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## PEROXYACETYL NITRATE (PAN): HISTORICAL PERSPECTIVE

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## 1. INTRODUCTION

*But if any man undertake to write a history that has to be collected from materials gathered by observation and the reading of works not easy to be got in all places, nor written always in his own language, but many of them foreign and dispersed in other hands, for him, undoubtedly, it is in the first place and above all things most necessary to reside in some city of good note, addicted to liberal arts, and populous; where he may have plenty of all sorts of books, and upon inquiry may hear and inform himself of such particulars as, having escaped the pens of writers, are more faithfully preserved in the memories of men, lest his work be deficient in many things, even those which it can least dispense with. But for me, I live in a little town, where I am willing to continue, lest it should grow less.*

- Plutarch (AD 46?-120)

Interestingly, the place Plutarch suggested is best for writing a history – a city or urban area – is where photochemical smog and other associated air pollutants were first observed.

Peroxyacetyl nitrate (PAN) has an interesting history: a story based on collaboration and discussion among biologists and chemists, which has led to the identification of a unique set of molecules that we are just now beginning to understand.

This paper is an overview of the history of PAN's discovery and its connection to plant damage observed in the South Coast Air Basin of southern California. The focus will be the work done by pioneers in this research area, particularly the long-path infrared spectroscopy and the chromatography with electron capture detection that enabled further exploration of PAN chemistry. The period from the 1950s to the present will be highlighted. Advances addressed include synthetic procedures, measurement techniques, laboratory properties (rates of reaction, ultraviolet photolysis, aqueous solubilities), and field measurements.

The work summarized here has led to the determination that PAN and its analogs play key roles in urban, regional, and global tropospheric chemistry. The phytotoxicity of PAN is discussed, along with its

connections to other key trace species, namely the organic peracids, peroxides, and nitrates.

## 2. BACKGROUND – EARLY AIR POLLUTION PIONEERS

The South Coast Air Basin in southern California was known for its "photochemical smog" during the early 1940s (Stephens 1987). In the late 1940s and early 1950s, farmers began to note serious damage to some crops, especially to romaine lettuce and parsley in the San Gabriel Valley. Rubber products were found to deteriorate at an accelerated rate. Various oxidants were suspected.

John Middleton, a professor of plant pathology at the University of California, and his research group first noted that SO<sub>2</sub> and HF were not the cause of the damage, but that oxidation, not reduction, was at hand (Middleton et al., 1950a,b). As Edgar Stephens pointed out in his paper on smog studies of the 1950s (Stephens 1987), ". . . the state of the art of analytical chemistry in 1945 was inadequate to deal with the problem." The problem was to identify the key oxidants causing the damage by using the analytical tools available at that time.

A perfumery chemist at the California Institute of Technology in Pasadena, Arie J. Haagen-Smit, noted that smog smelled like his terpene laboratory. Ellis Darley of the Citrus Experiment Station at the University of California, Riverside (UCR), began to expose plants with a fumigation system to a wide variety of chemicals, attempting, with little success, to determine the cause of plant bronzing. In 1950, Haagen-Smit fumigated a test plant with the products from the ozonolysis of gasoline vapors and was able to produce the plant pathology (Haagen-Smit 1950). His theory was that partially ozonized hydrocarbons were the cause.

Haagen-Smit followed these studies with photochemical investigations using nitrogen dioxide and hydrocarbons (known to be emitted in vehicle exhaust), which produced ozone and the observed damage to the plants and also replicated rubber damage (Haagen-Smit et al., 1952a,b). Other key aspects of photochemical smog included eye irritation and aerosol production leading to the characteristic brown haze observed in the boundary layer of the South Coast Air Basin. The demonstration that olefins are more reactive than other hydrocarbons in producing smog symptoms led to the pursuit of the sources of these emissions. The two likely candidates were automobiles and oil refineries.

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The real question that arose from the Haagen-Smit studies was the identities of the actual products and which ones triggered smog production. Was ozone the cause, or were other reactive gases responsible for the plant damage and eye irritation observed?

### 3. PEROXYACETYL NITRATE – ITS DISCOVERY

Edgar Stephens, Philip Hanst, Robert Doerr, and William Scott from the Franklin Institute Laboratories in Philadelphia used the first long-path infrared gas cell to identify some of the products. This instrument, constructed in 1954, enabled probing of the infrared spectrum of olefin-NO<sub>x</sub> photolyzed mixtures (Stephens et al., 1956a,b).

