REVIEW ARTICLE

THE ATMOSPHERIC CHEMISTRY OF ORGANIC NITRATES

JAMES M. ROBERTS

Environmental Chemistry Division, Brookhaven National Laboratory, Upton, NY 11973, U.S.A.

Abstract—The chemistry of organic compounds containing the covalently-bound nitrate group is reviewed with the purpose of summarizing the state of knowledge concerning their importance in atmospheric chemistry. Information pertinent to the conduct of research is contained in sections titled Nomenclature; Preparation, Properties and Spectroscopic Data; and Measurement Techniques. Information specific to atmospheric chemistry is contained in sections titled Atmospheric Formation Processes, Atmospheric Removal Processes, Atmospheric Observations, and Modeling Studies. Areas of potential importance and areas of major uncertainty are identified throughout to provide focus for future research activities.

Key word index: Alkyl nitrates, peroxycarboxylic nitric anhydrides, atmospheric chemistry.

INTRODUCTION

The oxides of nitrogen, NO_x ($= NO + NO_2$) play a central role in the chemistry of the atmosphere (Leighton, 1961; Crutzen, 1979; Logan, 1983; Singh, 1987). These oxides and their photochemical products (collectively termed odd nitrogen, NO_y) have tremendous importance in a variety of atmospheric processes such as acid formation, tropospheric and stratospheric ozone production and destruction, and urban- and regional-scale oxidant formation. Direct impacts of these compounds are human health impairment and phytotoxicity. It has been estimated that over half of the NO_x emissions to the atmosphere result from human activity (Logan, 1983); therefore it is crucial to understand the processes that govern the formation, removal and distribution (both spatial and chemical) of atmospheric NO_y if the anthropogenic perturbation of the atmosphere is to be assessed. In order to achieve this understanding, the chemistry of compounds that constitute NO_y must be thoroughly studied.

For the purposes of this review the term "odd nitrogen" (NO_y) is defined as the sum of NO_x plus all oxidized nitrogen species that represent sources or sinks of NO_x through processes that occur on relatively short time scales. Thus NO_y consists of NO, NO_2, nitric acid (HNO_3), inorganic aerosol nitrate (NO_3^-), nitrous acid (HNO_2), nitrate radical (NO_3), peroxynitric acid ($HOONO_2$), chlorine nitrate

($ClONO_2$), dinitrogen pentoxide (N_2O_5), 'peroxyacetyl nitrate' (PAN), and other organic nitrates of various types. As will be seen later, this definition of NO_y has something of an empirical basis, reflecting not only chemical processes but also the methods used to measure total NO_y in the atmosphere. Although nitrous oxide (N_2O) is an NO_x source in the upper atmosphere, and NH_3 can be a source of NO_x under certain circumstances, these compounds are not usually considered NO_y compounds.

The major processes involved in the interconversion of NO_y among species are shown in Fig. 1. Nitric oxide and NO_2 are rapidly interconverted ($\tau \leqslant 100\,s$) through the reaction of NO with O_3 and the photolysis of NO_2 by solar radiation. These two processes, in conjunction with the reaction of atomic oxygen (from NO_2 photolysis) with O_2 to form O_3, comprise what has been termed a 'photostationary state'. The reactions of HO_2, RO_2, and ClO with NO represent perturbations on this photostationary state which lead to the net formation of O_3, evidence from tropospheric measurements suggesting that there is nearly always an imbalance due to these additional reactions (Kelly *et al.*, 1980; Bollinger, 1982; Parrish *et al.*, 1986; Carroll *et al.*, 1987; Singh *et al.*, 1988). The major pathway for the removal of NO_y from the atmosphere appears to be through reaction of NO_2 (with OH) to form HNO_3 and subsequent wet and dry deposition of HNO_3 and NO_3^-. The remaining inorganic species shown in Fig. 1, HNO_2, NO_3, N_2O_5, $ClONO_2$, $HOONO_2$ are photolytically and/or thermally unstable and therefore represent reservoir species, which are, at times, involved in very important chemistry. The reactions of NO_3 with organic compounds can be an efficient loss process for some compounds (Carter *et al.*, 1981; Winer *et al.*, 1984). The uptake of N_2O_5 on

- STRATOSPHERIC SPECIES
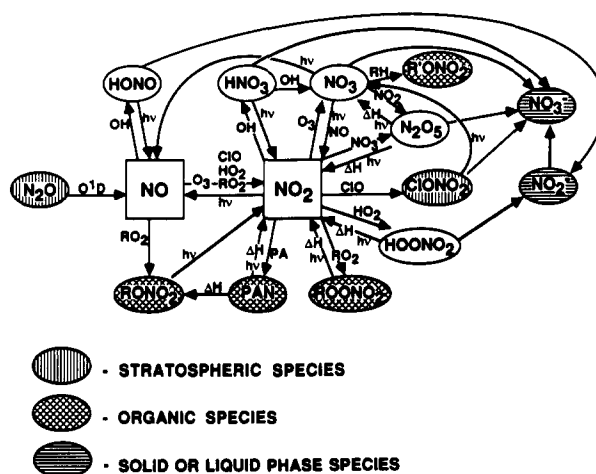
- ORGANIC SPECIES

- SOLID OR LIQUID PHASE SPECIES

Fig. 1. Tropospheric and stratospheric odd-nitrogen cycle.

particles and fog and cloud droplets may represent a significant process leading to acid deposition. The heterogeneous chemistry of $ClONO_2$ on ice is extremely important in stratospheric chemistry because such reactions involve both the removal of NO_y (as NO_3^-) and the liberation of active chlorine (Molina *et al.*, 1987; Tolbert *et al.*, 1987).

This review will demonstrate that organic nitrates (defined as organic compounds containing the covalently-bound $-ONO_2$ group) are important NO_y reservoir species. Atmospheric measurements show that PAN is often present in concentrations much greater than NO_x in the global atmosphere (Singh *et al.*, 1985). In addition, the measurement of the individual NO_y species, NO_x, HNO_3, particulate NO_3^-, and PAN, in parallel with measurements of total NO_y, indicate that in some circumstances there can be substantial fractions of unaccounted-for NO_y (Fahey *et al.*, 1986; Williams *et al.*, 1987; Singh *et al.*, 1988). This NO_y 'deficit' is very likely comprised of organic nitrates. Since these organic nitrates have much longer lifetimes than other inorganic NO_y species, they have an important effect on the geographic distribution of NO_y. Organic nitrate chemistry is an area in which the atmospheric cycles of nitrogen and organic carbon are strongly coupled. The far-reaching and long-term changes that are occurring in these cycles will quite probably be manifested in dramatic changes in the spatial and chemical distribution of organic nitrates. In fact, there is already some evidence that this is happening.

This review summarizes what is known concerning the atmospheric chemistry of organic nitrates, and identifies major areas of uncertainty. Another goal of this review is to compile and summarize data pertinent to the conduct of research on organic nitrates. The review is organized into sections entitled: Nomenclature; Preparation, Properties and Spectroscopic Data; Atmospheric Formation Processes; Atmospheric Removal Processes; Measurement Techniques; Atmos-

pheric Observations; Modeling Studies; and Conclusions.

NOMENCLATURE

For historical reasons the nomenclature of organic chemistry contains numerous misnomers and ambiguities and that of organic nitrates is no exception. The most widely known organic nitrate name "nitroglycerin" is a misnomer, it should be called glycerol trinitrate. Martinez (1980) points out that the most familiar atmospheric organic nitrate, "peroxyacetyl nitrate" (PAN), also has been misnamed and should be called ethaneperoxoic nitric anhydride (EPNA), since it is a mixed acid anhydride. A cursory glance through the recent literature finds the prefixes nitro-, nitrato-, nitroxy-, and nitrooxy- used to denote the covalently bound $-ONO_2$ group. For the purposes of facilitating communication and eliminating errors and uncertainties, it is useful to discuss the nomenclature of organic nitrates here. Although not explicitly covered in this review, organic nitrates will be included in the nomenclature discussion. The emphasis here is on the elimination of structural ambiguities, so common names such as 'acetic' acid need not be replaced by the more formal ethanoic acid.

Compounds of the structural type $RONO$, $RONO_2$ and $ROONO_2$, where R is a simple alkyl or aryl group, are esters of the alcohol ROH with the corresponding acids, nitrous acid (HONO), nitric acid ($HONO_2$) and peroxynitric acid ($HOONO_2$). Hence, they are termed nitrites, nitrates or peroxynitrates. Since esters are dehydration products of an alcohol and an acid, the nomenclature of the organic group follows directly from that of the parent alcohol. For example, the names methyl nitrite, benzyl nitrate, and *n*-propyl peroxynitrate unambiguously refer to the compounds CH_3ONO, $C_6H_5CH_2ONO_2$, and $CH_3CH_2CH_2OONO_2$, respectively. This is the most straightforward way to name $R-ONO_2$ compounds

and should be used wherever possible (IUPAC rule 5.33 for esters of oxo acids, 1965).

In naming complicated compounds, having several functional groups, it is often necessary or desirable to refer to the nitrogen group as a substituent by using a prefix name. The formally accepted anion, ligand and prefix names, and corresponding structures of nitrogen oxide groups, are summarized in Table 1 (IUPAC, 1977). The anion names are the same as the ester names discussed above with the exception of peroxonitrate. The ligand names are used to describe the structures of coordination complexes in which the ligand–metal bond is ionic in character. In general, such ligand–metal bonds are weaker than the bonds within the ligand molecule. In the case of the NO_2 group, ligand bonds can occur either through the nitrogen (nitro) or an oxygen (nitrito).

Substituent names are used to describe compounds in which a covalent bond exists. For the purposes of this review, this means a carbon–oxygen or carbon–nitrogen bond. The proper name for the $-ONO_2$ substituent is "nitrooxy" (pronounced nitrooxy), which is derived from the nitro ($-NO_2$) substituent and the term "oxy" which refers to the –O– linkage. Similarly, the term nitrosooxy (pronounced nitroso-oxy) (–O–N=O) follows from the terms "nitroso" (–N=O) and "oxy". Thus it is clear that the terms "nitro" and "nitrato" are not to be used to describe the covalent $-ONO_2$ substituent. The term "nitroxy", a natural contraction of "nitrooxy", is probably not misleading to an experienced chemist, hence is acceptable. However, a novice wishing to 'look it up' will not find nitroxy in descriptions of nomenclature.

The IUPAC rules give no definitive name for the substituent $-OONO_2$; however, one can be constructed in the same manner as that for "nitrooxy". Since the IUPAC rules specify the term "dioxy" be used to denote the –O–O– linkage (IUPAC, 1977), the name "nitrodioxy" is arrived at. Although this name is the most proper, dioxy is not commonly used. A substitution of the term "peroxy" results in "nitroperoxy", which sounds better and should permit unambiguous arrival at the correct structure.

Organic compounds are often named by linking two different group names. Such was the case with

peroxyacetyl nitrate $CH_3C(O)OONO_2$ (Stephens et al., 1961). However, as pointed out by Martinez (1980) the term "peroxyacetyl nitrate" is more appropriate to the structure $CH_3C(O)OOONO_2$. In either case, the name does not conform to IUPAC conventions, but more importantly leads to ambiguity. Compounds such as PAN are not esters of HNO_3 but rather anhydrides of two different acids, commonly known as mixed anhydrides. According to IUPAC Rule No. C-491.3, mixed anhydrides are named by giving the specific part of each acid name, in alphabetical order or order of complexity, followed by the term "anhydride". As a consequence, the name ethaneperoxoic nitric anhydride is the proper name for the "PAN" compound. Unfortunately, this leads to a different acronym, EPNA, a fact which may partially explain why the proper name has not been widely adopted. A proposed compromise recognizes the anhydride structure of the compound, but retains the acronym "PAN", as denoting peroxyacetic nitric anhydride. This convention permits the retention of the other acronyms, PPN, peroxypropionic nitric anhydride and PBzN for peroxybenzoic nitric anhydride, commonly employed in the literature. The class of compounds should be referred to as peroxycarboxylic nitric anhydrides.

PREPARATION, PROPERTIES AND SPECTROSCOPIC DATA

The synthetic methods discussed in this section will be limited to liquid phase chemistry, and gas phase chemistry carried out under anoxic conditions. Gas phase synthetic routes in the presence of oxygen will be discussed in a subsequent section since these are essentially the atmospheric formation mechanisms. The physical properties presented here have been assembled with the intent of providing a convenient references. The infrared (i.r.) and proton nuclear magnetic resonance (^1H NMR) spectral data, and mass spectrometric data are compiled here to provide a guide to the qualitative characterization and quantitative determination of these compounds.

The synthesis of nitrate esters, $RONO_2$, is generally accomplished through esterification of the parent

Table 1. Nomenclature of nitrogen oxide groups*

Group	Anion	Ligand	Substituent
NO_2	Nitrite	Nitro	Nitro, $-N\genfrac{}{}{0pt}{}{\diagup O}{\diagdown O}$
		Nitrito	Nitrosooxy, –O–N=O
NO_3	Nitrate	Nitrato	Nitrooxy, $-O-N\genfrac{}{}{0pt}{}{\diagup O}{\diagdown O}$
NO_4	Peroxonitrate	—	Nitroperoxy[†], $-O-O-N\genfrac{}{}{0pt}{}{\diagup O}{\diagdown O}$

*From IUPAC (1977).
†Proposed herein, see text for discussion.

alcohol, ROH, in nitric or mixed acid solution, or by reaction of the corresponding alkyl halide, RX, with silver nitrate or mercury (I/II) nitrate. However, more specialized methods have been used for the preparation of nitrates, especially those having other functional groups. The preparation of peroxyalkyl nitrates, $ROONO_2$, and the peroxycarboxylic nitric anhydrides, $RC(O)OONO_2$, has been accomplished through the reaction of the corresponding organic peroxy compound, ROOH or RC(O)OOH, with nitric acid in acidic solution or with N_2O_5 in non-aqueous solvents.

Simple nitrate esters have been synthesized for a wide range of hydrocarbon substituents. The preparations of 38 different nitrates by alcohol–acid esterification, or reaction of the parent halide with $AgNO_3$ under a variety of conditions, has been summarized by Boschan et al. (1955). Acid esterifications must be carried out by slow addition of the alcohol to cold acid in order to minimize the oxidation of the organic group or the formation of nitrate ion, both of which can lead to explosion. Preparation of nitrates through reactions of organic halides with $AgNO_3$ has been proven useful. The reaction can be carried out either in heterogeneous systems wherein $AgNO_3$ and the product AgX (X=Cl, Br, I) are insoluble, or in CH_3CN solution saturated with $AgNO_3$. Bromides or iodides must be used for the preparation of simple primary or secondary nitrates, but chlorides may be used where sufficiently reactive (tertiary, allylic or benzylic groups). The main disadvantages of this method are the expense and photosensitivity of $AgNO_3$. Several methods have been developed to avoid the safety problems of direct acid esterification or the expense of the $AgNO_3$ method, either by reaction of mercuric or mercurous nitrates with the parent halide, (McKillop and Ford, 1974) or reactions of primary amines (Katritzky and Marzorati, 1980) or alcohols (Olah et al., 1978) with specialized organic reagents.

Nitrate esters with more than one functional group can be somewhat more difficult to prepare. Nitric acid esterification with the di- and trialcohols leads to the formation of only the di- and trinitrates, for example glycerol trinitrate (commonly termed nitroglycerin). Primary nitrate esters of di- and trihydroxy compounds can be made through the use of a selective nitrating reagent, thionyl chloride nitrate $[ClS(O)ONO_2]$ (Hakimelahi, 1984). The reactions of $AgNO_3$ with bromohydrins (Henry, 1872; Marans and Zelinski, 1950) and HNO_3 with ethylene oxide ring (oxirane) compounds (Hanriot, 1879; Nichols et al., 1953) have also been used to make hydroxy nitrate esters. The former technique suffers from side reactions, the latter yields both isomers from unsymmetrical oxirane compounds. The occurrence of the oxirane reaction and the facility with which ethers can be hydrolyzed in strong acid suggest that the reaction of cyclic ethers with nitric acid is a synthetic route to hydroxy nitrates. Compounds of the α-nitrooxy ketone type, $RC(O)CH_2ONO_2$, have been prepared either by reaction of the α-bromo ketone

with $AgNO_3$ (Ferris et al., 1953; Kornblum and Frazier, 1966) or by reaction of the parent ketone with thallium (III) trinitrate (McKillop et al., 1978). In both methods, the major impurities produced are the α-dicarbonyl compounds formed via oxidative elimination.

The first suggestion that PAN could be synthesized in the liquid phase was given by Stephens (1969), who noted that both reaction of peroxyacetic acid with nitric acid (in mixed acid solution), and the treatment of peroxyacetic acid with silver nitrate yielded PAN. However, Stephens discounted both of these as useful synthetic methods, perhaps because of the success of the gas phase methods (to be discussed later) available at that time. The work of Louw et al. (1975) demonstrated that reaction of peroxycarboxylic acids with N_2O_5 in CH_2Cl_2 solution, or HNO_3 in SO_3/H_2SO_4 could be a viable synthetic route to peroxycarboxylic nitric anhydrides. This basic method has been used in a number of subsequent studies (Hendry and Kenley, 1977; Kravetz et al., 1980; Nielsen et al., 1982; Gaffney et al., 1984). The latter three references describe procedures that permit the preparation of high purity peroxyacetic nitric anhydride in alkane solvents for use as measurement standards. Syntheses involving peroxycarboxylic acids are inherently limited by the stability of the organic substituent in highly acid and oxidizing solution. For example, such syntheses of peroxyacrylic, $[CH_2CHC(O)OONO_2]$, or peroxymethacrylic, $[CH_2C(CH_3)C(O)OONO_2]$, nitric anhydrides may not be possible due to tendency of these conjugated alkenes to polymerize.

Liquid phase syntheses of esters of peroxynitric acid, $ROONO_2$, have been reported in three different studies. Lachowicz and Krevz (1967) and Duynstee et al. (1971) report the preparation of β-nitroalkyl peroxynitrates, $RCH(NO_2)CH_2OONO_2$, from the reaction of N_2O_4 and O_2 with olefins in hexane solution. Partially in response to the work of Stephens (1969), Duynstee et al. (1973) undertook the synthesis of t-butyl and methyl peroxynitrates by reaction of the corresponding dialkyl peroxide with N_2O_5 in $CHCl_3$ solution, however the results were somewhat ambiguous. Trifluoromethyl peroxynitrate has been synthesized through the reactions of CF_3OOH and CF_3OOF with N_2O_5 and N_2O_4, respectively (Hohorst and Des Marteau, 1974).

The purification of reaction products is limited by the thermal and mechanical instability of many of the nitrate compounds. Indeed for some compounds, such as PAN and glycerol trinitrate, it is not advisable to isolate the pure liquid (Stephens, 1969). As a rule, organic nitrates are not very soluble in water, thus it is often possible to wash a reaction mixture with water to remove the more soluble impurities. PAN prepared from peroxyacetic acid in alkane solution, and alkyl nitrates prepared as pure liquids from alcohols ($\leq C_4$), are easily purified in this way. Reaction mixtures can often be fractionally distilled if care is taken to stay well below the thermal decomposition temperature of

the nitrate and provided that a high boiling solvent is added to the flask to prevent concentration of explosive impurities. The above temperature limitation often requires distillation under vacuum.

Some physical properties of organic nitrates are compiled in Table 2, for compounds that have been isolated in the condensed phase, and for which condensed phase properties have been determined. These data are listed here to provide a reference for the chemical characterization or measurement of these compounds, and to suggest how these compounds might be distributed between the gas and aerosol phases in the atmosphere. In general, the nitric acid esters are slightly less volatile than the corresponding alcohol. Due to thermal instability, the boiling points of CF_3OONO_2 and PAN at 760 torr were obtained by extrapolation of vapor pressure values at lower temperatures. However, it is not clear that these measurements were free of thermal decomposition problems. This is evident from the data of Kacmarek et al. (1977), listed in Table 3, along with the corresponding PAN thermal decomposition lifetime. Because of the short PAN lifetime at the higher temperature the vapor pressure measurement may be in error (too high) depending on the fate of the decomposition products.

Spectroscopic methods have provided the backbone for research in atmospheric chemistry and have been particularly important in the study of organic nitrate chemistry. Infrared absorption spectroscopy has proven to be the most powerful technique for structural determination and is the method of choice for gas phase mechanistic studies. Nuclear magnetic resonance spectroscopy has been useful in structural studies where a relatively pure product can be isolated. Mass spectrometry has seen only limited use in the analysis of organic nitrates; however chemical- and photoionization techniques appear to be more useful than the traditional electron impact methods.

Early electron diffraction studies of fluorine nitrate and methyl nitrate (Pauling and Brockway, 1937), interpreted with simple models, indicated a planar $O-NO_2$ group with the F- or CH_3- perpendicular to the plane, although the planar configuration for these could not be ruled out. Subsequent spectroscopic studies and molecular orbital calculations of nitric acid (Maxwell and Moseley, 1940), methyl nitrate (Cox and Waring, 1971; Odeurs et al., 1984; Bock et al., 1985) and halogen nitrates (Arvia et al., 1963; Miller et al., 1967; McGrath et al., 1988) established the coplanarity of the heavy atoms in $R-ONO_2$ molecules. Ethyl nitrate has been shown by microwave spectroscopy to have the preferred *trans* structure shown in Fig. 2 (Scroggin et al., 1974).

Infrared absorption frequencies have been compiled in Table 4 for molecules containing the $-O-NO_2$ group. The major features of these spectra are the $-NO_2$ asymmetric $[v_a(NO_2)]$ and symmetric $[v_s(NO_2)]$ stretches, the O–N $[v(NO)]$ stretch and the NO_2 out-of-place bending $[\gamma_w(NO_2)]$ modes. Assignments of the frequencies to each band appear to be in

agreement throughout for $v_a(NO_2)$, $v_s(NO_2)$ and $\gamma_w(NO_2)$ modes. Some disagreement exists between the assignments for the O–N stretching vs NO_2 scissors $\delta(NO_2)$ mode for the inorganic nitrates (Arvia et al., 1963; Miller et al., 1967). The assignments for nitric acid esters follow those of Bock et al. (1985) and Brand and Cawthon (1955). The assignments for $v(NO)$ in peroxynitrate esters follow those of Hohorst and DeMarteau (1974). Absorptivities (or band strengths) have been reported for several peroxycarboxylic nitric anhydrides by Stephens (1964), Heuss and Glasson (1968), Glasson and Heuss (1977), Edney et al. (1979b), Gaffney et al. (1984), Niki et al. (1985) and Rogers and Rhead (1987).

The nuclear magnetic resonance (NMR) spectroscopy of organic nitrates has not been studied extensively; however, since it is routinely used for structure and purity determination, it will be summarized here. Early work of Hammond (1962) on the proton NMR of methyl nitrate demonstrates that the electronegativity of the nitrate group causes a downfield shift, $\delta = 4.15$ (CCl_4), relative to unsubstituted compounds. The methyl hydrogen resonance is also broader than typical proton resonances. The proton resonances of α hydrogens in simple alkyl nitrates fall in the range $\delta = 4.1–4.6$, and are somewhat solvent-dependent. The α proton resonances of alkyl groups having other functionalities exhibit additivity of substituent effects, for example: allyl $\delta = 4.91$ ($CDCl_3$), methylallyl $\delta = 4.84$ ($CDCl_3$), and benzyl $\delta = 5.4$ ($CDCl_3$) (Ochiai et al., 1984). Compilation of H^1NMR data for nitrate esters should permit the formulation of group additivity relations that could be used to predict chemical shifts of new compounds.

Observations of the NMR spectra of peroxynitrates are sparse. Duynstee et al. (1973) report a sharp ^1H resonance at $\delta = 4.17$ in $CDCl_3$ at $-30°C$ for CH_3OONO_2. Lachowicz and Krevz (1967) report $\delta = 4.90$ for the α protons of 2-nitroperoxy-nitrodecane. The methyl proton resonance of PAN has been observed by Nicksic et al. (1967) and Kravetz et al. (1980) to be solvent-dependent, varying from $\delta = 2.28$ in pure CCl_4 to $\delta = 1.29$ in benzene solution. Kravetz et al. (1980) have interpreted this to be due to PAN–benzene complex formation.

Nitrogen NMR is a technique that may have considerable utility in the characterization of organic nitrates. As will be seen in a later section, sensitive methods are available for the measurement of total odd-nitrogen (NO_y) in a gas stream, and these methods have been applied to the quantitation of organic nitrate standard streams. Thus it is desirable to have a nitrogen-specific method of chemical characterization of products to be used as standards. The technique of ^{14}N NMR appears to be ideal for this purpose (Witanowski and Webb, 1973).

The mass spectra of organic nitrates have been studied by electron impact (Stephens et al., 1961; Stephens, 1961, 1969; Fraser and Paul, 1968a,b; Heuss and Glasson, 1968; Louw et al., 1975), photoionization

Table 2. Physical properties of organic nitrates of potential atmospheric importance

Name	Structural formula	Molecular weight[*]	Melting point (°C)	Boiling point (°C) pressure (torr)	Density	Reference
Nitric acid esters						
Methyl	CH_3ONO_2	77.04	-82.3	64.6/760	1.2075^{20}_4	Cowley and Partington, 1933
Ethyl	$CH_3CH_2ONO_2$	91.07	-94.6	87.2/762	1.1084^{20}_4	Cowley and Partington, 1933
n-Propyl	$CH_3(CH_2)_2ONO_2$	105.09	—	110/762	1.0538^{20}_4	Vogel, 1948
2-Propyl	$(CH_3)_2CHONO_2$	105.09	—	101.7/760	1.043^{20}_4	Steinburger et al., 1955
2-Propenyl	$CH_2CHCH_2ONO_2$	103.08	—	102–106	—	Pattison and Brown, 1956
n-Butyl	$CH_3(CH_2)_3ONO_2$	119.12	—	135.5/763	1.0228^{30}	Vogel, 1948
2-Butyl	$CH_3CH_2CH(CH_3)ONO_2$	119.12	—	124/760 59/80	1.029^{20}	Kornblum et al., 1948
Methyl propyl	$CH_3CH(CH_3)CH_2ONO_2$	119.12	—	123	1.0152^{20}_4	Lowenherz, 1890 Gray and Pratt, 1957
1,1 Dimethyl ethyl	$(CH_3)_3CONO_2$	119.12	-34 – 35	22–23/4.0	—	Lucas and Hammett, 1942
4-Chlorobutyl	$Cl(CH_2)_4ONO_2$	153.56	—	92–93/11	—	Pattison and Brown, 1956
2-Methyl-2-propenyl	$CH_2C(CH_3)CH_2ONO_2$	117.11	—	83–88/215	1.064	Ferris et al., 1953
n-Pentyl	$CH_3(CH_2)_4ONO_2$	133.15	—	157/760 47–48/9.5	0.9962^{20}_4	B1[3] 1612§ Ross et al., 1968
3-Methyl butyl	$(CH_3)_2CH(CH_2)_2ONO_2$	133.15	—	147–148	0.9971^{20}	Schiff, 1886 Harkins et al., 1920
2-Pentyl	$CH_3(CH_2)_2CH(CH_3)ONO_2$	133.15	—	144	0.992^{20}	B1[3] 1605
2-Methyl-2-butyl	$(CH_3)_2C(CH_2CH_3)ONO_2$	133.15	—	118–120/240 52/12 26–27/5	1.010^{26}_4	Kuhn, 1946 Michael and Carlson, 1935
Cyclopentyl	$CH_2(CH_2)_3CHONO_2$	131.13	—	161/760 74/30	1.1261	Kornblum and Teitelbaum, 1952
n-Hexyl	$CH_3(CH_2)_5ONO_2$	147.18	—	∼171/760 67–69/12	—	B1[3] 1657 Pattison and Brown, 1956
Cyclohexyl	$CH_2(CH_2)_4CHONO_2$	145.16	—	181/760	1.1043	Kornblum and Teitelbaum, 1952
2-Heptyl	$CH_3(CH_2)_4CH(CH_3)ONO_2$	161.20	—	98–100/40	0.9621^{20}_4	B1[4] 1741
4-Heptyl	$(CH_3CH_2CH_2)_2CHONO_2$	161.20	—	85/25	—	Kornblum et al., 1955
n-Octyl	$CH_3(CH_2)_7ONO_2$	175.23	—	110–112/20	0.8419^{17}_{17}	B1 419
2-Octyl	$CH_3(CH_2)_5CH(CH_3)ONO_2$	175.23	—	90–91/8 92.5–94.5/18 82–83/8	0.951	Ross et al., 1968 Shriner and Parker, 1933
n-Decyl	$CH_3(CH_2)_9ONO_2$	203.28	—	127–128/11	0.951^0_4	Ross et al., 1968 B1 425
n-Dodecyl	$CH_3(CH_2)_{11}ONO_2$	231.34	—	143–144/5	—	Pattison and Brown, 1956

Name	Formula	MW	mp (°C)	bp/pressure	density	Reference
Benzyl	$C_6H_5CH_2ONO_2$	153.14	—	107–111/22, 101–104/12, 95/11, 43/0.5	—	Olah et al, 1978; Pattison and Brown, 1956; Ross et al, 1968; Baker and Nathan, 1936
p-Methyl benzyl	$p\text{-}CH_3C_6H_4CH_2ONO_2$	167.17	—	115–118/10, 60/0.2, 44–49/0.015	—	Katritzky and Mazorati, 1980; Baker and Nathan, 1936; Ross et al, 1968
3,5-Dimethyl benzyl	$(CH_3)_2C_6H_3CH_2ONO_2$	181.19	—	58–60/0.25	—	Ross et al, 1968
p-Chloro benzyl	$p\text{-}ClC_6H_4CH_2ONO_2$	187.56	—	109/7	—	Ross et al, 1968
p-Nitro benzyl	$p\text{-}NO_2C_6H_4CH_2ONO_2$	198.15	66–68	—	—	Ross et al, 1968
Nitric acid diesters						
Ethylene glycol	$CH_2(ONO_2)CH_2ONO_2$	152.06	—	25/0.071	1.4956^{15}_{15}	Crater, 1929
1,2-Propylene glycol	$CH_3CH(ONO_2)CH_2ONO_2$	166.09	—	25/0.098	1.3939^{15}_{15}	Crater, 1929
Hydroxy nitric acid esters						
2-Nitrooxyethanol	$HOCH_2CH_2ONO_2$	107.07	—	75/5, 44–46/1	1.333^{25}, 1.34834^{20}	Marans and Zelinski, 1950; Nichols et al, 1953
Nitrooxypropanol	$C_3H_7NO_4$‖	121.09	—	50–52/1	1.2233	Nichols et al, 1953
3-Nitrooxy propanol	$CH_2(ONO_2)CH_2CH_2OH$	121.09	—	123–124/42, 103–104/16	—	Pattison and Brown, 1956
3-Nitrooxy-2-butanol	$CH_3CH(ONO_2)CH(OH)CH_3$	135.12	—	44–45/1	1.1811	Nichols et al, 1953
Peroxynitric acid esters						
Trifluoro methyl	CF_3OONO_2	147.01	—	0.9/760¶	1.682^{-58}	Hohorst and DesMarteau, 1974
1,1 Dimethyl ethyl	$(CH_3)_3COONO_2$	135.12	—	~22/11	—	Duynstee et al, 1973
Peroxycarboxylic nitric anhydrides						
Peroxyacetic (PAN)	$CH_3C(O)OONO_2$	121.05	−48.5	104/760¶	—	Kacmarek et al, 1977
Peroxybenzoic (PBzN)	$C_6H_5C(O)OONO_2$			37/0.2	—	Heuss and Glasson, 1968
m-Chloroperoxybenzoic	$m\text{-}ClC_6H_4C(O)OONO_2$	217.56	−15	—	—	Louw et al, 1975
p-Nitroperoxybenzoic	$p\text{-}NO_2C_6H_4C(O)OONO_2$	228.12	43	—	—	Louw et al, 1975
2-Peroxynaphthoic	$C_{10}H_7C(O)OONO_2$	233.18	64–65	—	—	Louw et al, 1975

* Average based on natural isotope abundances.
† Where no pressure was reported, 760 torr is to be assumed.
‡ The superscript denotes the temperature of the material, the subscript the temperature of pure water used as the density standard.
§ Beilstein's Handbook, BI³ 1612 denotes p. 1612 of the third supplement to Volume 1.
‖ A mixture of the two vicinal isomers.
¶ Extrapolated from vapor pressure–temperature data.

