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## Observations of APAN during TexAQS 2000

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**Abstract.** Measurements of peroxyacetylic nitric anhydrides (PANs) made in Houston, Texas during TexAQS (Texas Air Quality Study) 2000 showed a relatively abundant PAN compound that had not been identified in previous studies in North America [*cf. Williams et al., 2000*]. This compound was hypothesized to be peroxyacetylic nitric anhydride {CH<sub>2</sub>=CH-C(O)OONO<sub>2</sub>, APAN} based on the work of *Tanimoto and Akimoto, [2001]*. APAN was synthesized and characterized on one of the two GC systems used to make those measurements, subsequent to the TexAQS 2000 field study, confirming that APAN was observed during TexAQS 2000, both on the ground and in airborne measurements. Mixing ratios of APAN were estimated from the response of the system to PAN and PPN and ranged up to 502 pptv, which was 30% of PAN. High APAN values were associated with the precursor species 1,3-butadiene and acrolein, which had local petrochemical sources. The presence of APAN at these unprecedented levels demonstrates the impact of these reactive VOC species, and may have associated health effects.

### 1. Introduction

Peroxyacetylic nitric anhydrides (also known as peroxyacetyl nitrates) are important tropospheric photochemical product species [*Gaffney et al., 1989; Roberts, 1990; Kleindienst, 1994*]. Peroxyacetylic nitric anhydride (PAN) is the simplest and most abundant in the troposphere. Other PAN compounds that have been observed include propionic, iso- and n-butyric, methacrylic and benzoic derivatives. Measurements of these derivatives, along with PAN itself, have been used to discern the hydrocarbon NO<sub>x</sub> photochemistry and by extension, O<sub>3</sub> production, operative in given environments [*Williams et al., 1997; Roberts et al., 1998*]. *Tanimoto and Akimoto, [2001]*, recently reported the observation of peroxyacetylic nitric anhydride {CH<sub>2</sub>=CH-C(O)OONO<sub>2</sub>, APAN} in Tokyo and on an island in Northern Japan, at abundances usually less than 1%, but as high as 4% of PAN. Through its synthesis and characterization, they demonstrated that it was the unidentified compound first noted in the work described by *Tanimoto et al., [1999]*. APAN had been previously observed as a product in chamber studies of allyl chloride [*Edney et al., 1986*] and acrolein [*Grosjean et al.*

1994a], and its thermal decomposition rate measured [*Grosjean et al., 1994a*], but atmospheric measurements of it had not been reported until *Tanimoto and Akimoto [2001]*.

The measurements reported here were made both on the ground at the La Porte Municipal Airport site and on board the NCAR Electra aircraft (based at Ellington Field) in August and September, 2000, during the Texas Air Quality Study (TexAQS 2000) conducted in and around Houston, Texas. Five PAN compounds were observed that had been previously identified in North America atmospheres: PAN, peroxypropionic nitric anhydride (PPN), peroxyisobutyric nitric anhydride (PiBN), peroxy-methacrylic nitric anhydride (MPAN), and peroxy-n-butyric nitric anhydride (PnBN, not measured on the aircraft). In addition, a compound was observed that eluted between PAN and PPN, similar to the observations of *Tanimoto et al., [1999]*, that had not been recognized in our previous studies. Prompted by the work of *Tanimoto and Akimoto [2001]*, a synthesis of APAN was developed and the product characterized by retention time and thermal properties. This confirmed that APAN was observed during the TexAQS 2000 study. Ambient mixing ratios of APAN were derived from the instrumental responses measured for PAN and PPN. Likely atmospheric formation pathways and its relationship to other measured species are given.

### 2. Experimental Approach

PAN compounds were measured using instrumentation similar to that described by *Williams et al., [2000]* and *Roberts et al., [2001a]*, with the following modifications. The ground-based instrument was fitted with a 7.5 m x 0.53 mm ID fused silica capillary column, coated with 1 μm trifluoropropyl silicone liquid phase (Restek RTX-200). During the Houston measurements, the column was held at 20°C and had a helium flow of 9 cm<sup>3</sup>min<sup>-1</sup> STP and the detector had a nitrogen make-up flow of 9 cm<sup>3</sup>min<sup>-1</sup> STP. Additional tests done in Boulder in 2001 used this system, except that the column was held at 15°C and had a helium flow rate of approximately 10 cm<sup>3</sup>min<sup>-1</sup> STP.