A very interesting, unexpected set of infrared bands observed in chemical reactions with 3-methylpentane was very strong when biacetyl was studied (Stephens et al., 1956b). The strong bands at 1740 cm<sup>-1</sup> and 1841 cm<sup>-1</sup> were quite unique, and the molecule responsible was labeled "Compound X" by the Franklin Institute research team. These workers attempted to isolate Compound X from the biacetyl reaction, but a two-drop sample trap exploded violently before they were able to obtain a mass spectrum. The five structures suggested all proved to be incorrect. The correct structure, CH<sub>3</sub>CO-OO-NO<sub>2</sub>, was not really determined until the leading candidate, acetyl nitrate, was synthesized by Edward Schuck and George Doyle and their results were presented in 1959 (Schuck and Doyle, 1959). This work showed similarities with the nitrate but also proved that acetyl nitrate was not identical to Compound X.

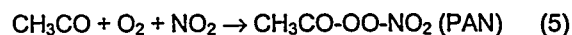
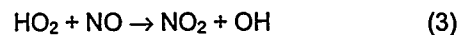
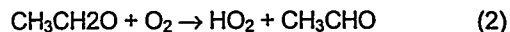
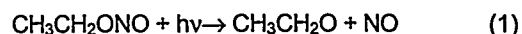
In 1961, Philip Leighton's classic textbook, *Photochemistry of Air Pollution* (Leighton, 1961), did a wonderful job of laying out the series of events that finally led Edgar Stephens to produce the correct structure for Compound X: peroxyacetyl nitrate (PAN). This structure was accepted as correct and finally confirmed by use of isotopically labeled PAN in infrared studies in 1974 (Varetti and Pimentel, 1974).

Further studies initiated in 1958 identified PAN as a key compound causing the bronzing of leaves of petunias and other susceptible plants. These studies, done with O. Clifton Taylor at the UCR Horticulture Department (Taylor et al., 1960), led to the use of gas chromatographic separation of PAN from the photochemical reaction mixture. Further characterization showed that PAN is a potent eye irritant. This collaboration between chemists and plant pathologists led to the observation that PAN and some of its analogs are 10-50 times more toxic than ozone to plants. Indeed, PAN, hydrogen peroxide, and nitrogen dioxide were identified in the first air pollution criteria documents, but they were later omitted from the Clean Air Act of 1970 because of difficulties in measuring and synthesizing standards at that time. This important collaboration at the UCR Statewide Air Pollution Research Center was one of the first to begin interdisciplinary work on air quality

problems and to demonstrate the value of and need for this approach.

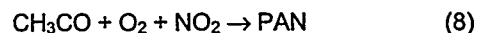
### 4. PANS – SYNTHESIS, PROPERTIES, AND MEASUREMENT

The first routine method for synthesis and isolation of PAN was developed by Edgar Stephens and colleagues at UCR (Stephens and Price, 1973). Ethyl nitrite was photolyzed in air to produce PAN. This chemistry represented the following processes:



The reaction products were gas chromatographed on preparatory-sized columns to separate and collect the PAN with cryogenic trapping. The PAN was placed in large air canisters, diluted in zero air, and stored in a cold room for use in fumigation and chemistry studies. This approach was quite successful, and a number of publications on PAN's toxicity and its chemical and physical properties resulted from use of this photoreactor system (Gaffney et al., 1989; Roberts, 1990).

Explosions reported with use of this system (Gaffney et al., 1989) usually were associated with the condensation of the explosive peroxyacyl nitrates (PANs) in a vacuum or pressure gauge system. Other photochemical production methods employed followed the general photochemical reaction scheme using halogens, where X is Cl or Br:



Similarly, NO<sub>3</sub> radical has been used to produce PAN, with NO<sub>3</sub> being generated by dark reaction of nitrogen dioxide and ozone (Gaffney et al., 1989).

These methods require photochemical apparatus and chromatographic or distillation equipment to separate the PAN for instrument calibration or laboratory study. The fact that PAN can be considered a mixed anhydride of peracetic acid and nitric acid (Roberts, 1990) led Hendry and co-workers to use the strong acid nitration of peroxyacetic acid in aqueous solution to synthesize PAN, followed by the extraction into a normal alkane solvent (Gaffney et al., 1989). Gaffney and co-workers modified the procedure to overcome potential safety hazards of working with PAN dissolved in a high-volatility solvent and recommended that n-tridecane be used for high-

purity PAN and derivative synthesis (Gaffney et al., 1984).

