The Impacts of Peroxyacetyl Nitrate in the Atmosphere of Megacities and Large Urban Areas: A Historical Perspective

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ABSTRACT: This paper is an overview of the history, discovery, and measurement of peroxyacetyl nitrate (PAN) and its analogs, the peroxyacyl nitrates (PANs), in highly populated urban areas and their downwind environments. The PANs are known to be strong lachrymators and highly phytotoxic. The discovery and characterization of PAN and its analogs helped to confirm that photochemical smog chemistry involved the oxidation of organics by the OH radical to produce organoperoxy radicals, which rapidly convert nitric oxide to nitrogen dioxide and lead to enhanced ozone formation. Advances in the knowledge of the chemistry of PAN and the PANs are reviewed including synthetic procedures, measurement techniques, field and satellite measurements, and important properties (rates of reaction, ultraviolet photolysis, and aqueous solubilities). Ground based measurements obtained in urban centers are highlighted, and the role of these large population centers is examined as sources of the PANs that impact downwind concentrations of tropospheric ozone. The phytotoxicity of PAN is discussed briefly along with its connections to other key trace species including the organic peracids, peroxides, and nitrates. The future potential of increasing wildfires due to climate change that are likely leading to large scale formation of the PANs is discussed along with the need to address the reactions of the PANs with polycyclic hydrocarbons on the surfaces of oily carbonaceous aerosols emitted from these fires. The work summarized here has led to the determination that PAN and its analogs play key roles in urban, regional, and global tropospheric chemistry.

KEYWORDS: *Peroxyacetyl nitrate, peroxyacyl nitrates, ozone, tropospheric chemistry, urban air pollution, PAN measurements, organic peracids, organic nitrates, organic peroxides, PAN synthesis, PAN properties*
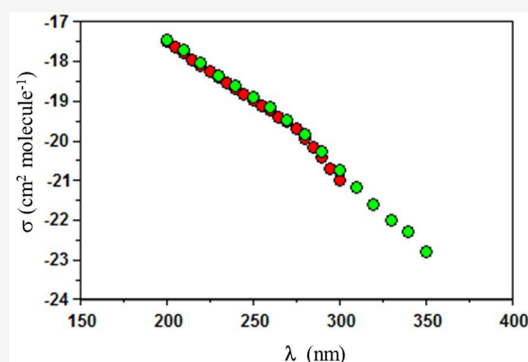
INTRODUCTION

The urban center where "photochemical smog" was first observed was the city of Los Angeles in southern California, commonly referred to as The South Coast Air Basin. Observations of reduced visibility, eye irritation, and people having difficulty breathing due to the presence of photochemical smog in Los Angeles was first reported in the early 1940s.[1] During this time, rubber tires and windshield wiper blades along with other rubber products exposed to the outside air were found to undergo deterioration more rapidly than normal.[1] In the late 1940s and early 1950s, farmers began to report serious unexplained crop damage in the surrounding farmlands including leaf chlorosis and bronzing, especially to romaine lettuce and parsley.[2,3] Various atmospheric pollutants were suspected to be the cause of this crop damage including SO_2 and HF, which were known plant damaging air pollutants. However, plant pathologist John Middleton and other agricultural researchers at the University of California, Riverside Citrus Experiment Station, eliminated these two pollutants as possible causal agents since the responsible air pollutant was determined to be an oxidant.[2,3] At the time,

analytical methods for trace gas oxidant identification and measurement were sadly lacking.[1] Plant pathologists at the Citrus Experiment Station developed a fumigation system for the study of plant exposure to known air pollutants in an attempt to identify the pollutants responsible for causing the leaf chlorosis and bronzing observed in the field. Initial exposure studies met with little success. However, Arie Haagen-Smit, a perfumery chemist at the California Institute of Technology, fumigated plants with the products from the photolysis of gasoline vapors and was successful in producing the plant pathology seen in the fields.[4] Haagen-Smit hypothesized that when automobile exhaust was photolyzed by sunlight, the photochemical reactions produced oxidants and oxidized hydrocarbons. His experiments exposed mixtures

of nitrogen dioxide (NO_2) and unsaturated organics (alkenes also termed olefins), which were known to be emitted in auto exhaust, to sunlight and found that ozone (O_3) was produced. Subsequently, the O_3 was found to be responsible for some of the observed plant damage and also explained the observed damage to rubber products.[5−7] The presence of NO_2, which is a red-brown gas, also helped to explain the reddish-brown color of the smog observed in Los Angeles, often called the "brown cloud". Haagen-Smit's experiments also showed that the likely candidates for the primary emissions of reactive hydrocarbons in the region were automobiles and oil refineries. This determination led to the initial control strategies of reducing emissions from these sources in order to control the levels of photochemical smog in the Los Angeles area.

DISCOVERY OF PEROXYACETYL NITRATE

While the production of O_3 in urban photochemical smog explained some of the crop damage, it did not explain all of the observations of plant phytotoxicity or health effects including severe eye irritation. More detailed investigations were needed to determine the presence of other air pollutants that could be responsible for these additional effects that were not explained by O_3 exposure. In 1954, pioneering research in analytical infrared spectroscopy was carried out at the Franklin Institute Laboratories in Philadelphia.[8,9] The results of this research included the construction of the first long-path infrared gas cell, which was used to examine the products from the photolysis of NO_2 and reactive olefins. The products identified included oxidized organics, primarily aldehydes and ketones including acetaldehyde and acetone. One compound that stood out in the infrared analysis was butane-2,3-dione or biacetyl. Further study showed that the photolysis of biacetyl in the presence of NO_2 produced very strong infrared bands at 1740 and 1841 cm^{-1}. Since these bands were unique, the unknown organic compound responsible for their presence was called "Compound X" by the research team.[8,9] In an attempt to isolate Compound X from the photochemical reaction of biacetyl and NO_2, the product mixture was condensed into a cold trap. Unfortunately, the sample trap exploded violently as it was thawed, and the attempt was a failure.

