this work are displayed. Optimal inlet dissociation temperatures of 150 °C for the detection of PAN, PPN, and APAN and 130 °C for the detection of MPAN were determined for this system.