Temperature (K)	P_{VAP}(torr)*	τ(sec)†
277.15	9.5	5.6×10^4
285.85	14.9	1.4×10^4
290.40	19.5	6900
293.55	23.1	4400
300.80	34.0	1600
307.50	47.3	630
315.95	71.5	210
330.15	108.8	38

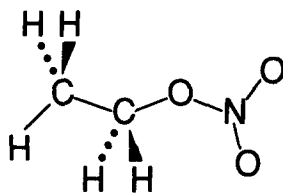*From Kacmarek et al. (1977).
†See data in later section.

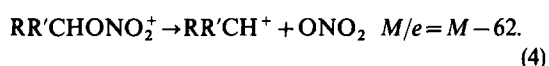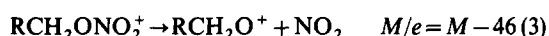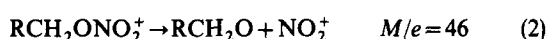
Fig. 2. The structure of ethyl nitrate.

(Kacmarek et al., 1977; Tagaki et al., 1981a) and chemical ionization (Pate et al., 1976; Suzuki et al., 1978; Das et al., 1979; Atlas, 1988). The fragmentation processes characteristic of organic nitrates under photo- and electron impact ionization are summarized below:

$$RCH_2ONO_2^+ \rightarrow R + CH_2ONO_2^+ \qquad M/e = 76 \qquad (1)$$

$$RCH_2ONO_2^+ \rightarrow RCH_2O + NO_2^+ \qquad M/e = 46 \qquad (2)$$

$$RCH_2ONO_2^+ \rightarrow RCH_2O^+ + NO_2 \qquad M/e = M - 46 \qquad (3)$$

$$RR'CHONO_2^+ \rightarrow RR'CH^+ + ONO_2 \qquad M/e = M - 62. \qquad (4)$$

The results of Takagi et al. (1981a) obtained with an (11.83 eV and 11.62 eV) Ar photoionization source, and 70 eV electron impact source indicate that only process (2) is operative in the case of PI of methyl nitrate, while EI appears to also proceed by process (3). In C_2–C_4 primary alkyl nitrates (Suzuki et al., 1978; Das et al., 1979; Takagi et al., 1981a) processes (1) and (2) predominate for both PI and EI, and significant ion abundances are observed at $M/e = 29$ (CHO^+, $C_2H_5^+$), 30(NO^+, CH_3O^+) and 31 (CH_3O^+). The PI mass spectra are less complicated than EI, which contain some common ions $M/e = 29$ ($C_2H_5^+$), 43 ($C_3H_7^+ + CH_3CO^+$), etc. Although no significant $M/e = M - 46$ ions are observed, C_2–C_4 alkyl nitrates, ethylene and 1, 2-propylene glycol dinitrates exhibit significant $M - 76$ (CH_2ONO_2) fragmentation in PI and EI. Cyclic nitrates (C_5–C_7) exhibit complicated mass spectra from both PI and EI with $M/e = M - 62$, arising from process (4), as a major

ion. The benzyl nitrate mass spectrum was comprised mainly of the parent ion, $M/e = 153$, and $M - 46$ ($M/e = 107$), in the PI mode, and the EI spectrum was more characteristic of aromatic hydrocarbons with the ions $M/e = 77$ and 91 present in high abundance. Positive ion chemical ionization of nitrates leads to observable abundances of $(M + 1)^+$ and $(M - 1)^+$ ions and simpler fragmentation patterns arising from the above processes, however, masses larger than M are also observed, especially in the cases of methyl and ethyl nitrate (Suzuki et al., 1978; Das et al., 1979). Negative ion chemical ionization (NICI) mass spectra of $RONO_2$ compounds of 3–7 carbons have recently been reported by Atlas (1988). The major features of these spectra are base peaks of $M/e = 46$ (NO_2^-), and major peaks at $M/e = 57 + 14n$, where $n = 0$–5 and increases with carbon number. This series corresponds to the loss of H_2 from the RCH_2O^- ion (Hayes et al., 1985).

The EI mass spectra of PAN and related compounds $RC(O)OONO_2$ are all very similar, exhibiting $M/e = 28$ (CO^+), 30 (NO^+), 44(CO_2^+), 46 (NO_2^+), and masses corresponding to R^+ and RCO^+ at 70 eV (Stephens et al., 1961; Stephens, 1961, 1969; Heuss and Glasson, 1968; Louw et al., 1977). No molecular ions were observed in EI mass spectra with the exception of a 20 eV EI MS of PBzN, for which $M/e = 183$ was observed (Heuss and Glasson, 1968). The 10.2 eV PI mass spectral analysis of PAN has been reported by Kacmarek et al. (1977) to result in the formation of $M/e = 15(CH_3^+)$, 30(NO^+), 42(CH_2CO^+), and 43(CH_3CO^+) ions. The CI/MS of PAN using both methane and isobutane, has been reported to result in the formation of $M/e = 43(CH_3CO^+)$, 46(NO_2^+, Base), 61(CH_3ONO^+), 77($CH_3ONO_2^+$), 88($O \equiv CCH_2ONO^+$), and 122($M + H^+$) for methane and 61, 71, 88, $(M - 1)$, M, and $(M + 1)$ ions for isobutane (not scanned < 57) (Pate et al., 1976). The isobutane CI mass spectrum showed a much higher abundance of $M + 1$ and M, relative to the lower mass ions, than did methane CI spectrum.

FORMATION PROCESSES

The sources of organic nitrates to the atmosphere can be roughly divided into primary emissions from combustion and chemical processes, and secondary formation from atmospheric photooxidation of organic compounds in the presence of NO_x. The emission of $RONO_2$ from specialized industrial processes certainly occurs, and has been observed in the explosives industry (Thompson et al., 1979), however, such sources are probably quite minor. Several alkyl nitrates have been observed in the exhaust of the turbine engines (Conkle et al., 1976), however the importance of such sources as well as emissions from diesel, and spark-ignition engines using petroleum and/or alcohol fuels, is uncertain. Long chain alkyl nitrates (e.g. n-octyl nitrate) are used as 'cetane impr-

Table 4. Selected fundamental frequencies (cm^{-1}) of the –O–NO$_2$ group in various molecules and structural types

Compound or type	–NO$_2$ stretch asymmetric	Symmetric	O–N stretch	NO$_2$ out-of-plane	Phase*	Reference
Inorganic nitrates						
HNO$_3$	1708	1325	879	762	v	Cohn et al., 1952; McGrath et al., 1988
			647			McGraw et al., 1965
FONO$_2$	1759	1301	804	709	v	Arvia et al., 1963
			633			Miller et al., 1967
ClONO$_2$	1735	1292	788	711	v	Arvia et al., 1963
			560			Miller et al., 1967
			434			McGrath et al., 1988
Nitric acid esters						
Methyl nitrate	1672	1287	854	759	v	Brand and Cawthon, 1955
	1634	1285	860	760	l	Brown, 1955
Ethyl nitrate	1661	1288	852	—	v	Niki et al., 1986
Alkyl nitrates	1639–1626	1282–1272	870–855	760–756	l	Carrington, 1960 Brown, 1955
Benzyl nitrate	1639	1284	861	758	l	Brown, 1955
Benzoyl nitrate	1730			786		Heuss and Glasson, 1968
1,2-Propylene Glycol dinitrate	1672	1280	836		v	Hoshino et al., 1978b
2-Hydroxy-2-methyl- propyl nitrate	1634	1284	872	756	l	Brown, 1955
1,2-Cyclohexandiol mononitrate	1629	1272	866	756	l	Brown, 1955
Nitro alkyl nitrates	1645–1631	1299–1271	872–844	756–749	l	Brown, 1955
Peroxynitric acid and esters						
HOONO$_2$	1728.3	1303.9	802.7	—	v	Niki et al., 1977
CF$_3$OONO$_2$	1760	1305	783	702	v	Hohorst and DeMarteau, 1974
CF$_2$ClOONO$_2$	1761	—	—	—	v	Niki et al., 1979
CFCl$_2$OONO$_2$	1757	1300	~780	—	v	Niki et al., 1979
CCl$_3$OONO$_2$	1754	1301	785	—	v	Niki et al., 1979
CHCl$_2$OONO$_2$	1743	—	—	—	v	Niki et al., 1979
CH$_2$ClOONO$_2$	1734.3	—	—	—	v	Niki et al., 1979
CH$_3$OONO$_2$	1723.8	1299.2	791.4	—	v	Niki et al., 1978
	1698	—	—	—	l	Duynstee et al., 1973
HOCH$_2$OONO$_2$	1725	1302	794			Niki et al., 1980
Ethyl	1718.9	1297.4	793.6	—	v	Niki et al., 1978
	1720	1298	797		v	Edney et al., 1979b
	1712	—	—	—	v	Duynstee et al., 1973
tert-Butyl	1692	—	—	—	l	Duynstee et al., 1973

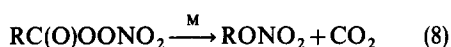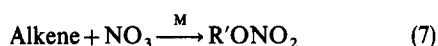| Peroxycarboxylic nitric acid	–NO$_2$ stretch asymmetric	Symmetric	O–N stretch	C=O stretch	Phase*	Reference
Peroxyfluoroformic	1760	1300	790	1910	v	Edney et al., 1979b
Peroxychloroformic	1756	1300	790	1844	v	Spence et al., 1978
Peroxyacetic	1736	1302	793	1838	v	Stephens, 1969
	1735	1300	791	1835	s	Varetti and Pimentel, 1974
	1740.6	1302.1	793.9†	1841.3	v	Gaffney et al., 1984
	1741	1302	791.5†	1842		Bruckmann and Willner, 1983
	1741.35	1301.28	793.75	1841	v	Niki et al., 1985
Peroxyacetic ^{15}N-nitric	1696	1287	781	1835	s	Varetti and Pimentel, 1974
	1701	1289	784		v	Niki et al., 1985
Peroxyglycolic	1747	1300	791	1831		Niki et al., 1987
Peroxypropionic	1736	1302	794.9	1838	v	Stephens, 1969
	1738.6	1301.3	799.2	1832.2	v	Gaffney et al., 1984
Peroxybutyric	1739	1299	794.9	1838	v	Stephens, 1969
Peroxyglutaric	1741	1302	793	1830	v	Rogers and Rhead, 1987
Peroxybenzoic	1739	1307	789.3	1805	v	Heuss and Glasson, 1968
Peroxycyclohexane- carboxylic	1739	1300	794.9	1828	v	Glasson and Heuss, 1977
o-Methylperoxybenzoic	1739	1300	794.3	1812	v	Glasson and Heuss, 1977
m-Methylperoxybenzoic	1739	1300	793.0	1805	v	Glasson and Heuss, 1977
p-Methylperoxybenzoic	1739	1300	794.3	1802	v	Glasson and Heuss, 1977
β-Phenylperoxyacetic	1748	1306	792.4	1835	v	Glasson and Heuss, 1977
2,4-Dimethylperoxybenzoic	1739	1302	789.9	1795	v	Glasson and Heuss, 1977
2,4,6-Trimethyl- peroxybenzoic	1736	1302	789.3	1799	v	Glasson and Heuss, 1977

*v-Vapor, l-liquid, s-solid in cryogenic matrix.
†Assigned to $\delta(NO_2)$ (scissor) mode.

overs' to enhance the performance of diesel engines and therefore may be present if unburned. Organic nitrates may be formed in the exhaust from spark ignition engines, especially those utilizing alcohol fuels, by processes favored by low O_2-high NO_x conditions (see below).

Organic nitrates are formed in secondary reactions through the atmospheric oxidation of organic compounds initiated by O_3, OH and NO_3. The nitrate formation mechanisms operating in all of these processes are often minor pathways and therefore have been difficult to quantify. There are a multitude of organic compounds found in, or emitted to, the atmosphere (Graedel *et al.*, 1986) and a complete description of atmospheric organic photooxidation chemistry is beyond the scope of this review. The interested reader is referred to several recent works in this area (Atkinson and Lloyd, 1984; Finlayson-Pitts and Pitts, 1986; Lurmann *et al.*, 1986; Kasting and Singh, 1986; Calvert and Madronich, 1987). Organic photooxidation chemistry will be discussed below only where necessary to illustrate features of organic nitrate chemistry.

The known gas-phase reactions resulting in the formation of $RONO_2$ and $ROONO_2$ compounds can be summarized schematically as follows:

$$RO_2^. + NO \xrightarrow{M} RONO_2 \qquad (5)$$

$$RO_2^. + NO_2 \xrightarrow{M} ROONO_2 \qquad (6)$$

$$Alkene + NO_3 \xrightarrow{M} R'ONO_2 \qquad (7)$$

$$RC(O)OONO_2 \xrightarrow{M} RONO_2 + CO_2 \qquad (8)$$

$$RO^. + NO_2 \xrightarrow{M} RONO_2. \qquad (9)$$

The oxy ($RO^.$) and peroxy ($RO_2^. \doteq ROO^.$) radicals shown above are products of OH–, O_3–, NO_3– and hv-initiated oxidation of organic compounds. Note that Reactions (9) and (6), for R = H, constitute major formation pathways of HNO_3 and $HOONO_2$.

Reactions of $RO_2^.$ radicals with NO are thought to be the most important sources of atmospheric alkyl nitrates. The formation of organic nitrates through the reaction of alkylperoxy radicals with NO (5) was first suggested by Spicer *et al.* (1973) for methylperoxy and Darnall *et al.* (1976) for larger alkylperoxy radicals and has been the subject of recent work (Hoshino *et al.*, 1978a; Takagi *et al.*, 1981b; Atkinson *et al.*, 1982b, 1983, 1984a, 1987a; Gery *et al.*, 1985; Shepson *et al.*, 1985; Harris and Kerr, 1989). The extent of this reaction is only a fraction of that of Reaction (10):

$$RO_2^. + NO \rightarrow RO^. + NO_2 \qquad (10)$$
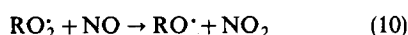
which constitutes a key step in the production of ozone from photooxidation of organic compounds.

Thus the branching ratios between Reactions (5) and (10) have implications not only for the efficiency of organic nitrate production but also as to the degree to which O_3 is formed from particular compounds.

It has been hypothesized that reaction of $RO_2^.$ with NO proceeds through the following mechanism (Atkinson *et al.*, 1983):

$$RO_2^. + NO \rightarrow ROONO^* \rightleftharpoons RONO_2^{\ddagger}$$
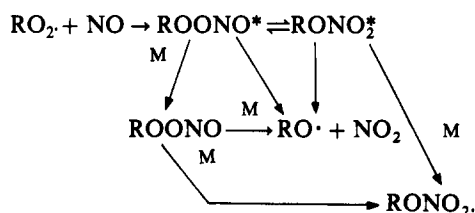
The addition of NO to $RO_2^.$ to form an unstable vibrationally excited peroxy nitrite has been proposed as the first step (Spicer *et al.*, 1973; Darnall *et al.*, 1976). It is interesting to note that the notion of the alkylperoxy nitrite product dates back to early air pollution studies (see Leighton, 1961). The excited peroxy nitrite undergoes rearrangement to form an excited nitrate, possibly through a three-membered ring transition state (Atkinson *et al.*, 1982b) shown in Fig. 3. Either excited species may decompose to form $RO^. + NO_2$ or may be collisionally deactivated to form the corresponding thermalized species. The formation of a peroxynitrite is plausible since the analogous acid HOONO has been observed as an intermediate in solution (Halfpenny and Robinson, 1952; Anbar and Taube, 1954; Benton and Moore, 1970). In addition, nitrate has been observed as a product of HOONO decomposition. However, it appears that a fraction of that decomposition probably occurs through a HO–ONO bond homolysis (Mahoney, 1970) and the remainder presumably through a unimolecular process. Attempts at gas phase generation of HOONO through the reaction of OH with NO_2 have proven unsuccessful (Burkholder *et al.*, 1987). Thermochemical data presented by Burkholder *et al.* (1987) for the

reaction $HOONO \xrightarrow{M} HO^. + NO_2$ indicate the bond dissociation (and therefore activation energy) for the reaction $ROONO \rightarrow RO^. + NO_2$ is at most ~ 20 kcal mole^{-1}. Given a reasonable pre-exponential factor of $\cong 10^{16}$, a short lifetime for ROONO against
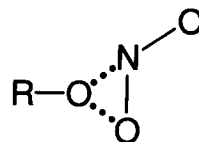
Fig. 3. Hypothesized transition state for the isomerization of an alkyl peroxynitrite to an alkyl nitrate.

bond homolysis is expected, and unimolecular rearrangement to $RONO_2$ must occur on that timescale.

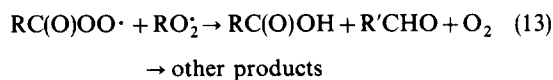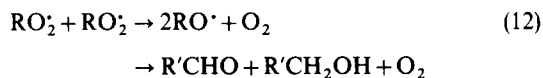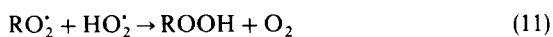It has recently been proposed that radicals of the type $CX_3OO^{\cdot}$ (where $X = F$ or Cl) react with NO to form the CX_3OONO intermediate. This suggestion was made on the basis of the large rate constant and negative temperature dependence observed for the reaction (Dognon et al., 1985) and through observations of the reaction of $CF_3OO^{\cdot}$ with NO in matrix isolation experiments (Clemitshaw and Sodeau, 1987). The gas phase products were observed to be exclusively $CX_3O + NO_2$, in a system in which CX_3ONO_2 could have been sensitively detected, strongly implying that CX_3ONO_2 is not formed through this reaction. In the matrix isolation study, CF_3OONO was not observed but CF_3ONO_2 was, however the reaction conditions do not rule out CF_3OONO as an intermediate. Either product could have been the source of CF_2O and FNO_2 that were also observed as products. Since low temperatures (4.2 K) were used and matrix cage effects are possible in such systems, the applicability of this study to gas phase is doubtful.

Evidence in support of the above mechanism for hydrocarbon radicals is found in the dependencies of alkyl nitrate yields, α (where $\alpha = k_5/(k_5 + k_{10})$) on carbon number, temperature, and pressure. Yields are observed to increase with increasing carbon number (Atkinson et al., 1982b), consistent with the general precept that rates of unimolecular decomposition of vibrationally excited species (in this case $ROONO^*$ and $RONO_2^*$) decrease as the number of degrees of freedom of the molecule increase. The yields of alkyl nitrates increase with increasing pressure and decreasing temperature (Atkinson et al., 1983). Pressure dependences of the nitrate yields are expected for three-body association reactions (NASA, 1987); and in this case the high pressure limits of the yields appear to be well above 760 torr. The magnitude of the temperature dependence of the yields suggests that a fraction of the nitrate formation proceeds through thermalized peroxynitrite isomerization.

Alkyl nitrate yields for normal, branched and cyclic alkyl peroxy radicals are summarized in Table 5, which has been constructed from the aforementioned chamber studies. Yields were calculated from the measured concentration increase of nitrates with decreasing alkane concentration and were corrected for OH reaction with the nitrate, and the fractional reaction rate of OH at a given position on the molecule (Carter and Atkinson, 1985). Two studies report Arrhenius equations for the relative rates of (5) and (10), for heptane reactions at 730–740 torr that are in good agreement; $k_5/k_{10} = 1.7 \times 10^{-3} \exp[1600/T]$ (Atkinson et al., 1983), and $k_5/k_{10} = 1.4 \pm 1.1 \times 10^{-3} \exp[(1640 \pm 250)/T]$ (Harris and Kerr, 1989), the latter study extending to 253 K. A generalized expression involving temperature and pressure dependencies has been developed to predict yields to within $\sim 25\%$ (Atkinson et al., 1983, 1987a). The equations predict a

maximum yields at 300K (high-pressure limit) of 0.435, which is consistent with the trend in yields from C_2–C_8, under the assumption that the limiting pressure decreases with increasing size of the molecule. Such yields have substantial implications for modeling of the organic photochemistry of smog formation, and can lead to significant amounts of alkyl nitrates in the atmosphere.

The reactions of $RO_2^{\cdot}$ with NO_2 have been observed to lead to peroxy nitrate formation (6) via three-body association. Table 6 lists the known rate constants for these reactions for particular R groups that have been studied. Temperature and pressure dependencies are noted where they have been determined. The data for $R = H$, CH_3, CCl_3, $CFCl_2$, CF_2Cl, CF_3, and $CH_3C(O)$ have been fit to general expressions for temperature and pressure-dependence (Troe, 1979; NASA, 1987). The rate constants for $R = H$ and CH_3 do not achieve their high pressure limits until approximately 760 torr. However, as R becomes larger, this rate constant approaches its high-pressure limit at lower pressures. The rate constants for $R = CH_3CH_2$ and $(CH_3)_2CH$ are essentially independent of pressure above approximately 50 torr. Some pressure dependence was observed for $CH_3C(O)$, however, the range was only a factor of 2 between 28 and 760 torr. In addition to the above compounds for which formation rate constants have been measured, the reactions where $R = FC(O)$, $ClC(O)$, C_NH_{2N+1} $(N = 1-6)$, $HOCH_2$, $CH_2OHC(O)$, $C_2H_5C(O)$, $C_3H_7C(O)$, $CHOCH_2CH_2C(O)$, $C_6H_5C(O)$ have also been observed (Stephens, 1969; Spence et al., 1978; Niki et al., 1978, 1979, 1980, 1987; Edney et al., 1979a,b; Lesclaux et al., 1986; Rogers and Rhead, 1987). There are several studies in which the ratio k_{10}/k_6 has been determined. Determinations of this rate constant ratio for PAN have ranged from 1.7 to 3.1 (Cox et al., 1976; Cox and Roffey, 1977; Hendry and Kenley, 1977); the variation most likely due to the pressure dependence of (6). A ratio of 1.52 ± 0.12 was found for PBzN (Kenley and Hendry, 1982). Atkinson and Lloyd (1984) recommend a ratio of 1.5 for all reactions of these types based on the modeling study of Carter et al. (1979). Under ambient conditions of T, P and $[NO_2] \cong 1$ ppbv, Reaction 6 can be relatively rapid $\tau < 10^3$ s. Aside from Reactions 5 and 10, the $RO_2^{\cdot}$ Reactions (11–14)

$$RO_2^{\cdot} + HO_2^{\cdot} \rightarrow ROOH + O_2 \tag{11}$$

$$RO_2^{\cdot} + RO_2^{\cdot} \rightarrow 2RO^{\cdot} + O_2 \tag{12}$$

$$\rightarrow R'CHO + R'CH_2OH + O_2$$

$$RC(O)OO^{\cdot} + RO_2^{\cdot} \rightarrow RC(O)OH + R'CHO + O_2 \tag{13}$$

$$\rightarrow \text{other products}$$

$$2RC(O)OO^{\cdot} \rightarrow RC(O)O^{\cdot} + O_2 \tag{14}$$

must also be considered in evaluating $RONO_2$ formation. Rate measurements indicate that these reactions can be rapid (Cox and Tyndall, 1979; Addison et al., 1980; Adachi and Basco, 1982a; Basco and Parmar,

Table 5. Rate constant ratios $\alpha_i = k_5/(k_5 + k_{10})$ for individual alkyl peroxy radicals at 299 ± 2 K and 735–740 torr

Parent compound	Primary RO$_2$	α	Secondary RO$_2$	α	Tertiary RO$_2$	α	References
Ethane	Ethyl	$\leqslant 0.014$					Atkinson et al., 1984a
Propane	1-Propyl	0.020 ± 0.009	2-Propyl	0.042 ± 0.003			Atkinson et al., 1987a
Propene	2-Hydroxy-1-propyl	0.015 ± 0.008	1-Hydroxy-2-propyl	0.017 ± 0.009			Shepson et al., 1985
n-Butane	1-Butyl	< 0.040	2-Butyl	0.090 ± 0.008			Atkinson et al., 1987a
n-Pentane			2-Pentyl	0.129 ± 0.016			Atkinson et al., 1984a
			3-Pentyl	0.131 ± 0.016			Atkinson et al., 1987a
Cyclopentane			Cyclopentyl	0.045 ± 0.015			Takagi et al., 1981b
Neopentane	Neopentyl	0.0513 ± 0.0053					Atkinson et al., 1987a
2-Methyl butane			2-Methyl-3-butyl	0.141 ± 0.003	2-Methyl-2-butyl	0.0533 ± 0.002	Atkinson et al., 1984a; 1987a
n-Hexane			2-Hexyl	0.209 ± 0.032			Atkinson et al., 1987a
			3-Hexyl	0.230 ± 0.031			Atkinson et al., 1987a
Cyclohexane			Cyclohexyl	0.160 ± 0.015			Atkinson et al., 1987a
				0.090 ± 0.044			Takagi et al., 1981b
2-Methylpentane			2-Methyl-3-and 2-Methyl-4-pentyl	0.190 ± 0.018	2-Methyl-2-pentyl	0.035 ± 0.096	Atkinson et al., 1984a; 1987a
3-Methylpentane			3-Methyl-2-pentyl	0.162 ± 0.009			Atkinson et al., 1987a
Toluene	Benzyl	0.12 ± 0.02					Hoshino et al., 1978a
		$\sim 0.09 \pm 0.02^*$					Gery et al., 1985
n-Heptane			2-Heptyl	0.291 ± 0.022			Atkinson et al., 1987a
			3-Heptyl	0.323 ± 0.048			Atkinson et al., 1987a
			4-Heptyl	0.285 ± 0.015			Atkinson et al., 1987a
			2,3 and 4-Heptyl†	0.251 ± 0.50			Harris and Kerr, 1989
Cycloheptane			Cycloheptyl	0.050 ± 0.011			Takagi et al., 1981b
n-Octane			2-Octyl	0.323 ± 0.024			Atkinson et al., 1987a
			3-Octyl	0.348 ± 0.032			Atkinson et al., 1987a
			4-Octyl	0.329 ± 0.032			Atkinson et al., 1987a

*From toluene photooxidation studies; not corrected for subsequent reactions of benzaldehyde and benzyl nitrate.

†The overall yield for the sum of 2-, 3- and 4-heptyl isomers.

Table 6. Rate constants of the reaction of peroxy radicals ($RO_2 \cdot$) with nitrogen dioxide (NO_2)

RO$_2$	Low pressure limit		High pressure limit			Reference
	$k_0^{300}*$	n	$k_\infty^{300}*$	m		
HO_2	$1.8 \pm 0.3 \times 10^{-31}$	3.2 ± 0.4	$4.7 \pm 1.0 \times 10^{-12}$	1.4 ± 1.4		NASA, 1987
CH_3O_2	$1.5 \pm 0.8 \times 10^{-30}$	4.0 ± 2.0	$6.5 \pm 3.2 \times 10^{-12}$	2.0 ± 2.0		NASA, 1987
$CFCl_2O_2$	$3.5 \pm 0.5 \times 10^{-29}$	4.0 ± 2.0	$6.0 \pm 1.0 \times 10^{-12}$	2.0 ± 2.0		Lesclaux and Caralp, 1984
	k_0^{298}†	n_0	k_∞^{298}†	n_∞	C	
CCl_3O_2	$9.2 \pm 3.0 \times 10^{-29}$	6.0 ± 1.5	14.9×10^{-12}	0.30 ± 0.3	260	Caralp et al., 1988
$CFCl_2O_2$	$5.5 \pm 1.6 \times 10^{-29}$	5.5 ± 1.5	8.3×10^{-12}	0.66 ± 0.3	342	Caralp et al., 1988
CF_2ClO_2	$4.0 \pm 2.0 \times 10^{-29}$	5.1 ± 1.0	10.2×10^{-12}	0.66 ± 0.3	373	Caralp et al., 1988
CF_3O_2	$2.7 \pm 0.8 \times 10^{-29}$	4.7 ± 1.0	8.9×10^{-12}	0.72 ± 0.3	416	Caralp et al., 1988
$CH_3CH_2O_2$			$1.2 \pm 0.07 \times 10^{-12}$‡			Adachi and Basco, 1979
$CH_3C(O)O_2$	$2.1 \pm 0.1 \times 10^{-12}$§		$4.7 \pm 0.3 \times 10^{-12}$||			Addison et al., 1980
	5.1×10^{-29}		6.1×10^{-12}¶			Basco and Parmar, 1987
$(CH_3)_2CHO_2$			$5.6 \pm 0.17 \times 10^{-12}**$			Adachi and Basco, 1982b

*Fit to the expression:

$$k(M, T) = \left[\frac{k_0(T)[M]}{1 + k_0(T)[M]/k_\infty(T)} \right] 0.6^{\{1 + [\log_{10}(k_0(T)[M]/k_x(T))^2]\}^{-1}}$$

where: $k_0(T) = k_0^{300}(T/300)^{-n} \, cm^6 \, molec^{-1} \, s^{-1}$; $k_x(T) = k_\infty^{300}(T/300)^{-m} \, cm^3 \, molec^{-1} \, s^{-1}$.

†Fit to the expression:

$$\log k(T) = \frac{k_0[M]}{1 + k_0[M]/k_\infty} + \frac{\log F_c}{1 + \{[\log(k_0[M]/k_x)]/N_c\}^2}$$

where: $k_0(T) = k_0^{298}(T/298)^{-n_0}$, $cm^6 \, molec^{-1} \, s^{-1}$, $k_x(T) = k^{298}(T/298)^{-n_x}$, $cm^3 \, molec^{-1} \, s^{-1}$, $F_c = \exp(T/C)$, and $N_c = 0.75 - 1.27 F_c$.