There were five structures suggested for Compound X in this early work (Figure 1a−e).[10] The correct structure for
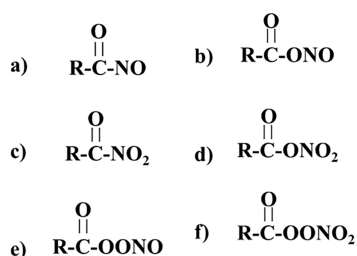
Figure 1. Proposed chemical structures for the PANs (a−e). The actual structure of the PANs is shown in panel f.

Compound X (Figure 1f) was not proposed until acetyl nitrate (Figure 1e) was synthesized by Edward Schuck and George Doyle in 1959.[10] This work showed that Compound X had similarities to acetyl nitrate but that it was not identical. Published in 1961, Philip Leighton's classic textbook "Photochemistry of Air Pollution"[11] describes the use of gas chromatography coupled with a photochemical reactor by

Edgar Stephens and co-workers in 1960.[12,13] This work finally led to the correct structure for Compound X (Figure 1f) and its identification as PAN. This structure was accepted as correct and finally confirmed by infrared analysis of isotopically labeled PAN in 1974.[14]

Further studies initiated in 1958 identified PAN as a key phytotoxic compound causing the bronzing of leaves of petunias and oxidative damage to other susceptible plants.[15] These plant exposure studies, carried out at the University of California at Riverside, were made possible due to the isolation of PAN using gas chromatography after it was photochemically produced.[15] The cooperative research between plant pathologists and atmospheric chemists, which led to the discovery of PAN and its initial isolation, showed that the PANs were from 10 to 50 times more potent plant phytotoxins than O_3.[16] This important collaboration evolved into the Statewide Air Pollution Research Center at the University of California at Riverside, which was one of the first environmental research centers to conduct interdisciplinary work on air quality problems and demonstrated the value of this approach.

PAN was also found to be a strong lachrymator or eye irritant that, along with formaldehyde, acetaldehyde, and acrolein, was responsible for most of the eye irritation observed in the Los Angeles smog. PAN, NO_2, and O_3 were all found to be the chemical oxidants associated with the Los Angeles smog that caused the observed oxidative damage. These air pollutants, along with hydrogen peroxide, were included in the first air pollution criteria documents. Indeed, PAN, hydrogen peroxide, NO_2, and O_3 were included in oxidant criteria documents that were part of the United States Clean Air Act of 1963. PAN and hydrogen peroxide were later omitted from the Clean Air Act of 1970 primarily due to difficulties in measuring and synthesizing standards for them at that time.

PEROXYACYL NITRATES: SYNTHESIS AND PROPERTIES

The first routine method for the synthesis and isolation of PAN was developed by Edgar Stephens and colleagues in the 1960s. By 1973, Stephens had determined that he could obtain a good yield for PAN synthesis by photolyzing ethyl nitrite in air.[17] The photochemical reaction steps involved in this synthesis are shown in Figure 2.

Ethyl nitrite (CH_3CH_2ONO) photolyzes rapidly with ultraviolet radiation in the region of 300−400 nm producing the ethoxy radical (CH_3CH_2O) and nitric oxide (NO) with a quantum yield of unity. In the presence of oxygen, the CH_3CH_2O rapidly produces the hydroperoxyl radical (HO_2)

1) $CH_3CH_2ONO + h\nu \rightarrow CH_3CH_2O + NO$

2) $O_2 + CH_3CH_2O \rightarrow HO_2 + CH_3CH=O$

3) $HO_2 + NO \rightarrow OH + NO_2$

4) $OH + CH_3CH=O \rightarrow H_2O + CH_3C=O$

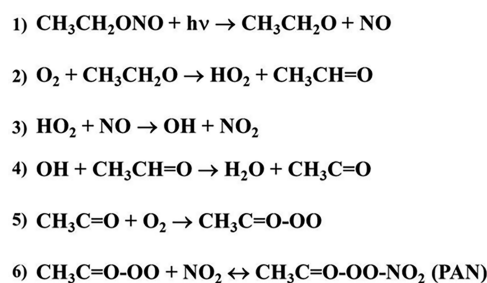5) $CH_3C=O + O_2 \rightarrow CH_3C=O-OO$

6) $CH_3C=O-OO + NO_2 \leftrightarrow CH_3C=O-OO-NO_2$ (PAN)

Figure 2. Photochemical and radical reactions leading to the formation of PAN ($CH_3C=O-OO-NO_2$) from the photolysis of ethyl nitrite (CH_3CH_2ONO).

and acetaldehyde ($CH_3CH{=}O$). The HO_2 radical can react with NO to produce the hydroxyl radical (OH) and NO_2. The OH radical then abstracts the aldehydic hydrogen from the $CH_3CH{=}O$ forming the acetyl radical ($CH_3C{=}O$), which rapidly adds O_2 to form the peroxyacetyl radical ($CH_3C{=}O$—OO). The $CH_3C{=}O$—OO radical forms PAN upon addition of NO_2. This same set of reactions can be produced by the photolysis of biacetyl ($CH_3COCOCH_3$) in the presence of NO and NO_2 in air as observed by researchers at the Franklin Institute.[8,9]

There are also side reactions that occur during the photochemical production of PAN using this method. The main side reactions are shown in Figure 3. These side reactions

1) $NO_2 + h\nu \rightarrow NO + O$

2) $O + O_2 + M \rightarrow O_3 + M$

3) $PAN \leftrightarrow CH_3C{=}O{-}OO + NO_2$

4) $CH_3C{=}O{-}OO + NO \rightarrow CH_3CO_2 + NO_2$

5) $CH_3CO_2 \rightarrow CH_3 + CO_2$

6) $CH_3 + O_2 \rightarrow CH_3O_2$

7) $CH_3O_2 + NO \rightarrow CH_3O + NO_2$

8) $CH_3O + O_2 \rightarrow CH_2O + HO_2$

Figure 3. Main side reactions in the photochemical production of PAN from the photolysis of ethyl nitrite in air that leads to the production of ozone (O_3) and formaldehyde (CH_2O) as byproducts.

