

PEROXYACETYL NITRATE (PAN) IN THE UNPOLLUTED ATMOSPHERE:
 AN IMPORTANT RESERVOIR FOR NITROGEN OXIDES

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Abstract. Based on the measured atmospheric distributions of ethane and propane (at midlatitudes in the northern hemisphere) and a simplified mechanism for their oxidation, it is predicted that acetaldehyde, acetone, and PAN [$\text{CH}_3\text{C}(\text{O})\text{OONO}_2$] are ubiquitous components of the troposphere and the lower stratosphere. Average acetaldehyde concentrations (from ethane oxidation) of 22 parts per trillion (ppt), 3 ppt, and 7 ppt; average acetone concentrations (from propane oxidation) of 111 ppt, 15 ppt, and 3 ppt and average PAN concentrations of 17 to 34 ppt, 90 to 360 ppt, and 40 to 85 ppt are estimated for the lower troposphere (~ 2 km), upper troposphere (~ 9 km), and the lower stratosphere (~ 15 km), respectively. These calculations suggest that in the troposphere, nitrogen oxides (NO_x) contained in their organic form may be as much or more abundant as their inorganic form. This organic form of reactive nitrogen is in chemical equilibrium [$\text{CH}_3\text{C}(\text{O})\text{OONO}_2 \rightleftharpoons \text{CH}_3\text{C}(\text{O})\text{OO} + \text{NO}_2$] with inorganic NO_2 and acts as reservoir of inorganic NO_x . Measurement methods for PAN are currently available to verify these predicted results.

Introduction

In the unpolluted atmosphere, the chemical role of methane is widely recognized (Levy, 1974). Recently, however, it has been found that other hydrocarbons, such as ethane, are also ubiquitously distributed, although at levels that are about three orders of magnitude lower than methane (Singh et al., 1979a). The role of nonmethane hydrocarbons in CO formation (Chameides and Cicerone, 1978; Hanst et al., 1980) and as a possible scavenger of Cl atoms in the lower stratosphere (Singh, 1977; Rudolph et al., 1980; Hanst, 1981) has been suggested. The object of the present study is to point out that peroxy nitrate formation can also give to the nonmethane hydrocarbons an important role in the transport of combined nitrogen through the atmosphere. Peroxyacetyl nitrate (PAN) is well known as a product of reactions among hydrocarbons and nitrogen oxides in polluted urban atmospheres (Stephens, 1969). The compound is also found at ground level in rural air, but at concentrations much lower than in the urban areas (Singh et al., 1979b).

In this study we conduct a preliminary but quantitative analysis of the oxidation of ethane and propane to suggest that despite their low abundance, these nonmethane hydrocarbons can form organic nitrogen compounds in relatively large concentrations in the unpolluted atmosphere.

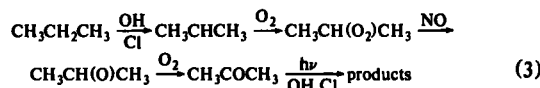
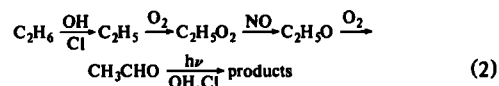
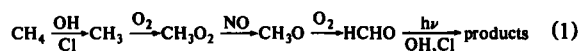
Analysis

Table 1 summarizes the atmospheric conditions that apply to the midlatitude region in the northern hemisphere. For the purposes of this analysis, three levels representative of the lower troposphere (~ 2 km), upper troposphere (~ 9 km), and the lower stratosphere (~ 15 km) are chosen. Based on available measurements, ethane (C_2H_6) and propane (C_3H_8) are found to be the dominant nonmethane hydrocarbons. In the lowest troposphere, other hydrocarbons (e.g., butanes, ethylene, isoprene) may also be important (Rudolph et al., 1979). However, their ubiquitousness in other parts of the troposphere has not yet been fully established. Although we limit the analysis of this study to ethane and propane, the presence of other hydrocarbons would further strengthen the conclusions of this study.