The aircraft instrument is a two-channel system using the same column material (3.25m pre-column and 3.75m long main column) in a back-flush configuration. The system was pressure and temperature controlled, and the carrier gas stream humidified with a CuSO<sub>4</sub>·6H<sub>2</sub>O filled cartridge, minimizing effects of variations in ambient humidity. Both systems employed direct injection for sample introduction, and both systems used Shimadzu Mini-2 ECDs.

PAN compounds thermally decompose at relatively low temperatures at similar rates [*Roberts and Bertman, 1992; Grosjean et al., 1994a*]. Thermal decomposition was used as a diagnostic in each GC system, to provide a qualitative check on compound identities and the extent of any interferences, and to provide an authentic calibration matrix. The ground system incorporated a stainless steel loop, held at 125°C, which was switched in-line at the top of the inlet every 5hrs [*Roberts et al., 2001a*], and the aircraft instrument employed a stainless steel decomposition loop as part of a constant pressure inlet system.

Calibrations of both instruments for PAN were accomplished using a modification of the acetone photolysis source [*Meyrahn et al., 1987; Warneck and Zerbach, 1992*] [METCON GmbH].

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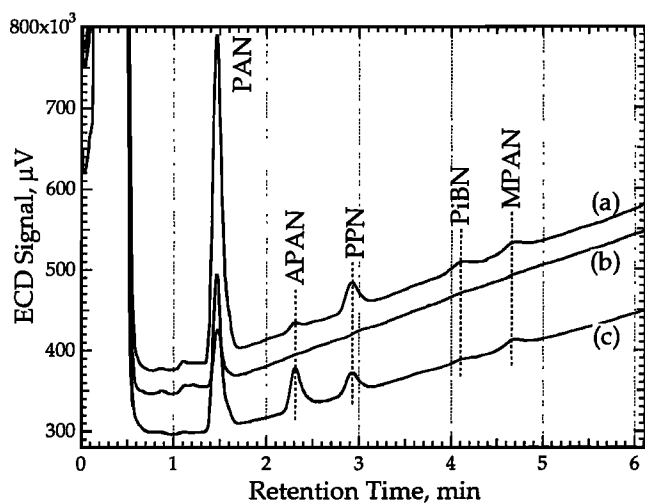


Figure 1. Chromatograms from the TexAQS 2000 La Porte ground site; (a) an ambient sample injected 8/31/00 at 1245 LST, (b) a PAN standard added to decomposed ambient air, and (c) an ambient sample injected 9/3/00 at 1215 LST.

The ground instrument was also calibrated for PAN, PPN, and MPAN with a capillary diffusion source and  $\text{NO}_y$  analysis [Williams *et al.*, 2000]. The aircraft system uses a pressure-controlled version of the photolytic source compatible with the pressure controlled inlet system, and was also calibrated on the ground using diffusion sources, and directly compared to the ground instrument. The relative responses of the instruments to the various PAN compounds were very similar with a slight decrease in response with the retention time of the compound, probably due to a slight amount of decomposition on the column.

APAN was synthesized following the general scheme of Nielsen *et al.*, [1982] and Gaffney *et al.*, [1984]. The peracid was made directly by reaction of the acid chloride,  $\text{CH}_2=\text{CH}-\text{C}(\text{O})\text{Cl}$ , with 90%  $\text{H}_2\text{O}_2$  at ice/water temperatures, and was nitrated by slow addition of  $\text{H}_2\text{SO}_4/\text{HNO}_3$  at  $0^\circ\text{C}$ . Products were extracted into tridecane, washed several times with water, and dried with anhydrous  $\text{MgSO}_4$ . The tridecane solution was then placed in a diffusion cell at  $0^\circ\text{C}$ . The flow from the diffusion cell was added to an ambient air stream, which was sampled either directly, or after decomposition.