result in the formation of O_3 (Figure 3, reaction 2) and formaldehyde (Figure 3, reaction 8) as byproducts. The presence of these unwanted byproducts along with excess acetaldehyde formed in the original photolytic reaction sequence (Figure 2, reaction 2) requires the use of separation methods to isolate the PAN. This separation was accomplished by using preparative gas chromatography. The purified PAN was then diluted with high purity nitrogen or zero air and stored in large gas canisters in a cold room to reduce the thermal decomposition and subsequent loss of PAN. One of the problems with this methodology is that, if PAN condenses at cold temperatures it can lead to an explosion as described by Stephens and co-workers.[18] These problems with unwanted product formation, separation requirements, and the possibility of explosion during storage led other researchers to investigate alternative methods of synthesizing and isolating PAN that would avoid the need for separation and safety concerns.

One of the alternative approaches that was first investigated was to use the dark reaction of the nitrate radical (NO_3) with acetaldehyde to form PAN. The reaction steps of this synthesis are outlined in Figure 4. Nitrogen pentoxide (N_2O_5) was used as the source of the NO_3 radical since it is in equilibrium with NO_3 and NO_2 (Figure 4, reaction 1). The NO_3 radical abstracts the aldehydic hydrogen of acetaldehyde in a similar manner as occurs with OH radical in the ethyl nitrate synthesis (Figure 2, reaction 4). Similar approaches have used Cl and Br atoms, generated from Cl_2 and Br_2 photolysis, to perform the abstraction of the aldehydic hydrogen to form PAN in air with NO and NO_2 added.[19]

1) $N_2O_5 \leftrightarrow NO_3 + NO_2$

2) $NO_3 + CH_3CH{=}O \rightarrow HNO_3 + CH_3C{=}O$

3) $CH_3C{=}O + O_2 \rightarrow CH_3C{=}O{-}OO$

4) $CH_3C{=}O{-}OO + NO_2 \leftrightarrow CH_3C{=}O{-}OO{-}NO_2$
                                                 (PAN)

Figure 4. Dark reaction of dinitrogen pentoxide (N_2O_5) with acetaldehyde ($CH_3CH{=}O$) in the presence of air leading to the formation of PAN.

The N_2O_5 reaction synthesis must be carried out in total darkness as NO_3 will rapidly photolyze. It also requires very dry reaction conditions since N_2O_5, as the anhydride of nitric acid, reacts rapidly with any available water. In addition, N_2O_5 is a very strong oxidant and nitrating agent and can react explosively with organics presenting similar safety problems as with the gas phase photolytic synthesis. Despite the safety issues, both the gas phase photochemical and the dark reaction synthetic approaches were used successfully and allowed for studies of the toxicity and physical properties of PAN.[19−21]

It was found that PAN could be concentrated from the gas phase into nonpolar deuterated solvents, such as deutero-chloroform and deuterated methylene chloride, which led to studies of liquid phase reactions of PAN with simple alkenes, alcohols, and amines.[19] The fact that PAN can be considered as a mixed anhydride of peracetic acid and nitric acid led researchers to use the strong acid nitration of peroxyacetic acid in aqueous solution to synthesize PAN at ice temperatures. The PAN could then be extracted into a nonpolar solvent separating it from the major reactants, peracetic acid and nitric acid, which are all soluble in ice water while PAN has a low water solubility.[22−24] By using low volatility solvents, in this case tridecane, high purity PAN samples could be safely handled and stored frozen, avoiding the safety problems associated with earlier gas phase synthetic methods.[25] Upon thawing of the samples, the higher volatility PAN can be released at room temperature with essentially no solvent contaminant, since tridecane has a very low vapor pressure. This procedure has also been used for the synthesis of the higher analogs of PAN by simple modification of the peracid.[25] For example, peroxypropionyl nitrate (PPN) can be synthesized by using peroxypropionic acid instead of peroxyacetic acid.

Advances in the synthesis of PAN and the PANs has led to improvements in analytical procedures as well as in the determination of their chemical and physical properties. As noted earlier, the infrared spectrum of PAN has a number of very characteristic bands that were assigned to the $C{=}O$ stretch in the peroxyacetyl functional group and used to confirm the formation of PAN in the different synthetic approaches.[19−21] There are five principal infrared bands for PAN located at 794, 1163, 1302, 1741, and 1842 cm^{-1}. These infrared bands are used for the measurement of PAN by using long-path Fourier transform infrared spectrometers on the ground, while the 794 and 1163 cm^{-1} bands are used for upper atmosphere satellite retrievals.

Key structural information was obtained by Stephens and by Nicksic and colleagues who observed that nitrite, acetate, and oxygen were produced by the rapid base hydrolysis of PAN, which helped to confirm the chemical structure.[26] Later, studies of PAN reactions in solution with ammonia and amines

showed the formation of oxygen, nitrous acid, and acetamides, also supporting the chemical structure identification.[27]

While the unique infrared spectrum of PAN is useful in its determination, PAN was found to have an ultraviolet spectrum with no dominant band structures giving essentially an exponentially decaying absorption spectrum.[28−30] The absorption cross sections for PAN are shown in Figure 5 for the
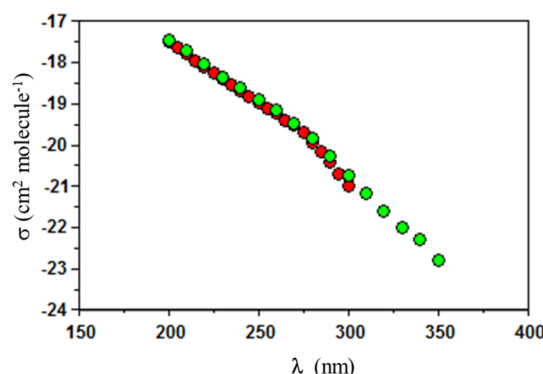