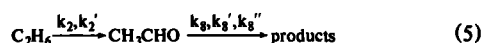
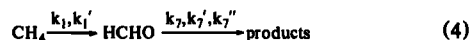
Methane data in Table 1 are taken from Hudson and Reed (1979). Ethane and propane concentrations are from Rudolph et al. (1980). Formaldehyde data are available from one-dimensional models and have been verified by a limited number

of measurements (Ehhalt and Tönnissen, 1980). NO_x data are based on the recent work of Kley et al. (1981) and for the stratosphere are taken from Hudson and Reed (1979). Daytime average NO_2/NO ratios are derived from the global photochemical model of Liu (1981). OH levels chosen here (daily average) are consistent with the best estimates of OH from models: Direct OH measurements suggest higher OH levels than those used in Table 1. Levels higher than those listed in Table 1 make the results of this study correspondingly more important. Chlorine atom concentrations have not been measured below 30 km. The Cl atom concentration listed in Table 1 is derived from a one-dimensional model (Rudolph et al., 1980). Rate constant symbols and data utilized in this study are presented in Table 2.

Oxidation of ethane is initiated when an OH or Cl radical abstracts hydrogen. The C_2H_5 radical is converted to a peroxide radical and then to acetaldehyde (CH_3CHO). These steps are similar to those in the oxidation of CH_4 to formaldehyde. The propane oxidation also proceeds along the same lines but the OH attack occurs at the middle carbon leading to the formation of acetone (CH_3COCH_3).



Overall we can summarize these sequences as follows:



Reactions (4), (5), and (6) are so similar that CH_3CHO and CH_3COCH_3 levels can be estimated by knowing the rate constants in these reaction sequences, as shown in Table 2, and the abundance of HCHO that has been relatively well characterized from 1-D models and limited measurements (Table 1). As a first approximation, the concentration of CH_3CHO from ethane and CH_3COCH_3 from propane can be estimated as follows:

$$[\text{CH}_3\text{CHO}]\text{C}_2\text{H}_6 = \left[\frac{k_2(\text{C}_2\text{H}_6)(\text{OH}) + k_2'(\text{C}_2\text{H}_6)(\text{Cl})}{k_1(\text{CH}_4)(\text{OH}) + k_1'(\text{CH}_4)(\text{Cl})} \right] \left[\frac{[\text{HCHO}]}{p_1} \right] \quad (7)$$

$$[\text{CH}_3\text{COCH}_3]\text{C}_3\text{H}_8 = \left[\frac{k_3(\text{C}_3\text{H}_8)(\text{OH}) + k_3'(\text{C}_3\text{H}_8)(\text{Cl})}{k_1(\text{CH}_4)(\text{OH}) + k_1'(\text{CH}_4)(\text{Cl})} \right] \times \left[\frac{[\text{HCHO}]}{p_2} \right] \quad (8)$$

where

$$p_1 = \frac{k_8(\text{OH}) + k_8'(\text{Cl}) + k_8''}{k_7(\text{OH}) + k_7'(\text{Cl}) + k_7''} \quad (9)$$

$$p_2 = \frac{k_9(\text{OH}) + k_9'(\text{Cl}) + k_9''}{k_7(\text{OH}) + k_7'(\text{Cl}) + k_7''} \quad (10)$$

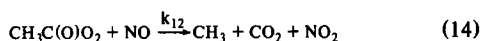
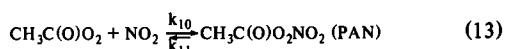
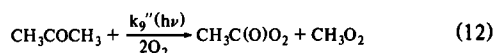
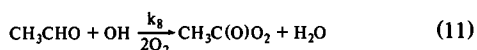
The quantities p_1 and p_2 essentially account for the fact that the CH_3CHO and CH_3COCH_3 decay rates are slower than HCHO. It is noted here that a small part of OH attack in pro-

TABLE 1. Atmospheric Abundance of Trace Species of Interest at Selected Elevations

Atmospheric Region	Temperature (K)	Trace Species Concentrations (ppb)						Free Radical Concentrations molec/cm ³	
		CH ₄	C ₂ H ₆	C ₃ H ₈	HCHO	NO _x	Average NO ₂ /NO ratio (daytime)	OH	Cl
Lower troposphere (~ 2 km)	285	1600	1.5	0.25	0.4	0.015	2.0	10 ⁶	(~ 0)
Upper troposphere (~ 9 km)	240	1600	1.5	0.20	0.04	0.15	0.5	5 × 10 ⁵	(~ 0)
Lower stratosphere (~ 15 km)	215	1400	0.3	0.01	0.035	0.6	0.5	5 × 10 ⁵	5 × 10 ³

pane can occur at the end carbon, leading largely to the formation of propionaldehyde. We have chosen to multiply the estimated CH₃COCH₃ concentration (Eq. 8) by 0.8 to correct for this minor branching as suggested by Hanst (1981).

The intermediates acetaldehyde and acetone are the precursors of PAN. Once CH₃CHO is formed it is either photolyzed or can react with OH or Cl radicals. The photolysis reaction results in a CH₃O₂ radical formation that can eventually form HCHO. In the case of acetaldehyde, the reaction with OH is of most interest. Photolysis is the key reaction for acetone, reaction with OH being too slow. The following sequence is known to take place (Cox and Roffey, 1977; Hendry and Kenley, 1977):



Assuming a steady state for PAN, the following concentration expression can be derived:

$$\text{PAN} = \left[\frac{k_{10}}{k_{11}k_{12}} \right] \times \left[\frac{k_8(\text{CH}_3\text{CHO})(\text{OH}) + k_9''(\text{CH}_3\text{COCH}_3)}{1 + \left[\frac{1}{k_{11}} + \frac{k_{10}(\text{NO}_2)}{k_{11}k_{12}(\text{NO})} \right] (k_{13}(\text{OH}) + k_{13}'(\text{Cl}) + k_{13}'')} \right] \left[\frac{\text{NO}_2}{\text{NO}} \right] \quad (18)$$

A number of observations regarding (11)–(17) must be made. First, the reactions CH₃CHO + Cl, CH₃COCH₃ + OH, and CH₃COCH₃ + Cl, even if they were to form CH₃C(O)O₂ radicals, are slow and can be neglected (Table 2). Similarly, CH₃C(O)O₂ + HO₂ is unimportant. The steep temperature dependence of k₁₁ plays a dominant role in the atmospheric distribution of PAN. Temperature-dependent rate constants for k₁₀ and k₁₂ are not available. However, the ratio k₁₀/k₁₂ [eq. (18)] is expected to be relatively temperature-independent.

The series of reactions (11) through (17) have no analogues in the oxidation of HCHO. The compound peroxy formyl nitrate has never been observed. Formyl radicals do not react with oxygen to form peroxyacyl radicals. Instead, the hydrogen is removed, yielding CO and HO₂ radicals (Hanst and Gay, 1977). Eq. (18) was independently verified at 300K for the conditions operating within a smog chamber (Singh et al., 1979c).

Expression (18) is derived assuming a stationary atmosphere. For the upper troposphere, exchange with the lower troposphere could provide an important removal mechanism because of the rapid decomposition of PAN in the lower troposphere. Thus the upper-tropospheric calculations have been performed with—as

well as without—this sink. A 60-day exchange rate (k_e = 1.9 × 10⁻⁷ sec⁻¹) with the lower troposphere is utilized:

$$\text{PAN (upper troposphere)} \xrightarrow{k_e} \text{Loss (lower troposphere)} \quad (19)$$

Results and Discussion

From the data provided in Tables 1 and 2, equations (7), (8), and (18) can be readily solved to obtain an estimate of the expected concentrations of CH₃CHO, CH₃COCH₃, and PAN. These results for the three important regions of the atmosphere are summarized in Table 3. It is clear that ethane alone can produce about 20 ppt of acetaldehyde in the lower troposphere. In a manner similar to HCHO, a rapid drop with altitude is observed in the troposphere. The increase in CH₃CHO in the lower stratosphere is attributable to the important role of Cl atoms in the oxidation of ethane. The trend for CH₃COCH₃ is very similar. Its much higher concentration at the lower troposphere is largely attributable to its much slower loss rate.

The distribution of PAN in the atmosphere is found to be dramatically different from that of the intermediate products acetaldehyde and acetone. PAN levels of 17 ppt, 360 ppt, and 85 ppt are estimated for the lower troposphere, upper troposphere, and the lower stratosphere, respectively. When the exchange process described in reaction (19) is considered, PAN concentrations in the upper troposphere decrease to about 90 ppt. The PAN distribution (Table 3) is largely a result of the highly temperature-dependent sinks of PAN. In the lower troposphere, the thermal decomposition of PAN (reaction k₁₂) is extremely rapid and is the only important sink. This thermal loss of PAN becomes relatively unimportant at the colder temperatures of the upper troposphere and the lower stratosphere. The UV absorption cross section of PAN is not highly reliable (Stephens, 1969) but photolytic loss of PAN below the ozone layer is relatively small (k₁₃'). PAN + OH and PAN + Cl reactions provide the important chemical removal processes at these higher altitudes. For the upper troposphere, exchange with the lower troposphere is an important removal process.

Estimated levels of PAN shown in Table 3 clearly point to the potential importance of organic nitrogen compounds in the atmosphere. Comparison of NO_x data from Table 1 with PAN levels shows that in the troposphere NO_x contained in its organic form may be as much or more abundant as the inorganic form. In the middle troposphere the reactive organic nitrogen could be 50 to 100 percent of the inorganic reactive nitrogen (NO_x + HNO₃). In the lower stratosphere only 10 to 15 percent of all nitrogen oxides may exist in their organic form. At 20 km, PAN levels are estimated to be a quarter of 15-km levels.

The calculations in this study have been made for those conditions listed in Table 1. The suggested higher OH levels and the presence of other hydrocarbons (Rudolph et al., 1979) could easily double the estimated CH₃CHO, CH₃COCH₃, and PAN concentrations in the lower troposphere. In addition, transport from polluted areas may also provide an additional source (Hendry and Kenley, 1977; Crutzen, 1979). Chlorine atom levels in the lower troposphere could be a factor of 2 to 4 lower than those utilized in Table 1 (Rudolph et al., 1980). This could reduce estimated PAN levels in the lower stratosphere by a factor of about 2 (~ 40 ppt). The effect is not linear because Cl atoms are both an important source as well as a sink for PAN. Part of this reduction could also be compensated by a higher

TABLE 2. List of Rate Constants Used in This Study

Reaction	Rate Constants*	Source†
$\text{CH}_4 + \text{OH} \rightarrow$	$k_1 = 2.4 \times 10^{-12} \exp (-1710/T)$	Hudson and Reed (1979)
$\text{CH}_4 + \text{Cl} \rightarrow$	$k_1' = 9.9 \times 10^{-12} \exp (-1359/T)$	Hudson and Reed (1979)
$\text{C}_2\text{H}_6 + \text{OH} \rightarrow$	$k_2 = 1.86 \times 10^{-11} \exp (-1230/T)$	Greiner (1970)
$\text{C}_2\text{H}_6 + \text{Cl} \rightarrow$	$k_2' = 7.3 \times 10^{-11} \exp (-61/T)$	Manning and Kurylo (1977)
$\text{C}_3\text{H}_8 + \text{OH} \rightarrow$	$k_3 = 1.82 \times 10^{-11} \exp (-675/T)$	Greiner (1970) and Darnall et al. (1978)
$\text{C}_3\text{H}_8 + \text{Cl} \rightarrow$	$k_3' = 1.36 \times 10^{-10} \exp (+44/T)$	Lewis et al. (1980)
$\text{HCHO} + \text{OH} \rightarrow$	$k_7 = 1.1 \times 10^{-11}$	Stief et al. (1980)
$\text{HCHO} + \text{Cl} \rightarrow$	$k_7' = 9.2 \times 10^{-11} \exp (-68/T)$	Hudson and Reed (1979)
$\text{HCHO} \xrightarrow{h\nu}$	$k_7'' = 2.8 \times 10^{-5}^\ddagger$	Hendry et al. (1980)
$\text{CH}_3\text{CHO} + \text{OH} \rightarrow$	$k_8 = 1.5 \times 10^{-11}$	Atkinson et al. (1979)
$\text{CH}_3\text{CHO} + \text{Cl} \rightarrow$	$k_8' = 1.1 \times 10^{-10}$	Estimated from HCHO data
$\text{CH}_3\text{CHO} \xrightarrow{h\nu}$	$k_8'' = 1.4 \times 10^{-5}^\ddagger$	Hendry et al. (1980)
$\text{CH}_3\text{COCH}_3 + \text{OH} \rightarrow$	$k_9 = k_2$	Cox et al. (1980), Atkinson (1981)
$\text{CH}_3\text{COCH}_3 + \text{Cl} \rightarrow$	$k_9' = k_2'$	Atkinson (1981)
$\text{CH}_3\text{COCH}_3 \xrightarrow{h\nu}$	$k_9'' = 5 \times 10^{-6}^\ddagger$	Estimated from Calvert and Pitts (1966)
$\text{CH}_3\text{C(O)O}_2 + \text{NO}_2 \rightarrow$	$k_{10} = 1.4 \times 10^{-12}$	Cox and Roffe (1977)
$\text{PAN} \xrightarrow{\text{Thermal}}$	$k_{11} = 7.9 \times 10^{14} \exp (-12540/T)^\ddagger$	Cox and Roffe (1977)
$\text{CH}_3\text{C(O)O}_2 + \text{NO} \rightarrow$	$k_{12} = 2.4 \times 10^{-12}$	Cox and Roffe (1977)
$\text{PAN} + \text{OH} \rightarrow$	$k_{13} \leq 1.7 \times 10^{-13} \text{ at } 300\text{K}^\S$	Winer et al. (1977)
$\text{PAN} + \text{Cl} \rightarrow$	$k_{13}' \sim 2.8 \times 10^{-11} \text{ at } 215\text{K}$	Atkinson (1981)
$\text{PAN} \xrightarrow{h\nu}$	$k_{13}'' = 2 \times 10^{-8} \text{ (max)}^\ddagger$	U.V. spectrum from Stephens (1969)

*All rate constants in units of $\text{cm}^3 \text{molec}^{-1} \text{sec}^{-1}$ unless otherwise indicated. †Many of these references are compilations that also contain original sources of rate data. ‡In units of sec^{-1} . §PAN + Cl rate constant is estimated by Atkinson (1981) to be half of $\text{C}_2\text{H}_6 + \text{Cl}$. Temperature dependence of PAN + OH and PAN + Cl reaction is estimated from C_2H_6 data.

than 0.5 NO_2/NO ratio in the lower stratosphere. Similarly, k_{12} may be larger than utilized in Table 2 (Sander and Watson, 1980). This will tend to reduce PAN levels in the lower troposphere but will have virtually no effect elsewhere. The pressure dependence of $\text{RO}_2 + \text{NO}_2 + \text{M}$ (forward reaction 13) has been measured to be negligible (Cox and Tyndall, 1979; Adachi and Basco, 1980). Sander and Watson (1980), however, do find a pressure dependence. If true, its effect would be to reduce estimated PAN levels with increasing altitude. The significance of the conclusions of this study, however, remains unaltered despite these uncertainties in our current understanding of the atmosphere. A schematic of the vertical distribution of PAN, when these uncertainties are considered, is shown in Figure 1.

Since PAN and NO_2 equilibrium can shift rapidly with temperature [reaction (13)], PAN can regenerate NO_2 at warmer temperatures. Thus, a constant exchange of PAN and NO_2 in the lower and upper troposphere associated with turbulent weather conditions can exist. Rapid absorption of UV light above the ozone layer could cause PAN to transport inorganic nitrogen from the lower to the upper stratosphere. In the future, higher Cl concentration in the lower stratosphere (from man-made activities such as release of halocarbons) could increase this role of PAN. Similarly, increasing levels of man-made pol-

lution (including those from aircraft exhaust) could increase the levels of these and other nonmethane hydrocarbons, thereby further increasing the organic content of reactive nitrogen.

Although measurements of acetaldehyde and acetone at these levels must await further developments in instrumentation, methods currently exist (electron capture gas chromatography) to measure PAN at these estimated concentration levels (Singh et al., 1979b). In addition, one should attempt to apply the spectroscopic method. When the solar spectrum is recorded at grazing incidence through the upper atmosphere, the strong PAN bands at 795 cm^{-1} and 1165 cm^{-1} should appear.

These preliminary calculations can be further improved by the exercise of more sophisticated photochemical models and the development of more accurate UV absorption (e.g., acetone, PAN) and temperature-dependent rate-constant (especially PAN + OH, PAN + Cl, and acetone + OH reactions) data. The possibility that methane-initiated reactions ($\text{CH}_3\text{O}_2 + \text{NO}_2 \rightarrow \text{CH}_3\text{OONO}_2$; $\text{CH}_3\text{O} + \text{NO}_2 \rightarrow \text{CH}_3\text{ONO}_2$) may provide additional sources of organic nitrogen compounds, especially at the colder

TABLE 3. Estimated Concentration of Acetaldehyde, Acetone, and PAN

Atmospheric Region	CH_3CHO (ppt) (from C_2H_6)	CH_3COCH_3 (ppt) (from C_3H_8)	PAN (ppt)*
Lower troposphere	22	111	17†
Upper troposphere	3	15	90‡, 360†
Lower stratosphere	7	3	85†

*Parts per trillion. †Assumes stationary atmosphere. ‡Assuming a 60-day exchange between the upper tropospheric and lower tropospheric air.

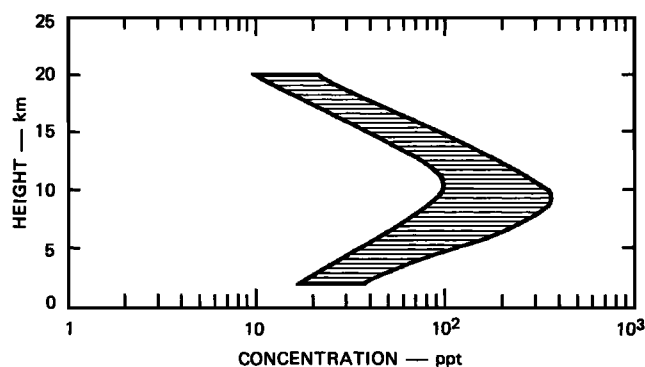


Figure 1 Schematic of PAN Profile in the Atmosphere

temperatures of the upper troposphere and the stratosphere, should be further explored. Other peroxy nitrates may also contribute in small degree to this organic reservoir of NO_x . These include peroxy nitric acid, peroxy propionyl nitrate, peroxy benzoyl nitrate, and halogenated peroxy nitrates.

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