‡$cm^3 \, molec^{-1} \, s^{-1}$ at 298 K, independent of pressure 44–676 torr.

§$cm^3 \, molec^{-1} \, s^{-1}$, at 302 K, 28 torr.

\|\|$cm^3 \, molec^{-1} \, s^{-1}$, 302 K, 715 torr.

¶Fit to the expression:

$$\log k = \log\left(\frac{k_\infty k_0[M]}{1 + k_0[M]} \right) + \frac{\log F_c}{1 + \{\log(k_0[M]/k_\infty)\}^2}$$

where: k_0 ($cm^6 \, molec^{-1} \, s^{-1}$), and k_∞ ($cm^3 \, molec^{-1} \, s^{-1}$) are for 298 K and $F_c = 0.19$. This includes the data of Addison et al. (1980).

**$cm^3 \, molec^{-1} \, s^{-1}$ at 298 K, independent of pressure 55–400 torr.

1985), especially (11). Thus (11–14) can limit organic nitrate formation, especially in low NO_x environments.

Studies of the reaction of NO_3 with alkenes (Reaction 7) (Japar and Niki, 1975; Hoshino et al., 1978b; Shepson et al., Bandow et al., 1980; Dlugokencky and Howard, 1989; Canosa-Mass et al., 1988a,b) indicate that it proceeds through addition to the double bond, forming a carbon radical and a nitrooxy group:

$$\underset{\diagup}{\overset{\diagdown}{C}} = \underset{\diagdown}{\overset{\diagup}{C}} + NO_3 \xrightarrow{M} \underset{\diagup}{\overset{\diagdown}{C}} - \underset{\diagdown}{\overset{ONO_2}{\overset{\diagup}{C}}} \cdot \qquad (7)$$
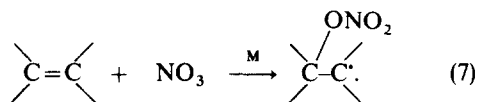
The carbon radical rapidly reacts with O_2 to form a peroxy radical. NO_3 will have significant abundances only at night and the coexistence of NO_3 and NO is precluded by their rapid reaction. Therefore, the likely fates of peroxy radicals formed by NO_3 reaction are Reactions (6) and (11–13). The resulting difunctional

products, i.e. nitrooxy ketones and aldehydes, dinitrates or nitrooxy peroxynitrates, have been observed in chamber studies (Hoshino et al., 1978b; Bandow et al., 1980; Shepson et al., 1985).

The rate constants of initial reactions of NO_3 with alkenes are summarized in Table 7. These reactions can be quite rapid especially for compounds having highly substituted or conjugated double bonds. The temperature dependencies of some NO_3 reactions with alkenes and alkynes have recently been determined, and are summarized in Table 8. Measurements of NO_3 in the troposphere have shown mixing ratios up to 100 pptv (Platt et al., 1980, 1981, 1984; Noxon et al., 1980; Noxon, 1983) and have indicated the presence of rapid sink reactions. Thus, Reaction (7) may initiate significant formation pathways for multifunctional organic nitrates.

The unimolecular decomposition of peroxycarboxylic nitric anhydrides to form the corresponding C_{N-1} alkyl nitrate

$$RC(O)OONO_2 \rightarrow RONO_2 + CO_2 \qquad (15)$$

has been observed and quantified for PAN (Stephens, 1969; Fild and Lovell, 1970; Senum et al., 1986), but appears to be a general process based on several studies involving R(CO)OONO₂ chemistry (Darley et al., 1963; Kopczynski et al., 1974). The rate measured for PAN decomposition through this channel was several hundred times slower than the bond homolysis channel:

$$RC(O)OONO_2 \rightarrow RC(O)OO^\cdot + NO_2 \quad (-6)$$

but exhibited a similar temperature dependence (Senum et al., 1986) (see next section). This represents a loss mechanism for PAN that occurs in the absence of NO. Given other possible formation pathways, abundance of the parent compounds, and similar rates, Reaction (15) is likely to be an important source of methyl nitrate but not larger compounds. The importance of this methyl nitrate source must be evaluated in the context of rates of methyl nitrate removal, PAN concentrations and ambient temperatures.

Reaction (9) involves the pressure-dependent addition reaction of an alkoxy radical RO$^\cdot$ with NO$_2$ to form RONO$_2$. While such reactions are fast, there are a number of competing reactions that RO$^\cdot$ may undergo. H-atom transfer reactions occur if R con-

Table 7. Rate constants for the reaction of NO$_3$ with alkenes and alkynes at 294–298 ($\pm$2) K

Compound	k^* (cm^3 molec^{-1} s^{-1})	Reference
Ethene	$2.14 \pm 0.32 \times 10^{-16}$‡	Atkinson et al., 1988
	$9.3 \pm 1.0 \times 10^{-16}$	Japar and Niki, 1975
	$1.85 \pm 0.24 \times 10^{-16}$	Canosa-Mas et al., 1988a
Acetylene	$\leqslant 0.23 \times 10^{-16}$	Atkinson et al., 1987b
	$0.51 \pm 0.35 \times 10^{-16}$	Canosa-Mas et al., 1988a
Propene	$9.40 \pm 1.19 \times 10^{-15}$‡	Atkinson et al., 1988
	$5.3 \pm 0.30 \times 10^{-15}$	Japar and Niki, 1975
Propyne	$0.94 \pm 0.44 \times 10^{-16}$	Atkinson et al., 1987b
	$2.66 \pm 0.32 \times 10^{-16}$	Canosa-Mas et al., 1988a
1-Butene	$9.70 \pm 2.10 \times 10^{-15}$	Atkinson et al., 1984c
	$7.80 \pm 0.80 \times 10^{-15}$	Japar and Niki, 1975
1-Butyne	$4.55 \pm 0.46 \times 10^{-16}$	Canosa-Mas et al., 1988a
2-Butyne	$6.7 \pm 1.5 \times 10^{-14}$	Canosa-Mas et al., 1988a
Isobutene	$3.05 \pm 0.34 \times 10^{-13}$	Atkinson et al., 1984c
	$3.4 \pm 0.7 \times 10^{-13}$	Canosa-Mas et al., 1988a
	$3.30 \pm 0.43 \times 10^{-13}$	Ravishankara and Mauldin, 1985
	$1.1 \pm 0.1 \times 10^{-13}$	Japar and Niki, 1975
cis-2-Butene	$3.39 \pm 0.39 \times 10^{-13}$	Atkinson et al., 1984c
	$1.8 \pm 0.2 \times 10^{-13}$	Japar and Niki, 1975
trans-2-Butene	$3.78 \pm 0.41 \times 10^{-13}$	Ravishankara and Mauldin, 1985
	$3.96 \pm 0.48 \times 10^{-13}$	Dlugokencky and Howard, 1989
	$1.4 \pm 0.1 \times 10^{-13}$	Japar and Niki, 1975
1,3-Butadiene	$9.57 \pm 1.10 \times 10^{-14}$	Atkinson et al., 1984b
	$2.1 \pm 0.4 \times 10^{-13}$	Benter and Schindler, 1988
	$2.2 \pm 0.6 \times 10^{-13}$	Canosa-Mas et al., 1988a
2-Methyl-2-butene	$9.33 \pm 1.18 \times 10^{-12}$‡	Atkinson et al., 1988
	$5.5 \pm 0.5 \times 10^{-12}$	Japar and Niki, 1975
Cyclopentene	$4.52 \pm 0.52 \times 10^{-13}$	Atkinson et al., 1985b
1-Pentyne	$7.54 \pm 0.75 \times 10^{-16}$	Canosa-Mas et al., 1988a
Isoprene	$5.79 \pm 0.68 \times 10^{-13}$	Atkinson et al., 1984b
	$1.3 \pm 0.14 \times 10^{-12}$	Benter and Schindler, 1988
	$6.52 \pm 0.78 \times 10^{-13}$	Dlugokencky and Howard, 1989
1-Hexyne	$1.6 \pm 0.19 \times 10^{-15}$	Canosa-Mas et al., 1988a
2,3-Dimethyl-2-butene	$5.69 \pm 0.73 \times 10^{-11}$‡	Atkinson et al., 1988
	$3.7 \pm 0.5 \times 10^{-11}$	Japar and Niki, 1975
2,3-Dimethyl-1,3-butadiene	$2.3 \pm 0.3 \times 10^{-12}$	Benter and Schindler, 1988
Cyclohexene	$5.14 \pm 0.61 \times 10^{-13}$	Atkinson et al., 1984b
1,3-Cyclohexadiene	$1.30 \pm 0.30 \times 10^{-11}$	Atkinson et al., 1984b
	$1.1 \pm 0.1 \times 10^{-11}$	Benter and Schindler, 1988
1,4-Cyclohexadiene	$5.17 \pm 0.63 \times 10^{-13}$	Atkinson et al., 1984b
	$7.8 \pm 0.7 \times 10^{-13}$	Benter and Schindler, 1988
Cycloheptene	$4.71 \pm 0.56 \times 10^{-13}$	Atkinson et al., 1985b
1,3-Cycloheptadiene	$6.80 \pm 1.60 \times 10^{-12}$	Atkinson et al., 1984b
Bicyclo[2.2.1]-2-heptene	$2.41 \pm 0.28 \times 10^{-13}$	Atkinson et al., 1985b
Bicyclo[2.2.1]-2,5-heptadiene	$9.92 \pm 1.13 \times 10^{-13}$	Atkinson et al., 1985b
1,3,5-Cycloheptatriene	$1.3 \pm 0.3 \times 10^{-12}$	Atkinson et al., 1985b
Bicyclo[2.2.2]-2-octene	$1.44 \pm 9.18 \times 10^{-13}$‡	Atkinson et al., 1988
α-Pinene	$6.10 \pm 1.40 \times 10^{-12}$	Atkinson et al., 1984b
	$6.18 \pm 0.74 \times 10^{-12}$	Dlugokencky and Howard, 1989

Table 7. (Continued)

Compound	$k*$ (cm^3 molec^{-1} s^{-1})	Reference
β-Pinene	$2.36 \pm 0.28 \times 10^{-12}$‡	Atkinson et al., 1988
Δ^3-Carene	$1.05 \pm 0.23 \times 10^{-11}$	Atkinson et al., 1984b
d-Limonene	$1.38 \pm 0.30 \times 10^{-11}$	Atkinson et al., 1984b
Myrcene	$1.10 \pm 0.30 \times 10^{-11}$†	Atkinson et al., 1985a
cis- and trans-Ocimene	$2.4 \pm 0.6 \times 10^{-11}$†	Atkinson et al., 1985a
α-Terpinene	$1.94 \pm 0.47 \times 10^{-10}$†	Atkinson et al., 1985a
γ-Terpinene	$3.1 \pm 0.7 \times 10^{-11}$†	Atkinson et al., 1985a
α-Phellandrene	$9.1 \pm 2.3 \times 10^{-11}$†	Atkinson et al., 1985a
Acrolein	$5.9 \pm 1.8 \times 10^{-16}$	Atkinson et al., 1987b
Crotonaldehyde	$4.1 \pm 0.9 \times 10^{-15}$	Atkinson et al., 1987b
Vinyl chloride	$2.3 \pm 1.1 \times 10^{-16}$	Atkinson et al., 1987b
1,1-Dichloroethene	$6.6 \pm 3.1 \times 10^{-16}$	Atkinson et al., 1987b
cis-1,2-Dichloroethene	$7.5 \pm 3.5 \times 10^{-17}$	Atkinson et al., 1987b
trans-1,2-Dichloroethene	$5.7 \pm 2.7 \times 10^{-17}$	Atkinson et al., 1987b
Trichloroethene	$1.5 \pm 0.7 \times 10^{-16}$	Atkinson et al., 1987b
Tetrachloroethene	$<0.4 \times 10^{-16}$	Atkinson et al., 1987b
Allyl chloride	$2.9 \pm 1.3 \times 10^{-16}$	Atkinson et al., 1987b

*The rate constants reported in Atkinson et al. (1984b, c) were determined using the best value for the $N_2O_5 = NO_3 + NO_2$ equilibrium constant available at that time. Atkinson et al. (1987b) have used the absolute measurement of $NO_3 + trans$-2-butene by Ravishankara and Mauldin (1985) for their rate constant measurements, and to recalculate previously determined rate constants. Accordingly, the rate constant of Ravishankara and Mauldin was adopted here as the absolute standard and other rate constants determined by relative rates were recalculated relative to it.

†These rate constants are based on a more recent N_2O_5 equilibrium constant, which results in good agreement between rate constants derived from the data of Atkinson et al. (1985b) and those based on the measurements of Ravishankara and Mauldin (1985).

‡The rate constants reported by Atkinson et al. (1988) were measured by relative rates using the average of the trans-2-butene rate constants measured by Ravishankara and Mauldin (1985), and Dlugokencky and Howard (1989) as the absolute standard.

Table 8. Temperature dependencies in the reaction of NO$_3$ with some alkenes and alkynes*

Compound	Temperature range (K)	A (cm^3 molec^{-1} s^{-1})	E_a/R	Reference
Acetylene	295–523	$4.9 \, (^{+16}_{-4}) \times 10^{-13}$	2800 ± 1100	Canosa-Mas et al., 1988b
Ethene	295–523	$6.3 \, (^{+2.9}_{-2.0}) \times 10^{-12}$	3100 ± 480	Canosa-Mas et al., 1988b
Propyne	295–473	$1.5 \, (^{+4.0}_{-1.1}) \times 10^{-11}$	3200 ± 600	Canosa-Mas et al., 1988b
1-Butyne	295–473	$3.2 \, (^{+5.0}_{-2.0}) \times 10^{-11}$	3400 ± 480	Canosa-Mas et al., 1988b
1-Pentyne	295–473	$3.0 \, (^{+2.5}_{-1.4}) \times 10^{-11}$	3200 ± 480	Canosa-Mas et al., 1988b
trans-2-Butene	204–378	†	†	Dlugokencky and Howard, 1989
Isoprene	251–381	$3.03 \pm 0.45 \times 10^{-12}$	450 ± 70	Dlugokencky and Howard, 1989
1-Hexyne	295–473	$9.0 \, (^{+5.1}_{-3.2}) \times 10^{-12}$	2600 ± 360	Canosa-Mas et al., 1988b
α-Pinene	261–384	$1.19 \pm 0.31 \times 10^{-12}$	-490 ± 70	Dlugokencky and Howard, 1989

*Fit to the equation $k(T) = A \exp(-E_a/RT)$.

†A four parameter fit $k(T) = (1.78 \pm 0.36) \times 10^{-12} \exp[-(530 \pm 100)/T] + (2.28 \pm 0.26) \times 10^{-14} \exp[(570 \pm 110)/T]$ was found to best describe the substantial curvature in this temperature dependence.

tains a hydrogen α to the oxygen;

$$RR'CHO^\cdot + NO_2 \rightarrow RR'CO + HONO \quad (16)$$

$$RR'CHO^\cdot + O_2 \rightarrow RR'CO + H_2O^\cdot. \quad (17)$$

Alternatively RO$^\cdot$ may decompose in a unimolecular fashion,

$$RR'R''CO^\cdot \xrightarrow{M} RR'C=O + R''^\cdot, \quad (18)$$
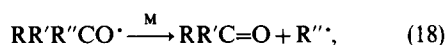
where R and R' may be alkyl groups or hydrogens and R'' is an alkyl group. The reactions of RO$^\cdot$ with NO to form RONO are rapid, however, RO$^\cdot$ is reformed

rapidly (τ photolysis <5 min) in the daytime so this reaction does not constitute a loss process. Alkoxy radicals of carbon number greater than 3 may also isomerize through 1,4 or 1,5 hydrogen shifts to form 4- or 5-hydroxy peroxy radicals (following rapid addition of O$_2$ to the carbon radical).

Determinations of rate constants for (9) where $R = CH_3$ (Batt and Rattray, 1979), C_2H_5 (Batt and Milne, 1977) and $i - C_3H_7$ (Balla et al., 1985) indicate that this reaction is rapid ($k = 1-4 \times 10^{-11}$ cm^3 molec^{-1} s^{-1}) and evidence suggests that the rate constant of (16) is small relative to that of (9) ($k_{16}/k_9 < 0.05$) (Batt and Rattray, 1979; Batt 1980).

Reaction (17) has been found to be slow for $R = CH_3$ (Barker *et al.*, 1977; Batt and Robinson, 1979; Cox *et al.*, 1980; Gutman *et al.*, 1982; Wantuck *et al.*, 1987), C_2H_5 (Gutman *et al.*, 1982; Zabarnick and Heicklen, 1985a), n-C_3H_7 (Zabarnick and Heicklen, 1985b), i-C_3H_7 (Balla *et al.*, 1985), and i-C_4H_9 (Zabarnick and Heicklen, 1985c) with a rate constant ranging from 1.3×10^{-15} to 1.9×10^{-14} cm³/molec-s. Akimoto *et al.* (1978) determined $k_{17}/k_9 = 1.4 \times 10^{-4}$ $R = C_6H_5CH_2$. Considering the atmospheric mixing ratios of O_2 and NO_2 in the polluted troposphere, 0.21 (5×10^{18} molec cm^{-3}) and $<2 \times 10^{-7}$ (200 ppbv; 5×10^{12} molec cm^{-3}), respectively, Reaction (17) is the dominant fate of $RO^\cdot$ and (9) constitutes a very small atmospheric source of $RONO_2$.

Reaction (18) proceeds at significant rates at atmospheric temperatures for some compounds (Atkinson and Lloyd, 1984; Carter and Atkinson, 1985). The analogous reactions of trihalomethoxy radicals CX_3O to form carbonyl halides, CX_2O, and a halogen atom have been observed and predicted to be rapid enough under stratospheric conditions that the fraction reacting with NO_2 to form CX_3ONO_2 is negligibly small (Carr *et al.*, 1986; Rayez *et al.*, 1987; Francisco *et al.*, 1987; Lesclaux *et al.*, 1987).

The formation of organic nitrates in combustion effluents must be considered as a possible source. The chemistry in exhaust streams of internal combustion engines involve substantially different conditions relative to the atmosphere. For example, in motor vehicle exhaust, $[NO_2]$ is much higher (~ 100 ppmv) and $[O_2]$ lower (<0.05 mole fraction). However, gas temperatures are much higher (200–400°C), and potentially catalytic materials and surfaces are present. Thus, higher $[NO_2]$ increases the fraction of $RO^\cdot$ that undergoes Reaction (9) (unknown temperature dependence) relative to Reaction (17), the rate of which increases ~ 10 fold due to temperature (Cox *et al.*, 1980; Gutman *et al.*, 1982) but decreases due to lower $[O_2]$. The unimolecular decomposition reaction (18), isomerization through the 1,4- and 1,5-hydroxy shift mechanism, and (-9):

$$RONO_2 \xrightarrow{M} RO^\cdot + NO_2 \qquad (-9)$$
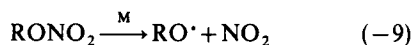
are significantly faster at exhaust stream temperatures (Batt and Robinson, 1987; Balla *et al.*, 1985; Zabarnick and Heicklen, 1985b,c), and should constitute the major loss mechanisms for $RO^\cdot$. The extent of formation of $RONO_2$ compounds in combustion effluents depends critically on the combination of gas composition and temperature, and nitrate formation may occur upon mixing of the exhaust with ambient air. However, the abundance of aldehydes and ketones in gasoline engine exhaust and the fact that alkyl nitrates have not been observed in exhaust from internal combustion engines (Jonsson, 1985) support the notion that (9) does not constitute a major exhaust source of $RONO_2$.

ATMOSPHERIC REMOVAL PROCESSES

The gas-phase processes responsible for the destruction of organic nitrates are reaction with OH radicals, photolysis, and thermal decomposition. Multi-phase processes of potential importance are uptake by cloudwater, aerosol or precipitation, and deposition on ground surfaces. The relative importance of each of the above processes is different for each compound type, varies from one compound to another within a type, and is different for a given compound depending on location in the atmosphere (e.g. upper troposphere, surface layer).

Rate constants for the reaction of OH with some alkyl nitrates and PAN are listed in Table 9. These reactions appear to proceed via hydrogen abstraction from the alkyl group. With the exceptions of methyl and ethyl nitrates, the measured alkyl nitrate rate constants are lower than those of the parent alkane (Atkinson, 1986). Atkinson (1986), Atkinson *et al.* (1982a, 1984a) and Gaffney *et al.* (1986) have calculated group rate constants and subsitutent factors to estimate OH–alkyl nitrate rate constants. These approximations yield rate constants that are within a factor of 2 of measured values. Based on the above rate constants and a seasonally-, spatially-, and diurnally-averaged OH concentration of 6×10^5 mol cm^{-3}, atmospheric lifetimes against OH reaction of between 5 days (3-octyl nitrate) and 1.6 years (methyl nitrate) are predicted.

The rate constant for the reaction of chlorine atoms (Cl) with PAN was recently determined to be 3.7 (± 1.7) $\times 10^{-13}$ cm³ molec^{-1} s^{-1} (Tsalkani *et al.*, 1988), approximately 10^2 smaller than a previous estimate, which was based on the Cl + ethane rate constant (Singh and Hanst, 1981). The new rate constant, coupled with estimated relative abundances of Cl and OH implies that reaction with OH will dominate that of Cl by about 10^3 throughout the upper troposphere and stratosphere.

The photolysis of organic nitrates through absorption of solar radiation in the near-u.v. region appears to be a significant atmospheric loss mechanism. Rates of photolysis may be estimated from the u.v.-absorption spectrum of a given compound, solar actinic flux estimates, and known or assumed quantum efficiencies. The state of knowledge concerning photolysis processes is summarized below.

It has been known since the work of Hartley (1903) that the absorption spectrum of ethyl nitrate was a featureless continuum in the near-u.v. region. Early quantitative absorption data were obtained by Goodeve (1934) for ethyl nitrate. The u.v. spectra of compounds containing the NO_2 group (Harris, 1973) and $RONO_2$ compounds (Csizmadia *et al.*, 1973) have been the subject of molecular orbital and liquid phase studies. The spectra (Figs 4–6) are all quite similar in appearance, the spectra of $HONO_2$ and $HOONO_2$ are also shown for comparison purposes, exhibiting

Table 9. Rate constants for the reaction of OH radicals with organic nitrates

Compound	k $(cm^3\ molec^{-1}\ s^{-1})$ $(\times 10^{12})$	Conditions (K), (torr)	Reference
Methyl nitrate	0.034 ± 0.004	298, 1.98–3.15	Gaffney et al., 1986
	0.37 ± 0.09	303, 750	Kerr and Stocker, 1986
Ethyl nitrate	0.48 ± 0.2	303, 750	Kerr and Stocker, 1986
n-Propyl nitrate	0.70 ± 0.22	303, 750	Kerr and Stocker, 1986
2-Propyl nitrate	$0.18 \pm 0.05*$	299, 735	Atkinson et al., 1982a
n-Butyl nitrate	$1.39 \pm 0.11*$	299, 735	Atkinson et al., 1982a
2-Butyl nitrate	$0.67 \pm 0.10*$	299, 735	Atkinson et al., 1982a
2-Pentyl nitrate	$1.83 \pm 0.12*$	299, 735	Atkinson et al., 1982a
3-Pentyl nitrate	$1.10 \pm 0.20*$	299, 735	Atkinson et al., 1982a
2-Methyl-3-butyl nitrate	$1.72 \pm 0.05†$	298, 735	Atkinson et al., 1984a
2,2-Dimethyl-1-propyl nitrate	$0.85 \pm 0.20†$	298, 735	Atkinson et al., 1984a
2-Hexyl nitrate	$3.13 \pm 0.15*$	299, 735	Atkinson et al., 1982a
3-Hexyl nitrate	$2.66 \pm 0.21*$	299, 735	Atkinson et al., 1982a
Cyclohexyl nitrate	$3.29 \pm 0.36†$	298, 735	Atkinson et al., 1984a
2-Methyl-2-pentyl nitrate	$1.71 \pm 0.22†$	298, 735	Atkinson et al., 1984a
3-Methyl-2-pentyl nitrate	$3.01 \pm 0.08†$	298, 735	Atkinson et al., 1984a
3-Heptyl nitrate	$3.64 \pm 0.43*$	299, 735	Atkinson et al., 1982a
3-Octyl nitrate	$3.82 \pm 0.78*$	299, 735	Atkinson et al., 1982a
Peroxyacetic nitric anhydride	0.113 ± 0.06	273, 25–100	Wallington et al., 1984
	0.137 ± 0.05	297, 25–100	Wallington et al., 1984
	0.075 ± 0.014	298, 0.6–1.9	Tsalkani et al., 1988

*The rate constant was measured relative to that of cyclohexane and was corrected for the slight change in cyclohexane rate constant resulting from the review of Atkinson (1986).

†The rate constant was measured relative to that of n-butane and was corrected for the slight change in n-butane rate constant resulting from the review of Atkinson (1986).

$\pi \to \pi^*$ transitions at $\lambda \leqslant 190$ nm and lower energy $n \to \pi^*$ transitions in the 250–270 nm range, which appear as inflections in an otherwise exponential decrease with wavelength. The exception to the above is the spectrum of nitrooxy acetone (NOA) in which the additional carbonyl chromophere is evident.

Recent measurement of gas-phase absorption spectra of compounds of the type $RONO_2$ and $ROONO_2$ are summarized in Tables 10 and 11, respectively. The absorption cross-sections of a number of alkyl nitrates have recently been measured by Roberts and Fajer (1989). Increases in the magnitudes of cross-sections were observed for primary alkyls with increasing carbon chain length, and for alkyl groups with increasing degree of substitution, Fig. 5. In addition, the cross-section of nitrooxy ethanol, $HOCH_2CH_2ONO_2$, was observed to be approximately a factor of 5 below that of methyl nitrate in the actinic region $\lambda > 290$ nm. It was also found that the spectra could be fit by second degree exponential equations of the form $\sigma(\lambda) = \exp(a\lambda^2 + b\lambda + c)$, such fits are summarized in Table 12. A number of determinations have been made of methyl and ethyl nitrate cross-sections. Those of methyl nitrate (Calvert and Pitts, 1966; Maria et al., 1973; Taylor et al., 1980; Roberts and Fajer, 1989) agree within stated experimental errors; however, those errors are almost a factor of 2 range for $\lambda > 290$ nm. Two recent ethyl nitrate cross-section measurements (Takacs, unpublished results, 1988; Roberts and Fajer, 1989) are in
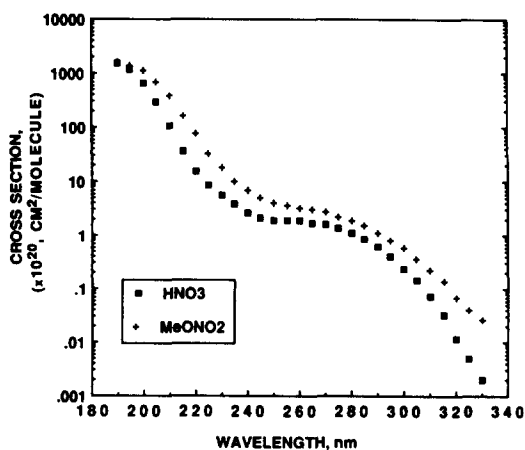
Fig. 4. The u.v. absorption spectra of HNO_3 (Molina and Molina, 1981) and methyl nitrate (Taylor et al. 1980) between 190 and 330 nm.

excellent agreement, while that of Calvert and Pitts (1966) is higher and diverges from the other two in the region $\lambda > 290$ nm, and that of Goodeve (1934, as reported by Leighton, 1961) exhibits the opposite curvature and is higher in the region $\lambda > 310$ nm.

Spectra of various $ROONO_2$ compounds have also been measured in a number of different studies. Methyl peroxynitrate has been studied at 298 K by Sander and Watson (1980), at 296 K by Morel et al.

Table 10. Gas phase u.v. absorption cross-sections of compounds of the type $RONO_2$

λ(nm)	H*	CH_3†	CH_3‡	C_2H_5‡	$i\text{-}C_3H_7$‡	$t\text{-}C_4H_9$‡	NOA‡§
			$\sigma(\times 10^{20}$ cm^2 molecules$^{-1})$				
190	1560	1600					
195	1150	1400					
200	661	1100					
205	293	700					
210	105	380					
215	35.6	160					
220	15.1	78					
225	8.62	33					
230	5.65	18					
235	3.72	10					
240	2.57	6.7					
245	2.10	5.0					
250	1.91	4.1 ± 0.8					
255	1.90	3.7					
260	1.88	3.2					
265	1.71	3.0					
270	1.59	2.7	2.4	3.1	4.1	4.3	
275	1.35	2.2	2.0	2.8	3.6	4.0	
280	1.10	1.9	1.6	2.3	2.9	3.7	
285	0.848	1.5	1.2	1.8	2.3	3.1	5.2
290	0.607	1.1	0.83	1.3	1.7	2.6	5.2
295	0.409	0.80	0.56	0.84	1.2	2.0	4.8
300	0.241	0.57	0.35	0.52	0.80	1.5	4.1
305	0.146	0.36	0.21	0.30	0.51	1.0	3.4
310	0.071	0.22 ± 0.18	0.12	0.16	0.30	0.70	2.5
315	0.032	0.14	0.067	0.081	0.17	0.45	1.8
320	0.012	0.070	0.035	0.038	0.092	0.27	1.2
325	0.005	0.040	0.017	0.017	0.047	0.15	0.73
330	0.002	0.026	0.008	0.007	0.022	0.086	0.42

*Molina and Molina (1981). $T = 298$ K.
†Taylor et al. (1980). $T = 298$ K. Error estimates: $\lambda = 1100 \pm 200$ ($\times 10^{20}$) at 200 nm, 4.1 ± 0.8 at 250 nm, 0.22 ± 0.18 at 310 nm.
‡Roberts and Fajer (1989).
§Nitrooxy acetone.

(1980), and at 275 K by Cox and Tyndall (1979) and are in reasonable agreement ($\pm 50\%$), with the latter measurements showing a distinct band at ~ 240 nm rather than an inflection, but none of the spectra extend beyond ~ 290 nm. Cross-sections of the CH_3OONO_2, CCl_3OONO_2 and $CFCl_2OONO_2$ are not significantly different from that of $H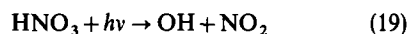OONO_2$. The absorption cross-section of PAN has been determined by Stephens (1969), and Senum et al. (1984), the latter measurements, which extended to 300 nm, were 20–30% lower.