Figure 5. Plot of the absorption cross sections (σ) of PAN in the ultraviolet from 200 to 350 nm. Data taken from ref 29 (red dots) and ref 30 (green dots).

region of 200−350 nm.[29,30] The absorption cross sections in the ultraviolet confirm that PAN is slow to photolyze in the atmosphere below altitudes lower than 5−7 km.[30] PAN was also found to react very slowly with both the OH radical and O_3.[30−32] In addition, the aqueous solubility of PAN was determined to be 3−5 M atm^{-1} indicating that PAN has a slow rate of uptake into acidic rain droplets and wet aerosols.[19,20,33,34] Therefore, the only significant loss process for PAN and the PANs, was found to be due to the thermal equilibrium of PAN with the peroxyacetyl radical and NO_2 (Figure 3, reaction 3) followed by the loss of either of the forward reaction products. If no loss occurs, the back reaction is favored and PAN will reform.[19,20]

The equilibrium has been determined to be strongly temperature dependent with the back reaction favored at colder temperatures. The kinetic data for the forward reaction has been reviewed and evaluated.[35] The recommended value for the rate is $5.4 \times 10^{16} \exp(-13830/T)$, which at 298 K yields a decomposition rate of 5.7×10^{-4} s^{-1} and an apparent atmospheric lifetime for PAN of about 30 min. This represents the maximum loss rate and assumes that the peroxyacetyl radical is lost by reaction with NO (Figure 3, reaction 4). The atmospheric lifetime of PAN is thus dependent on the NO/NO_2 ratio since the rate of peroxyacetyl radical loss is dependent on the NO concentration. The higher the NO concentration, the shorter the apparent PAN lifetime. The reformation of PAN by the equilibrium back reaction is dependent on the NO_2 concentration as outlined in Figure 3 (reaction 4).[36] Thus, the higher the NO_2 concentration, the longer the apparent PAN lifetime. Therefore, the apparent atmospheric lifetimes of PAN and the PANs depend upon the NO to NO_2 ratio in the air mass. It is also important to note that there are other important loss mechanisms in remote areas where the NO concentrations are very low. These include the reaction of the peroxyacetyl radical with HO_2 radical, organoperoxy radicals (RO_2), and other peroxyacyl radicals (RC=O—OO) to form peracids and acyl peroxides.[37−39] Of particular importance is the reaction of peroxyacetyl radical

with the hydroperoxyl HO_2 to form peracetic acid and molecular oxygen (O_2).

The calculated maximum rates for PAN decomposition and atmospheric lifetimes at some relevant tropospheric temperatures are given in Table 1. With a low water solubility, low

Table 1. Maximum Thermal Decomposition Rates and Atmospheric Lifetimes of PAN as a Function of Tropospheric Temperature[35,37]

tropospheric temp (K)	decomposition rate, k (s^{-1})	half-life (min)
243	2.6×10^{-8}	6.4×10^{5}
253	1.9×10^{-7}	8.7×10^{4}
263	1.4×10^{-6}	1.2×10^{4}
273	1.0×10^{-5}	1.6×10^{3}
283	7.7×10^{-5}	2.2×10^{2}
293	2.1×10^{-4}	7.9×10^{1}
298	5.7×10^{-4}	2.9×10^{1}
303	1.6×10^{-3}	1.0×10^{1}
313	4.2×10^{-3}	3.0

reactivity to oxidation, slow photolysis rates, and strong thermal dependence on its equilibrium, PAN and its analogs are found to have longer atmospheric lifetimes during wintertime and at high altitudes, where the tropospheric temperatures are lower, and fairly short lifetimes during the summertime and at lower altitudes, where tropospheric temperatures are higher. However, recall that these lifetimes are dependent on the atmospheric levels of NO and NO_2, which in turn are strongly connected to the levels of the HO_2 radical (Figure 2, reaction 3) as well as organoperoxy radicals (RO_2). The importance of PAN acting as a potential means of transporting NO_2 long distances, as evidenced by the temperature dependence of the equilibrium reaction (Figure 3, reaction 3) led to the recognition of its potential importance in both urban and global atmospheric chemistry.[37,40,41]

■ MEASUREMENT METHODS

A number of analytical methods have been used to measure the concentrations of PAN and its analogs the PANs in both laboratory and urban and global atmospheric field studies. The first methods used long-path infrared spectroscopy in laboratory studies at fairly high concentrations. The adaptation of long-path infrared methods to the polluted urban atmosphere found in the Los Angeles and surrounding areas was successful in measuring PAN levels in the few to tens of parts per billion concentrations using kilometer path lengths.[42,43] However, better sensitivity was needed for measuring the lower concentrations anticipated in less polluted regions. One of the first devices used to determine PAN concentrations at lower levels was the electron capture detector (ECD), invented by James Lovelock.[44,45] The ECD was initially designed to detect low levels of oxygen in planetary atmospheres for NASA. However, Lovelock and others quickly found it to be extremely useful for determining gas phase species containing electronegative atoms in their structures such as the chlorofluorocarbons (CFCs). As PAN contains five oxygen atoms in its structure and it had been shown to be able to be separated using gas chromatography, the ECD was the first gas chromatographic detector to be able to detect PAN at the tens of parts per trillion levels and above.[46] This allowed for the measurement of PAN to be performed by injecting a few cubic centimeters of air directly

into a gas chromatograph operated with the injector and column at ambient temperature to minimize thermal decomposition of the PAN. The columns used were relatively short (6 ft) packed columns (1/8 in. diameter) using a nonpolar packing material. The PAN elutes after the large oxygen signal observed at about 2−3 min. However, the analysis typically takes about 20 min to complete since there is a significant baseline shift in the instrument from water vapor, which elutes at about 15 min and takes about 5 min for baseline to return to normal before the next sample can be injected.[19,20]