Measurements of hydrocarbons and acrolein during TexAQS 2000 were made either by direct cryogenic sampling, or by canister sampling followed by cryogenic concentration, and GC/MS analysis. The methods used for the ground measurements of 1,3-butadiene were described in Roberts *et al.*, [2001b] and those for acrolein were described by Apel *et al.*, [2001]. The methods for the aircraft VOC measurements are described by Friedli *et al.*, [2001], however only relative concentrations of acrolein are available at this point.

### 3. Identification and Quantitation

PAN GC analyses made during TexAQS 2000 showed the obvious anomalous presence of a peak in between PAN and PPN that was thermally unstable under the same conditions as the PAN-type compounds (Figure 1). The work of Tanimoto and Akimoto [2001] demonstrated that this compound was APAN and that it elutes between PAN and PPN. The GC analyses of the APAN synthesis product added to ambient air in Boulder showed a peak between PAN and PPN, that thermally decomposed in the same manner as the other PANs. The correlation between retention times, measured on the same instrument under slightly different conditions, was good,  $R^2 > 0.9999$ , given that the variability of absolute retention times observed in the Houston data set ranged from 1.5% for PAN to 3% for MPAN, but the

relative variation was much less. This, coupled with the thermal decomposition behavior and the work of Tanimoto and Akimoto, [2001], effectively demonstrates that the peak observed in Houston 2000 is APAN.

Ambient concentrations of APAN were calculated using a calibration factor mid-way between that of PAN and PPN. This is deemed appropriate because the response factors for PAN-type compounds in these systems have been observed to decrease slightly with compound elution time. This approximation should add only a small uncertainty to the resulting measurements, since those calibration factors were different by only 20%. The resulting uncertainties were estimated to be  $\pm(5\text{pptv}+15\%)$  of PAN and PPN, and  $\pm(5\text{pptv}+20\%)$  of APAN, PiBN and MPAN. Limit of detection of each of the PANs was 5 pptv. The same uncertainties apply to the aircraft instrument.

### 4. Results

The PANs data from the La Porte site is summarized in Table 1 for all data points and for the period 1000-1900 LST. The averages and medians were calculated by setting all data below detection limit to one half the limit of detection (LoD), 2.5 pptv. Ratios were calculated only when both compounds were above the LoD. Levels of PAN and PPN are similar to those measured in other urban areas, and the average PPN/PAN is typical of  $\text{HC-NO}_x$  photochemistry dominated by anthropogenic hydrocarbons [Roberts *et al.*, 1998]. Less is known about mixing ratios of PiBN, however the daytime average PiBN/PAN was 2.3%, in agreement with observations in Nashville, Tennessee [Roberts *et al.*, 2001a]. The APAN mixing ratio was as high as 502 pptv, and the APAN/PAN averaged 3.3%. Houston differs from Nashville, and indeed every other urban area in the United States, having a large concentration of petrochemical plants along the Houston Ship Channel, approximately 2-5 km north of the La Porte site. APAN/PAN was high (up to 30%) in a handful of instances, as a result of the local effects of petrochemical sources.

The NCAR Electra data is summarized in Table 2. Typical takeoff times were 1100 to 1300 LST with a 1700-2000 return. In general the flight legs over the Houston urban area were flown at altitudes ranging from 500 to 1000 meter AGL, the few samples taken above the boundary layer (2000m) over the city had APAN mixing ratios at or below 20 pptv. The data should therefore be compared to the daytime subset in Table 1. In general the aircraft data showed higher maxima but comparable or lower averages or medians, because the aircraft sampled source regions ranging

Table 1. Summary of PANs Measured at the La Porte Site.

| Compound/Quantity     | Max <sup>1</sup> | Min   | Avg.  | Median | N <sup>2</sup> |
|-----------------------|------------------|-------|-------|--------|----------------|
| PAN <sup>3</sup>      | 6500             | 15    | 480   | 140    | 2296           |
| PAN <sup>4</sup>      | 6500             | 17    | 950   | 610    | 910            |
| APAN <sup>3</sup>     | 502              | <5    | 12    | <5     | 605            |
| APAN <sup>4</sup>     | 502              | <5    | 25    | <5     | 445            |
| PPN <sup>3</sup>      | 1360             | <5    | 74    | 23     | 1739           |
| PPN <sup>4</sup>      | 1360             | <5    | 150   | 90     | 870            |
| PiBN <sup>3</sup>     | 266              | <5    | 13    | <5     | 730            |
| PiBN <sup>4</sup>     | 266              | <5    | 25    | 13     | 558            |
| MPAN <sup>3</sup>     | 210              | <5    | 15    | <5     | 701            |
| MPAN <sup>4</sup>     | 210              | <5    | 30    | 18     | 535            |
| APAN/PAN <sup>3</sup> | 0.30             | 0.003 | 0.033 | 0.019  | 605            |
| APAN/PAN <sup>4</sup> | 0.30             | 0.003 | 0.032 | 0.019  | 445            |
| PPN/PAN <sup>3</sup>  | 0.47             | 0.033 | 0.158 | 0.156  | 1739           |
| PPN/PAN <sup>4</sup>  | 0.35             | 0.046 | 0.163 | 0.144  | 870            |
| PiBN/PAN <sup>3</sup> | 1.95             | 0.004 | 0.033 | 0.026  | 730            |
| PiBN/PAN <sup>4</sup> | 0.20             | 0.004 | 0.029 | 0.026  | 558            |

<sup>1</sup>All mixing ratios in pptv.

<sup>2</sup>Number of observations above detection limit.

<sup>3</sup>All Data

<sup>4</sup>1000-1900 LST

**Table 2.** Summary of PANs Measured on the Electra.

| Compound/Quantity | Max   | Min    | Avg.  | Median | N <sup>2</sup> |
|-------------------|-------|--------|-------|--------|----------------|
| PAN               | 12100 | <5     | 611   | 405    | 1096           |
| APAN              | 421   | <5     | 21    | 8.6    | 243            |
| PPN               | 1955  | <5     | 75    | 37     | 976            |
| PiBN              | 359   | <5     | 22    | 13     | 632            |
| MPAN              | 733   | <5     | 51    | 41     | 645            |
| APAN/PAN          | 0.15  | 0.0036 | 0.014 | 0.010  | 230            |
| PPN/PAN           | 0.27  | 0.019  | 0.100 | 0.092  | 965            |
| PiBN/PAN          | 0.27  | 0.0043 | 0.032 | 0.026  | 615            |

<sup>1</sup>All mixing ratios in pptv.

<sup>2</sup>Number of observations above detection limit.

from directly over the ship channel to rural areas. MPAN was an exception because higher isoprene areas were also sampled. Observations of APAN outside the Houston area, over Denver, Dallas, Oklahoma City, and Tulsa were all below 15 pptv, even in instances where PAN was up to 1700 pptv.

## 5. Discussion

APAN is formed in the atmosphere primarily by reaction of acrolein  $\{\text{CH}_2=\text{CH}-\text{C}(\text{O})\text{H}\}$  with hydroxyl radical (OH) and reaction of the acrylyl radical with  $\text{O}_2$  and then  $\text{NO}_2$ . Acrolein is directly emitted in automobile exhaust and petrochemical activities, and is formed through the reaction of 1,3-butadiene with OH or  $\text{O}_3$ . Rate constants have been measured for the reactions of 1,3-butadiene and acrolein with OH at  $6.7 \times 10^{-11}$  and  $2.0 \times 10^{-11}$  respectively [Atkinson, 1997; Atkinson, 1989]. A molar yield of  $0.58 \pm 0.04$  has been measured for the production of acrolein from OH reaction with 1,3-butadiene in the presence of  $\text{NO}_x$  (corrected for OH+acrolein) [Tuazon *et al.*, 1999]. Acrolein + OH is said to proceed primarily through aldehyde H atom abstraction [Atkinson, 1990]. Loss of APAN will be primarily through reaction with OH and thermal decomposition, and to a minor extent through reaction with  $\text{O}_3$ . The rate constant for OH+APAN has not been reported, but should be in the range 1 to  $2 \times 10^{-11}$ , based on the recent measurement of the MPAN + OH of  $2.5 \times 10^{-11}$  [Orlando *et al.*, 2001]. The thermal decomposition of APAN has been measured by Grosjean *et al.*, [1994a] to be similar to PAN at 298 °K, although the Arrhenius parameters obtained are quite different and appear specious. High temperatures during the TexAQS 2000 study, up to 42°C, resulted in PANs thermal lifetimes as short as 5 min. Therefore,

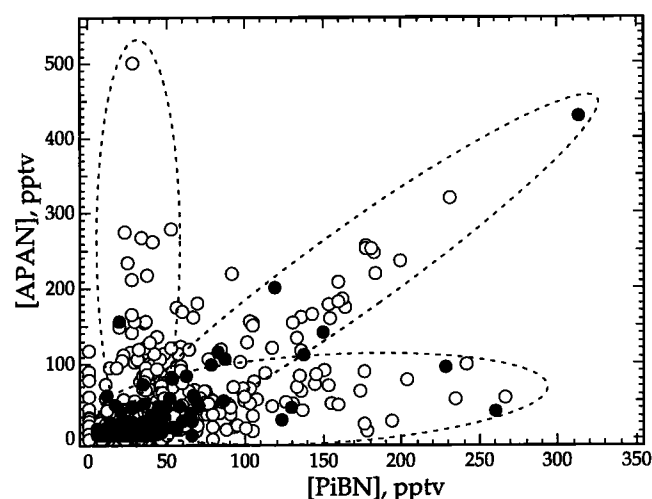


Figure 2. Mixing ratios of APAN versus mixing ratios of PiBN measured at the La Porte site and aboard the NCAR Electra, during the TexAQS 2000 field study. The open circles are from the La Porte site and the solid circles are from the NCAR Electra.

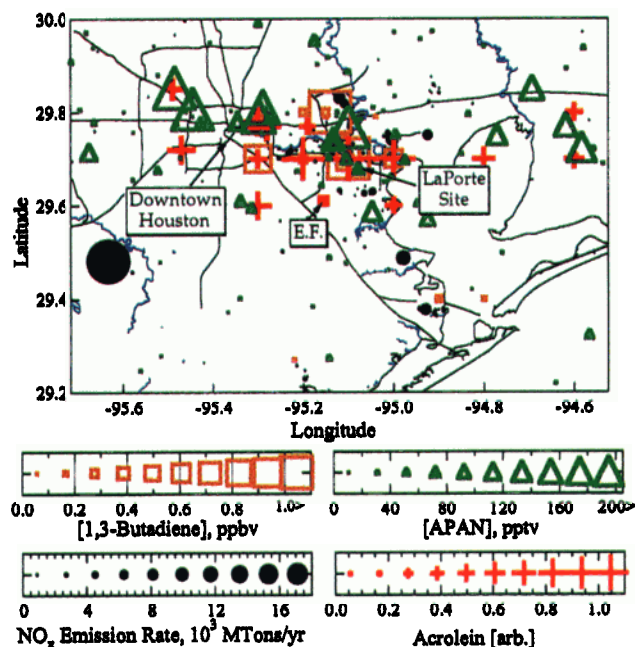


Figure 3. 1,3-butadiene, acrolein, and APAN measured from the NCAR Electra, super-imposed on a map of greater Houston and associated  $\text{NO}_x$  sources. Also noted are Ellington Field, downtown Houston, and the La Porte Municipal Airport site (29.669°N, 95.064°W). The largest  $\text{NO}_x$  source is the Parrish power plant. The other sources are stand-alone power plants, flares, or co-generation facilities associated with industrial plants.

the formation of APAN from 1,3-butadiene and acrolein photooxidation in the presence of  $\text{NO}_x$  should be relatively rapid and efficient, and the net lifetime of APAN should be relatively short (< a few hours).

The correlation between PAN species can be used to discern the nature of precursors of those compounds [cf. Williams *et al.*, 1997]. The correlation of APAN versus PiBN (Figure 2) shows three distinct populations: points high in APAN low in PiBN, points high in both PiBN and APAN, and points that were high in PiBN low in APAN. The presence of these populations underscores the difference between the Houston urban air shed and that of a typical urban North American. In general, urban atmospheres are dominated by mobile source emissions, and to some extent biogenic hydrocarbons, while that of Houston has significant petrochemical sources, the effect of which was to produce distinctly different ambient concentrations of APAN and PiBN. Although recognized as incomplete, the EPA 1999 Toxics Release Inventory [U.S. EPA, 2001] lists point sources of 1,3 butadiene that totaled over  $10^5$  kg/year in the Houston-Galveston area.

The measurements of acrolein and 1,3-butadiene at the La Porte site are particularly instructive. Median mixing ratios of 1,3-butadiene and acrolein were 0.087 and 0.021 ppbv respectively, however, large short-term perturbations, “plumes” were observed in both species with maxima as high as 16.7 and 6.8 ppbv, respectively. The 1,3-butadiene plumes tended to come from areas north and west of the La Porte site while acrolein seemed to have more widely distributed sources, perhaps because it had both primary and photochemical sources. The plumes clearly indicate the impact of petrochemical sources and not mobile sources, which have much smaller concentrations relative to markers such as acetylene. Longer chain 1,3-dienes are also possible sources of APAN, but none were observed in the ground or aircraft measurements.

With the exception of few data points, all the aircraft data shown in Figure 2 lie within the two populations where both

APAN and PiBN are elevated or where APAN is low. This is not surprising because the probability of getting a GC sample inside a narrow plume of either 1,3-butadiene or acrolein is very low. Aircraft observations are superimposed on a map of the greater Houston area in Figure 3. Also shown are stationary NO<sub>x</sub> sources, La Porte Municipal Airport, and Ellington Field. The body of water and cluster of NO<sub>x</sub> sources east of downtown Houston define the petrochemical complex along the ship channel. Highest 1,3-butadiene and acrolein were observed along the ship channel. High APAN was also observed around the ship channel and just south of the La Porte site, but the highest level, 400 pptv was observed NW of downtown Houston. Almost all these high APAN samples were taken on August 25 during two passes near the downtown area in the afternoon. The high APAN and somewhat elevated acrolein here could be a result of photochemical production from 1,3-butadiene emitted from the petrochemical complex and transported to the downtown area by light southeasterly winds. Another cluster of high APAN along with elevated acrolein was observed just northeast of Trinity Bay. These data were also observed during a single flight on September 1 and may be explainable by a similar mechanism.

## Conclusions

The observation of APAN during the TexAQS 2000 study has been confirmed through laboratory synthesis, retention time and thermal decomposition. The ambient levels of APAN were as high as 502 pptv, and as high as 30% relative to PAN. The variation of APAN and APAN precursors with other PAN species, with location, and with meteorology demonstrates that high concentrations of APAN result from petrochemical sources. Aircraft observations imply that APAN is much less abundant in other urban areas, as low as 1% or less of PAN. This explains why APAN had escaped detection in the atmosphere prior to Tanimoto *et al.*, [1999].

These observations have several implications. Local sources of reactive compounds cause locally high abundances of PAN compounds that are otherwise not observed. The presence of APAN means that acrolein and 1,3-butadiene are taking part in O<sub>3</sub> production in this environment, underscoring the importance of these sources of reactive VOC in this chemistry.

1,3-Butadiene is not particularly toxic but has been classified as a probable carcinogen, while acrolein is extremely toxic and possibly carcinogenic [U.S. EPA, 1994]. PAN is not particularly toxic at the levels found in ambient air [Vyskocil *et al.*, 1998] and only moderately mutagenic [cf. Kleindienst, 1994]. However, based on the toxic nature of acrolein, the biological effects of APAN may be categorically different, or more intense, than those of PAN and will need to be investigated.

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