Over the years, advances in the synthesis of PANs have led to improvements in analytical procedures and in determinations of the chemical and physical properties of PANs. Noteworthy are studies of Karen Darnall and James N. Pitts, Jr., who used PAN canister samples obtained from Edgar Stephens to produce high-concentration PAN samples in deuterated chloroform and methylene chloride. These studies led to the understanding that PAN is highly soluble in nonpolar solvents. These researchers used nuclear magnetic resonance (NMR) to study the liquid-phase reactions of this novel oxidant with olefins; studies examining alcohols etc. followed (Gaffney et al., 1989; Roberts, 1990).

Key structural information was obtained by Stephens and by Nicksic and colleagues, who observed products of base hydrolysis that helped to confirm the PAN structure (Nicksic et al., 1966). Later studies with ammonia and amines that showed the formation of oxygen, HONO, and acetamides supported these observations (Wendschuh et al., 1973).

The very simple ultraviolet absorption spectrum of PAN observed by Stephens was confirmed by Senum, Lee, and Gaffney at Brookhaven National Laboratory in the early 1980s (Gaffney et al., 1989; Roberts, 1990). Recent reexamination of the data led to the conclusion that the PAN molecule is not readily photolyzed at altitudes below 5-7 km. In 1984, Tim Wallington, Roger Atkinson, and Arthur Winer at UCR showed the reaction rates with OH to be quite slow. The aqueous-phase solubilities of PAN were examined by Yin-Nan Lee of Brookhaven and found to be 3-5 M atm<sup>-1</sup>; these results were confirmed by Chester Spicer's group at Battelle Columbus Laboratory (Gaffney et al., 1989; Roberts, 1990).

In the meantime, PAN was observed by Stephens and others to decompose thermally to form methyl nitrate, carbon dioxide, and other minor products. What has been determined is that PAN is in thermal equilibrium with NO<sub>2</sub> and the peroxyacetyl radical and that this equilibrium is strongly temperature dependent (Gaffney et al., 1989; Roberts, 1990; Finlayson-Pitts and Pitts, 2000). At the cold temperatures found at higher altitudes and in wintertime PAN is quite stable, while at lower altitudes in the summertime PAN has a fairly short lifetime that depends on the ratio of NO to NO<sub>2</sub> and the abundance of HO<sub>2</sub> radicals, which can remove the peroxyacetyl radical. Hanwant Singh was the first to point out that PAN could act as a means of transporting NO<sub>2</sub> over very long distances and therefore was a globally important molecule and not just an urban air pollutant (Singh, 1987).

The first measurements of PAN were made in the laboratory by using long-path infrared techniques that worked reasonably well at the higher concentrations

found in the Los Angeles air shed (Tuazon et al., 1978; Hanst et al., 1982). However, the infrared instruments of the early 1960s were clearly not capable of routine monitoring of PAN. With the invention of the electron capture detector (ECD) by James Lovelock, Ellis Darley and co-workers in 1963 developed a method for PAN analysis that has been used since then quite successfully (Darley et al., 1963). Many others have used a similar approach that employs a nonpolar column to separate PANs from the various other ECD-sensitive gases (oxygen, Freons, organic nitrates, etc.) (Roberts, 1990). Used in the 1960s and 1970s to monitor PAN in the air in the Riverside area, this method found very high values of the phytotoxin (20-50 ppb). In 1974, James Lovelock and Stewart Penkett used a similar analysis system to measure PAN off the coast of England, observing a level of 2 ppb and alerting the community to PAN's ubiquity (Lovelock and Penkett, 1974).

Calibration of the above instruments was usually accomplished by using base hydrolysis to yield acetate and nitrite. These methods had some difficulties, and thermal decomposition to NO<sub>2</sub> and direct measurement with a chemiluminescent nitrogen oxides monitor have seen more use in recent years (Roberts, 1990).

Other approaches were examined in the mid-1980s, when luminol chemiluminescence was observed to occur with PAN, as well as with NO<sub>2</sub>. Two groups, Gaffney's at Los Alamos and Stedman's at the University of Denver, demonstrated in 1986 that chromatography works for this application. Stedman published the method in 1988, documenting a five-minute analysis for PAN with a packed column (Burkhardt et al., 1988). Gaffney and Marley reported a modification of this method that employs fast capillary chromatography to obtain 30-second time resolution for PAN and its analogs and also gives measurements of NO<sub>2</sub> (Gaffney et al., 1998).

Mass spectrometry of PAN was first reported by Ron Steer, Karen Darnall, and James N. Pitts, Jr., in electron impact mode in 1969. The chemical ionization spectrum was reported in 1976 by Chris Pate, Jerry Sprung, and Pitts, who used one of the first Finnigan gas chromatograph-mass spectrometer systems equipped with this capability. Because of its very large ECD cross section, the negative-ion mass spectrometric sensitivity for PAN is quite high. This was predicted in 1989 to be a reasonable approach (Gaffney et al., 1989), and it has been pursued in recent years by Chester Spicer of Battelle Columbus and by Hiroshi Tanimoto and Hajime Akimoto in Japan.

Because of its rather undistinctive ultraviolet spectrum, direct ultraviolet absorption spectroscopy has not been used for PAN analyses. NMR has been used for laboratory studies of PAN, and that method, along with circular internal reflectance infrared spectroscopies, may be important in future studies of PANs in solution.

## 5. FUTURE NEEDS – PANS, PERACIDS, PEROXIDES, NITRATES

Since the initial work at the Franklin Institute in Philadelphia and the original observation of PANs in Los Angeles photochemical smog, PANs have been measured in every corner of the world (Gaffney et al., 1989; Roberts, 1990). Measured PANs include the commonest (PAN), as well as peroxypropionyl nitrate (PPN) and peroxybutyryl nitrate (PBN). Other PANs deemed important include those derived from isoprene oxidation (MPAN) and aromatics (PBzN) (Gaffney et al., 1989; Roberts, 1990).

PANs are strongly connected with peracids by the following reactions in low-NO conditions:



The peracids are known to be produced in rural air masses, where NO levels allow the buildup of HO<sub>2</sub>. However, methods for measurement of these species, along with other organic peroxides, need to be given serious examination, especially as we begin to control NO<sub>x</sub> emission levels to reduce the urban and regional ozone problems.

The PAN levels in urban U.S. regions like the Los Angeles air basin and surrounding air shed have dropped significantly in recent years. Levels are rarely observed above 5 ppb, a tenfold reduction compared to the 1960s and 1970s. However, in other areas of the world, PANs can also be produced in large quantities if NO<sub>x</sub> levels and the reactive hydrocarbon species leading to PAN and ozone formation are not controlled. Indeed, in Mexico City we recently measured total PANs of 40 ppb by gas chromatography with ECD (Gaffney et al., 1999).

Another concern is that the production of PANs from aldehydes is a direct process, as noted in the early synthetic procedures. The use of oxygenated fuels that lead to increased emissions of aldehydes or aldehyde precursors such as ethanol or methyl-*t*-butyl ether should continue to be accompanied by assessment for PANs and other oxidants (Gaffney et al., 1997; Gaffney et al., 1999). In addition, the potential for long-range transport of PANs on continental scales and for PANs to function as a source of regional ozone should not be forgotten (Singh, 1987; Gaffney et al., 1993; Gaffney et al., 1999).

The PANs are indicators of peroxy radical activity and are indicative of the potential importance of organic nitrates. PAN decomposition is known to lead to methyl nitrate formation, which is fairly stable in the atmosphere. The nighttime thermal decomposition of methyl nitrate may be an important source of radicals for the oxidation of NO to NO<sub>2</sub> and for the formation of HONO. Our understanding of the

chemical toxicity and radiative behavior of these compounds needs to be evaluated. A number of research groups, notably Paul Shepson's at Purdue University (Roberts, 1990), are beginning to explore the organic nitrates in detail by using methods mentioned above.

Peroxy nitrates might play important roles in the transport of NO<sub>2</sub> under cold conditions:



These species were first examined by Edward Edney, John Spence, and Philip Hanst at the U.S. Environmental Protection Agency laboratories. Because of their short lifetimes at room temperature, the compounds were assumed not to act as key storage modes in the lower atmosphere (Edney et al., 1979). However, at middle latitudes in the wintertime they may have lifetimes that approach days, and, like PAN (depending upon NO, HO<sub>2</sub>, and NO<sub>2</sub> levels), they might be reformed to actively transport NO<sub>2</sub> and also tie up peroxy radicals that would lead to ozone formation.

The PANs are known to be quite sensitive to walls in laboratory studies and therefore are likely to react on aerosol surfaces. PANs are very soluble in nonpolar organics and indeed may undergo important oxidation reactions on soot surfaces, leading to the formation of oxidized and nitrated polynuclear aromatic hydrocarbons potentially having high mutagenicity (Finlayson-Pitts and Pitts, 2000).

We have known about these fascinating molecules for over 40 years, but our fundamental understanding and ability to measure PANs is just now beginning to expand. Interestingly, many physical chemists are beginning to explore the unusual properties of these highly energetic molecules.

The future of PAN chemistry, opened to us by Edgar Stephens and his colleagues, looks bright, and its further exploration should lead us to a much better understanding of the key oxidation reactions occurring in the troposphere.

## 6. ACKNOWLEDGMENTS

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