Gas chromatography with electron capture detection (GC/ECD) was successful in obtaining measurements of PAN in the urban atmospheres of Los Angeles and Riverside, California, during the 1960s and 1970s.[46] These studies found that PAN levels could reach 20−50 ppb during air pollution events. While it was initially assumed that PAN was only to be found in polluted urban air, measurements taken off the coast of England in 1972−1973 and over the mid-Atlantic Ocean in 1974 indicated that PAN was present in remote atmospheres at levels of 1−2 ppb.[47,48] Thus, PAN and its analogs were found to be present at easily measurable levels in both urban and rural atmospheres. These measurements showed that the role of PAN in urban, regional, and global atmospheric chemistry needed to be understood.

Calibration of the GC/ECD was initially accomplished by base hydrolysis of the PAN followed by measurement of the acetate and nitrite products. This approach is time-consuming and requires a significant amount of PAN. Other calibration methods were based upon comparison to the response of PAN in NO/O_3 chemiluminescent monitors. The chemiluminescent reaction of NO with O_3 to form electronically excited NO_2 (NO_2^*) had been known for some time.[49,50] Once formed, the NO_2^* then decays to the ground state emitting a broad chemiluminescence (590−3000 nm) with a maximum intensity in the near-infrared at 1270 nm. This reaction has become a standard method for the determination of NO. It has also been used for the determination of NO_2 after decomposition to NO using a thermal catalyst.[37,51] The instrument is commonly called a "NO_x box", where the combined concentrations of NO and NO_2 are known as NO_x.[51] The instrument measures the NO_x signal from the thermally decomposed NO_2 combined with the NO present in the air. It then measures the NO concentration alone without the use of the thermal catalyst. NO_2 is determined by difference ($NO_x − NO = NO_2$).[51] The measurement of the chemiluminescent emission requires the use of red sensitive photomultipliers, which limits the detection of the method to about a 1 ppb NO_x, NO, and NO_2. PAN will also decompose in the thermal catalyst to form NO and thus can be detected by the chemiluminescent reaction. Although the instrument can be used to determine the concentration of PAN standards in zero air, atmospheric PAN actually acts as an interferent in the NO_x box measurements of NO and NO_2 along with other nitrogen oxides, which can be decomposed by the thermal catalyst to NO to give erroneously high NO_2 readings.[52] In major urban centers where PAN levels can be in the tens of parts per billion, this interference requires correction to the NO_x values obtained with the NO_x box in order to obtain reliable NO_2 results.[53]

While GC/ECD detection was successful in determining both PAN and the PANs, it has a number of drawbacks that limited its use in the field. The GC/ECD typically takes about

15−30 min to complete an analysis. The ECD also makes use of a radioactive ^{63}Ni foil, a beta emitter, which can lead to safety concerns when used in the field. These issues led to the investigation of other methods for PAN analysis, especially in aircraft operations where shorter analysis times are required. One of the approaches initially examined in the early 1980s was the use of the chemiluminescent reaction of luminol with NO_2, which uses a wetted luminol wick with air containing the NO_2 flowed over the wick. The chemiluminescent emission has a maximum at 425 nm, which is easily detectable using inexpensive phototubes equipped with photon counting technology.[54−56] The sensitivity for the detection using the NO_2−luminol reaction was found to be in the tens of parts per trillion levels. It was demonstrated that both PAN and NO_2 could be determined separately by using luminol chemiluminescence coupled with a short gas chromatographic column.[57] The first commercial instrument using this approach made use of a large packed column, which led to very broad chromatographic separation and times for analysis of about 5−10 min. The long separation times on the packed column led to baseline drift. The application of fast capillary gas chromatography to the luminol detector shortened the analysis time to about 30 s while maintaining the detection limits to about 10 ppt.[58,59] The fast capillary gas chromatographic luminol method has been automated and successfully used in aircraft measurements for PAN and NO_2 using small compressed gas bottles or charcoal filtered air pumps to supply the carrier gases.[59,60]

The mass spectrum of PAN was first determined using electron impact ionization in 1969 as part of a study showing the release of singlet molecular oxygen ($O_2{}^1\Delta_g$) occurring during the base decomposition of PAN.[61] The chemical ionization mass spectrum of PAN was obtained in 1976.[62] Being an energetic molecule, the parent peak of PAN was not observed in the positive ion mass spectrum. However, since PAN has a high ECD cross section, the negative ion mass spectrum of PAN can be detected with high sensitivity.[19,63,64] While the negative ion mass spectrum of PAN does not yield a molecular ion, it has been demonstrated that the monitoring of PAN using the base peak (62 m/e) corresponding to the NO_3^- ion yields sensitivity for PAN in the parts per trillion range.[65] Analysis times for methods using gas chromatography/negative ion mass spectrometry are typically in range of 5−10 min. Although this approach has been used successfully in field studies, it requires the use of compressed gases, high voltage electronics, and vacuum pumps, which limit its widespread field usage. The method is also sensitive to the detection of other organic nitrates and has been used with high sensitivity for these species.

A number of techniques have also been developed for more rapid determinations of PAN and analogs by making use of the thermal decomposition leading to the measurement of either NO_2 or the peroxyacyl radical. There are three main methods that have been used for aircraft and eddy flux measurements of PANs. Laser-induced fluorescence (LIF) monitoring[66−69] and cavity ring down spectroscopy (CRDS)[70−77] are both used to follow the production of NO_2 immediately following the thermal decomposition of the PANs. The third method, chemical ionization mass spectroscopy (CIMS) using I^-,[78−84] follows the carboxylate ion formed from the peroxyacyl radicals. The first two methods are indirect and yield a total PANs level, while the third method gives specific concentrations for the individual PANs including the predominant

PAN compound. All of the methods have approximately 10 ppt detection limits and are able to yield measurements on a time scale of a few seconds.