The products and quantum yields of photolysis of $RONO_2$ and RO_2NO_2 compounds have not been studied extensively. The lack of structure in the absorption spectra of $RONO_2$ compounds has led to the assumption of dissociation quantum yields of unity (Taylor et al., 1980). Johnston et al. (1974) measured a quantum yield of 1 (± 0.05) for the process:

$$HNO_3 + h\nu \rightarrow OH + NO_2 \qquad (19)$$

between 200 and 315 nm. Gray and Rogers (1954) concluded that CH_3ONO_2 was photodissociated (by a low-pressure Hg lamp) through the analogous process:

$$CH_3ONO_2 + h\nu \rightarrow CH_3O^{\cdot} + NO_2 \qquad (20)$$

however, they did not measure the quantum yield. Gray and Style (1953) measured a quantum yield of 0.31 for the photolysis of $CH_3CH_2ONO_2$ by the 253.7 and 265 nm Hg lines and deduced that (21) was the sole photolysis pathway:

$$CH_3CH_2ONO_2 + h\nu \rightarrow CH_3CH_2O^{\cdot} + NO_2. \quad (21)$$

Rebbert (1963) deduced the following three pathways for the photolysis of $CH_3CH_2ONO_2$ at 313 nm:

$$CH_3CH_2ONO_2 + h\nu \rightarrow CH_3CH_2O + NO_2 \qquad \phi \geqslant 0.24 \qquad (21)$$

$$\rightarrow CH_3CHO + HONO \qquad \phi \leqslant 0.09 \qquad (22)$$

$$\rightarrow CH_3CH_2ONO + O \qquad \phi \leqslant 0.14 \qquad (23)$$

where ϕ is the quantum yield for a given process; the overall quantum yield was estimated at ~ 0.5. Renlund and Trott (1984) conclude that the photo-

Table 11. u.v. Absorption cross-sections of compounds of the type RO_2NO_2

λ(nm)	H^*	CH_3†	CCl_3†	$CFCl_2$†	$CH_3(CO)$‡	$CH_3CH_2(CO)$‡
			$\sigma(\times 10^{20}$ cm^2 molec$^{-1})$			
190	1010					
195	816					
200	563	528			317	269
205	367				237	211
210	241	278		125	165	155
215	164				115	101
220	120	133	136	85	77	69
225	95.2		117		55	48
230	80.8	62	97	70	40	35
235	69.8		79		29	24
240	59.1	50	65	56	21	17
245	49.7	44	53		15	12
250	41.8	35	51	39	11	9
255	35.1	30	40	35	8.0	6.5
260	27.8	26	30	29	5.7	4.6
265	22.4	23	25	18	4.0	3.2
270	17.8	16	14	12	2.8	2.3
275	13.4	12	11	6	1.8	1.5
280	9.3	7	9	4	1.1	1.0
285	6.3				0.72	0.60
290	4.0				0.41	0.33
295	2.6				0.22	0.16
300	1.6				0.11	0.097
305	0.1					
310	0.7					
315	0.4					
320	0.3					
325	0.2					
330	0.1					

*Molina and Molina (1981): $T = 298$ K; uncertainty estimated from 5% at 200 nm to 30% at 330 nm.

†Morel et al. (1980): $T = 296$ K; estimated relative standard deviations: 10% for 220–260 nm, 25% for 265–275 nm, and 50% for 280–290 nm.

‡Senum G. I. et al. (1984). Ultraviolet absorption spectrum of peroxyacetyl nitrate and peroxypropionyl nitrate. J. phys. Chem. 88, 1269–1270.

$T = 298 \pm 1$ K, Relative standard deviations varied from 1–2% at 200 nm, to 20–25% at 300 nm.
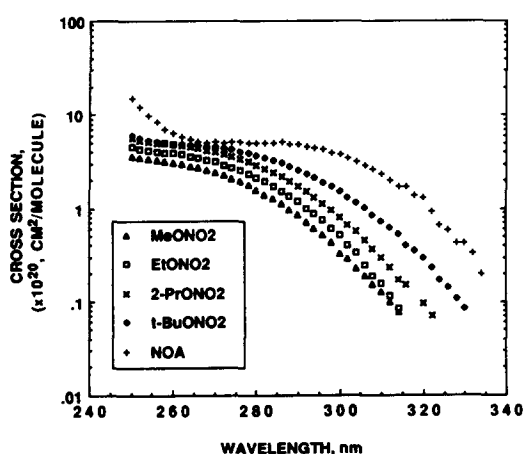
Fig. 5. The u.v. absorption spectra of methyl, ethyl, 2-propyl and t-butyl nitrates, and nitrooxy acetone (NOA) between 250 and 335 nm, from Roberts and Fajer (1989).

dissociation of $CH_3CH_2CH_2ONO_2$ at 193 nm proceeds through the process analogous to 21. Although no studies of larger organic nitrates have been re-ported, similar pathways may be expected for these compounds. It should be noted that the particular distribution of pathways should not have much effect on radical chemistry because expected concentrations of organic nitrates are small and photolysis rates slow relative to other photolytic radical sources such as O_3. Direct measurement of the rates of ethyl n-propyl, n-butyl and 2-butyl nitrate photolysis to yield NO_2 have been made by Luke and Dickerson (1988) and Luke et al. (1990). Those measurements, coupled with the absorption spectra determined by Roberts and Fajer (1989), result in quantum yields close to unity ($\pm 50\%$) for process [21] (and analogs) at temperatures of $\sim 25°$C. A pronounced temperature dependence was observed in the photolysis rates of ethyl, n-propyl and 2-butyl nitrates which yielded a factor of 2 larger rate between 6 and 26°C (Luke et al., 1989). Quantum efficiencies for photodissociation are probably close to unity and are unlikely to exhibit any temperature dependence since the actinic wavelength are so far above the bond dissociation energy threshold of ~ 700 nm (41 kcal mole^{-1}). Temperature de-

Table 12. Least squares fits of the organic nitrate absorption spectra to equations of the form: $\sigma(\lambda)=\exp(a\lambda^2+b\lambda+c)$ in the region $\lambda \geqslant 270$ nm (from Roberts and Fajer, 1989)

Compound	$a(\times 10^3)$	b	c	R^2	Uncertainty[†]
Methyl	-1.044	0.5309	-112.4	1.000	25
Ethyl	-1.442	0.7626	-145.7	0.999	25
1-Propyl	-1.344	0.7110	-138.9	0.999	25
2-Propyl	-1.086	0.5649	-118.0	0.999	25
1-Butyl	-1.384	0.7305	-141.2	0.999	20
2-Butyl	-1.250	0.6578	-131.1	1.000	20
t-Butyl	-0.993	0.5307	-115.5	0.999	25
2-Pentyl	-1.231	0.6454	-129.1	1.000	25
3-Pentyl	-1.446	0.7712	-147.4	0.999	25
Cyclopentyl	-1.884	1.0109	-180.5	0.997	100
Nitrooxyacetone*	-1.365	0.7834	-156.8	0.994	25
					70[‡]
Nitrooxyethanol	-2.359	1.2478	-210.4	0.998	140[§]

*$\lambda \geqslant 284$ nm.
[†]Relative uncertainty at 310 nm (%).
[‡]Relative uncertainty at 330 nm (%).
[§]Relative uncertainty at 300 nm (%).

Table 13. Photodissociation rate estimates for $RONO_2$ and $ROONO_2$ compounds

Compound	$J(s^{-1}(\times 10^6))$	Conditions	Reference
CH_3ONO_2	2.2	Surface, ZA* $=45°$	Taylor et al., 1980
	1.5	0.98 km alt. ZA $=0°$	Roberts and Fajer, 1989
$CH_3CH_2ONO_2$	1.9	0.98 km, ZA $=0°$	Roberts and Fajer, 1989
	1.4	Surface, ZA $=0$[†]	Luke et al., 1990
$CH_3CH_2CH_2ONO_2$	1.3	Surface, ZA $=0$[†]	Luke et al., 1990
$(CH_3)_2CHONO_2$	3.9	0.98 km, ZA $=0°$	Roberts and Fajer, 1989
$CH_3CH_2CH(ONO_2)CH_3$	3.5	0.98 km, ZA $=0°$	Roberts and Fajer, 1989
	2.5	Surface, ZA $=0$[†]	Luke et al., 1990
$(CH_3)_3/CONO_2$	10	0.98 km, ZA $=0°$	Roberts and Fajer, 1989
$CH_3C(O)CH_2ONO_2$	42	0.98 km, ZA $=0°$	Roberts and Fajer, 1989
$HOONO_2$	9.6	Troposphere	Molina and Molina, 1981
$CH_3C(O)OONO_2$	0.06–0.21	Surface, ZA $=0$–$60°$	Senum et al., 1984
$CH_3CH_2C(O)OONO_2$	0.07–0.23	Surface, ZA $=0$–$60°$	Senum et al., 1984

*ZA $=$ solar zenith angle.
[†]From the equations:
$J_{EN}=\exp\{[-3.341\times10^{-3}[O_3]_{total}\sec(\theta)]-8.396-(1211.2/T)\}$
$J_{NPN}=\exp\{\{-3.575\times10^{-3}[O_3]_{total}\sec(\theta)]-8.415-(1211.2/T)\}$
$J_{2BN}=\exp\{[3.594\,k\times10^{-3}[O_3]_{total}\sec(\theta)]-7.291-(1350.7/T)\}$
where: θ is the solar zenith angle, $[O_3]_{total}$ is the column ozone abundance in Dobson units, and T is the temperature in K. Conditions used were $\theta=0°$, $[O_3]=295$, $T=298$ K.

pendencies of absorption cross-sections are well known, especially at small cross-sections on the tails of absorption features, however that implied for alkyl nitrates is unusually large (NASA, 1987). An explanation for this is a significant contribution to the absorption cross-section by a higher vibrational level (Luke and Dickerson, 1988; Luke et al., 1990).

To date no product studies of $ROONO_2$ photolysis have been reported; plausable pathways are

$$ROONO_2 + hv \rightarrow RO^{\cdot} + NO_3 \qquad (24)$$

$$\rightarrow RO_2^{\cdot} + NO_2 \qquad (25)$$
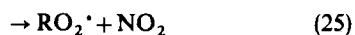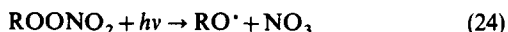
with (25) being favored thermochemically (see below).
Atmospheric photodissociation rates of $RONO_2$ and $ROONO_2$ may be calculated using the following

expression:

$$J=\int \phi(\lambda)\sigma(\lambda)I(\lambda)d\lambda \qquad (II)$$

where $\phi(\lambda)=$ the quantum efficiency as a function of wavelength.

$\sigma(\lambda)=$ the absorption cross-section as a function of wavelength.

$I(\lambda)=$ the spherically-integrated solar actinic flux as a function of wavelength (e.g. Demerjian et al., 1980).

Such estimates have been reported for some $RONO_2$ and $ROONO_2$ compounds and are summarized in Table 13. These estimates were all made assuming quantum efficiencies of unity for $RONO_2$ or $ROONO_2$ destruction. Resulting lifetimes range from

<1 to >100 days and most certainly would exhibit strong altitude dependencies (see Taylor et al., 1980). The major uncertainties in these estimates lie in the absorption cross-sections, especially for $\lambda > 300$ nm, quantum efficiencies, and the temperature dependencies thereof.

The direct photolytic rates measured by Luke and

Pressure dependencies are observed in Reactions -9 and -6, the extent of which depends on the size and nature of the R group. Such a pressure dependency is expected given that the combination Reaction (6) exhibits a pressure dependence. Graham et al. (1978) determined the pressure dependence of $HOONO_2$ decomposition and arrived at the following equation:

$$k(M) = \{5.2 \times 10^{-6} \exp(-19.9/RT)[M]/(1 + 4.86 \times 10^{-12}[M]^{0.61})\}\, s^{-1} \qquad \text{(III)}$$

Dickerson (1988) and Luke et al. (1990) were observed to vary not only with temperature, but also with total column O_3 concentration. This follows from the fact that O_3 is responsible for most of the absorption of solar radiation in the wavelength region just below 310 nm. Predictive equations were derived for J of ethyl, n-propyl and 2-butyl nitrates as a function of zenith angle, total column ozone and temperature. Estimates from these equations are reasonably close to estimates made from absorption spectra and solar flux data (Table 13). The photolysis rate measurements for n-butyl nitrate (Luke et al., 1990) although not as extensive, appear to be close to those that would be predicted from absorption spectra.

Thermal decomposition is an important process because it constitutes the major atmospheric loss mechanism of $ROONO_2$ compounds and can limit the extent to which $RONO_2$ compounds will survive in combustion sources. These reactions occur via the following pathways (Gray and Rogers, 1954; Hendry and Kenley, 1977, 1979).

$$RONO_2 \xrightarrow{M} RO + NO_2 + M \qquad (-9)$$

$$ROONO_2 \xrightarrow{M} ROO + NO_2 + M. \qquad (-6)$$
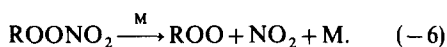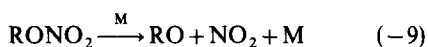
Therefore, in the presence of sufficient O_2 or NO, Reactions 17 and 10 prevent the reformation of $RONO_2$ and $ROONO_2$, respectively.

Thermal decomposition rate constants are presented in Table 14 in the Arrhenius form. The A factors are all within the range 10^{14}–10^{17} with the exception of the PAN decomposition involving a cyclic intermediate. The activation energies (E_a) are very close to the $RO–NO_2$ ($ROO–NO_2$) bond energies, consistent with the lack of any appreciable activation energies for reactions of the type RO (ROO) $+ NO_2$. For example: ΔH for $CH_3ONO_2 \rightarrow CH_3O + NO_2 = 40.0 \pm 0.5$ kcal mole^{-1} (Benson, 1976), $E_a + RT = 41 \pm 1$ kcal mole^{-1} (Batt et al., 1977). This is a useful approximation that can be used to estimate the thermal stability of a compound for which thermochemical quantities are known or can be estimated. For example, ΔH for $ROONO \rightarrow ROO$ is estimated to be ~ 20 kcal mole^{-1}, and coupled with a reasonable A factor $\sim 10^{16}\, s^{-1}$ (Benson, 1976) gives a lifetime for $ROONO$ compounds at 298 K that is quite short (0.05 s).

where $[M]$ is in molec cm^{-3}, RT in kcal mole^{-1}. The rate constant does not approach its high-pressure limit at 1 atm. Similar results were obtained by Bahta et al. (1982) with CH_3OONO_2, in which the results were fit to Equation I. The following rate coefficients and dependencies were found

$$k_0(T) = (1.5 \pm 0.8) \times 10^{-30}(T/300)^{-(4.0 \pm 2.0)}$$

$$k_\infty(T) = (6.5 \pm 3.2) \times 10^{-12}(T/300)^{-(2.0 \pm 2.0)}.$$

The pressure dependence of PAN decomposition by simple fission has been observed but not quantified by Bruckmann and Willner (1983) in the range 1.48–32.4 torr. However, Addison et al. (1980) observed a relatively slight pressure dependence of the formation reaction (Table 6) in the range 28–715 torr. Therefore, only slight pressure dependence of Reaction -6 is expected for PAN. Senum et al. (1986) reported no discernable pressure dependence in the rearrangement reaction of PAN from 2.5 to 21 torr initial pressure. Calculations by Jullien et al. (1983) for 2-propyl nitrate thermal decomposition indicate that the rate is close to the high pressure limit at 1 atm (450 K).

Several general conclusions can be arrived at from the above thermal decomposition data. Compounds of the type $RONO_2$ are stable at atmospheric temperatures; however will decompose at significant rates in exhaust streams and at temperatures present in instrumentation used to make chemical measurements, such as NO_2 reduction catalysts, and GC injection ports. The peroxycarboxylic nitric anhydrides (e.g. PAN) are moderately stable at temperatures typical of the tropospheric boundary layer and very stable at temperatures typical of the upper troposphere/lower stratosphere. Compounds such as $ClONO_2$ and $ROONO_2$, where R is an alkyl group, are unstable at lower tropospheric temperatures, and moderately stable at upper tropospheric temperatures.

Since the atmosphere is a multi-phase system, containing liquid and solid phase material, the uptake by, and subsequent reaction of organic nitrates in these phases must be considered. In addition, it is useful to examine the aqueous chemistry of organic nitrates since it has some bearing on how these species may behave in chemical analysis systems. It is safe to say that there is much less known, especially in a quantitative sense, about the multi-phase behavior of or-

Table 14. Rate constants for thermal decomposition of $RONO_2$ and $ROONO_2$ compounds; $k(T) = Ae^{-E_a/RT}$

Compound	$\log_{10}(A, s^{-1})$	E_a, (kcal mole^{-1})	k (298 K) (s^{-1})	Conditions	References
$HONO_3$	16 ± 1*	$\cong 49.3$*	5×10^{-20}		Estimated here
$ClONO_2$	14.3*'	23.5 ± 0.2	1.2×10^{-3}	313–333 K 1–180 torr	Schönle et al., 1979
CH_3ONO_2	14.23	39.4		485–512 K	Appin et al., 1936
	13.52	36.1		470–520 K	[as quoted by Gary et al., 1981]
	15.7 ± 0.6	40.5 ± 1	7.8×10^{-15}	0.8–1.9 kN m^2	Gary et al., 1981 Batt et al., 1977
$C_2H_5ONO_2$	16.85	41.2 ± 0.5	3.4×10^{-14}	434–454 K 18–81 torr	Levy, 1954
	16.0*	40.0*			Batt and Milne, 1977
n-$C_3H_7ONO_2$	16.5	40.0	1.1×10^{-13}	575–100 K 10^{-4}–10^{-3} torr	Mendenhall et al., 1975
i-$C_3H_7ONO_2$	16.51 ± 0.55	40.5 ± 0.4	5×10^{-14}	533–635 K	Jullien et al., 1983
t-$C_4H_9ONO_2$†	15.9	40.2	2×10^{-14}		Batt and Milne, 1976
$HOONO_2$	14.15	20.7 ± 0.5	8.2×10^{-2}	254–283 K 760 torr	Graham et al., 1977
CH_3OONO_2	15.78	21.3	1.4	256–268 K 350 torr	Bahta et al., 1982
$C_3H_7OONO_2$‡	14.7§	19.8	1.5	285–289 K 700 torr	Edney et al., 1979a,b
$ClC(O)OONO_2$	16.8 ± 1.6	27.7 ± 2.3	3.0×10^{-4}	293.7–300.2 K 760 torr	Spence et al., 1978
$CH_3C(O)OONO_2$‖	14.9 ± 0.6	24.9 ± 0.8	4.3×10^{-4}	294–328 K 760 torr	Cox and Roffey, 1977
	16.3 ± 0.6	26.9 ± 0.9	3.7×10^{-4}	298–313 K	Hendry and Kenley, 1977
	16.5	27.0	4.9×10^{-4}	295–315 K	Schurath and Wipprecht, 1979
$CH_3C(O)OO^{15}NO_2$			$3.3(\pm 0.2). \times 10^{-4}$	700 torr	Niki et al., 1985
$CH_3C(O)OONO_2$¶	12.32	24.8 ± 1.8	1.2×10^{-6}	298–338 K 2–30 torr	Senum et al., 1986
$CH_3CH_2C(O)OONO_2$	17.2	28.0	4.6×10^{-4}	295–315 K	Schurath and Wipprecht, 1979
n-$C_5H_{11}C(O)OONO_2$	15.3	26.7	4.4×10^{-5}	298–333 K**	Van Swieten et al., 1978
$C_6H_5C(O)OONO_2$	14.93	25.2 ± 3.0	2.8×10^{-4}	290.3–304.7 K 750 torr	Ohta and Mizoguchi, 1981
	15.2 ± 0.6	25.9 ± 0.9	1.6×10^{-4}	291–314 K 800 torr	Kenley and Hendry, 1982

* The A factor is taken as typical of simple fission reactions and E_a is essentially equal to the bond dissociation energy (Benson, 1976).

* First-order A-factor at 760 torr.

‡ A mixture of the 1- and 2-isomers resulted from the Cl atom-initiated chemistry.

§ Estimated from $RO_2 + NO$ and $RO_2 + NO_2$ rate constant ratios.

‖ PAN decomposition in the presence of NO:

$CH_3C(O)OONO_2 \rightarrow CH_3C(O)OO \cdot + NO_2$

$CH_3C(O)OO \cdot + NO \rightarrow CH_3C(O)O \cdot + NO_2$

$CH_3C(O)O \cdot + M \rightarrow CH_3 \cdot + CO_2$.

¶ PAN decomposition in the absence of NO:

** In cyclohexane solution, 0.01–0.1 M concentration.

ganic nitrates compared to the homogeneous gas-phase.

The extent of adsorption of organic nitrates on solid particulate matter would seem, by analogy to other polar organic compounds, to be governed by the compound's vapor pressure, hence size. On this basis, compounds having vapor pressures <0.01 torr can be expected to be significantly partitioned onto solid particles. Therefore, organic nitrates of ~ 7 carbons or more, and difunctional nitrates of ~ 4 carbons or more may be found on solid particles to some extent.

Studies of the solubility of gas-phase organic nitrates have been limited to the study of PAN and a few alkyl nitrates. Lee (1984) and Holdren et al. (1984) have studied the solubility and decomposition of PAN in water samples having a range of pHs typical of

cloudwater and precipitation. The Henry's Law solubility of PAN was found by Lee (1984) to be 3.6 ± 0.2 M atm^{-1} at $22.0°C$ and 8.3 ± 0.5 M atm^{-1} at $10.2°C$ $(\Delta H°_{Sol} = -11.75$ kcal mol$^{-1})$, and 5 ± 1 M atm^{-1} at $10°C$ by Holdren et al. (1984). Henry's Law solubilities of 3 M atm^{-1} for methylnitrate (Lee et al., 1983), 1.6 ± 0.12 M atm^{-1} for 1-butyl and 0.74 ± 0.04 M atm^{-1} for 2-butyl nitrates at 295 K (Luke et al., 1989) and 3.94 ± 0.59 M atm^{-1} for 1-butyl and 2.27 ± 0.23 M atm^{-1} for 2-butyl nitrates at 279 K (Luke et al., 1989) have been reported. Solubilities of other alkyl nitrates are expected to be similar, however, those of difunctional nitrates, especially hydroxynitrates may be significantly larger. Since PAN and alkyl nitrates are of intermediate solubility, its importance in liquid phase chemistry may depend on the rates of subsequent liquid-phase reactions.
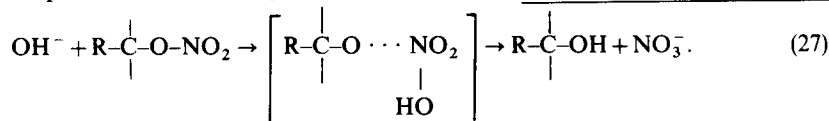
The deposition of PAN on natural surfaces has been studied by Garland and Penkett (1976). Deposition velocities of around 0.25 cm s^{-1} were observed over soil and grass, which corresponded to surface resistances of 2.9–7.0 s cm^{-1}. These results are in qualitative agreement with those of Hill (1971) who observed PAN uptake by alfalfa that was about a factor of 2 slower than O_3. No discernable (<0.04 cm s^{-1}) deposition was observed over deionized water or sea water surfaces. A deposition velocity of ~ 0.006 cm s^{-1} was determined by Schurath et al. (1984) over waters of pH < 7. It was further concluded that while the surface deposition of PAN will lead to relatively slow removal $(\tau_e \sim 2$ days) for mixing heights of 1 km, mixing heights below 100 m caused by nocturnal inversions will cause fairly rapid depletion of PAN within the surface layer.

Reactions of organic nitrates in aqueous solution that are of interest here include hydrolysis, redox and dehydration reactions under mildly acidic to alkaline conditions and possible reactions with other trace species or radicals. The hydrolysis of simple nitrate esters has been observed to occur via the following pathways (Cannon, 1970; Baker and Easty, 1950);
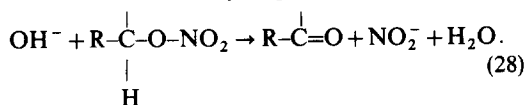
Nucleophilic attack on carbon:

$$OH^- + R-\overset{|}{\underset{|}{C}}-ONO_2 \rightarrow R-\overset{|}{\underset{|}{C}}-OH + NO_3^-. \quad (26)$$
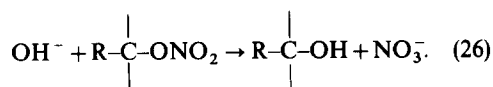
Nucleophilic attack on nitrogen:

$$OH^- + R-\overset{|}{\underset{|}{C}}-O-NO_2 \rightarrow \left[R-\overset{|}{\underset{|}{C}}-O \cdots \overset{NO_2}{\underset{HO}{|}} \right] \rightarrow R-\overset{|}{\underset{|}{C}}-OH + NO_3^-. \quad (27)$$

Abstraction of an α-hydrogen:

$$OH^- + R-\overset{|}{\underset{H}{C}}-O-NO_2 \rightarrow R-C=O + NO_2^- + H_2O. \quad (28)$$

Abstraction of a β-hydrogen:

$$OH^- + R-\overset{|}{C}-\overset{|}{\underset{H}{C}}-O-NO_2 \rightarrow R-C=C + NO_3^- + H_2O. \quad (29)$$
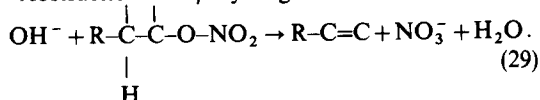
Table 15. The hydrolysis rate of PAN in water

Temperature (°C)	$k(s^{-1}(\times 10^4))$	References
5	1.17 ± 0.05	Holdren et al., 1984
15	2.17 ± 0.05	Holdren et al., 1984
22	4.0 ± 1.2	Lee, 1984
25	6.83 ± 1.7	Holdren et al., 1984

Although mechanistically distinct, Reactions (26) and (27) produce the same end products. Reactions (28) and (29) are redox and dehydration reactions, respectively, and it should be noted that Reaction (28) produces nitrate ion.

Hydrolysis in neutral or acidic solution has been observed to be relatively slow (10^{-5}–10^{-3} s^{-1}) for a variety of alkyl nitrates (Robertson et al., 1982) and was not acid catalyzed. The products of neutral hydrolysis of four secondary alkyl nitrates: 2-propyl, 2-butyl, cyclopentyl, and cyclohexyl were the corresponding alcohols (Robertson et al., 1982). The neutral hydrolyses of t-butyl nitrate and benzyl nitrate were found by Lucas and Hammett (1942) to be quite slow, and to result in some formation of isobutene ($\sim 15\%$) and benzaldehyde ($\sim 6\%$).
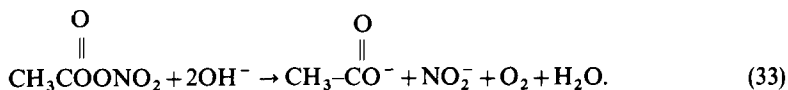
The hydrolysis of nitrate esters appears to be base catalyzed for some species but not for others. For instance, benzyl nitrate hydrolysis is base catalyzed whereas that of t-butyl nitrate is not (Lucas and Hammett, 1942). It should be noted that even with basic catalysis, these reactions can still be quite slow. Studies of the aqueous phase chemistry of peroxycarboxylic nitric anhydrides has been limited largely to PAN, with some work having been done on PBzN. PAN hydrolysis in acidic solution has been observed to be relatively slow, but appears to be a strong function of temperature. Lee (1984) observed a rate constant at $22°C$ which was roughly independent of pH in the range 4.2–5.6. Holdren et al. (1984) measured the rate constant as function of temperature from 5 to 25°C (independent of pH, 4.0–5.6), and observed that NO_3^- was the principal nitrogen decomposition product in this pH range. These data are summarized in Table 15. The decomposition of PAN in neutral or acidic solution may be dominated by the same homolytic pathway as the gas-phase decomposition. Therefore in the laboratory studies of Holdren et al. (1984) which were done at relatively high concentration, the following reactions pertain:
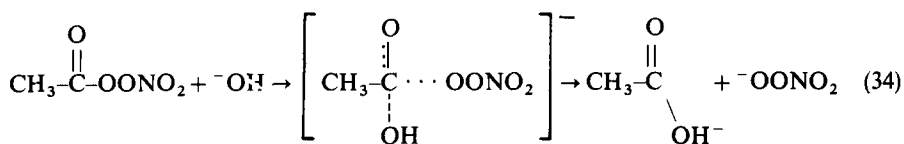
$$PAN \rightarrow PA + NO_2 \quad (-6)$$

$$2NO_2 \rightarrow NO_3^- + NO_2^- \quad (30)$$

$$H^+ + NO_2^- \rightleftharpoons HNO_2, \quad pKa\ 3.37 \quad (31)$$

$$2HNO_2 \rightarrow NO + NO_2 + H_2O \quad (32)$$
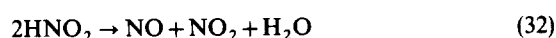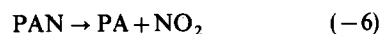
which may account for the observation that NO_3^- was the principal product.

The hydrolysis of PAN in basic solution has been observed to be rapid by Stephens (1967) and Nicksic et al. (1967). The products of hydrolysis were found to be acetate and nitrite ions and molecular oxygen, consistent with the following overall reaction:

structures were originally hypothesized for "Compound X", none of which proved to be correct. Through subsequent work (Stephens et al., 1961) the structure, and corresponding name, of "peroxyacetyl nitrate" were arrived at. An interesting account of this early research can be found in Stephens (1987). Long-

$$\overset{\overset{\displaystyle O}{\displaystyle \|}}{CH_3COONO_2} + 2OH^- \rightarrow CH_3\text{-}\overset{\overset{\displaystyle O}{\displaystyle \|}}{C}O^- + NO_2^- + O_2 + H_2O. \qquad (33)$$

Steer et al. (1969) further showed that some of the molecular oxygen was formed in an excited state. Emission from O_2 $(^1\Delta_g)$ was observed and initial formation of O_2 $(^1\Sigma_g^+)$ was deemed possible. The following is a plausible mechanism:

path i.r. absorption remains a useful method for the measurement of PAN at the higher concentrations characteristic of urban areas (Tuazon et al., 1978; Hanst et al., 1982). More recently matrix-isolation

$$CH_3\text{-}\overset{\overset{\displaystyle O}{\displaystyle \|}}{C}\text{-}OONO_2 + {}^-OH \rightarrow \left[CH_3\text{-}\overset{\overset{\displaystyle O}{\displaystyle \vdots}}{\underset{\underset{\displaystyle OH}{\displaystyle |}}{C}} \cdots OONO_2 \right]^- \rightarrow CH_3\text{-}\overset{\overset{\displaystyle O}{\displaystyle \|}}{C}\underset{\displaystyle OH^-}{\diagdown} + {}^-OONO_2 \quad (34)$$

$$^-OONO_2 \rightarrow O_2(O_2^*) + NO_2^-. \qquad (35)$$

Hydroxyl ion attack on the carbonyl carbon is most probable by analogy to hydrolysis of esters and other anhydrides, with elimination of the peroxynitrate $(OONO_2^-)$ anion and subsequent decomposition to molecular oxygen and nitrite.

The following general statements can be made concerning the atmospheric removal pathways of organic nitrates. Alkyl nitrates are lost in all regions of the troposphere primarily by photolysis at wavelengths < 330 nm, although reaction with OH may be significant for compounds of high carbon number $(\gtrsim C_5)$. Alkyl peroxynitrates are thermally unstable at temperatures characteristic of the lower troposphere, and will be destroyed by photolysis $(\tau \lesssim 1 \text{ day})$ in the upper troposphere. The thermal decomposition of peroxycarboxylic nitric anhydrides is the dominant tropospheric loss mechanism, however photolysis, reaction of OH with higher carbon number species, such as PBzN, will surely be significant in the upper troposphere.

MEASUREMENT TECHNIQUES

The first identifications of organic nitrates in laboratory organic photooxidation systems were made by i.r. spectroscopy. In these studies, the presence of alkyl nitrates and an unidentified species "Compound X" were noted by Stephens et al. (1956a,b). The presence of "Compound X" in the atmosphere of Los Angeles was confirmed by long-path i.r. absorption a short time later (Scott et al., 1957). Five possible

FT–i.r. spectroscopy has been used for the measurement of PAN in ambient air (Griffith and Schuster, 1987). While the long-path measurements have detection limits of a few ppbv mixing ratio of PAN, the matrix isolation technique has a reported limit of 0.05 ppbv.

PAN and other organic nitrates have generally been measured by gas chromatography with electron capture detection (GC/ECD). The original method described by Darley et al. (1963) for PAN and larger homologues has been refined and adapted by numerous practitioners over the ensuing years: however, several of the essential features of the technique have not changed. Column and detector temperatures have been kept relatively low (< 50° and < 100°C, respectively) to minimize thermal decomposition, and short packed columns coated with polyethylene glycol-type phases have been used. In general, the more inert materials of construction such as glass, Teflon and polyethylene have been used in these systems, however there are numerous reports of the use of stainless steel with apparently satisfactory results.

Samples are most often injected directly into PAN GC/ECD systems using a gas switching valve with a sample loop, limited by chromatographic considerations to a volume of approximately 20 cm³ (for 760 torr samples). Samples have been transported to the GC systems either with gas tight syringes or by a continuously flowing sample line, constructed of some inert material such as Teflon. Pyrex glass has been observed to catalyze the apparent formation of PAN
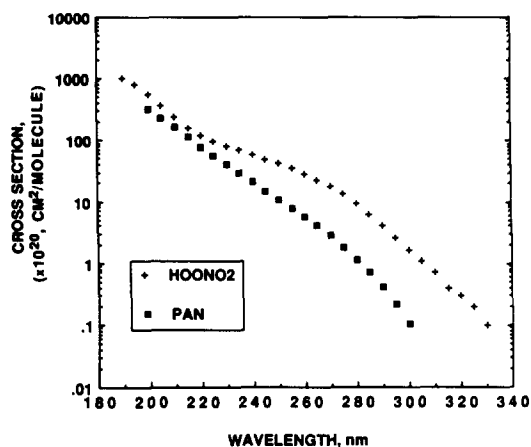
Fig. 6. The u.v. absorption spectra of $HOONO_2$ (Molina and Molina, 1981) and PAN (Senum et al. 1984) between 190 and 330 nm.

problem in their system. The elution of water as a large peak relatively late in the analysis is often the limiting factor in sampling repetition rate. A two-column system, consisting of a pre-column and analysis column of identical material, has been devised by Vierkorn-Rudolph et al. (1985) to eliminate water from the analysis through back-flushing. Water has also been observed to greatly reduce the response of the GC/ECD system to PAN at water concentrations below 60% r.h., and PAN mixing ratios below 100 ppbv, often to the point of complete disappearance (Holdren and Rasmussen, 1976). A humidity effect was alluded to by Nieboer and van Ham (1976), but no details were given. Lonneman (1977) found no humidity effect in his PAN measurements, while Watanabe and Stephens (1978) observed some humidity affect in their GC/ECD systems $<5-10\%$ for ^{3}H-ECD and 5-70% for [63]Ni, but only at 2-5% r.h. and complete loss of PAN in an acid-washed glass flask at 2-5% r.h. Clearly systems of this type need to be examined in order to understand the nature of any humidity problem. Improvements on the GC/ECD system for PAN measurements may be possible through the use of capillary or coupled packed capillary (so-called "multi-dimensional") GC methods (Liberti and Ciccioli, 1986). Recently, Roberts et al. (1989) have reported the separation of PAN, PPN, and C_1–C_4 alkyl nitrates on a capillary column, but the application of this method to ambient analysis has not yet been demonstrated.

Electron capture has been the detection method most widely used in chromatographic analysis of PAN. The response of ECDs to PAN has been shown to decrease with increasing temperature (Singh and Salas, 1983a) probably due to thermal dissociation. The most reliable operation is generally achieved at temperatures somewhat above the column temperature. Thermal conversion of PAN to NO and measurement of the resulting NO by O_3-chemiluminescence has also been used in chromatographic analysis (Glavas and Schurath, 1983; Joos et al., 1986). This thermal conversion has been shown to proceed at close to 100% efficiency for PAN and alkyl nitrates on commercially available converters containing molybdenum or molybdenum on activated carbon (Winer et al., 1974; Schurath et al., 1984; Grosjean and Harrison, 1985), and gold catalysts (Bollinger et al., 1983; Fahey et al., 1985a). Therefore, this detection method has the advantage that it can be independently calibrated with a stable compound such as NO. Such catalytic conversion methods have been used to make NO_y measurements. However, the NO_y chemiluminescence method is not as sensitive as the electron capture detector, and requires the use of much more elaborate instrumentation. Recent work by Burkhardt et al. (1988) and Drummond et al. (1988) has shown that a luminol chemiluminescence detector can be used to detect PAN with attendant advantages of good sensitivity and less stringent carrier gas purity requirements.

during sampling (Lovelock and Penkett, 1974). However, Singh and Salas (1983a) report a 20% loss of PAN in Pyrex wool, and Glavas and Schurath (1983) report 12% loss of PAN in a Pyrex cryosampler. Singh and Viezee (1988) describe an enhancement in observed PAN concentrations by as much as a factor of 6 in marine air sampled through glass chambers. Cryogenic concentration of PAN has been reported by Singh and Salas (1983a), Glavas and Schurath (1983), Meyrahn et al. (1984) and Vierkorn-Rudolf (1985). These studies have found only slight overall losses of PAN (10-20%) associated with cryosampling, provided that samples are warmed only to room temperature prior to injection. Water need not be removed from the gas stream prior to cryosampling because PAN hydrolysis is slow in such systems (Glavas and Schurath, 1983), however, Singh and Salas (1983) used a Nafion® semi-permeable membrane dryer for sampling with no discernable loss of PAN.

The gas chromatographic separation of PAN has nearly always been done at low temperatures (20–35°C) with short packed columns (0.14–2.0 m) coated with polyethylene glycol phases. Conditions (retention time, temperature) can be adjusted to minimize thermal decomposition and to determine methyl nitrate and PPN as well. However, even under optimal conditions PAN losses in the column can be substantial (Singh and Salas, 1983a) and methyl nitrate may not be completely separated from chlorocarbons such as tetrachlorethylene (Brice et al., 1984). The work of Darley (1963) shows that the larger homologs of PAN and PPN, as well as ethyl and propyl nitrates should be observable with PAN measurement systems, but alkyl nitrates larger than methyl nitrate have only recently been reported in ambient air measurements (Buhr et al., 1988). Coelution of ECD-sensitive species in real air samples has been checked through selective removal of PAN and PPN by KOH (Vierkorn-Rudolph et al., 1985), and was found not to be a

The most difficult aspect of the PAN measurement is calibration. Gas phase standards have been produced either as static mixtures in steel, glass or plastic containers, or as flowing streams involving photochemical synthesis or diffusion sources of pure PAN. Such standards have been calibrated by i.r. spectroscopy, collection in basic solution as acetate or nitrite, measurement of the decrease in a photochemical reactant used to make PAN, or NO_y chemiluminescence.

The early work of Stephens and colleagues (Darley et al., 1963; Stephens, 1969; Stephens and Price, 1973) was based on i.r. spectroscopic calibration, the original absorption coefficients having been measured by Stephens using PAN purified after photochemical synthesis. Stephens (1969) demonstrated that alkaline hydrolysis of PAN leads to formation of acetate and nitrite ions, and that colorimetric determination of the nitrite ion could be used for calibration. Such an analysis (more recently accomplished by ion chromatography) has been extensively used for PAN calibration. Photolysis of the $Cl_2/NO_2/air/acetaldehyde$ system was used by Gay et al. (1976) to produce PAN in nearly quantitative yield (95%, based on acetaldehyde loss). This has been used as a basis of PAN calibration by Singh and Salas (1983a), after a slight correction for the presence of NO from NO_2 photolysis, and by Grosjean et al. (1984). Lonneman et al. (1982) described a PAN calibration procedure based on thermal deomposition in the presence of NO, in which the consumption of NO was determined by O_3-chemiluminescence and an experimental stoichiometric factor was applied.

The selective collection of PAN in basic solution (KOH, NaOH) has been used in conjunction with NO_y chemiluminescence for the measurement of PAN in standard streams containing NO_2 (Singh and Salas, 1983a; Grosjean and Harrison, 1985). NO_y chemiluminescence has also been utilized for the direct calibration of PAN in gas steams containing only PAN (Fehsenfeld et al., 1987), or after separation of PAN from other NO_y species via gas chromatography (Joos et al., 1986).

It is difficult to designate one calibration method as clearly superior to the others since each has advantages or disadvantages based on portability, ease of operation, sensitivity limit or chemical specificity. There are several reported studies in which methods have been intercompared with excellent to good agreement: i.r. spectroscopy and alkaline hydrolysis/colorimetric nitrite analysis in the concentration range 20–1600 ppmv (Stephens, 1969); the $Cl_2/NO_2/acetaldehyde/air$ photochemical source, based on acetaldehyde loss and the difference in NO_y chemiluminescence signal downstream of an alkaline scrubber in the range 160–550 ppbv (Singh and Salas, 1983a); GC/FID analysis (which was based on an alkaline hydrolysis/colorimetric NO_2^- determination) and a GC/NO_y analysis at a concentration of PAN of about 100 ppbv (Meyrahn et al., 1984); alkaline hy-

drolysis, with acetate ion determination, and NO_y chemiluminescence measurement using an alkaline scrubber ranging up to 400 ppbv (Grosjean and Harrison, 1985); and the alkaline hydrolysis/colorimetric NO_2^- determination and GC/NO_y determination of PAN standard streams in the range 3–80 ppbv (Joos et al., 1986).

Several studies have indicated that the response of electron capture detectors is very similar for the C_1-C_3 alkyl nitrates, and PAN and PPN (Stephens and Price, 1973; Vierkorn-Rudolph et al., 1985), however, reports of the observation of alkyl nitrates $\geqslant C_2$ are limited to a few studies. Buhr et al. (1988) report much higher sensitivities for C_3-C_5 alkyl nitrates relative to PAN, and were able to measure 2-propyl, 2-butyl and 2-pentyl nitrates with a conventional packed column coupled to a sealed ECD that was thought to have generally enhanced sensitivity. Most measurements of methyl nitrate and PPN have usually assumed ECD responses equivalent to that of PAN as a basis for calibration, however loss of PAN in the analytical system impacts on the validity of this assumption. Williams (1965) found ethyl nitrate in 2.5 ℓ air samples collected at $-80°C$ and analyzed by packed column GC/ECD. The identification of ethyl nitrate was made by comparison of retention time, ECD response, and lack of retention on a $MgClO_4$ drying column of the ambient air sample and an authentic ethyl nitrate sample. No quantitative information was given, and it was noted that ethyl nitrate was only 'occasionally' observed. Jonsson and Berg (1983) describe qualitative identification of isopropyl nitrate in the atmosphere of Stockholm using cryogenic sampling and a two-dimensional GC analytical scheme. Jüttner (1988) reported one measurement of isopropyl nitrate made in a forested area near Tübingen, F.R.G., using a cryogenic collection technique involving a solid sorbent material, and GC analysis.

Atlas (1988) has recently observed C_4 and C_5 (and possibly C_3) alkyl nitrates in shipboard measurements in the northern Pacific Ocean, and in ambient air samples from College Station, Texas. Samples were collected and analyzed using a method based on the technique of Grob and Grob (1971), in which large volumes (10–300 ℓ) of air were passed through 5 mg charcoal traps, and the traps were subsequently extracted with small volumes of benzene ($\sim 40 \mu l$). The solvent extracts were then analyzed, without further concentration, by capillary GC with electron capture detection via splitless injection at relatively high temperature. Explicit gas-phase standards were not generated and tested in this study because these compounds were identified in the samples subsequent to collection. Quantitation was achieved using solution standards and by assuming complete collection in, and recovery from, the sampling system. The alkyl nitrates were identified by retention time and negative ion mass spectrometry and confirmed where possible with authentic samples, with positive results for 2-butyl nitrate, and the 2- and 3- pentyl nitrates. The presence

of other nitrates, in particular a propyl nitrate, was also indicated, but interferences from the presence of halocarbons or solvent precluded quantitation.

There are a few measurements of peroxybenzoic nitric anhydride (PBzN) in ambient air. The early work of Heuss and Glasson (1968), showing that base-catalyzed solvolysis of PBzN by methanol gave quantitative yields of methyl benzoate, formed the basis of the measurement technique first employed by Appel (1973) and later by Meijer and Nieboer (1977) wherein PBzN was collected in bubblers containing methanol–NaOH solution. Appel (1973) demonstrated that benzoic acid was not converted to methyl benzoate under sampling conditions and, hence, would not interfere with the measurement. The resulting methyl benzoate was solvent extracted and analyzed by GC/FID, with a detection limit of 0.07 ppbv with packed column separation (Appel, 1973) and 0.03 ppbv with capillary column with separation (Meijer and Nieboer, 1977). Fung and Grosjean (1985) describe the measurement of PBzN by collection in aqueous KOH solution, then analyzed as benzoic acid by ion chromatography with u.v. absorption detection. Although their studies indicate that gas-phase benzoic acid is efficiently collected by this technique, they argue that benzoic acid should be found mostly in the aerosol phase and that the aerosol concentrations that have been observed would constitute a very small interference in their method. Their detection limit is estimated at 0.03 ppbv of PBzN in a 60 ℓ sample.

Qualitative evidence of the presence of difunctional organic nitrates in carbonaceous aerosol was reported by Schuetzle et al. (1975). Analyses were performed by high resolution mass spectrometry after direct thermal evolution from the sampling medium (gold plates, or glass fiber filters). The structures identified were of the type X–$(CH_2)_n$-Y where $n = 3$–5; X = –COOH (presumably a carboxylic acid group), and –CHO; and Y = CH_2ONO, CH_2ONO_2, –$COONO_2$, and –COONO. The last two structures are doubtful since it is unlikely that compounds of the type $ROONO_2$ and ROONO are stable. Estimated concentrations ranged up to 1.0 $\mu g\,m^{-3}$ but were generally quite a bit lower than that.

ATMOSPHERIC OBSERVATIONS

Although many organic nitrates have been identified in laboratory studies, extensive atmospheric measurements, generally in urban areas, have been limited to PAN. It is only in the past 10 years or so that the global impact of PAN has been recognized and its measurement in the remote troposphere undertaken. In addition it is now clear that measurements of other major NO_y species, and total NO_y, are extremely valuable in interpreting PAN measurements. Investigations of other organic nitrates have been limited to PPN, PBzN and simple alkyl nitrates. Although the data for these are sparse, they exhibit some interesting features, and suggest many avenues of future study.

The PAN data presented below have been classified according to the nature of the air masses in which the measurements were made. PAN is a secondary species formed from both NO_x and organic precursors with the formation rate being roughly first order in each precursor. Both NO_x and organic species have diffuse background sources and large anthropogenic sources confined to relatively small urban areas. It is well established that the concentrations of these anthropogenic precursors decrease rapidly as air masses are advected from urban areas; therefore, the air masses are classified roughly according to the time elapsed since the impact of urban sources. The categories and times to be used here are as follows: urban, $t < 1$ day; regional, $t = 1$–3 days; and remote, $t \geqslant 3$ days. Obviously the boundaries between categories are somewhat ill-defined, resulting in somewhat arbitrary classifications. In addition, reported measurements do not always contain information necessary to make classifications. Nevertheless, these categories will provide a context in which to discuss relevant points of atmospheric chemistry.

Urban PAN measurements

PAN has been measured in urban areas since the early 1960s. There have been several recent summaries of these measurements (Altshuller, 1983; Temple and Taylor, 1983a; Grosjean, 1984). Important features of these measurements are reviewed here; measurements reported since the previous summaries are listed in Table 16.

There are a number of interesting features in the urban PAN measurements. The highest average and maximum concentrations reported have been found in Los Angeles and the surrounding areas, where daily averages range from 10 to 30 ppbv with maxima up to 210 ppbv. Other cities in the continental U.S. have exhibited averages and maximum concentrations somewhat lower than those of Los Angeles. Observations in cities outside the U.S. have shown in general lower PAN concentrations although maximum concentrations have approached those reported for some U.S. cities.

It has been well established from these urban data sets that PAN is a photochemical reaction product. Diurnal profiles have consistently shown daytime, usually mid-afternoon, maxima for PAN concentrations, and higher PAN concentrations in the summer relative to the winter months. The diurnal profiles reported by Grosjean (1984), are shown for example in Fig. 7. These profiles were generated from a large set of measurements made in Riverside, CA (Pitts and Grosjean, 1979). Thus in urban areas close to sources of NO_x and organic compounds ambient concentrations of PAN are heavily dependent on the formation rate of PAN, which is dependent on solar radiation.

Annual and seasonal trend data on PAN concentration are sparse, as there are only a few data sets available of any extent. The general observation of higher summertime concentrations relative to winter-

Table 16. Recent measurements of PAN in urban air masses

Site	Sampling period	PAN(ppbv) Avg	PAN(ppbv) Max	Reference
Delft, The Netherlands	1973–1985	0.42*	0.94*	Guicherit, 1987
Bonn, F.R.G.	June–July 1980	0.41	1.6	Löbel et al., 1980
Simcoe, Canada	June 1980–March 1981	1.3	5.6	Corkum et al., 1986
Univ. of Calgary, Canada	19 November 1980–30 August 1981	0.22	2.4	Peake and Sandhu, 1983
Calgary, Canada,	12 July 1981–7 April 1982	0.14	6.6	Peake and Sandhu, 1983
Bonn, F.R.G.	18–27 August 1982	0.08	0.17	Glavas and Schurath, 1983
Athens, Greece	14–16 September 1982	0.53	0.78	Glavas and Schurath, 1983
Patras, Greece	17 September 1982	0.07†		Glavas and Schurath, 1983
Edmonton, Canada	December 1982–May 1984	0.28	7.5	Peake et al., 1988
Philadelphia, PA	4–22 April 1983	1.0	3.7	Singh and Salas, 1989
Staten Island, NY	25 April–1 May, 1983	1.6	5.5	Singh and Salas, 1989
Fort Saskatchewan, Canada,	August–September 1983	0.25	0.66	Peake et al., 1988
Downey, CA	18–27 February 1984	1.2	6.7	Singh and Salas, 1989
Houston, TX	9–17 March 1984	0.75	7.9	Singh and Salas, 1989
Denver, CO	24 March–1 April 1984	0.64	2.04	Singh and Salas, 1989
Birmensdorf, Switzerland	15 June–18 July 1984	0.4	5.5	Landolt et al., 1985
Athenes, Greece	February–October 1985	0.68	3.7	Tsani-Bazaca et al., 1988
Rio de Janeiro	1–11 July 1985		5.4	Tanner et al., 1988
Paris, France	18–31 October 1985	1.0	9.0	Tsalkani et al., 1987
	7–26 February 1986	1.8	6.7	Tsalkani et al., 1987
Claremont, CA	11–19 September 1986	3.2	11.8	Grosjean, 1988

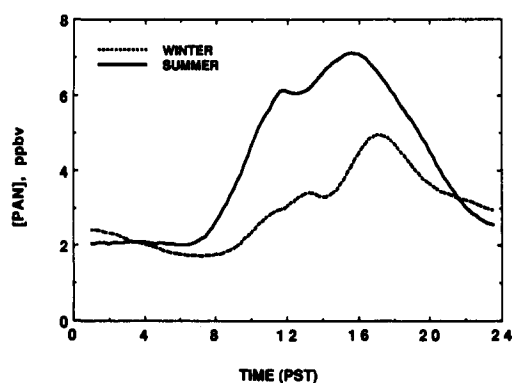*Quarterly averages.
†Single measurement.

Fig. 7. Six month-averaged diurnal concentration-time profiles for PAN (ppb), Riversidle, CA, 1975–1976. Solid line = summer, May–October 1987; Dashed line = winter, November 1975–April 1976. Reported by Grosjean (1984) as having been adapted from Pitts and Grosjean (1979).
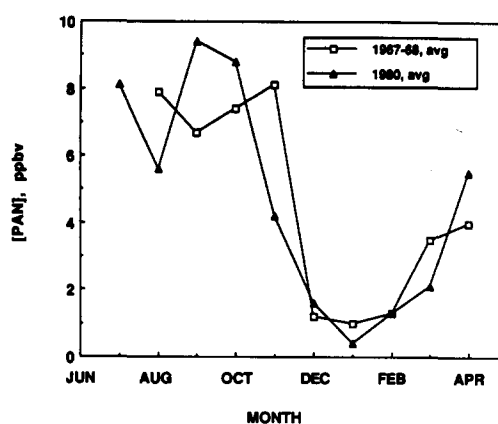

Fig. 8. The annual trend in PAN concentrations measured in Riverside, CA, as monthly means of observations made between the hours of 0800 and 2000, for 1967–1968 and 1980 (Temple and Taylor, 1983b).

time is borne out by several large measurement sets made in urban and regional areas (Temple and Taylor, 1983a; Grosjean, 1984). The only two data sets that involve measurements by the same research group at the same site for extended periods of time were made by Temple and Taylor (1983a,b) in Riverside, CA, from August–April 1967–1968 and July–April 1980, using essentially the same techniques. PAN concentrations are shown as monthly averages between the hours of 0800 and 2000 in Fig. 8. If the month-to-month variability is taken into account, the 1968–1969 and 1980 do not indicate any long term change in PAN concentration during this period. In addition, the same seasonal dependence in PAN concentration is observed in both periods. The 24-h concentrations of Grosjean (1984) are somewhat lower in the summer months due to the inclusion of lower night-time values, but is still consistent with the 1968–1969 and 1980 data. In contrast with these results, Guicherit (1987) reports a large increase in PAN concentration (of approximately 10% per year) between 1973 and 1985 at Delft in The Netherlands. These data are plotted in Fig. 9 as quarterly averages and exhibit not only an increase with time but a distinct seasonal trend, that, as will be seen below, is more characteristic of remote or rural sites that are influenced by air masses of remote origin.

Measurements on this time scale and of this scope

are extremely valuable in examining the long term trends in oxidant formation and the impact of anthropogenic emissions. The data from Riverside indicate that in spite of the population growth that took place from 1967 to 1980 with that air-basin, PAN concentrations have not grown. This trend is consistent with the trends in NO_x and NMHC concentration in the South Coast air basin, which have not changed, or perhaps declined slightly in the period 1968-1985 (Kuntasal and Chang, 1987). Conversely, the Delft data probably reflect the fact that NO_x and HC emissions have grown, largely unchecked, in Europe over the past 15 years.

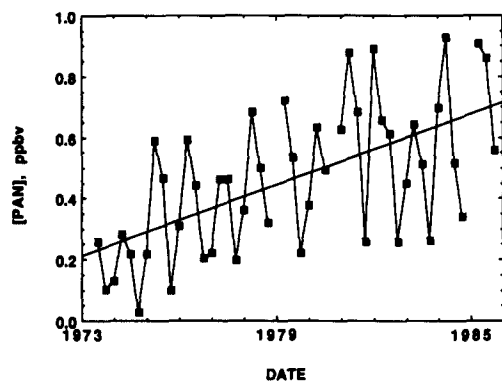### Regional PAN measurements

PAN measurements have been made less frequently in air masses that are regional in character. The working definition of regional air masses effectively places all non-urban continental sites in this category at least part of the time. However, the air masses observed at continental sites, especially coastal sites, are occasionally clean enough that they are characteristic of remote tropospheric air masses. For the purposes of this review, all non-urban continental measurements will be summarized in this category and it will be noted where such measurements are thought to be more representative of the remote troposphere.

Table 17 lists the average and maximum PAN

Fig. 9. Quarterly average PAN concentrations observed at Delft in The Netherlands, between 1973 and 1985, from Guicherit (1987).

Table 17. Measurements of PAN in non-urban continental air masses

Site	Sampling period	PAN(ppbv) Avg	Max	Reference
Wilmington, OH	3–30 August 1974		4.1	Lonneman et al., 1976
Mill Valley, CA	January 1977	0.30	0.83	Singh et al., 1979
Badger Pass, CA	May 1977	0.13	0.22	Singh et al., 1979
Reese River, NV	May 1977	0.11	0.26	Singh et al., 1979
Jetmore, KA	June 1978	0.25	0.52	Singh et al., 1979
Sheldon Wildlife Reserve, TX	October 1978	0.64	2.8	Westberg et al., 1978
Van Hiseville, NJ	July–August 1979	0.50		Spicer et al., 1983
Huntington Lake, IN	April 1981	0.46		Spicer et al., 1983
East Central Missouri	February	0.74		Spicer et al., 1983
Harwell, U.K.	1974–1975	0.27*	0.78†	Brice et al., 1984
	1980–1981	0.43*	0.78†	Brice et al., 1984
Risø, Denmark	11 June–23 September 1980		0.9‡	Nielsen et al., 1981
Göteburg, Sweden	17 July–9 September 1980		0.8‡	Nielsen et al., 1981
Simcoe, Ontario	1–15 June 1982	0.4	1.7	Bottenheim et al., 1984
Kananaskis Valley, Alberta	April–August 1982	~ 0.5	2.3	Peake et al., 1983
North Bay, Ontario	23–27 July 1982	0.13	0.36§	Bottenheim et al., 1984
Longwoods, Ontario	March 1983	0.7	1.4‖	Bottenheim et al., 1984
Chalk River, Ontario	November–December 1983	0.25		Brice et al., 1988
North Bay, Ontario	January–February 1984	0.61	2.5	Anlauf et al., 1986
Allegheny Mountain, PA	5–28 August 1983	1.2		Pierson et al., 1987
Niwot Ridge, CO	28 June–20 July 1984	0.3		Fahey et al., 1986
	22 October–6 November 1984	0.25		Fahey et al., 1986
Suburban (Rome), Italy	July 1984		> 4	Ciccioli et al., 1986a,b
	April 1985–February 1987	0.33	9.6	Ciccioli et al., 1988
Alert, NW Territories	5–19 March 1985	0.207		Bottenheim et al., 1986
Kejimkujik Natl. Park, Nova Scotia	June 1984–September 1986	0.13	0.83‡	Bottenheim et al., 1987
Various Airports, N and S Hemisphere	June 1984	0.05	0.31	Rudolph et al., 1987
Alert, NW Territories	1–22 April 1986	0.47		Barrie et al., 1990
Donon, France	September 1986–July 1987	0.2	~ 2	Perros et al., 1988

*Average of monthly means.
†Highest monthly mean.
‡Average of daily maxima.
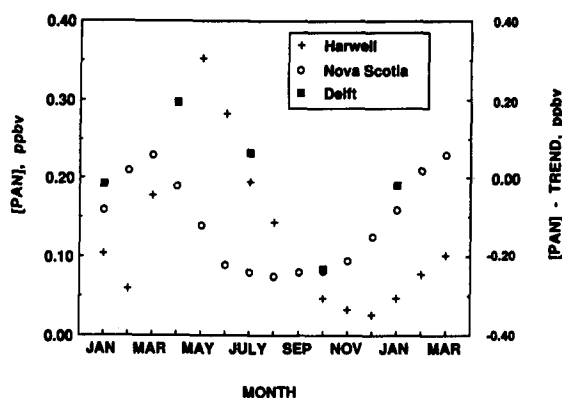§For 6 h averages.
‖For 12 h averages.

Fig. 10. Season variation in PAN concentration in air masses more characteristic of remote air masses. The Harwell data were selected according to chlorofluorocarbon concentrations (Penkett and Brice, 1986), the Nova Scotia data are simple overall monthly averages (Bottenheim et al., 1987), and the Delft data have been transformed by subtraction of the PAN concentration calculated from the trend line in Fig. 9, and sorted according to season (Guicherit, 1987).

concentrations observed at various non-urban continental sites. In general, average concentrations are substantially lower than those observed in urban air masses. Peak or maximum concentrations approach the range 1–40 ppbv at times when heavy anthropogenic impact occurs. Several features of PAN chemistry are apparent in the data from studies in which extensive PAN measurements were made and where information on other NO_y component species and meteorology was obtained. The measurements of Nielsen et al. (1981) show that PAN can be transported long distances (> 1000 km). Extensive PAN data sets have been obtained at Harwell, U.K. (Brice et al., 1984; Penkett and Brice, 1986), and Kejimkujik National Park, Nova Scotia (Bottenheim et al., 1987). The seasonal variation in monthly averages at Harwell, U.K., show summertime maxima due to the photochemical nature of PAN sources (Brice et al., 1984). In addition several wintertime–early spring pollution episodes resulted in high monthly averages for February and March 1981 (Brice et al., 1984). A slight summertime peak was also observed in the daily maximum PAN concentration measured at the Nova

Scotia site (Bottenheim et al., 1987). Both the Harwell and Nova Scotia data sets exhibit springtime maxima in 'clean-air' or overall averages, as shown in Fig. 10. The Nova Scotia data are simple monthly averages. The Harwell data are averages of measurements selected from periods of at least 4 h, during which $[CFCl_3] < 189$ ppbv and $[CH_3CCl_3] < 200$ pptv, indicating air characteristic of remote air masses was being sampled. Also shown are the data from Delft, The Netherlands, in which the average difference between measured PAN and the trend line shown in Fig. 9 has been calculated for winter, spring, summer and fall. These springtime maxima are thought to result from the elevated concentrations and wider distribution of the PAN precursors caused by the reduced photochemical activity of wintertime coupled with lower average temperatures relative to summertime. Ozone concentrations characteristic of the remote Northern Hemisphere have shown a similar springtime maxima. Based on their PAN data, Penkett and Brice (1986) have suggested that tropospheric photochemistry is responsible for the springtime O_3 maximum.

Several sets of the PAN measurements listed in Table 17 have been made in conjunction with other NO_y species. The ratio of [PAN] to [PAN] + inorganic nitrate, IN ($[IN] = [HNO_3] + [NO_3^-]$), Table 18, has been used as a measure of the relative importance of these major NO_x product species. Observed values range from 0.07 to 0.9, and higher values seem to be associated with air masses that have been well 'aged' photochemically, or in which recent precipitation has occurred (Bottenheim et al., 1984, 1986; Anlauf et al., 1986; Daum et al., 1989; Barrie et al., 1989). Both factors are consistent with a much more rapid wet and dry deposition of inorganic nitrate than of PAN. Lower PAN fractions appear to be associated with air masses that have been more recently impacted by anthropogenic emissions. This is supported by the model calculations of Derwent and Hov (1982) in which HNO_3 was produced more rapidly from simulated urban emissions than PAN. The results of Grosjean (1983) in which this ratio is much higher on average are somewhat at odds with the above picture. However, the sampling site at Clarement, CA is the middle of the Los Angeles air basin and is therefore

Table 18. The ratio [PAN]/[PAN] + [IN] observed at non-urban continental sites

Site	Sampling period	Ratio Range	Mean	Reference
Simcoe, Ontario	1–7 June 1982	0.11–0.70	0.31	Bottenheim et al., 1984
	9–14 June 1982	0.07–0.36	0.21	Bottenheim et al., 1984
North Bay, Ontario	23–27 July 1982	0.17–0.53	0.34	Bottenheim et al., 1984
	15 January–24 February 1984	0.2–0.7	0.32	Anlauf et al., 1986 Daum et al., 1989
Harwell, U.K.	January 1980–June 1981	0.08–0.34		Brice et al., 1984
Alert, NW Territories	March 1985	0.76–0.90	0.84	Bottenheim et al., 1986
	April 1986		0.88	Barrie et al., 1989

surrounded by sources. In such a case the above simple arguments concerning the [PAN]/[PAN] + [IN] ratio may not be applicable, and the relative formation rates may be more dependent on the nature of the HCs present, and the HC:NO_x ratio.

There are several data sets of simultaneous measurements of PAN, NO_x, total NO_y and other NO_y constituents. The work at Niwot Ridge, CO, described by Singh et al. (1985) and Fahey et al. (1986) appears to be the most extensive in which a NO, NO_2, HNO_3, aerosol NO_3^-, PAN, and total NO_y were measured. Measurements were made in the summer and fall of 1984. The Niwot Ridge site is at high altitude (3 km) approximately 60 km northwest of the Denver metropolitan area. The proximity to Denver, combined with the lack of appreciable urban areas between the West Coast and the site, provide air masses that have experienced a wide range of anthropogenic impact. This is expressed in the concentration of PAN, which varied by almost three orders-of-magnitude (Singh et al., 1985). The higher concentrations are associated with urban air masses that have been aged perhaps half a day, whereas the lowest observed concentrations approach those of the background troposphere. Therefore comparisons can be made with other measurements that are characteristic or urban, regional and remote air masses.

Singh et al. (1985) divided the PAN and NO_x data into summer and autumn periods, and into day and night periods. A correlation between PAN and NO_x was observed only in the summer daytime. PAN concentrations were relatively constant during the other periods. The ratio of PAN to NO_x varied systematically with NO_x. Summer (day and night) ratios varied from an average of 0.5 at high NO_x (> 1 ppbv) to just over 1 at low NO_x (0.1–0.2 ppbv). Autumn ratios varied from an average of 0.3 at NO_x > 1 ppbv, to well above 3 at 1 ppbv > NO_x > 0.1 ppbv. These features are a result of the photochemical nature of PAN sources, and the thermal stability of PAN, in that photochemical formation of PAN is rapid in the summertime and relatively slow in the autumn and winter, and the atmospheric lifetime of PAN is much longer in the cooler seasons than in summertime. As a result, PAN concentrations are at least several times higher than those of NO_x in air masses far removed from anthropogenic impact.

Fahey et al. (1986) show summer PAN to be an almost constant fraction of NO_y of between 0.15 to 0.20 except under conditions of high night-time NO_y (> 1.5 ppbv) when the PAN fraction decreased slightly to ~0.10, probably because such air masses have been impacted by relatively fresh anthropogenic NO_x emissions that have not undergone photochemistry. This is supported by a corresponding increase in the NO_x/NO_y ratio under these conditions. The autumn daytime ratios varied from ~0.2 at high NO_y (> 1 ppbv) to >0.4 at low NO_y (>0.5 ppbv). The autumn nighttime ratios were relatively constant at 0.3–0.4, but the

range of NO_y concentrations was much narrower than summer during these periods. The interpretation of these results is similar to that of the PAN/NO_x data. Fast photochemistry and relatively rapid thermal decomposition maintain an almost constant PAN to NO_y ratio in the summertime, with the exception of the high night-time NO_y periods. The longer lifetime of PAN in the autumn results in a larger fraction of NO_y being 'stored' as PAN.

Other measurements of PAN and NO_y, although not extensive, permit the determination of the PAN to NO_y ratio. Pierson et al. (1987) report chemiluminescent measurements of NO and the sum $NO_2 + PAN$, and GC/ECD measurements of PAN during August 1983 at Allegheny Mountain, PA. Although details of the measurements are lacking, the quantity [$NO_2 + PAN$] probably includes all other NO_y species. Therefore if the sum [NO] + [NO_2 + PAN] is taken to be [NO_y] the ratio of [PAN] to [NO_y] was 0.2, and [NO_y] was 5.9 ppbv. Grosjean (1983, 1988) reported PAN and NO_y data from measurements in September and October of 1980 and again in September 1985 at Claremont, CA. In 1980, the PAN to NO_y ratio varied from 0.004 to 0.31 and [NO_y] ranged from 36 to 170 ppbv, while in 1985 the ratio varied from 0.003 to 0.74 and [NO_y] ranged from 11 to 137 ppbv, however, there was no apparent relationship between [PAN]/[NO_y] and [NO_y] during either period. During both periods the average [PAN]/[NO_y] was 0.12, average [NO_y] was 97 ppbv in 1980, and 43 ppbv in 1985. Although the Pierson et al. (1987) and Grosjean (1983, 1988) measurements were made in air masses much more highly impacted by anthropogenic emissions, the resulting PAN to NO_y ratios are very similar to those of the high NO_y data at Niwot Ridge, CO. Summertime measurements of PAN and NO_y (reported as NO_x) by Spicer et al. (1975) in St. Louis, MO and West Covina, CA exhibited PAN-to-NO_y ratios somewhat lower than those above. An average ratio of 0.045 at [NO_y] = 43 ppbv was found in St. Louis, and an average ratio of 0.073 at [NO_y] = 136 ppbv was found in West Covina, CA.

Remote PAN measurements

Relatively few measurements of PAN have been made at what can truly be considered remote sites. The results of those measurements are listed in Table 19 and show the following general features: concentrations are often quite low and are seen to increase with altitude, wintertime concentrations are higher than summertime, and PAN is present in the stratosphere. From the few measurements of NO_x and NO_y that have been made in remote areas (Singh et al., 1988), it is clear that PAN is a major fraction of NO_y. This is expected from the extrapolation of the results of Singh et al. (1985) and Fahey et al. (1986) to low NO_x and NO_y concentrations.

Table 19. Measurements of PAN in remote air masses

Site	Sampling period	PAN(ppbv) Avg	Max	Reference
Pt. Arena, CA	August–September 1978	0.08	0.28	Singh et al., 1979
N. Pacific Ocean*	September 1982	0.074	0.4	Singh and Salas, 1983b
Pt. Arena, CA	25–29 August 1982	0.032	0.05†	Singh and Salas, 1983b
	15–28 January 1984	0.12	1.0	Singh and Salas, 1989
	25 April 1984–3 March 1985	0.046	0.13	Singh and Salas, 1989
N. Pacific Ocean	November–December 1984	0.038	0.083‡	Singh et al., 1986
S. Pacific Ocean	November–December 1984	~ 0.005	0.012‡	Singh et al., 1986
N. Pacific Ocean	August 1984	0.025	0.036§	Singh et al., 1986
N. Pacific Ocean	February 1985	0.15	0.23§	Singh et al., 1986
S. Hemisphere	June 1984	~ 0.01	0.024	Rudolph et al., 1987
N. Hemisphere	June 1984	~ 0.05	0.16	Rudolph et al., 1987
Stratosphere	June 1984	0.021	0.035	Rudolph et al., 1987
Western Atlantic PBL‖	January 1986	0.18	0.51	Bottenheim and Gallant, 1987
FT¶	January 1986	0.094	0.23	Bottenheim and Gallant, 1987

*1–8 km altitude.
†The maximum 3 h average.
‡The maximum daily average.
§The maximum of composite average.
‖Planetary boundary layer.
¶Free troposphere.

Table 20. Measurements of PPN

Site	Sampling period	Average PPN/PAN	Reference
Pt. Arena, CA	25–29 August 1982	≤ 0.07	Singh and Salas, 1983
Philadelphia, PA	4–22 April 1983	0.13	Singh and Salas, 1989
Staten Island, NY	25 April–1 May 1983	0.14	Singh and Salas, 1989
Point Arena, CA	15–28 January 1984	0.04	Singh and Salas, 1989
Downey, CA	18–27 February 1984	0.05	Singh and Salas, 1989
Denver, CO	24 March–1 April 1984	0.03	Singh and Salas, 1989
Point Arena, CA	24 April 1984–3 March 1985	0.09	Singh and Salas, 1989
Colorado	July 1984	0.05	Singh et al., 1986
Niwot Ridge, CO	July–November 1984	0.05	Singh et al., 1985
Suburban (Rome), Italy	July 1984	~ 0.14	Ciccioli et al., 1986a
Suburban (Rome), Italy	July 1985	~ 0.09	Ciccioli et al., 1986b
Rio de Janeiro, Brazil	July 1985	0.20	Tanner et al., 1988

Peroxypropionic nitric anhydride (PPN)

Since PPN can be observed with the same analytical technique as PAN, many studies report at least some PPN data, usually given as a fraction relative to PAN, and almost always assumed to exhibit the same instrumental response. Reported concentrations are summarized in Table 20 as fractions of measured PAN, but do not include those summarized previously by Altshuller (1983). The lower concentrations of PPN relative to PAN are a reflection of the fact that sources of the parent compounds, acetaldehyde and acetone are much larger than those of propionaldehyde. An illustration of this can be seen in the OH radical initiated oxidation of propane, in which reaction at the secondary carbon is preferred to reaction at the primary carbon by almost 6-to-1 (Atkinson, 1986). In addition, the abundance of PPN relative to PAN appears to be greater closer to pollution sources, a feature interpreted by Singh and Salas (1989) as indicating that faster reaction of PPN precursors, such as 1-butene, limit the production of PPN in air masses of greater age.

Peroxybenzoic nitric anhydride (PBzN)

Only a few attempts to measure PBzN have been reported. Appel (1973) observed [PBzN] < 0.07 ppbv (limit of detection) in the San Francisco Bay area during 'light smog'. Meijer and Nieboer (1977) found an average concentration of 4.6 ppbv between 1400 and 1600 h on 24 June 1976, at Delft, The Netherlands. Subsequent analyses on 4 days in 1978 and 1979 revealed PBzN concentrations between 0.2 and 1.0 ppbv, during periods when PAN was between 2 and 5 ppbv (Meijer unpublished results). Hanst et al. (1982) measured PBzN < 1 ppbv with long-path i.r. in the Los Angeles atmosphere. Fung and Grosjean (1985) observed from 0.15 to 0.62 (median = 0.32) ppbv

in urban Los Angeles, and from 0.08 to 1.81 (median 0.37) ppbv at an unspecified industrial site.

Alkyl nitrates

Reports of atmospheric measurements of the broad category of compounds, alkyl nitrates, are sparse. Although methyl nitrate can be observed using the GC-ECD method for PAN, few studies give any quantitative data, partly because of the real possibility of interference in the method from the unimolecular decomposition of PAN or coelution of chlorinated HCs. Grosjean (1983) reports methyl nitrate concentrations of "up to ~5 ppbv" in Los Angeles during a study in which [PAN] was as high as 39 ppbv and total [NO_y] as high as 170 ppbv. Ciccioli *et al.* (1986a,b) report methyl nitrate concentrations as high as 1.5 ppbv, and several night-time episodes in which methyl nitrate concentrations were much higher than those of PAN. Interference from coelution of a chlorinated HC must be considered a possible explanation for these anomalous results. Hanst *et al.* (1982) estimate a total concentration of alkyl nitrates of "not more than 2 ppbv" in long-path i.r. absorption measurements in Los Angeles. The qualitative observations of ethyl nitrate (Williams, 1965) and isopropyl nitrate (Jonsson and Berg, 1983) have been mentioned previously. Jüttner (1988) described a single measurement of 0.0025 ppbv isopropyl nitrate in a forested area near Tübingen, F.R.G., in August 1987. Atlas (1988) has made observations of several alkyl nitrates in the Northern Pacific Ocean from a shipboard platform. Three compounds, 2-butyl, 2-pentyl, and 3-pentyl nitrates have been tentatively quantified, and qualitative evidence was found for the presence of other C_3 and C_5 compounds. Concentrations of up to 0.03 ppbv 2-butyl nitrate and up to 0.009 ppbv of the sum of 2 and 3-pentyl nitrates were observed. In general, the concentrations of nitrates were quite well correlated with one another, and with simultaneous Rn measurements, indicating a continental or continentally-derived source of these nitrates. Although measurements of other NO_y compounds were not made, the absolute concentration of these nitrates is probably a significant fraction of total NO_y in such remote air masses.

The observation of 2-propyl, 2-butyl, and 2- and 3-pentyl nitrates at Scotia Range, PA, July–August 1988, has recently been reported by Buhr *et al.* (1988). Individual mixing ratios of between 0.001 and 0.060 ppbv were measured via a packed column GC/ECD method, and the total of the three or four compounds was approximately 1.5% of total NO_y (D. Parrish, private communication, 1988). It should be noted however, that the column employed did not separate either ethyl from 2-propyl nitrate, or 1-propyl from 2-butyl nitrate.

Measurements of alkyl nitrates during the springtime, 1988, at Mauna Loa, and in late winter to early spring at Alert, Canada, have been reported by Atlas and Schauffler (1988). At Mauna Loa eight alkyl nitrates were observed: 1- and 2-propyl, 1- and 2-butyl, and 1-, 2-, 3-pentyl and 2-isopentyl nitrates, with secondary nitrates more abundant than the primary compounds. The average relative distribution was: C_3-54%, C_4-30%, and C_5-16%, and total mixing ratio ranged from <0.002 to >0.010 ppbv with a mean of 0.004 ppbv. Extensive measurements of other NO_y species were also made during this campaign, however, the relationships between these and the $RONO_2$ have not yet been examined. The compounds observed at Alert were C_3–C_7, primary and secondary nitrates having both straight and branched chains. The average relative distribution was; C_3-16%, C_4-25%, C_5-25%, C_6-18%, and C_7-14%. The total mixing ratio ranged from 0.090 to 0.25 ppbv and the mean was 0.16 ppbv. Simultaneous measurements of PAN ranged from 0.15 to 0.5 ppbv (Bottenheim, as reported by Atlas and Schauffler, 1988) and the ratio of total alkyl nitrates to PAN ranged from 1:3 to 2:3.

The composition of NO_y

A number of studies have involved simultaneous measurements of NO_x, the major product species HNO_3, PAN, and aerosol NO_3^-, as well as total NO_y. The results of these measurements are summarized in Table 21 as the average ratio of the individual species to NO_y. The locations of these measurements span the range from very clean, Eastern Pacific boundary layer, to moderately polluted, Scotia Range, PA. Many features of the PAN, NO_x and NO_y relationships have been discussed previously in this paper. It is interesting to note here that the sum of the individual species, ΣNO_{yi}, is often significantly less than the corresponding total NO_y measurements. Such an NO_y "deficit" is indirect evidence of the presence of organic nitrate species.

MODELING STUDIES

A fairly recent evaluation of kinetic and mechanistic data on the photochemistry pertaining to smog has been published by Atkinson and Lloyd (1984). Several recent works have compared and evaluated air quality models and the chemical mechanisms used therein (Hough, 1988, Seinfeld, 1988). Mechanisms used for modeling of urban and regional scale chemistry are of two types: explicit and lumped. Explicit mechanisms seek to describe the chemistry of individual reactant and product compounds by keeping track of individual species, and require a great deal of computation due to the tremendous number of organic species emitted to the atmosphere. Examples of explicit mechanisms can be found in Leone and Seinfeld (1985), Carter *et al.* (1986) and Atherton and Penner (1988). It is often useful or necessary to combine reactant or product compounds of one generic type into a single 'lumped' species. These so-called lumped mechanisms must be used in LRT acid deposition models, for

example, because of computational limitations (Lurmann et al., 1986; Stockwell, 1986). Further examples of lumped mechanisms are described by Leone and Seinfeld (1985). In addition to the above mechanisms, which are meant to simulate conditions of high anthropogenic impact, models have been constructed to simulate the effect of a few of the longer-lived organic species on the global troposphere (Singh and Kasting, 1988; Isaksen and Hov, 1987; Kasting and Singh, 1986; Aikin et al., 1983; Brewer et al., 1983).

Urban scale modeling has been chiefly concerned with the simulation of oxidant, specifically, O_3 production. Often such models are compared with data from laboratory chamber experiments in order to determine how well the time variations of concentration of major species are simulated. Simulations of other species concentration profiles are used as additional diagnostic tests of chemical mechanisms. There are several reports of the successful simulation of PAN and alkyl nitrate concentrations produced in chamber experiments (Carter et al., 1979; Lurmann et al., 1986) and good agreement was found between explicit and condensed mechanism simulations of PAN and PAN analog concentrations (Lurmann et al., 1986; Atherton and Penner, 1988, 1990). However, Atherton and Penner (1988) note that because organic nitrates are not explicitly treated in condensed mechanisms, realistic simulations of them are not produced. The results of organic nitrate simulations with an explicit mechanism show that the fraction of NO_y stored as organic nitrates (other than PAN) can reach 24% at HC/NO_x ratios of 28 (Atherton and Penner, 1988, 1990).

Studies that attempt to simulate regional chemistry have also shown that PAN evolves as the major NO_y species (Hov, 1984; Artherton and Penner, 1988, 1990) a feature that appears to be born out by atmospheric observations (Singh et al., 1985; Fahey et al., 1986). The results of Atherton and Penner (1988, 1990) at $HC/NO_x = 28$ and the general product studies of Calvert and Madronich (1987), if taken as characteristic of regional chemistry, support the assertion that the NO_y 'deficit' (as detailed in Table 21) is comprised of organic nitrates, however, this organic nitrate category contains many more species and a greater variety (e.g. PAN analogs and difunctional compounds) than the few that have been measured to date. The species produced from isoprene and α-pinene, as described by Lloyd et al. (1983), were not important in the studies of Atherton and Penner (1988); however, they may have much greater relative importance in regional photochemistry, depending on the fate of these biogenically derived species (Atherton and Penner, 1990).

Modeling studies of the remote atmosphere involving organic nitrates have concentrated on the distribution of NO_y among species. Due to the greatly reduced numbers and concentrations of anthropogenic organic compounds, the chemical mechanisms used in these studies are much simpler than in urban or regional simulations. PAN was suggested to be an

Table 21. The distribution of NO_y among individual species

Location	Sampling period	NO$_x$/NO$_y$	PAN/NO$_y$	Average ratio HNO$_3$/NO$_y$	NO$_3^-$/NO$_y$	NO$_{yi}$/NO$_y$	Reference
Niwot Ridge, CO	5 July–31 August 1984	0.29	0.16	0.10	0.02	0.58	Fahey et al., 1986
Niwot Ridge, CO	October–November 1984	0.4	0.3	—	—	0.88	Fahey et al., 1985b
Point Arena, CA	April–May 1985	0.6	0.1	0.05	—	0.75*	Fahey et al., 1985b
Western Atlantic PBL	4 January 1986	0.32	0.08		0.30†	0.70	Bottenheim and Gallant, 1987
FT		0.27	0.11		0.18†	0.56	Bottenheim and Gallant, 1987
Scotia Range, PA	25 June–26 July 1986	0.59	0.14	0.16	0.04	0.93	Williams et al., 1987
Continental U.S. and Eastern Pacific	August–September 1986	0.10–0.16	0.25–0.40	0.25–0.45	—	0.77	Fehsenfeld et al., 1988; Singh et al., 1988
Niwot Ridge, CO	2 July –14 August 1987	0.32	0.24	0.13	0.04	0.73	Williams et al., 1987

*Measurement of total NO_y was made with a Teflon particle filter, thus NO_3^- was excluded from the data analysis.
†Total inorganic nitrate, $HNO_3(g)$ + particulate NO_3^-.

important, if not the most important, NO_y species in the remote troposphere based on both its long atmospheric lifetime at temperatures characteristic of the upper troposphere (Crutzen, 1979) and the simple chemistry of 2- and 3-C compounds (Singh and Hanst, 1981; Aikin et al., 1983; Brewer et al., 1983). More recent studies have produced seasonal and vertical profiles of PAN concentration that are in reasonable agreement with observation (Kasting and Singh, 1986) and the global distribution obtained by Isaksen and Hov (1987) is qualitatively consistent with that observed by Rudolph et al. (1987).

Singh and Kasting (1988) have recently included methyl nitrate in simulations of the chemistry of the remote marine troposphere, and calculated a concentration of less than 0.001 ppbv at the surface and a decrease with altitude. Until recently, simulations of alkyl or multifunctional nitrate chemistry have been limited by the absence of any quantitative data concerning their photolysis. The recent u.v. absorption cross-section measurements were used to estimate remote atmospheric concentrations of alkyl nitrates through a balance of formation and loss processes (Roberts and Fajer, 1989) and in a more detailed photochemical model (Atherton and Penner, 1990; Atherton, 1990). Both calculations predict that much lower concentrations would result from remote chemistry due to the increase in importance of $RO_2^* + HO_2^*$ and $RO_2^* + RO_2^*$ reactions relative to $RO_2^* + NO$. These studies imply that significant relative concentrations of $RONO_2$ compounds must be due to the long-range transport of these compounds.

CONCLUSIONS

Organic nitrates constitute an important class of atmospheric chemical compounds. Not only do they represent a major area of interaction between the N and organic C cycles, but because of the long atmospheric lifetimes of some of these compounds, relative to other NO_y species, they also comprise a major fraction of tropospheric NO_y. However, there are still a number of areas of uncertainty in the role that organic nitrates play in atmospheric chemistry.

Formation of organic nitrates occurs through a number of processes. Simple alkyl nitrates result primarily from a minor pathway of the reaction of RO_2^* radicals with NO. The branching ratio of $RONO_2$ formation varies systematically, increasing with carbon number from <0.014 for ethyl to >0.3 for octyl radicals, but needs to be determined for other RO_2^* radicals of atmospheric importance, especially difunctional radicals such as α- and γ-hydroxy RO_2^* radicals. The reaction of RO^* radicals with NO_2 will form alkyl nitrates; however, competing reactions of RO^* combined with the relatively low atmospheric abundance of NO_2 make this an unimportant atmospheric pathway. The possibility that formation of $RONO_2$ by this reaction may occur to some extent in exhaust streams,

especially those from engines burning alcohol-based fuels, needs to be studied. The unimolecular reaction of peroxycarboxylic nitric anhydrides appears to be a general pathway for the formation of the corresponding $RONO_2$ having one less C. While this reaction is relatively slow, it may be the major formation process of methyl nitrate, but is probably not important for higher C number homologs. The reaction of NO_3 with alkenes is a rapid process which appears to result in difunctional nitrates. Although the initial reaction rates have been measured for many compounds, the reaction pathways have not been clearly established. The reactions of alkyl peroxy and peroxyacyl radicals with NO_2 are fairly rapid and lead to the formation of alkyl peroxynitrates and peroxycarboxylic nitric anhydrides, respectively. The temperature and pressure dependencies of these reactions have been determined for only a relative few key species. In addition, the rates of the major competing reaction RO_2^* with NO, and RO_2^* with $R'O_2^*$ and HO_2^* must be known in order to derive the net formation rate of a given compound.

Comparatively little quantitative information concerning the rates of removal of organic nitrates from the atmosphere is available. Many alkyl nitrates are removed primarily through photolysis. The few measurements of absorption cross-sections that have been made, have relatively high uncertainties associated with them in the wavelength range of atmospheric importance ($\lambda > 290$ nm). Photolysis rate measurements indicate a strong temperature dependence. Information on the quantum efficiencies of photodissociation is also sparse. Quantum efficiencies are most likely close to 1.0, however several studies of ethyl nitrate report values closer to 0.5. The estimated photolytic lifetimes of alkyl nitrates range from <1 to >10 days depending on the compound and conditions assumed. The removal rates by OH radical reaction have been determined for a number of alkyl nitrates and there are now sufficient data to permit the estimation of rate constants through structure–reactivity relationships. Hydroxyl radical reaction appears to be a significant loss pathway only for the alkyl nitrates of higher C numbers ($\gtrsim C_5$). Alkyl nitrates are not very soluble in water, and therefore not significantly removed by wet deposition. Adsorption on aerosol particles or surfaces is likely to be an important removal pathway for only the larger ($\gtrsim C_5$) alkyl nitrates.

Difunctional nitrates may have much shorter photolytic lifetimes than alkyl nitrates, depending on the nature of the functional group. Compounds with a carbonyl group and an α-nitrooxy group are photodissociated relatively rapidly ($\tau < 1$ day), and hydroxy nitrates may be relatively soluble. Rates of reaction with OH have not been measured, however they can be estimated (Atkinson, 1987) and in many cases, such as α-nitrooxyacetone, the OH reaction rate appears to be slower than that of the corresponding nitrate (n-propylnitrate). Although heterogeneous losses to the aqueous or solid phase may be more important for

some of these compounds, little is known concerning their solubility in liquid water.

Alkyl peroxynitrates are removed from the atmosphere through several processes. Although absorption cross-sections of such compounds have not been measured above 290 nm, they are most likely very similar to that of peroxynitric acid and the chlorofluoromethyl peroxynitrates. Accordingly, photolysis lifetimes of alkyl peroxynitrates may be as short as 1 day. Estimated thermal decomposition rates of alkyl peroxynitrates vary dramatically with altitude, due to both temperature and pressure dependencies. For example, the lifetime of CH_3OONO_2 has been estimated to vary from ~ 1 s at the surface to ~ 40 days at the tropopause (Bahta et al., 1982). It should be noted that rates of thermal decomposition estimated from the bond homolysis rate constants represent upper limits to the atmospheric loss rate, because the resulting RO_2^* radical can recombine with NO_2 at appreciable rates compared to other reactions of RO_2^*. Reaction with OH and heterogenous losses probably do not occur for these compounds at significant rates relative to the above processes.

The removal of peroxycarboxylic anhydrides likewise occur through several different pathways. Thermal decomposition is the major loss mechanism in the lower troposphere. However, as in the $ROONO_2$ reactions, the net loss rate depends on the $NO:NO_2$ ratio in the daytime, and other losses such as reaction with RO_2^* (HO_2^*) or heterogenous removal at night. The lifetimes of these compounds due to thermal decomposition become quite long (years) at temperatures characteristic of the upper troposphere. Under such conditions, photolysis and reaction with OH become the major loss processes ($\tau \sim 100$ days). Considerable uncertainty still exists in the u.v. absorption cross-sections of these compounds, measurements having been made above 300 nm only for PAN and PPN. Although uptake by liquid water appears to be slow for PAN, solubilities of other such compounds are unknown. Surface deposition, although relatively slow, may be an important loss process for PAN within shallow surface layers characteristic of the night-time boundary layer.

Atmospheric measurements of organic nitrates have been limited to PAN and PPN, with a very few observations of alkyl nitrates and related compounds. The evidence is overwhelming that PAN is ubiquitous in the troposphere, with mixing ratios varying from tens-of-pptv to tens-of-ppbv. The higher concentrations are observed in, or close to, anthropogenic source regions (i.e. urban areas). One set of measurements shows a substantial increase in average PAN over the past 15 years or so, and one shows no apparent increase. PAN appears to constitute a major fraction of NO_y, and its relative abundance appears to increase with both distance away from sources due to photochemical aging of air masses, and season due to slower loss rates in the winter. PPN appears to be minor relative to PAN (5–15%) and the few measure-

ments of PBzN have shown widely different results, with concentrations ranging from <0.07 to 4.6 ppbv. There have been several reports of methyl nitrate measurements but little direct effort has been made to improve or verify techniques for these measurements. Several sets of measurements of higher C number $(C_3–C_7)$ alkyl nitrates have been reported, but must be regarded as preliminary until the methods used are verified. There is also evidence of difunctional nitrates in carbonaceous aerosol, but these measurements should be considered as somewhat circumstantial.

There is a pressing need to develop methods for the measurement of organic nitrates other than PAN, especially the alkyl nitrates, and these should be made in conjunction with as many other NO_y species as is practical in order to better define the spatial and chemical distribution of NO_y. Some long time-scale measurements of at least PAN and perhaps other organic nitrates should be undertaken at sites somewhat remote from anthropogenic impact in order to identify possible long-term trends.

Photochemical models have been fairly successful in simulating PAN concentrations observed in chamber studies under urban conditions. Models more suitable to regional air masses and remote air masses have been able to qualitatively reproduce some of the features of the relative NO_y distributions and the seasonal and spatial distributions observed in PAN measurements. Most models of alkyl nitrate chemistry have thus far not included realistic chemistry, especially with respect to photolytic loss rates of these compounds.

More complete descriptions of organic nitrate chemistry should be included in atmospheric chemical models as laboratory kinetic data become available. Models should address the quantitative effects of organic nitrate chemistry on important aspects of atmospheric chemistry such as the production of O_3 and other oxidants in the remote troposphere. Models should be evaluated as to the relative effect of NO_x and organic C emissions on $RONO_2$ chemistry so that future emission scenarios or control strategies can be evaluated. An additional aim should be the assessment of the likelihood or magnitude of any impacts that might result from long-term changes in organic nitrate concentrations.

REFERENCES

Adachi H. and Basco N. (1979) The reaction of ethylperoxy radicals with NO_2. *Chem. Phys. Lett.* **67**, 324–328.

Adachi H. and Basco N. (1982a) Spectra of propylperoxy radicals and rate constants for mutual interaction. *Int. J. Chem. Kinet.* **14**, 1125–1137.

Adachi H. and Basco N. (1982b) Reactions of isopropylperoxy radicals with NO and NO_2. *Int. J. Chem. Kinet.* **14**, 1243–1251.

Addison M. C., Burrows J. P., Cox R. A. and Patrick R. (1980) Absorption spectrum and kinetics of the acetylperoxy radical. *Chem. Phys. Lett.* **73**, 283–287.

Aikin A. C., Herman J. R., Maier E. J. R. and McQuillan C. J. (1983) Influence of peroxyacetyl nitrate (PAN) on odd-nitrogen in the troposphere and lower stratosphere. *Planet. Space Sci.* **31**, 1075–1082.

Akimoto H., Hoshino M., Inoue G., Okuda M. and Washida N. (1978) Reaction mechanism of the photooxidation of the toluene–NO_2–O_2–N_2 system in the gas phase. *Bull. Chem. Soc. Jpn.* **51**, 2496–2502.

Altshuller A. P. (1983) Measurements of the products of atmospheric photochemical reactions in laboratory studies and in ambient air–relationships between ozone and other products. *Atmospheric Environment* **17**, 2383–2427.

Anbar M. and Taube H. (1954) Interaction of nitrous acid with hydrogen peroxide and with water. *J. Am. Chem. Soc.* **76**, 6243–6247.

Anlauf K. G., Bottenheim J. W., Brice K. A., Fellin P., Wiebe H. A., Schiff H. I., MacKay G. I., Braman R. S. and Gilbert R. (1985) Measurement of atmospheric aerosols and photochemical products at a rural site in SW Ontario. *Atmospheric Environment* **19**, 1859–1870.

Anlauf K. G., Bottenheim J. W., Brice K. A. and Wiebe H. A. (1986) A comparison of summer and winter measurements of atmospheric nitrogen and sulfur compounds. *Water Air Soil Pollut.* **30**, 153–160.

Appel B. R. (1973) A new and more sensitive procedure for analysis of peroxy-benzoyl nitrate. *J. Air Pollut. Contr Ass.* **23**, 1042–1044.

Arvia A. J., Cafferata L. F. R. and Schumacher H. J. (1963) Das Infrarotspektrum und die Struktur von NO_3Cl und NO_3F. *Chem. Ber.* **96**, 1187–1194.

Artherton C. S. (1990) Organic nitrates in remote marine environments: evidence for long range transport. *Geophys. Res. Lett.* (submitted).

Atherton C. S. and Penner J. E. (1988) Nitrogen oxide transformation in a tropospheric model. *Tellus* **40B**, 380–392.

Artherton C. S. and Penner J. E. (1990) The transformation of nitrogen oxide in the urban and remote troposphere. *J. geophys. Res.* (submitted).

Atkinson R. (1986) Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions. *Chem. Rev.* **86**, 69–201.

Atkinson R. (1987) A structure activity relationship for the estimation of rate constants for the gas-phase reactions of OH radicals with organic compounds. *Int. J. Chem. Kinet.* **19**, 799–828.

Atkinson R., Aschmann S. M., Carter W. P. L. and Winer A. M. (1982a) Kinetics of the gas-phase reactions of OH radicals with alkyl nitrates at $299 \pm 2K$. *Int. J. Chem. Kinet.* **14**, 919–926.

Atkinson R., Aschmann S. M., Carter W. P. L., Winer A. M. and Pitts J. N., Jr. (1982b) Alkyl nitrate formation from the NO_x–air photooxidations of C_2–C_8 *n*-alkanes. *J. phys. Chem.* **86**, 4563–4569.

Atkinson R., Aschmann S. M., Carter W. P. L., Winer A. M. and Pitts J. N. Jr. (1984a) Formation of alkyl nitrates from the reaction of branched and cyclic alkyl peroxy radicals with NO. *Int. J. Chem. Kinet.* **16**, 1085–1101.

Atkinson R., Aschmann S. M. and Goodman M. A. (1987b) Kinetics of the gas-phase reactions of NO_3 radicals with a series of alkynes, haloalkenes, and α,β-unsaturated aldehydes. *Int. J. Chem. Kinet.* **19**, 299–307.

Atkinson R., Aschmann S. M., Long W. P. and Winer A. M. (1985b) Effects of ring strain on gas-phase rate constants: 3.

NO_3 radical reactions with cycloalkenes. *Int. J. Chem. Kinet.* **17**, 957–966.

Atkinson R., Aschmann S. M. and Pitts J. N., Jr. (1988) Rate constants for the gas-phase reactions of the NO_3 radical with a series of organic compounds at $296 \pm 2K$. *J. phys. Chem.* **92**, 3454–3457.

Atkinson R., Aschmann S. M. and Winer A. M. (1987a) Alkyl nitrate formation from the reaction of a series of branched RO_2 radicals with NO as a function of temperature and pressure. *J. atmos. Chem.* **5**, 91–102.

Atkinson R., Aschmann S. M., Winer A. M. and Pitts J. N., Jr. (1984b) Kinetics of the gas-phase reactions of NO_3 radicals with a series of dialkenes, cycloalkenes, and monoterpenes, at 295 ± 1 K. *Envir. Sci. Technol.* **18**, 370–375.

Atkinson R., Aschmann S. M., Winer A. M. and Pitts J. N., Jr. (1985a) Kinetics and atmospheric implications of the gas-phase reactions of NO_3 radicals with a series of mono-terpenes and related organics at 294 ± 2 K. *Envir. Sci. Technol.* **19**, 195–163.

Atkinson R., Carter W. P. L. and Winer A. M. (1983) Effects of temperature and pressure on alkyl nitrate yields in the NO_x photooxidations of *n*-pentane and *n*-heptane. *J. phys. Chem.* **87**, 2012–2018.

Atkinson R. and Lloyd A. C. (1984) Evaluation of kinetic and mechanistic data for modeling of photochemical smog. *J. Phys. Chem. Ref. Data.* **13**, 315–444.

Atkinson R., Plum C. N., Carter W. P. L., Winer A. M. and Pitts J. N., Jr. (1984c) Rate constants for the gas-phase reactions of nitrate radicals with a series of organics in air at 298 ± 1 K. *J. phys. Chem.* **88**, 1210–1215.

Atlas E. L. (1988) Evidence for $\geqslant C_3$ alkyl nitrates in rural and remote atmospheres. *Nature* **331**, 426–428.

Atlas E. and Schauffler S. (1988) Organic nitrates and selected halocarbons in the Pacific atmosphere. Presented at the American Geophysical Union Fall Meeting, San Francisco, CA, 5–9 December.

Bahta A., Simonaitis R. and Heicklen J. (1982) Thermal decomposition kinetics of $CH_3O_2NO_2$. *J. phys. Chem.* **86**, 1849–1853.

Baker J. W. and Easty D. M. (1950) Hydrolysis of organic nitrates. *Nature* **166**, 156.

Baker J. W. and Nathan W. S. (1936) The mechanism of aromatic side-chain reactions with special reference to the polar effects of substituents. Part VII. Attack at a saturated carbon atom by a charged ion. *J. Chem. Soc.* 236–241.

Balla R. J., Nelson H. H. and McDonald J. R. (1985). Kinetics of the reactions of isopropoxy radicals with NO, NO_2 and O_2. *Chem. Phys.* **99**, 323–335.

Bandow H., Okuda M. and Akimoto H. (1980) Mechanism of the gas-phase reactions of C_3H_6 and NO_3 radicals. *J. phys. Chem.* **84**, 3604–3608.

Barker J. R., Benson S. W. and Golden D. M. (1977) The decomposition of dimethyl peroxide and the rate constant for $CH_3O + O_2 \rightarrow CH_2O + HO_2$. *Int. J. Chem. Kinet.* **9**, 31–53.

Barrie L. A., den Hartog G., Bottenheim J. W. and Landsberger S. (1990) Anthropogenic aerosols and gases in the lower troposphere at Alert, Canada, in April 1986. *J. atmos. Chem.* (accepted).

Basco N. and Parmar S. S. (1985) Spectra and reactions of acetyl and acetylperoxy radicals. *Int. J. Chem. Kinet.* **17**, 891–900.

Basco N. and Parmar S. S. (1987) The reaction of acetylperoxy radicals with NO_2. *Int. J. Chem. Kinet.* **19**, 115–128.

Batt L. (1980) Reactions of alkoxy radicals relevant to atmospheric chemistry. *Proceedings of the First European Symposium on Physio-Chemical Behavior of Atmospheric Pollutants, Ispra, Italy, 1979* (edited by Versino B. and Ott H.), Commission of the European Communities.

Batt L. and Milne R. T. (1976) The gas phase pyrolysis of alkyl nitrites. I. *t*-butyl nitrite. *Int. J. Chem. Kinet.* **8**, 59–84.

Batt L. and Milne R. T. (1977) The gas-phase pyrolysis of

alkyl nitrites. IV. Ethyl nitrite. *Int. J. Chem. Kinet.* **9**, 549–565.

Batt L., Milne R. T. and McCulloch R. D. (1977) The gas-phase pyrolysis of alkyl nitrites. V. Methyl nitrite. *Int. J. Chem. Kinet.* **9**, 567–587.

Batt L. and Rattray G. N. (1979) The reaction of methoxy radicals with nitric oxide and nitrogen dioxide. *Int. J. Chem. Kinet.* **11**, 1183–1196.

Batt L. and Robinson G. N. (1979) Reaction of methoxy radicals with oxygen. I. Using dimethyl peroxide as a thermal source of methoxy radicals. *Int. J. Chem. Kinet.* **11**, 1045–1053.

Batt L. and Robinson G. N. (1987) Decomposition of the *t*-butoxy radical. I. Studies over the temperature range 402–443 K. *Int. J. Chem. Kinet.* **19**, 391–400.

Benson S. W. (1976) *Thermochemical Kinetics.* John Wiley, New York.

Benter Th. and Schindler R. N. (1988) Absolute rate coefficients for the reaction of NO_3 radicals with simple dienes. *Chem. Phys. Lett.* **145**, 67–70.

Benton D. J. and Moore P. (1970) Kinetics and mechanism of the formation and decay of peroxynitrous acid in perchloric acid solutions. *J. Chem. Soc.* (A), 3179–3182.

Bock Ch. W., Krasnoshchiokov S. V., Khristenko L. V., Panchenko Yu. N. and Pentin Yu. A. (1985) *Ab initio* analysis of structure and vibrational spectrum of methyl nitrate. *Chem. Phys.* **106**, 69–73.

Bollinger M. J. (1982) Chemiluminescent measurements of the oxides of nitrogen in the clean troposphere and atmospheric chemistry implications. Ph.D. Thesis, University of Colorado, Boulder, CO.

Bollinger M. J., Sievers R. E., Fahey D. W. and Fehsenfeld F. C. (1983) Conversion of nitrogen dioxide, nitric acid and *n*-propyl nitrate to nitric oxide by gold-catalyzed reduction with carbon monoxide. *Analyt. Chem.* **55**, 1980–1986.

Boschan R., Merrow R. T. and Van Dolah R. W. (1955) The chemistry of nitrate esters. *Chem. Rev.* **55**, 485–510.

Bottenheim J. W., Brice K. A. and Anlauf K. (1984) Discussion of a Lagrangian trajectory model describing long-range transport of oxides of nitrogen, the incorporation of PAN in the chemical mechanism, and supporting measurements of PAN and nitrate species at rural sites in Ontario, Canada. *Atmospheric Environment* **18**, 2609–2619.

Bottenheim J. W., Fricke W. and Brice K. A. (1987) Measurements of PAN, a highly sensitive tracer for photochemical oxidant chemistry. *Presented at the Air Pollution Control Association 80th Annual Meeting*, New York, 21–26 June.

Bottenheim J. W., Gallant A. J. and Brice K. A. (1986) Measurements of NO_y species and O_3 at 82°N latitude. *Geophys. Res. Lett.* **13**, 113–116.

Bottenheim J. W. and Gallant A. J. (1987) The occurrence of peroxyacetyl nitrate over the Atlantic Ocean east of North America during WATOX-86. *Global Biogeochem. Cycles* **1**, 369–380.

Brand J. C. D. and Cawthon T. M. (1955) The vibrational spectrum of methyl nitrate. *J. Am. Chem. Soc.* **77**, 319–323.

Brewer D. A., Augustsson T. R. and Levine J. S. (1983) The photochemistry of anthropogenic nonmethane hydrocarbons in the troposphere. *J. geophys. Res.* **88**, 6683–6695.

Brice K. A., Penkett S. A., Atkins D. H. F., Sandalls F. J., Bamber D. J., Tuck A. F. and Vaughan G. (1984) Atmospheric measurements of peroxyacetylnitrate (PAN) in rural, south-east England: seasonal variations winter photochemistry and long-range transport. *Atmospheric Environment* **18**, 2691–2702.

Brice K. A., Bottenheim J. W., Anlauf K. G. and Wiebe H. A. (1988) Long-term measurements atmospheric peroxyacetyl nitrate (PAN) at rural sites in Ontario and Nova Scotia; Seasonal variations and long-range transport. *Tellus* **40B**, 408–425.

Brown J. F. Jr. (1955) The infrared spectra of nitro and other oxidized nitrogen compounds. *J. Am. Chem. Soc.* **77**, 6341–6351.

Bruckmann P. W. and Willner H. (1983) Infrared spectro-

scopic study of peroxyacetyl nitrate (PAN) and its decomposition products. *Envir. Sci. Technol.* **17**, 352–357.

Buhr M., Fehsenfeld F. C., Parrish D. D., Sievers R. E. and Roberts J. M. (1988) Contribution of organic nitrates to the total odd-nitrogen budget at a rural, eastern U.S. site. Presented at the American Geophysical Union Fall Meeting, San Francisco, CA, 5–9 December.

Burkhardt M. R., Maniga N. I., Stedman D. H. and Paur R. J. (1988) Gas chromatographic method for measuring nitrogen dioxide and peroxyacetyl nitrate in air without compressed gas cylinders. *Analyt. Chem.* **60**, 816–819.

Burkholder J. B., Hammer P. D. and Howard C. J. (1987) Product analysis of $OH + NO_2 + M$ reaction. *J. phys. Chem.* **91**, 2136–2144.

Calvert J. G. and Madronich S. (1987) Theoretical study of the initial products of the atmospheric oxidation of hydrocarbons. *J. geophys. Res.* **92**, 2211–2220.

Calvert J. G. and Pitts J. N. Jr. (1966) *Photochemistry*, p. 454. John Wiley, New York.

Canosa-Mas C., Smith S. J., Toby S. and Wayne R. P. (1988a) Reactivity of nitrate radical towards alkynes and some other molecules. *J. Chem. Soc. Farad. Trans. 2* **84**, 247–262.

Canosa-Mas C., Smith S. J., Toby S. and Wayne R. P. (1988b) Temperature dependences of the reactions of the nitrate radical with some alkynes and with ethylene. *J. Chem. Soc. Farad. Trans. 2* **84**, 263–272.

Caralp F., Lesclaux R., Rayez M.-T., Rayez J.-C. and Forst W. (1988) Kinetics of the combination reactions of chlorofluoromethyl peroxy radicals with NO_2 in the temperature range 233–373 K. *J. Chem. Soc. Farad. Trans. 2* **84**, 569–585.

Carr R. W. Jr., Peterson D. G. and Smith F. K. Jr. (1986) Flash photolysis of 1,2-dichlorotetrafluoroacetone in the presence of oxygen. Kinetics and mechanism of the oxidation of chlorodifluoro radicals. *J. phys. Chem.* **90**, 607–614.

Carrington R. A. G. (1960) The infrared spectra of some organic nitrates. *Spectrochim. Acta.* **16**, 1279–1293.

Carroll M. A., Ridley B. A., Trainer M., Madronich S., Gregory G. L., Condon E., Singh H. B., Beck S. M. and Dunlap D. D. (1987) Photochemical stationary state examined by contrasting observed ratios of NO_2/NO with theoretical calculations, Presented at the American Geophysical Union 1987 Fall Meeting, San Francisco, CA, 7–11 December.

Carter W. P. L. and Atkinson R. (1985) Atmospheric chemistry of alkanes. *J. atmos. Chem.* **3**, 377–405.

Carter W. P. L., Lloyd A. C., Sprung J. L. and Pitts J. N. Jr. (1979) Computer modeling of smog chamber data: progress in validation of detailed mechanism for the photooxidation of propene and *n*-butane in photochemical smog. *Int. J. Chem. Kinet.* **11**, 45–101.

Carter W. P. L., Lurmann F. W., Atkinson R. and Lloyd A. C. (1986) Developement and testing of a surrogate species chemical reaction mechanism. Final Report for EPA Contract No. 68-02-4104.

Carter W. P. L., Winer A. M. and Pitts J. N. Jr. (1981) Major atmospheric sink for phenol and cresols. Reaction with the nitrate radical. *Envir. Sci. Technol.* **15**, 829–831.

Ciccioli P., Brancaleoni E., DiPalo C., Brachetti A. and Cecinato A. (1986a) Daily trends of photochemical oxidants and their precursors in a suburban forested area. A useful approach for evaluating the relative contributions of natural and anthropogenic hydrocarbons to the photochemical smog formation in rural areas in Italy. *Proceedings of the Fourth European Symposium on Physio-Chemical Behavior of Atmospheric Pollutants, Stresa, Italy*, 23–25 September.

Ciccioli P., Brancaleoni E., Cecinato A., Brachetti A., Sciortino M., Carillo A. and Bargagli A. (1988) Seasonal and daily trends of PAN in a suburban area of central Italy. In *Field Measurements and their Interaction, Air Pollution Research Report* **14** (edited by S. Bilke *et al.*). Comm. Eur. Commun. 1988.

Ciccioli P., Brancaleoni E., DiPalo V., Liberti M. and DiPalo

C. (1986b) Misura delle alterazoni della qualita dell'aria da fenomeni di smog fotochimico. *Acqua–Aria* 7, 675–683.

Clemitshaw K. C. and Sodeau J. R. (1987) Atmospheric chemistry at 4.2 K: A matrix isolation study of the reaction between CF_3O_2 radicals and NO. *J. phys. Chem.* 91, 3650–3653.

Cohn H., Ingold C. K. and Poole H. G. (1952) Infra-red spectrum of nitric and deutero nitric acid vapour. Completion of identification of the fundamental frequencies. Entropy of nitric acid. Barrier resisting rotation of the hydroxyl group. *J. Chem. Soc.* 4272–4282.

Conkle J. P., Lackey W. W., Martin C. L. and Miller R. L. (1976) Organic compounds in turbine combustor exhaust. In *Envir. Sensing and Assess.* I.E.E.E. Publication 75-CH-1004-1, ICESA, pp. 27-2.1 to 27-2.11, New York.

Connon N. W. (1970) Nitrate esters. *Eastman Org. Chem. Bull.* 42.

Corkum R., Giesbrecht W. W., Bardsley T. and Chernik E. A. (1986) Peroxyacetyl nitrate (PAN) in the atmosphere at Simcoe, Canada. *Atmospheric Environment* 20, 1241–1248.

Cox A. P. and Waring S. (1971) Microwave spectrum, structure and dipole moment of methyl nitrate. *Trans. Faraday Soc.* 67, 3441–3450.

Cox R. A., Derwent R. G., Holt P. M. and Kerr J. A. (1976) Photolysis of nitrous acid in the presence of acetaldehyde. *J. Chem. Soc. Faraday Trans. I.* 72, 2061–2075.

Cox R. A. and Tyndall G. S. (1979) Rate constants for reactions of CH_3O_2 in the gas phase. *Chem. Phys. Lett.* 65, 357–360.

Cox R. A., Derwent R. G., Kearsey S. V., Batt L. and Patrick K. G. (1980) Photolysis of methylnitrite: kinetics of the reaction of the methoxy radical with O_2. *J. Photochem.* 13, 149–163.

Cox R. A. and Roffey M. J. (1977) Thermal decomposition of peroxyacetylnitrate in the presence of nitric oxide. *Envir. Sci. Technol.* 11, 900–906.

Cowley E. G. and Partington J. R. (1933) Studies in dielectric polarization. Part VIII. The dipole moments of alkyl nitrates and nitrites. *J. Chem. Soc.* 1252–1254.

Crater W. de C. (1929) The vapor pressures of glycerol trinitrate and certain glycol dinitrates. *Ind. Eng. Chem.* 21, 674–676.

Crutzen P. J. (1979) The role of NO and NO_2 in the chemistry of the troposphere and stratosphere. *Ann. Rev. Earth Planet. Sci.* 7, 443–472.

Csizmadia V. M., Houlden S. A., Koves G. J., Boggs J. M. and Csizmadia I. G. (1973) The stereochemistry and ultraviolet spectra of simple nitrate esters. *J. Org. Chem.* 38, 2281–2287.

Darley E. F., Kettner K. A. and Stephens E. R. (1963) Analysis of peroxyacyl nitrates by gas chomatography with electron capture detection. *Analyt. Chem.* 35, 589–591.

Darnall K. R., Carter W. P. L., Winer A. M., Lloyd A. C. and Pitts J. N. Jr. (1976) Importance of $RO_2 + NO$ in alkyl nitrate formation from C_4–C_6 alkane photooxidations under simulated atmospheric conditions. *J. phys. Chem.* 80, 1948–1950.

Das R. C., Koga O. and Suzuki S. (1979) Chemical ionization mass spectrometry of alkyl nitrates and nitrites. *Bull. Chem. Soc. Jpn.* 52, 65–68.

Daum P. H., Kelly T. J., Tanner R. L., Tang X., Anlauf K., Bottenheim J., Brice K. A. and Wiebe H. A. (1989) Winter measurements of trace gas and aerosol composition at a rural site in southern Ontario. *Atmospheric Environment* 23, 161–173.

Demerjian K. L., Schere K. L. and Peterson J. T. (1980) Theoretical estimates of actinic (spherically integrated) flux and photolytic rate constants of atmospheric species in the lower troposphere. *Adv. Envir. Sci. Technol.* 10, 369–459.

Derwent R. G. and Hov O. (1982) The potential for secondary pollutant formation in the atmospheric boundary layer

in a high pressure situation over England. *Atmospheric Environment* 16, 655–665.

Dlugokencky E. J. and Howard C. J. (1989) Laboratory studies of NO_3 radical reactions with some atmospheric hydrocarbons. *J. Phys. Chem.* 93, 1091–1096.

Dognon A. M., Caralp F. and Lesclaux R. (1985) Reactions de radicaux chlorofluorométhyl peroxyles avec NO: Etude cinetique dans le domaine de temperature compres entre 230 et 430 K. *J. Chim Phys. Phys.-Chim. Biol.* 82, 349–352.

Drummond J. W., Schiff H. I. and Mackay G. I. (1988) Atmospheric measurements of PAN (peroxyacetyl nitrate) using a newly developed Luminox^R instrument. Presented at the American Chemical Society 196th National Meeting, Los Angeles, CA, 25–30 September.

Duynstee E. F. J., Hennekens J. L. J. P., van Raayen W. and Voskuil W. (1971) Synthesis and thermal decomposition of a tertiary β-nitroalkyl peroxynitrate. *Tet. Lett.* 34, 3197–3200.

Duynstee E. F. J., Housmans J. G. H. M., Vleugels J. and Voskuil W. (1973) Synthesis of t-butyl and methyl peroxynitrate. *Tet. Lett.* 25, 2275–2276.

Edney E. O., Spence J. W. and Hanst P. L. (1979a) Synthesis and thermal stability of peroxy alkyl nitrates. *J. Air Pollut. Control Ass.* 29, 741–743.

Edney E. O., Spence J. W. and Hanst P. L. (1979b) Peroxy nitrate air pollutants: synthesis and thermal stability. In *Nitrogenous Air Pollutants* (edited by Grosjean D.), pp. 111–135. Ann Arbor Science, Ann Arbor, MI.

Fahey D. W., Eubank C. S., Hübler G. and Fehsenfeld F. C. (1985a) Evaluation of a catalytic reduction technique for the measurement of total reactive odd-nitrogen, NO_y, in the atmosphere. *J. atmos. Chem.* 3, 435–468.

Fahey D. W., Hübler G., Parrish D. D., Williams E. J., Norton R. B., Ridley B. A., Singh H. B., Liu S. C. and Fehsenfeld F. C. (1986) Reactive nitrogen species in the troposphere: measurements of NO, NO_2, HNO_3, particulate nitrate, peroxyacetyl nitrate (PAN), O_3, and total reactive odd nitrogen (NO_y) at Niwot Ridge, Colorado. *J. geophys. Res.* 91, 9781–9793.

Fahey D. W., Parrish D. D., Williams E. J., Norton R. B., Hübler G., Fehsenfeld F. C., Ridley B. A., Gandrud B. W. and Shetter J. (1985b) Tropospheric measurements of NO_y, NO_x, HNO_3, and PAN at clean continental and coastal sites. Presented at the American Geophysical Union Fall Meeting, San Francisco, CA, 9–13 December.

Fehsenfeld F. C., Dickerson R. R., Hübler G., Luke W. T., Nunnermaker L. J., Williams E. J., Roberts J. M., Calvert J. G., Curran C. M., Delaney A. C., Eubank C. S., Fahey D. W., Fried A., Gandrud B. W., Langford A. O., Murphy P. C., Norton R. B., Pickering K. E. and Ridley B. A. (1987) A ground-base intercomparison of NO, NO_x and NO_y measurement techniques. *J. geophys. Res.* 92, 14,710–14,722.

Fehsenfeld F. C., Parrish D. D., and Fahey D. W. (1988) The measurement of NO_x in the non-urban troposphere. In *Tropospheric Ozone* (edited by I. Isaksen). D. Reidel, Dordrecht.

Ferris A. F., McLean K. W., Marks I. G. and Emmons W. D. (1953) Metathetical reactions of silver salts in solution III. The synthesis of nitrate esters. *J. Am. Chem. Soc.* 75, 4078.

Fild I. and Lovell D. J. (1970) Infrared studies of peroxyacetyl nitrate (PAN). *J. Opt. Soc. Am.* 60, 1315–1318.

Finlayson-Pitts B. J. and Pitts J. N. Jr. (1986) *Atmospheric Chemistry: Fundamentals and Experimental Techniques.* John Wiley, New York.

Francisco J. S., Li Z. and Williams I. H. (1987) Dissociation dynamics of the trifluoromethoxy radical. *Chem. Phys. Lett.* 140, 531–536.

Fraser R. T. M. and Paul N. C. (1968a) The mass spectrometry of nitrate esters and related compounds. Part I. *J. Chem. Soc.* 659–663.

Fraser, R. T. M. and Paul, N. C. (1968b) The mass spectrometry of nitrate esters. Part II. *J. Chem. Soc. B.*, 1407–1410.

Fung K. and Grosjean D. (1985) Peroxybenzoyl nitrate:

measurement in smog chambers and urban air. *Sci. Total Envir.* **46**, 29-40.

Gaffney J. S., Fajer R. and Senum G. I. (1984) An improved procedure for high purity gaseous peroxyacyl nitrate production: use of heay lipid solvents. *Atmospheric Environment* **18**, 215-218.

Gaffney J. S., Fajer R., Senum G. I. and Lee J. H. (1986) Measurement of the reactivity of OH with methylnitrate: implications for prediction of alkyl nitrate-OH reaction rates. *Int. J. Chem. Kinet.* **18**, 399-407.

Garland J. A. and Penkett S. A. (1976) Absorption of peroxyacetyl nitrate and ozone by natural surfaces. *Atmospheric Environment* **10**, 1127-1131.

Gay B. W. Jr., Noonan R. C., Bufalini J. J. and Hanst P. L. (1976) Photochemical synthesis of peroxyacyl nitrates in gas phase via chlorine-aldehyde reaction. *Envir. Sci. Technol.* **10**, 82-85.

Gery M. W., Fox D. L., Jeffries H. E., Stockburger L. and Weathers W. S. (1985) A continuous stirred tank reactor investigation of the gas-phase reaction of hydroxyl radicals and toluene. *Int. J. Chem. Kinet.* **17**, 931-955.

Glasson W. A. and Heuss J. M. (1977) Synthesis and evaluation of potential atmospheric eye irritants. *Envir. Sci. Technol.* **11**, 395-398.

Glavas S. and Schurath U. (1983) Concentration and storage of peroxyacetylnitrate (PAN) for mobile field measurements in tropospheric air. *Chimika Chronika* **12**, 89-97.

Goodeve J. W. (1934) The absorption spectra of ethyl nitrate, ethyl nitrite, and nitroethane. *Trans. Faraday Soc.* **30**, 504-508.

Graedel T. E., Hawkins D. T. and Claxton L. D. (1986) *Atmospheric Chemical Compounds, Sources, Occurrence, and Bioassay.* Academic Press, Orlando, FL.

Graham R. A., Winer A. M. and Pitts J. N. Jr. (1977) Temperature dependence of the unimolecular decomposition of pernitric acid and its atmospheric implications. *Chem. Phys. Lett.* **51**, 215-220.

Graham R. A., Winer A. M. and Pitts J. N. Jr. (1978) Pressure and temperature dependence of the unimolecular decomposition of HO_2NO_2. *J. Chem. Phys.* **68**, 4505-4510.

Gray J. A. and Style D. W. G. (1953) The photolysis of ethyl nitrate. *Trans. Farad. Soc.* **49**, 52-57.

Gray P., Griffiths J. F. and Hasegawa K. (1981) Non-isothermal decomposition of methyl nitrate: anomalous reaction order and activation energies and their correction. *Int. J. Chem. Kinet.* **13**, 817-831.

Gray P. and Pratt M. W. T. (1957) The latent heats of vaporization of the alkyl nitrates. *J. Chem. Soc.* 2163-2168.

Gray P. and Rogers G. T. (1954) The explosion and decomposition of methyl nitrate in the gas phase. *Trans. Farad. Soc.* **50**, 28-36.

Griffith D. W. and Schuster G. (1987) Atmospheric trace gas analysis using matrix isolation-Fourier transform infrared spectroscopy. *J. atmos. Chem.* **5**, 59-81.

Grob K. and Grob G. (1971) Gas-liquid chromatographic mass spectrometric investigation of C_6-C_{20} organic compounds in an urban atmosphere. *J. Chromatogr.* **62**, 1-13.

Grosjean D. (1983) Distribution of atmospheric nitrogenous pollutants at a Los Angeles area smog receptor site. *Envir. Sci. Technol.* **17**, 13-19.

Grosjean D. (1984) Discussion: Worldwide ambient measurements of peroxyacetyl nitrate (PAN) and implications for plant injury. *Atmospheric Environment* **18**, 1489-1491.

Grosjean D. (1988) Aldehydes, carboxylic acids and inorganic nitrate during NSMCS. *Atmospheric Environment* **22**, 1637-1648.

Grosjean D., Fung K., Collins J., Harrison J. and Breitung E. (1984) Portable generator for on-site calibration of peroxyacetyl nitrate analyzers. *Analyt. Chem.* **56**, 569-573.

Grosjean D. and Harrison J. (1985) Peroxyacetyl nitrate: Comparison of alkaline hydrolysis and chemiluminescence methods. *Envir. Sci. Technol.* **19**, 749-752.

Guicherit R. (1987) Ozone on an urban and regional scale: with special reference to the situation in The Netherlands. *Proceedings of the NATO Advanced Research Workshop on Tropospheric Ozone,* Lillehammer, Norway, 1-5 June.

Gutman D., Sanders N. and Butler J. E. (1982) Kinetics of the reactions of methoxy and ethoxy radicals with oxygen. *J. phys. Chem.* **86**, 66-70.

Hakimelahi G. H., Sharghi H., Zarrinmayeh H. and Khalafi-Nezhad A. (1984) The synthesis and application of novel nitrating and nitrosating agents. *Helv. Chim. Acta.* **67**, 906-915.

Halfpenny E. and Robinson P. L. (1952) Pernitrous acid. The reaction between hydrogen peroxide and nitrous acid, and the properties of the intermediate product. *J. Chem. Soc.* 928-938.

Hammond P. R. (1962) Nuclear magnetic resonance of the methyl esters of some inorganic oxyacids. *J. Chem. Soc.* 1370-1373.

Hanst P. L., Wong N. W. and Bragin J. (1982) A long-path infra-red study of Los Angeles smog. *Atmospheric Environment* **16**, 969-981.

Hanriot M. (1879) Derives de la glycerine. *Ann. Chim. Phys.* **17**, 62-119.

Harkins W. D., Clark G. L. and Roberts L. E. (1920) The orientation of molecules in surfaces, surface energy, adsorption and surface catalysis V. The adhesional work between organic liquids and water. *J. Am. Chem. Soc.* **42**, 700-712.

Harris L. E. (1973) The lower electronic states of nitrite and nitrate ion, nitromethane, nitramide, nitric acid, and nitrate esters. *J. Chem. Phys.* **58**, 5615-5626.

Harris S. J. and Kerr J. A. (1989) A kinetic and mechanistic study of the formation of alkyl nitrates in the photooxidation of *n*-heptane studied under atmospheric conditions. *Int. J. Chem. Kinet.* **21**, 207-218.

Hartley W. N. (1903) The absorption spectra of metallic nitrates. *J. Chem. Soc.* **83**, 221-246.

Hayes R. N., Sneldon J. C., Bowie J. H. and Lewis D. E. (1985) Elimination of molecular hydrogen and methane from collision-activated alkoxide negative ions in the gas phase. An ab initio and isotope effect study. *Aust. J. Chem.* **38**, 1197-1208.

Hendry D. G. and Kenley R. A. (1977) Generation of peroxy radicals from peroxy nitrates (RO_2NO_2). Decomposition of peroxyacyl nitrates. *J. Am. Chem. Soc.* **99**, 3198-3199.

Hendry D. G. and Kenley R. A. (1979) Atmospheric chemistry of peroxynitrates. In *Nitrogenous Air Pollutants* (edited by Grosjean D.), pp. 137-148. Ann Arbor Science, Ann Arbor, MI.

Henry M. L. (1872) Recherches sur les derives etheres des alcools et des acides polyatomiques. *Ann. Chim. Phys.* 4 **27**, 243-264.

Heuss J. M. and Glasson W. A. (1968) Hydrocarbon reactivity and eye irritation. *Envir. Sci. Technol.* **2**, 1109-1116.

Hill A. C. (1971) Vegetation: a sink for atmospheric pollutants. *J. Air Pollut. Control Ass.* **21**, 341-345.

Hohorst F. A. and DesMarteau D. D. (1974) Some reactions of CF_3OO derivatives with inorganic nitrogen compounds. Synthesis and vibrational spectrum of trifluoromethyl peroxynitrate. *Inorg. Chem.* **13**, 715-719.

Holdren M. W. and Rasmussen R. A. (1976) Moisture anomaly in analysis of peroxyacetyl nitrate (PAN). *Envir. Sci. Technol.* **10**, 185-187.

Holdren M. W., Spicer C. W. and Hales J. M. (1984) Peroxyacetyl nitrate solubility and decomposition rate in acidic water. *Atmospheric Environment* **18**, 1171-1173.

Hoshino M., Akimoto H. and Okuda M. (1978a) Photochemical oxidation of benzene, toluene, and ethylbenzene initiated by OH radicals in the gas phase. *Bull. Chem. Soc. Jpn.* **51**, 718-724.

Hoshino M., Ogata T., Akimoto H., Inove G., Sakamaki F. and Okuda M. (1978b) Gas phase reaction of N_2O_5 with propylene. *Chem. Lett.* 1367-1370.

Hough A. (1988) An intercomparison of mechanism for the

production of photochemical oxidants. *J. geophys. Res.* **93**, 3789–3812.

Hov O. (1984) Modeling of the long-range transport of peroxyacetylnitrate to Scandinavia. *J. atmos. Chem.* **1**, 187–202.

Isaksen I. S. A. and Hov O. (1987) Calculations of trends in the tropospheric concentration of O_3, OH, CO, CH_4 and NO_x. *Tellus* **39B**, 271–285.

IUPAC (1965) *Nomenclature of Organic Chemistry, Section C.* Butterworth, London.

IUPAC (1977) *How to Name an Inorganic Substance.* Pergamon Press, Oxford.

Japar S. M. and Niki H. (1975) Gas phase reactions of the nitrate radical with olefins. *J. phys. Chem.* **79**, 1629–1632.

Johnston H. S., Chang S.-G. and Whitten G. (1974) Photolysis of nitric acid vapor. *J. phys. Chem.* **78**, 1–7.

Jonsson A. (1985) Sampling and gas chromatographic analysis of volatile organic air pollutants. Ph.D. Thesis, University of Stockholm, Stockholm, Sweden.

Jonsson A. and Berg S. (1983) Determination of low-molecular-weight oxygenated hydrocarbons in ambient air by cryogenic sampling and two-dimensional gas chromatography. *J. Chromatogr.* **279**, 307–322.

Joos L. F., Landolt W. F. and Leuenberger H. (1986) Calibration of peroxyacetyl nitrate measurements with an NO_x analyzer. *Envir. Sci. Technol.* **20**, 1269–1273.

Jullien, J., Pechine J.-M., Perz F. and Sadek M. A. (1983) Decomposition thermique en phase gazeuse du nitrate d'isopropyle. *Propell. Expl. Pyrotech.* **8**, 99–101.

Jüttner F. (1988) A cryotrap technique for the quantitation of monoterpenes in humid and ozone-rich forest air. *J. Chromatogr.* **442**, 157–163.

Kacmarek A. J., Solomon I. J. and Lustig M. (1977) Preparation and properties of peroxyacetyl nitrate. *J. Inorg. Nucl. Chem.* **40**, 574–576.

Katritzky A. R. and Marzorati L. (1980) Conversion of primary amines to nitrate esters. *J. Org. Chem.* **45**, 2515–2516.

Kasting J. F. and Singh H. B. (1986) Nonmethane hydrocarbons in the troposphere: impact on the odd hydrogen and odd-nitrogen chemistry. *J. geophys. Res.* **91**, 13,239–13,256.

Kelly T. J., Stedman D. H., Ritter J. A. and Harvey R. B. (1980) Measurements of oxides of nitrogen and nitric acid in clean air. *J. geophys. Res.* **85**, 7417–7425.

Kenley R. A. and Hendry D. G. (1982) Generation of peroxy radicals from peroxynitrates ($ROONO_2$). Decomposition of peroxybenzoyl nitrate (PBzN). *J. Am. Chem. Soc.* **104**, 220–224.

Kerr J. A. and Stocker D. W. (1986) Kinetics of the reactions of hydroxyl radicals with alkyl nitrates and with some oxygen-containing organic compounds studied under simulated atmospheric conditions. *J. Atmos. Chem.* **4**, 253–262.

Kopczynski S. L., Altshuller A. P. and Sutterfield F. D. (1974) Photochemical reactives of aldehyde–nitrogen oxide systems. *Envir. Sci. Technol.* **8**, 909–918.

Kornblum N. and Frazier H. W. (1966) A new and convenient synthesis of glyoxals, glyoxalate esters, and α-diketones. *J. Am. Chem. Soc.* **88**, 865–866.

Kornblum N., Patton J. T. and Nordmann J. B. (1948) The basis for the reported optical activity of the salts of aliphatic nitro compounds: 2-nitrobutane. *J. Am. Chem. Soc.* **70**, 746–749.

Kornblum N., Smiley R. A., Ungnade H. E., White A. M., Taub B. and Herbert S. A. Jr. (1955) The reaction of silver nitrate with secondary and tertiary alkyl halides. *J. Am. Chem. Soc.* **77**, 5528–5533.

Kornblum N. and Teitelbaum C. (1952) The basis for the report that rearrangements occur when cyclopentyl iodide and cyclohexyl iodide react with silver nitrite. *J. Am. Chem. Soc.* **74**, 3076–3078.

Kravetz T. M., Martin S. W. and Mendenhall G. D. (1980)

Synthesis of peroxyacetyl and peroxyaroyl nitrates. Complexation of peroxyacetyl nitrate with benzene. *Envir. Sci. Technol.* **14**, 1262–1264.

Kuhn L. P. 1(946) Catalytic hydrogenolysis of nitrate esters. *J. Am. Chem. Soc.* **68**, 1761–1762.

Kuntasal G. and Chang T. Y. (1987) Trends and relationships of O_3, NO_x, and HC in the south coast air basin of California. *J. Air. Pollut. Control Ass.* **37**, 1158–1163.

Lachowicz D. R. and Krevz K. L. (1967) Peroxynitrates. The unstable products of olefin nitration with dinitrogen tetroxide in the presence of oxygen. A new route to α-nitro ketones. *J. Org. Chem.* **32**, 3885–3888.

Landolt W., Joos F. and Mächler H. (1985) Erste Messungen des PAN-Gehalt-es der Luft im Raume Birmensdorf (ZH). *Schweiz. Z. Forstwes.* **136**, 421–426.

Lee Y.-N., Senum G. I. and Gaffney J. S. (1983) Peroxyacetyl nitrate (PAN) stability, solubility, and reactivity—implications for tropospheric nitrogen cycles and precipitation chemistry. Presented at the Fifth International Conference of the Commission on Atmospheric Chemistry and Global Pollution, Oxford, England, 28 August –2 September.

Lee Y.-N. (1984) Kinetics of some aqueous-phase reactions of peroxyacetyl nitrate. Presented at the Conference on Gas–Liquid Chemistry of Natural Waters, Brookhaven National Laboratory, Upton, NY, 1–4 April.

Leighton P. A. (1961) *Photochemistry of Air Pollution.* Academic Press, NY.

Leone J. A. and Seinfeld J. H. (1985) Comparative analysis of chemical reaction mechanisms for photochemical smog. *Atmospheric Environment* **19**, 437–464.

Lesclaux R. and Carlap F. (1984) Determination of the rate constants for the reactions of $CFCl_2O_2$ radical with NO and NO_2 by laser photolysis and time resolved mass spectrometry. *Int. J. Chem. Kinet.* **16**, 1117–1128.

Lesclaux R., Carlap F., Dognon A. M. and Carioulle D. (1986) The rate of formation of halomethyl peroxy nitrates in the stratosphere and their possible role as temporary reservoirs for ClO_x and NO_x species. *Geophys. Res. Lett.* **13**, 933–936.

Lesclaux R., Dognon A. M. and Caralp F. (1987) Photooxidation of halomethanes at low temperature: the decomposition rate of $CDCl_3O$ and $CFCl_2O$ radicals. *J. Photochem. Photobio. A.* **41**, 1–11.

Levy J. B. (1954) The thermal decomposition of nitrate esters. II. The effect of additives on the thermal decomposition of ethyl nitrate. *J. Am. Chem. Soc.* **76**, 3790–3793.

Liberti A., Ciccioli P. (1986) High resolution chromatographic techniques for the evaluation of atmospheric pollutants. *J. High Res. Chromat. Chromat. Commun.* **9**, 492–501.

Lloyd A. C., Atkinson R., Lurmann F. W. and Nitta B. (1983) Modeling potential ozone impacts from natural hydrocarbons—I. Development and testing of a chemical mechanism for the NO_x–air photooxidation of isoprene and α-pinene under ambient conditions. *Atmospheric Environment* **17**, 1931–1950.

Löbel J., Wipprecht V. and Schurath U. (1980) Messungen von Peroxoiacetylnitrat (PAN) in Außenluft. *Staub.-Reinhalt. Luft.* **40**, 243–244.

Logan J. A. (1983) Nitrogen oxides in the troposphere: global and regional budgets. *J. geophys. Res.* **88**, 10,785–10,807.

Lonneman W. A. (1977) PAN measurement in dry and humid atmospheres. *Envir. Sci. Technol.* **11**, 194–195.

Lonneman W. A., Bufalini J. J. and Namie G. R. (1982) Calibration procedure for PAN based on its thermal decomposition in the presence of nitric oxide. *Envir. Sci. Technol.* **16**, 655–660.

Lonneman W. A., Bufalini J. J. and Seila R. L. (1976) PAN and oxidant measurement in ambient atmospheres. *Envir. Sci. Technol.* **10**, 374–380.

Louw R., Slvis G. J. and Vermeeren H. P. W. (1975) Facile preparation of peroxyacyl nitrates. *J. Am. Chem. Soc.* **97**, 4396–4397.

Lovelock J. E. and Penkett S. A. (1974) PAN over the Atlantic and the smell of clean linen. *Nature* **249**, 434.

Lowenherz R. (1890) Ueber die Molecularrefraction der Nitrate. *Ber. Deut. Chem. Ges.* **23**, 2180–2182.

Lucas G. R. and Hammett L. P. (1942) Rate and mechanism in the reactions of *t*-butyl nitrate and benzyl nitrate with water and hydroxyl ion. *J. Am. Chem. Soc.* **64**, 1928–1937.

Luke W. T. and Dickerson R. R. (1988) Direct measurements of the rate of photolysis of ethyl nitrate. *Geophys. Res. Lett.* **15**, 1181–1184.

Luke W. T., Dickerson R. R. and Nunnermarker L. J. (1990) Direct measurements of the photolysis rates coefficients and Henry's Law constants of several alkyl nitrates. *J. geophys. Res.* (submitted).

Lurmann F. W., Lloyd A. C. and Atkinson R. (1986) A chemical model for use in long-range transport/acid deposition computer modeling. *J. geophys. Res.* **91**, 10,905–10,936.

Mahoney L. R. (1970) Evidence for the formation of hydroxyl radical in the isomerization of pernitrous acid to nitric acid in aqueous solution. *J. Am. Chem. Soc.* **92**, 5262–5263.

Marans N. S. and Zelinski R. P. (1950) 2-Nitratoethyl esters of acrylic, crotonic and methacrylic acids. *J. Am. Chem. Soc.* **72**, 5330–5331.

Maria H. J., McDonald J. R. and McGlynn S. P. (1973) Electronic absorption spectrum of nitrate ion and boron trihalides. *J. Am. Chem. Soc.* **95**, 1050–1056.

Martinez R. I. (1980) A systematic nomenclature for the "peroxyacyl nitrates", the functional and structural misnomers for anhydride derivatives of nitrogen oxo acids. *Int. J. Chem. Kinet.* **12**, 771–775.

Maxwell L. R. and Moseley V. M. (1940) Molecular structure of nitrogen dioxide and nitric acid by electron diffraction. *J. Chem. Phys.* **8**, 738–742.

McGrath M. P., Francl M. M., Rowland F. S. and Hehre W. J. (1988) Isomers of nitric acid and chlorine nitrate. *J. phys. Chem.* **92**, 5352–5357.

McGraw G. E., Bernitt D. L. and Hisatune I. C. (1965) Vibrational spectra of isotopic nitric acids. *J. Chem. Phys.* **42**, 237–244.

McKillop A. and Ford M. E. (1974) Mercury-assisted solvolyses of alkyl halides, simple procedures for the preparation of nitrate esters, acetate esters, alcohols and ethers. *Tetrahedron* **30**, 2467–2475.

McKillop A., Young D. W., Edwards M. and Hug R. P. (1978) Thallium in organic synthesis. 51. oxidation of enolizable ketones to α-nitrato ketones by thallium (III) nitrate in acetonitrile. *J. Org. Chem.* **43**, 3773–3774.

Meijer G. M. and Nieboer H. (1977) Determination of peroxy benzoyl nitrate in ambient air. *VDI Berichte* **270**, 55–56.

Mendenhall G. D., Golden D. M. and Benson S. W. (1975) The very-low-pressure pyrolysis (VLPP) of *n*-propyl nitrate, *tert*-butyl nitrate and methyl nitrite. Rate constants for some alkoxy radical reactions. *Int. J. Chem. Kinet.* **7**, 725–737.

Meyrahn H., Hahn J., Helas G., Warneck P. and Penkett S. A. (1984) Cryogenic sampling and analysis of peroxyacetyl nitrate in the atmosphere. Presented at the Third European Symposium on Physio-Chemical Behavior of Atmospheric Pollutants, Varese, Italy, 10–12 April.

Michael A. and Carlson G. H. (1935) On the mechanism of the nitration process. *J. Am. Chem. Soc.* **57**, 1268–1276.

Miller R. H., Bernitt D. L. and Hisatune I. C. (1967) Infrared spectra of isotopic halogen nitrates. *Spectroch. Acta* **23A**, 223–236.

Molina L. T. and Molina M. J. (1981) UV absorption cross sections of HO_2NO_2 vapor. *J. Photochem.* **15**, 97–108.

Molina M. J., Tso T.-L., Molina L. T. and Wang F. C.-Y. (1987) Antarctic stratospheric chemistry of chlorine nitrate, hydrogen chloride and ice; release of active chlorine. *Science* **238**, 1253–1257.

Morel O., Simonaitis R. and Heicklen J. (1980) Ultraviolet

absorption spectra of HO_2NO_2, $CCl_3O_2NO_2$, $CCl_2FO_2NO_2$, and $CH_3O_2NO_2$. *Chem. Phys. Lett.* **73**, 38–42.

NASA Panel for Data Evaluation (1987) Chemical kinetics and photochemical data for use in stratospheric modeling. Evaluation Number 8, Jet Propulsion Laboratory, Pasadena, CA.

Nichols P. L. Jr., Magnusson A. B. and Ingham J. D. (1953) Synthesis of nitric esters by the addition of nitric acid to the ethylene oxide ring. *J. Am. Chem. Soc.* **75**, 4255–4258.

Nicksic S. W., Harkins J. and Mueller P. K. (1967) Some analyses for PAN and studies of its structure. *Atmospheric Environment* **1**, 11–18.

Nieboer H. and van Ham J. (1976) Peroxyacetyl nitrate (PAN) in relation to ozone and some meteorological parameters at Delft in the Netherlands. *Atmospheric Environment* **10**, 115–120.

Nielsen T., Hansen A. M. and Thomsen E. L. (1982) A convenient method for the preparation of pure standards of peroxyacetyl nitrate for atmospheric analysis. *Atmospheric Environment* **16**, 2447–2450.

Nielsen T., Samuelsson U., Grennfelt P. and Thomsen E. L. (1981) Peroxyacetyl nitrate in long-range transported air. *Nature* **293**, 553–555.

Niki H., Maker P. D., Savage C. M. and Breitenbach L. P. (1977) Fourier transform IR spectroscopic observation of pernitric acid formed via $HOO + NO_2 \rightarrow HOONO_2$. *Chem. Phys. Lett.* **45**, 564–566.

Niki H., Maker P. D., Savage C. M. and Breitenbach L. P. (1978) FTIR spectroscopic observation of peroxyalkyl nitrates formed via $ROO + NO_2 \rightarrow ROONO_2$. *Chem. Phys. Lett.* **55**, 289–292.

Niki H., Maker P. D., Savage C. M. and Breitenbach L. P. (1979) FTIR spectroscopic observation of haloalkyl peroxynitrates formed via $ROO + NO_2 \rightarrow ROONO_2$ ($R = CCl_3$, $CFCl_2$ and CF_2Cl). *Chem. Phys. Lett.* **61**, 100–104.

Niki H., Maker P. D., Savage C. M. and Breitenbach L. P. (1980) FTIR studies of the Cl-atom initiated oxidation of formaldehyde: detection of a new metastable species in the presence of NO_2. *Chem. Phys. Lett.* **72**, 71–73.

Niki H., Maker P. D., Savage C. M. and Breitenbach L. P. (1985) An FTIR study of the reactions $Br + CH_3CHO \rightarrow HBr + CH_3CO$ and $CH_3C(O)OO + NO_2 \rightarrow CH_3C(O)OONO_2$ (PAN). *Int. J. Chem. Kinetics* **17**, 525–534.

Niki H., Maker P. D., Savage C. M., Breitenbach L. P. and Hurley M. D. (1986) An FTIR spectroscopic study of the kinetics and mechanism for the NO_2-initiated oxidation of tetramethyl ethylene at 298 K. *Int. J. Chem. Kinet.* **18**, 1235–1247.

Niki H., Maker P. D., Savage C. M. and Hurley M. D. (1987) FTIR study of the kinetics and mechanisms for the Cl-atom and HO-radical initiated oxidation of glycolaldehyde CH_2OHCHO. *J. phys. Chem.* **91**, 2174–2178.

Noxon J. F. (1983) NO_3 and NO_2 in the mid-Pacific troposphere. *J. geophys. Res.* **88**, 11,017–11,021.

Noxon J. F., Norton R. B. and Marovich E. (1980) NO_3 in the troposphere. *Geophys. Res. Lett.* **7**, 125–128.

Ochiai M., Fujita E., Arimoto M. and Yamaguchi H. (1984) A new synthesis of allyl nitrates from allylmetal (Group IVb) compounds and thallium (III) nitrate. *Chem. Pharm. Bull.* **32**, 887–890.

Odeurs R. L., van der Veken B. J., Herman M. A. and Shamir J. (1984) Rigid asymmetric rotor theory and the gas phase structure of fluoronitrate. *J. Molec. Struct.* **118**, 81–88.

Ohta T. and Mizoguchi I. (1981) Thermal decomposition rate constant of peroxybenzoyl nitrate in the gas phase. *Envir. Sci. Technol.* **15**, 1229–1232.

Olah G. A., Narang S. C., Pearson R. L. and Cupas C. A. (1978) Synthetic methods and reactions; 48. Convenient and safe preparation of alkyl nitrates (polynitrates) via

transfer nitration of alcohols (polyols) with *n*-nitrocollidin-ium tetrafluoroborate. *Synthesis* **6**, 452–453.

Pate C. T., Sprung J. L. and Pitts J. N. Jr. (1976) Chemical ionization mass spectrum of peroxyacetylnitrate. *Org. Mass Spectrom.* **11**, 552–555.

Parrish D. D., Trainer M., Williams E. J., Fahey D. W. Hübler G., Eubank C. S., Liu S. C., Murphy P. C., Albritton D. L. and Fehsenfeld F. C. (1986) Measurements of the NO_x–O_3 photostationary state at Niwot Ridge, Colorado. *J. geophys. Res.* **91**, 5361–5370.

Pattison F. L. M. and Brown G. M. (1956) Organic nitrates as synthetic intermediates, preparations of nitrates and some representative reactions. *Can. J. Chem.* **34**, 879–884.

Pauling L. and Brockway L. O. (1937) The adjacent charge rule and the structure of methyl azide, methy nitrate, and fluorine nitrate. *J. Am. Chem. Soc.* **59**, 13–20.

Peake E., Maclean M. A. and Sandhu H. S. (1983) Surface ozone and peroxyacetyl nitrate (PAN) observations at rural locations in Alberta, Canada. *J. Air Pollut. Control Ass.* **33**, 881–883.

Peake E. and Sandhu H. S. (1983) The formation of ozone and peroxyacetyl nitrate (PAN) in the urban atmosphere of Alberta. *Can. J. Chem.* **61**, 927–935.

Peake E., MacLean M. A., Lester P. F. and Sandhu H. S. (1988) Peroxyacetylnitrate (PAN) in the atmosphere of Edmonton, Alberta, Canada. *Atmospheric Environment* **22**, 973–981.

Penkett S. A. and Brice K. A. (1986) The spring maximum in photo-oxidants in the Northern Hemisphere troposphere. *Nature* **319**, 655–657.

Perros P., Tasalkani N. and Tourance G. (1988) PAN measurements in a forested area (Donon, France). *Envir. Technol. Lett.* **9**, 351–358.

Pierson W. R., Brachaczek W. W., Gorse R. A. Jr., Japar S. M., Norbeck J. M. and Keeler G. J. (1987) Acid rain and atmospheric chemistry at Allegheny Mountain. *Envir. Sci. Technol.* **21**, 679–691.

Pitts J. N. Jr. and Grosjean D. (1979) Detailed character-ization of gaseous and size-resolved particulate pollutants at a South Coast Air Basin smog receptor site: Levels and modes of formation of sulfate, nitrate and organic particu-lates and their implications for control strategies. Report No. PB-301294/5WP, National Technical Information Service, Springfield, VA.

Platt U., Perner D., Schroder J., Kessler C. and Toennissen A. (1981) The diurnal variation of NO_3. *J. geophys. Res.* **86**, 11,965–11,970.

Platt U., Perner D., Winer A. M., Harris G. W. and Pitts J. N. Jr. (1980) Detection of NO_3 in the polluted troposphere by differential optical absorption. *Geophys. Res. Lett.* **7**, 89–92.

Platt U., Winer A. M., Biermann H. W., Atkinson R. and Pitts J. N. Jr. (1984) Measurement of nitrate radical concentrations in continental air. *Envir. Sci. Technol.* **18**, 365–369.

Ravishankara A. R. and Mauldin R. L. III (1985) Absolute rate constants for the reaction of NO_3 with trans-2-butene. *J. Phys. Chem.* **89**, 3144–3147.

Rayez J. C., Rayez M. T., Halvick P., Duguay B., Lesclaux R. and Dannenbert J. J. (1987) A theoretical study of the decomposition of halogenated alkoxy radicals. I. Hy-drogen and Chlorine extrusions. *Chem. Phys.* **116**, 203–213.

Rebbert R. E. (1963) Primary processes in the photolysis of ethyl nitrate. *J. phys. Chem.* **67**, 1923–1925.

Renlund A. M. and Trott W. M. (1984) ArF laser-induced decomposition of simple energetic molecules. *Chem. Phys. Lett.* **107**, 555–560.

Roberts J. M. and Fajer R. W. (1989) UV absorption cross sections of organic nitrates of potential atmospheric im-portance and estimation of atmospheric lifetimes. *Envir. Sci. Technol.* **23**, 945–951.

Roberts J. M., Fajer R. W. and Springston S. R. (1989) The capillary gas chromatographic separation of alkyl nitrates and peroxycarboxylic nitric anhydrides. *Analyt. Chem.* **61**, 771–772.

Robertson R. E., Koshy K. M., Annessa A., Ong J. N., Scott J. M. W. and Blandamer M. J. (1982) Kinetics of solvolysis in water of four secondary alkyl nitrates. *Can. J. Chem.* **60**, 1780–1785.

Rogers J. D. and Rhead L. A. (1987) Peroxyglutaryl nitrate: Formation and infrared spectrum. *Atmospheric Environ-ment* **21**, 2519–2523.

Ross S. D., Coburn E. R. and Finkelstein M. (1968) Some reactions of nitrate esters in acetic acid containing sulfuric acid. *J. Org. Chem.* **33**, 585–587.

Rudolph J., Vierkorn-Rudolph B. and Meixner F. X. (1987) Large-scale distribution of peroxyacetyl nitrate results from the STRATOZ III flights. *J. geophys. Res.* **92**, 6653–6661.

Sander S. P. and Watson R. T. (1980) Kinetics studies of the reactions of CH_3O_2 with NO, NO_2, and CH_3O_2 at 298 K, *J. phys. Chem.* **84**, 1664–1674.

Schiff R. (1886) Einige Molekularvolumina. *Ber. Deut. Chem. Ges.* **19**, 560–568.

Schönle G., Knauth H.-D. and Schindler R. N. (1979) Press-ure dependence of the exchange reaction between $ClONO_2$ and $^{15}NO_2$. *J. phys. Chem.* **83**, 3297–3302.

Schuetzle D., Cronn D., Crittendon A. L. and Charlson R. J. (1975) Molecular composition of secondary aerosol and its possible origin. *Envir. Sci. Technol.* **9**, 838–845.

Schurath U. and Wipprecht V. (1979) Reactions of per-oxyacyl radicals. *Proceedings of the First European Sym-posium on Physio-Chemical Behavior of Atmospheric Pollu-tants, Ispra, Italy* (edited by Versino B. and Ott H.). Commission of the European Communities.

Schurath U., Kortmann U. and Glavas S. (1984) Properties, formation and detection of peroxyacetyl nitrate. Presented at the Third European Symposium on Physio-Chemical Behavior of Atmospheric Pollutants, Varese, Italy, 10–12 April.

Scott W. E., Stephens E. R., Hanst P. L. and Doerr R. C. (1957) Further developments in the chemistry of the atmosphere. *Proc. Am. Pet. Inst. Sect.* 3, **37**, 171–183.

Scroggin D. G., Riveros J. M. and Wilson E. B. (1974) Microwave spectrum and rotational isomerism of ethyl nitrate. *J. Chem. Phys.* **60**, 1376–1385.

Seinfeld J. H. (1988) Ozone air quality models: a critical review. *J. Air Pollut. Control Ass.* **38**, 616–645.

Senum G. I., Lee Y.-N. and Gaffney J. S. (1984) The ultra-violet absorption spectrum of peroxyacetyl nitrate. *J. phys. Chem.* **88**, 1269–1271.

Senum G. I., Fajer R. and Gaffney J. S. (1986) Fourier transform infrared spectroscopic study of the thermal stability of peroxyacetyl nitrate. *J. phys. Chem.* **90**, 152–156.

Shepson P. B., Edney E. O., Kleindienst T. E., Pittman J. H., Namie G. R. and Cupitt L. T. (1985) The production of organic nitrates from hydroxyl and nitrate radical reaction with propylene. *Envir. Sci. Technol.* **19**, 849–854.

Shriner R. L. and Parker E. A. (1933) Asymmetric synthesis. II. The action of optically active nitrates on cyclic ketones. *J. Am. Chem. Soc.* **55**, 766–777.

Singh H. B. (1987) Reactive nitrogen in the troposphere. *Envir. Sci. Technol.* **21**, 320–327.

Singh H. B. and Hanst P. L. (1981) Peroxyacetyl nitrate (PAN) in the unpolluted atmosphere: an important re-servoir for nitrogen oxides. *Geophys. Res. Lett.* **8**, 941–944.

Singh H. B., Hübler G., Carroll M. A., Ridley B. A., Davis D. D., LeBel P. and Huebert B. (1988) Odd nitrogen in the troposphere: Results based on the NASA GTE/CITE-2 experiment. Presented at the American Chemical Society 196th National Meeting, Los Angeles, CA, 25–30 Sep-tember.

Singh H. B. and Kasting J. F. (1988) Chlorine–hydrocarbon photochemistry in the marine troposphere and lower stratosphere. *J. atmos. Chem.* **7**, 261–285.

Singh H. B. and Salas L. J. (1983a) Methodology for the analysis of peroxyacetyl nitrate (PAN) in the unpolluted atmosphere. *Atmospheric Environment* **17**, 1507–1516.

Singh H. B. and Salas L. J. (1983b) Peroxyacetyl nitrate in the free troposphere. *Nature* **302**, 326–329.

Singh H. B., Salas L. J., Ridley B. A., Shetter J. D., Donahue N. M., Fehsenfeld F. C., Fahey D. W., Parrish D. D., Williams E. J., Liu S. C., Hübler G. and Murphy P. C. (1985) Relationship between peroxyacetyl nitrate and nitrogen oxides in the clean troposphere. *Nature* **318**, 347–349.

Singh H. B., Salas L. J., Shigeishi H., Smith A. J., Scribner E. and Cavanagh L. J. (1979) