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Ecological Research Series

A STUDY OF PAN-TYPE COMPOUNDS AND RELATED PRECURSORS

Environmental Sciences Research Laboratory
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THE STRUCTURE OF PAN-TYPE COMPOUNDS AND RELATED PRECURSORS

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SECTION I

BACKGROUND AND INTRODUCTION

Peroxyacetyl nitrate, known by the acronym, PAN, is the sole member of an unusual new and novel class of compounds that have the proposed general formula $RC(O)OONO_2$ where R is a alkyl or aryl group. PAN was first discovered as an air pollutant[1] in 1956, although at that time its chemical formulation was not understood. It is the agent responsible for eye irritation and extensive crop damage. Other hydrocarbon members of this group were either discovered later in ambient air[2] or reported from synthetic mixtures.[3]

Most of the work concerning these compounds was performed using impure mixtures, for only in a few cases were these compounds examined after being obtained initially in a pure state. Even though PAN has been discovered about twenty years ago, fundamental information about it is very scant and even less is known about its congeners.

The research performed under the present grant indicates that acylated compounds present in ambient air are sufficient for the formation of PAN-type compounds. Also, the decomposition of PAN is more complex than reported previously because hydrocarbons and oxygen are formed in addition to the reported products, methyl nitrate and carbon dioxide and varying amounts of nitromethane.

PAN has been synthesized in high yield and in the quantities required for characterization and testing. This compound has been obtained in a very pure state using preparative g.l.c.

SECTION II

APPARATUS

VACUUM AND PURIFICATION APPARATUS

A vacuum apparatus and preparative gas chromatograph (with a GOW MAC thermistor detector) were constructed specifically for the manipulation and purification of PAN-type compounds. The chromatograph and vacuum system are interconnected so that the PAN compounds can be passed from one part of the system to the other with minimum manipulation. Vacuum stopcocks coated with KEL-F grease were used throughout the system. Pressures were measured using calibrated Wallace & Tiernan and Acco gauges. Reactors were fabricated from Pyrex. Plexiglass shielding was placed between the apparatus and the operators.

THE A-H6 MERCURY-ARGON SOURCE

Because of a number of factors, chief among them being economical operation, the Illumination Industries 1000-watt A-H6 lamp is employed as an ultraviolet source. Another factor that prompts its use is the high ratio of ultraviolet to total (radiant) energy.

SECTION III

SYNTHESIS AND PURIFICATION OF PAN

SYNTHESIS

Although there are five reported synthetic methods for PANs,[1] most are the more intellectual curiosities than realistic synthetic routes to these compounds, and there were no procedures that would conveniently produce the quantities of pure PAN required for this research. However, two previously reported methods were selected for scale-up. The first was based on a report by C. S. Tuesday[2] involving the "dark" reaction between acetaldehyde and nitrogen pentoxide in the presence of trace amounts of oxygen.

$$CH_3CHO + N_2O_5 \xrightarrow{\text{trace } O_2} CH_3C(O)OONO_2 \qquad (1)$$

The reactant concentration in this case was in the ppm range. But on scale-up to the pph (parts per hundred) range, an entirely different reaction took place, i.e.,

$$CH_3CHO + N_2O_5 \rightarrow CH_3CH(ONO_2)_2. \qquad (2)$$

When this gem-dinitrate was first detected, there was some question concerning its identity. Was it some sort of PAN-type compound? Was this compound important in air pollution chemistry? After an examination of the nature of this compound as well as its trifluoromethyl congener and the conditions required for the formation of compounds of this type, it was concluded that compounds of this type are not likely to be present in contaminated air. A manuscript regarding these compounds has been accepted for publication in the Journal or Organic Chemistry, (see Section VII).

Upon concluding that this synthesis was not leading to PAN compounds on increasing the reactant concentrations, the photolysis of biacetyl in the presence of NO_x and oxygen was then explored. This procedure was scaled-up by increasing the reactant concentrations to the several torr pressure range. In a typical reaction, biacetyl (1-1/2 torr) and NO_2 (4 torr) were loaded into a three-liter Pyrex bulb (7 in. diameter) and then oxygen was introduced. The partial pressure of the latter was 600 torr. The bulb was floated on an ice bath and cold water from the bath was flowed over the top of the bulb so that it was completely covered with cold water. The temperature of the bulb during photolysis never exceeded 3°C. The UV photo source was in Illumination Industries A-H6 lamp described above, and the irradiation period was 150 minutes. The distance between the lamp and the bottom of the reaction bulb was 14 inches. Over 5 mℓ of the gas (equivalent at STP) was produced from this run. The yield was in excess of 80%. The results suggest the reaction,

$$CH_3C(O)C(O)CH_3 + NO_2 \xrightarrow[h\nu]{O_2} CH_3C(O)OONO_2. \quad (3)$$

This process bares some similarities to that reported by Hanst[3] because the intermediate specie in both cases is probably $CH_3C(O)\cdot$. On further reaction the acylperoxy radical is formed and the terminating step involving NO_2 yields PAN.

PURIFICATION

The crude PAN was first purified by vacuum line fractionation. It was passed slowly through traps set at -80 and -196°. The PAN along with unreacted biacetyl was retained in the former, and methyl nitrate, carbon dioxide and the excess nitrogen dioxide were held in the latter. This procedure was followed by a gas chromatographic purification. The column used was a 5-ft, 1/4-in. O.D. Pyrex tube containing a Fluoropak 80 support with a KEL-F grease (10%) stationary phase. The

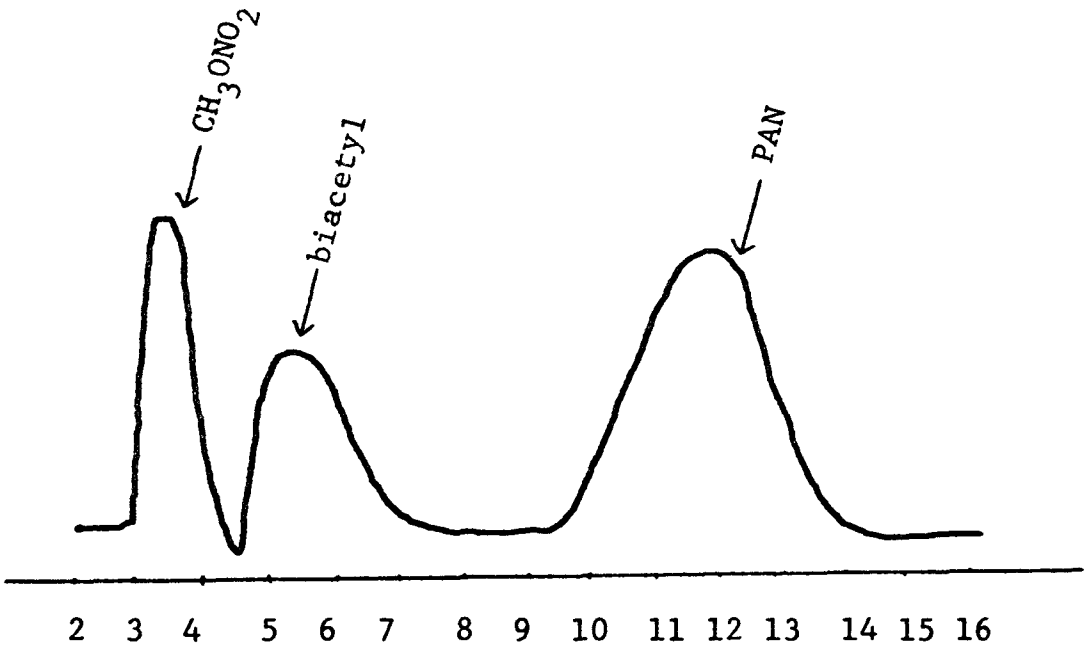


Figure 1. Chromatogram of PAN.

chromatograph is shown below in Figure 1. The shape of the curve labelled "PAN" is influenced by its presence in the inlet system as a liquid. The cooling effect of sweeping it out in a helium stream is probably the reason why its topology differs from the usual curves.

PROPERTIES

The average gas density molecular weight of PAN was found to be 128 g/GMV (calculated: 121) and its melting point is -48.5 $\pm$ 0.5°. Its vapor pressures were measured between 0.20 and 55.6°; at the higher temperature decomposition was observed. In this temperature range, the vapor pressure of PAN obeys the relationship $\log P_{(torr)} = -1991/T + 8.161$. Its extrapolated boiling point is 103.9° and its equilibrium vapor pressure at 24.25° is 28.7 torr. Its latent heat of vaporization is 9.111 kcal/mole and its entropy of vaporization is 24.2 e.u. calculated from the vapor pressure equation.

SECTION IV

DECOMPOSITION OF PAN

PAN at ca. 10 torr pressure was allowed to decompose in several different Pyrex containers as well as in a Pyrex infrared cell containing sodium chloride windows. The Pyrex containers contained either Teflon stopclocks or glass stopcocks coated with KEL-F grease. It was found that the nature of decomposition did depend somewhat on the container and its prior history. However, the products (in order to decreasing abundance) were found to be CO_2, CH_3ONO_2, CH_3NO_2, O_2, CH_4, C_2H_6 and smaller amounts of unidentified substances. The total carbon nitrogen and oxygen are well in balance. Interestingly, no NO_2 was found. The products were identified by their infrared and/or mass spectra. These studies are continuing in order to more clearly elucidate the decomposition of PAN. This data as well as the kinetic data below must be regarded as preliminary, and therefore any conclusions drawn are tentative.

SECTION V

KINETIC STUDY

The kinetics of decomposition were measured by the method used by P. Hanst for the decomposition of dimethylperoxide.[4] The infrared cell was charged with PAN at an initial pressure of 10.47 torr and the cell was kept at a 28 $\pm$ 0.5° temperature and monitored periodically.

The kinetic data plotted as f(p) (the pressure of PAN) vs time is found in Figure 2. Zero and first-order kinetics deviate more from linearity than do second- and third-order. The latter two are nearly linear and are about equally close (Figure 3). The results are not surprising because the number and kinds of products indicate the decomposition of PAN is complex and probably involved more than one process (see below for speculative discussion). The correlation coefficients also corroborate that the plots for second- and third-order relationships closely describe the kinetics of decomposition of PAN under the conditions to which it was subjected (see Table 1). A second-order rate constant, $k = 2.33 \times 10^{-4}$ $torr^{-1}$ min^{-1}, is calculated from the least squares straight-line parameters.

Table 1

CORRELATION COEFFICIENTS
(r)

0^{th} order :	$\|r\| = 0.93943$
1^{st} order :	$\|r\| = 0.978255$
2^{nd} order :	$\|r\| = 0.997862$
3^{rd} order :	$\|r\| = 0.997061$

2^{nd} order specific rate constant = 2.33×10^{-4} $torr^{-1}$ min^{-1}

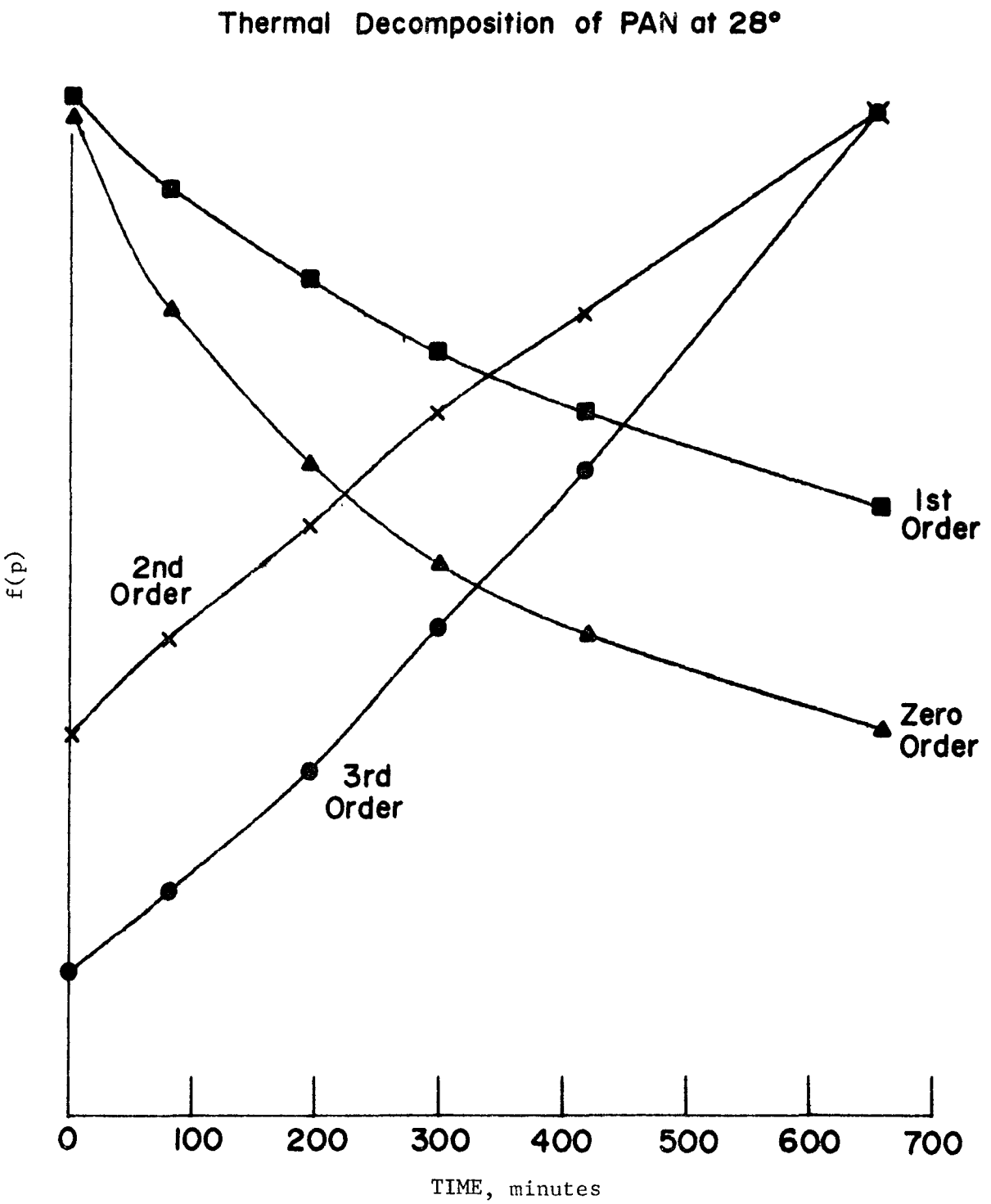


Figure 2. Thermal decomposition of PAN at 28°.

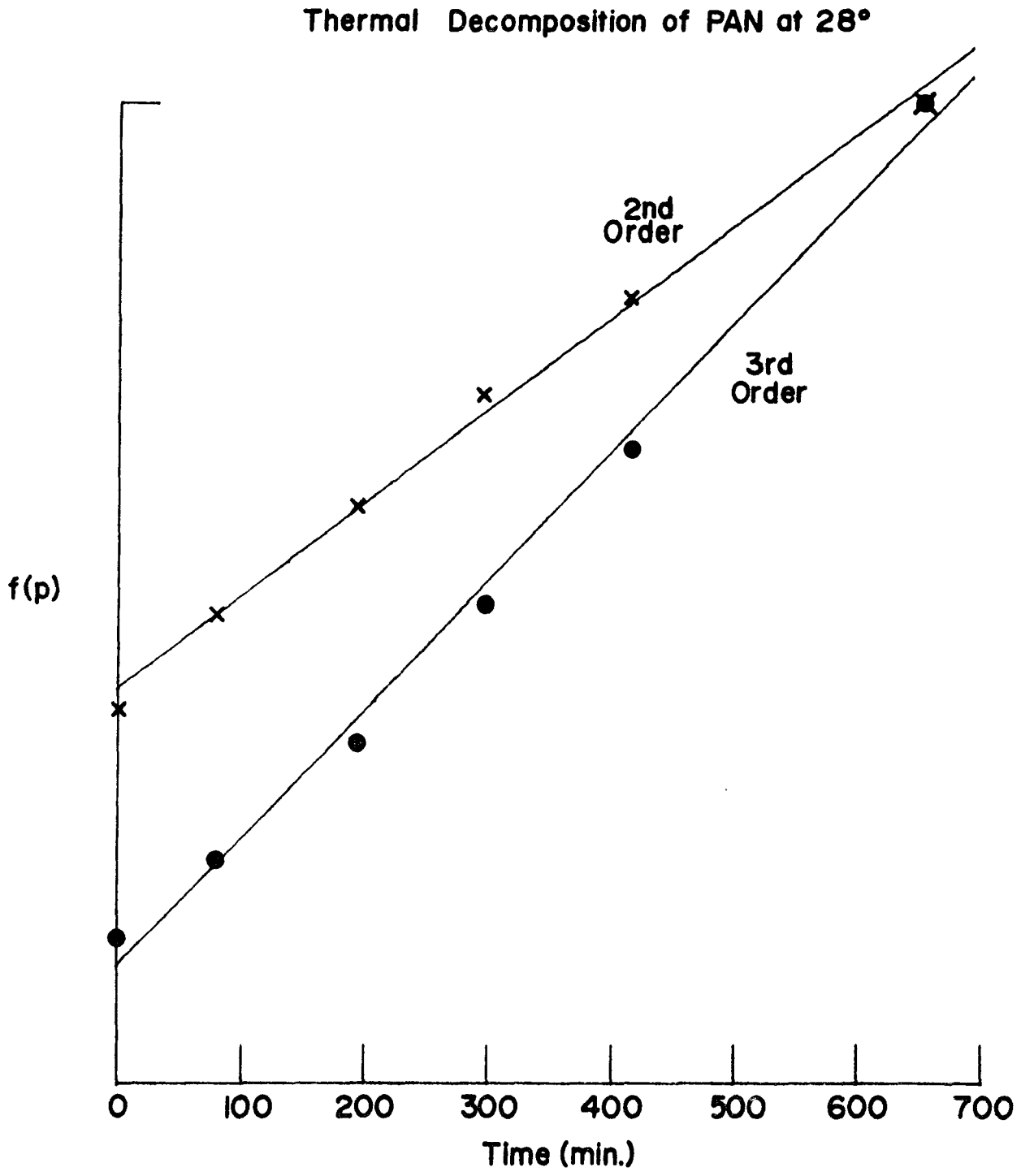
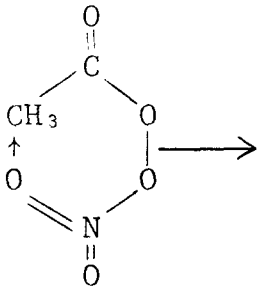

Thermal Decomposition of PAN at 28°
2nd Order
3rd Order
f(p)
0
100
200
300
400
500
600
700
Time (min.)

Figure 3

SECTION VI

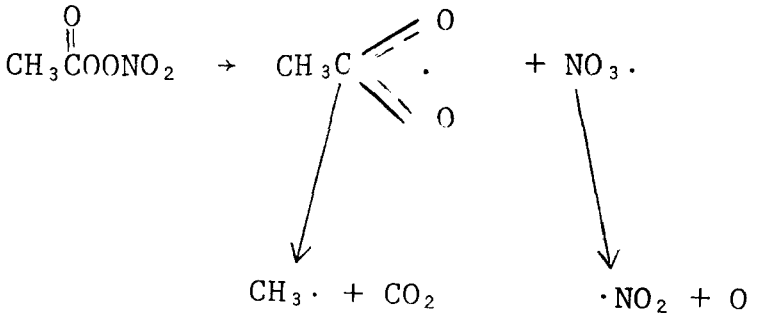
RECOMMENDATIONS FOR FUTURE RESEARCH

The kinetic results indicate that there is probably more than one mode for the decomposition of PAN and that the resultant order ($3 < x < 2$) is the sum of the different rate controlling reactions. It was previously reported that the decomposition of PAN in dilute mixtures produces only carbon dioxide and methyl nitrate by a cyclic intermediate and variable amounts of nitromethane.[3]



$$\longrightarrow CH_3ONO_2 + CO_2 \quad (4)$$

Under conditions of the experiments used in the present research the decomposition is more complicated. The above mechanism may indeed occur, but the results can also be interpreted in terms of another scheme which more comprehensively explains the products.



$$(5)$$

$$CH_3\cdot + NO_3\cdot \rightarrow CH_3ONO_2 \quad (6a)$$

$$CH_3\cdot + O + NO_2 \rightarrow CH_3ONO_2 \quad (6b)$$

$$CH_3\cdot + NO_2 \rightarrow CH_3NO_2 \quad (6c)$$

$$CH_3\cdot \xrightarrow{\text{dimerization}} C_2H_6 \quad (6d)$$

$$CH_3\cdot \xrightarrow{\text{H abstr}} CH_4 \quad (6e)$$

It is likely that the O-O single bond is the weakest bond in the molecule, so that the initiation step is the fission of the peroxide band. In CH_3OOCH_3, this bond energy is only ca. 35 kcal/mole. This bond energy is likely to be less in the case of PAN. Most simple unimolecular decompositions (A → B + C) follow the second-order rate law, although, acccording to the Lindemann theory, it is entirely possible for such reactions to be first-order. This is the case for the decomposition of CH_3OOCH_3.[4]

In order to more clearly understand the mechanism of the decomposition of PAN, ^{17}O labelling studies need to be made. NMR, infrared, Raman, EPR, and mass spectral techniques can be used to characterize the products and, therefore, it is likely that a determination can be made of the modes of decomposition.

SECTION VII

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4. Hanst, P. L., and Calvert, J. G., J. Phys. Chem., 63, 104 (1959).

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16. ABSTRACT

This work was undertaken to search for preparative procedures for PAN, to study its structure and properties, and to ellucidate more clearly the nature of its formation and decomposition. An ideal preparative procedure for PAN had been found, high yields of PAN have been obtained, and a statisfactory preparative g.l.c. technique has been adapted for its purification. The results of the synthetic studies tend to confirm prior conclusions, but the decomposition of PAN does not proceed entirely the way previously described.

The results from this research indicate that the acyl and acylperoxy radicals are precursors to PAN in photochemical environments containing acyl derivatives, NO_x, and oxygen. In contrast to prior investigations, however, several decomposition products of PAN have been found that were not previously reported, that is, hydrocarbons and oxygen have been found as products in the present study. Additional characterization data has been obtained that corroborate the structure established for PAN.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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