Both the LIF and CRDS methods measure total PANs, usually reported as $\sum$PAN, after thermal decomposition as NO_2. The measurement is similar to catalytic converters used in the NO_x/O_3 chemiluminescent instruments in that the thermal decomposition channels are corrected for the NO_2 present. Multiple temperature channels are used to attempt to separate the observed signals from other species such pernitric acid, HO_2NO_2, and alkyl peroxy nitrates, RO_2NO_2, which can be a significant interference at colder temperatures where they are stable.[19,20] Depending upon the temperature scheme, organic nitrates, nitric acid, and ammonia can also lead to signals. These techniques have significant errors if the air samples have high NO content, as the peroxyacyl radicals will react and convert the NO to NO_2 which is what is measured. The reactions that lead to errors are the same as those shown in Figure 4, which show the various RO_2 radicals that can be formed if NO is in excess. These peroxy radicals can react with the NO to form NO_2, which leads to higher values than actual. In most ambient cases and studies carried out in remote areas, the NO concentrations are not high, so these side reactions producing extra NO_2 are not significant. Both of these methods are laser-based systems that are affected by aerosols that can absorb or scatter the light leading to potential errors, so that the incoming gas sample requires filtration before the analysis. Care has to be taken in the calibrations of these systems to take into account losses of PANs on filter surfaces, which can change with time. This is done by calibrating the systems with PAN and PANs standards, as well as the other species that are measured in the various temperature channels. These other species include organic nitrates and nitrites, nitric acid, and ammonia. The advantage of these methods is that they can yield fast measurements for total PANs (i.e., $\sum$PAN) that can be used for eddy correlation methods designed to study surface deposition of PANs in a variety of environments. They also allow faster measurements on board aircraft, which allows better spatial determinations of total PANs.

The third method makes use of a chemical ionization reaction of I^- ions with PANs to form RCO_2^- ions, which are detected in a mass spectrometer. Note that the corresponding peracids will also give the RCO_2^- upon reaction with I^- in the chemical ionization source.[84] This approach can be used with or without chromatographic separation to determine the various PANs including the more complex PAN structures with a few to 10 ppt detection limits. To better determine the more complex PAN structures such as acryloyl peroxynitrate (APAN), methacryloyl peroxynitrate (MPAN), and crotonyl peroxynitrate (CPAN), which are difficult to synthesize, the photochemical production of these types of PANs has been accomplished using a simple photochemical system and the corresponding acyl chlorides in the presence of NO_2 in air.[85] This synthetic method makes use of preparative chromatography to purify the calibration samples used for the CIMS method.

GROUND BASED MEASUREMENTS OF PAN

Measurements of PAN were first reported in 1960 in the Los Angeles, CA, area.[86,87] Since that initial set of field measurements, PAN has been measured in many areas across the globe. The maximum daily values for PAN measured in various sites from 1960 to 2020 are given in Table 2.[86−128] In many cases,

Table 2. PAN Maximum Daily Values Reported in the Literature

location	maximum PAN (ppb)	years	refs
Los Angeles, CA, USA	70	1960	86, 87
Los Angles Air Basin, CA, USA	38	1968	16
Los Angeles, CA, USA	65.5	1968	88
Hoboken, NJ, USA	9.9	1970	88
St. Louis, MO, USA	25	1973	88
West Covina, CA, USA	46	1973	89
Wilmington, OH, USA	4.1	1974	88
Los Angeles, CA, USA	40	1977−1978	42
Claremont, CA, USA	37	1978	90
Claremont, CA, USA	47	1980	91
Riverside, CA, USA	30	1980	92
Simcoe, Canada	5.3	1980−1981	93
Bandelier, NM, USA	1.9	1987−1989	94
Athens, Greece	3.7	1988	95
Beijing, China	6.8	1988	96
Toronto, Ontario, Canada	4	1988−1990	97
Munich, Germany	5.6	1989−1990	98
Lindau, Germany	4.7	1989	99
Cape Town, South Africa	8.6	1989	100
Atlanta, GA, USA	2.9	1992	101
Claremont, CA, USA	9.9	1993	102
Mecklenburg, Germany	1	1994	103
Edinburgh, Scotland, UK	3	1994−1998	104
La Vergne, TN, USA	2.1	1995	105
Albuquerque, NM, USA	1.7	1995	106
Porto Alegre, Brazil	6.7	1996−1997	107
Los Angeles, CA, USA	6.9	1997	87
Azusa, CA, USA	4.8	1997	108
Simi Valley, CA, USA	3	1997	108
Mexico City, Mexico	34	1997	109
Berlin, Germany	2.5	1998	110
Nopigia,,Crete, Greece,	1.9	1999	111
Nashville, TN, USA	2.5	1999	112
La Porte, Houston, TX, USA	6.5	2000	113
Athens, Greece	6.6	2001	114
Pellston, MI, USA	1.3	2001	115
Gulf of Maine, USA	2.8	2002	116
Mexico City, Mexico	8	2003	117
Santiago, Chile	7.6	2003−2004	118
Seoul, Korea	10.4	2004−2005	119
Coastal Antarctica	0.05	2005−2006	120
Beijing, China	2.5	2005	121
Beijing, China	11.2	2006	122
Lanzhou, China	9.1	2006	123
Rome, Italy	30.3	2007−2008	124
Nam Co, Central Plateau, Tibet	1	2011−2012	125
Shanghai, China	7	2016−2017	126
Tianjin, China	3	2018	127
Beijing, China	4	2020	128

the PAN analogs (peroxypropionyl nitrate (PPN), n-peroxybutryl nitrate (PBN), iso-peroxybutryl nitrate (iPBN), and methacryloyl peroxynitrate (MPAN)) have also been reported.[129] The levels of PPN are typically are about 8−12% of the PAN observed, with the butyl PANs at levels of 3−6% of the PAN. In areas where there are high emissions of isoprene, which is a precursor of methacrolein, MPAN has been reported

at 5−10% of the PAN levels. In general, PAN levels in urban areas have decreased since the maximum value of 70 ppb was recorded in 1960 in Los Angeles.[86,87] Note that a maximum value for PAN of 30.3 ppb was reported in Rome, Italy, in 2007−2008. This indicates that, while highs in most urban areas since 2000 are not reaching levels above 20 ppb, it is possible that PAN levels may still reach high values in densely populated areas with high levels of motor vehicle traffic under certain weather conditions.[124]

As noted previously, PAN and its analogs are produced from the photooxidation of organic molecules in the presence of nitrogen oxides. The same peroxy radical species that produce the PANs are also involved in the formation of tropospheric ozone. Because of this close relationship between PAN and ozone formation, measurements of PAN have been used as a means of tracking smog chemistry. The PANs can be transported long distances and are an important reservoir of nitrogen oxides, especially in colder air masses.[19,20] PAN has been observed in Coastal Antarctica at a 1 ppt detection limit using sample preconcentration and GC/ECD.[120] Data reported in this remote region found a high of about 50 ppt in 2005−2006 confirming the long-range transport of PAN. PAN has also been measured at a maximum of 1 ppb on the Central Plateau in Nam Co, Tibet, again indicating long-range transport of PAN at high altitudes.[125]

High levels of PAN are usually associated with urban areas where there are significant emissions of both reactive organics and NO from industry and motor vehicle traffic. Although emission controls of reactive hydrocarbons from automotive exhaust and industrial plumes have reduced the amounts of the PANs in urban areas, their importance in the long-range transport of nitrogen oxides and ozone production in remote areas remains a concern. It has been recognized for some time that PAN and its analogs are ubiquitous in the troposphere.[130] The chemistry of the PANs and their formation, transport, and loss have been modeled on global scales.[131] Comparisons of the model results to aircraft and other field measurements have shown that, while there is some reasonable agreement, there remains a need for better data to validate the model results. In particular, while the levels of the PANs on urban scales tend to be strongly linked to the local emissions of reactive organics and nitrogen oxides, regional and global scale levels are likely strongly impacted by the large-scale emissions of organics, particularly aldehydes, and nitrogen oxides from wildfires.[131]

As PAN is formed by the oxidation of organics to form acetaldehyde, which is an immediate precursor to the peroxyacetyl radical, there has been some concern that the use of ethanol and ethanol/gasoline blends may lead to faster formation of PAN in urban areas where these fuels are being used in the presence of high NO.[132,133] In Brazil, the motor vehicle fuel is typically E25 (25% ethanol/gasoline blend). Initial measurements of aldehydes in the urban centers of Brazil showed acetaldehyde to be much higher than that in other urban centers due to the cracking of the ethanol in the combustion process leading to acetaldehyde as a primary pollutant.[134] Continued addition of catalytic converters can lead to some reduction of the acetaldehyde levels when E25 is the predominant automotive fuel.[135] Increasing the ethanol level to E85 (85% ethanol) will likely lead to higher emissions of acetaldehyde, which will lead to enhanced ozone and PAN production and a reduction in air quality.[136,137] Indeed, in areas that use E95 (95% ethanol) as a fuel for buses, the emissions of acetaldehyde and acetic acid are at levels

exceeding 150 ppm have been reported.[138] Comparison of the emissions from the combustion of the various fuels indicates that biofuels, especially ethanol, will likely contribute to enhanced PAN production.[139]

■ SATELLITE MEASUREMENTS

As PAN and its analogs can be transported over large distances and are more stable at higher altitudes where the temperatures are colder, a number of satellite measurements using high resolution Fourier transform infrared spectrometers have made determinations of the levels of PAN in the upper and lower stratosphere. These measurements include data obtained from the cryogenic infrared spectrometers and telescopes for the atmosphere (CRISTA),[140] the tropospheric emission spectrometer (TES),[141−147] the Michelson interferometer for passive atmospheric sounding,[148−150] the infrared atmospheric sounding interferometer (IASI),[151−153] and the atmospheric chemistry experiment-Fourier transform spectrometer (ACE-FTS).[154] The satellite methods make use of high-resolution instruments that are typically 0.25 cm^{-1} resolution or as high as 0.06 cm^{-1}. The instruments use the 794 cm^{-1} or the 1163 cm^{-1} absorption bands of PAN for the determinations in the infrared. There are a number of atmospheric gases that are active in the infrared in the same regions as those used for PAN that include gaseous CO_2, O_3, H_2O, and other trace species. Note that liquid water also is a strong infrared absorber and that it has broad band absorption especially in the 1163 cm^{-1} region.[155] At high water concentrations, the determination of PAN is very difficult. Thus, useful PAN data are obtained in the upper troposphere and lower stratosphere where the water is at low concentrations due to the very low temperatures. Resolutions of the instruments are usually over tens of square kilometers with a frequency of measurement ranging from a few hours to daily depending upon the satellite's orbit. Measurements are typically taken in a time frame that covers a few 100 km, so that the data are best used for large scale evaluations and intercomparisons. Spectral subtraction algorithms and data handling methods are used that make use of the known infrared characteristics of the various atmospheric gases for spectral analysis as well as atmospheric temperature are required to obtain the data. The algorithms are continually being improved with time as more high-resolution infrared spectra are obtained for the many trace gases. One example of this is the determination of trifluoromethane or CFC-23, which has been measured by satellite.[156] Since both PAN and CFC-23 have strong bands in the 794 cm^{-1} region, they need to be considered and corrected for in their measurement using satellite spectrometers. The spectral algorithms used for these determinations have been compared and evaluated with modeling data.[157] The satellite data typically have 30−50% error in the measurements with estimated detection limits of 0.1−0.2 ppb.

Satellite data do allow for longer large-scale data sets to be evaluated for PAN. Data analyses clearly indicate that the increases in large scale wildfires seen globally are qualitatively correlated with higher PAN values, indicative of the anticipated formation of PAN from the volatile organic and nitrogen oxide emissions from the fires. The large-scale data obtained from the satellites are also useful for the evaluation of the global scale atmospheric chemistry models but are limited to the upper troposphere due to water interferences as noted. Once the data is obtained it can be reexamined with improved spectral information as it becomes available. For example, the

CRISTA data obtained in 1997 has been reexamined and evaluated for PAN and ozone and was useful in showing the upper troposphere and lower stratospheric mixing occurrence.[140] Future improvements of the satellite methodologies will continue but will likely be limited to the upper troposphere due to the large interferences from water vapor and clouds over the long optical paths used by the satellites. Note that the data taken over the wet tropics regions typically has the highest errors.

■ FUTURE NEEDS AND RECOMMENDATIONS

Long-term data sets are still lacking for the levels of PAN on urban and regional scales. This was initially due to the lack of suitable measurement methods and to difficulties in producing standards for these methods. This is no longer the case. In the near future, there will certainly be changes in the emissions of organics and nitrogen oxides that can lead to the formation of PAN and its analogs, as well as increased tropospheric ozone levels. Many of these anticipated changes are linked to impacts of climate change, such as increasing wild fires, as well as to changes in our energy usage in attempt to mitigate greenhouse gas emissions.[51,131] For example, increased use of electric vehicles will lead to reductions in emissions of NO and reactive hydrocarbon, especially if the electric power is obtained from alternative energy sources that do not involve combustion (nuclear, hydroelectric, wind, solar, etc.).[51,139] Long-term measurements of NO, reactive hydrocarbons, and PAN at a number of surface sites globally would be extremely useful in documenting how these changes impact the tropospheric air quality. One possibility would be to implement high resolution long-path FTIR systems at universities throughout the world that would be able to monitor not only PAN but other important greenhouse gases, such as CO, CO_2, and O_3. These systems could be used to train students in high resolution spectroscopy, which will have future applications in many areas including improving satellite algorithms. These data could be extremely useful in ground truthing satellite measurements as well as for planning aircraft studies to be able to obtain measurements as a function of altitude. Long-term data sets would also allow for validation of atmospheric chemical and meteorological models and to improve predictive capabilities as we move toward more sustainable energy and environmental conditions.

If NO levels are successfully reduced as we move toward electric vehicles and other sustainable technologies, the formation of PANs would likely drop, coupled with a lowering of the background tropospheric ozone. However, if climate change should increase the emissions of reactive organics from the biosphere due to longer growing seasons and higher average temperatures, it is likely that the levels of organic peroxyalkyl and peroxyacyl radicals will increase. This will in turn give rise to the formation of higher levels of organic hydroperoxides and organic peracids. The peracids are known to be produced in rural air masses where low NO levels allow the buildup of HO_2 and RO_2 species. Methods for measurement of the peracids and hydroperoxides, as well as other organic peroxides, need to be given serious examination as we begin to control NO emissions in an attempt to reduce the urban and regional ozone problems. Since the organic hydroperoxides and peracids are known to have chemiluminescent reaction sensitivities with luminol, similar to hydrogen peroxide, they could be measured with a 10 ppt sensitivity in both air and water by using luminol chemiluminescent detection coupled with separation by high performance liquid chromatography.[51] The use of CIMS using I⁻ can also be useful for the determination of the organic peracids if used in conjunction with chromatography.

Since the PANs are usually higher in larger urban areas, their measurement is important to address how these city plumes are going to impact downwind sites. While the PAN levels in the urban U.S. regions like the Los Angeles air basin and surrounding air shed have dropped significantly in recent years, PAN levels in other areas such as the megacities Mexico City and Beijing have seen high levels of the PANs that can have downwind impacts. Continued measurements in these high population density regions as well as downwind sites are needed to ensure that mitigation strategies for PANs and other species are being effective. With the likelihood of climate change increasing reactive volatile organics such as isoprene and the monoterpenes, the potential formation of PAN, MPAN and other PANs as well as organic peroxides and organic nitrates should also not be ignored. While we know that the PANs can have significant impacts on crops and vegetation, the impacts of organic peroxides and peracids are not well determined and require further study.

The PANs are very soluble in nonpolar organics and may undergo important oxidation reactions on oily diesel soot surfaces as well as carbonaceous aerosols, called "tar balls", from wild fires. PAN has been reported to react with benzo(a)pyrene to form oxidized and nitrated products.[158,159] Hence, the surface reactions of the PANs on carbonaceous aerosols will likely lead to the formation of oxidized and nitrated polycyclic aromatic hydrocarbons (PAHs) that will potentially have high mutagenic activity.[37,158,159] While a number of studies have been conducted on the reactions of PAHs with O_3, NO_2, nitric acid, and OH radical photo-oxidations,[37] the reactions of PANs with PAHs need to be systematically studied in more detail to evaluate their potential in altering PAHs into the highly mutagenic nitro-PAH compounds.

PAN and its analogs have now been characterized, studied, and measured for over 60 years. These fascinating molecules still have many secrets to be determined as atmospheric chemists work with other scientists to expand our fundamental understanding of how the PANs can impact us and how their measurement can help us in our understanding of tropospheric chemistry and its interactions with the biosphere and geosphere. Further measurements and studies of the role of the PANs in both homogeneous and heterogeneous chemistry will be required if we are to continue to improve our understanding of the unusual properties of these highly energetic molecules and their potential impacts on health and the environment.

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Notes

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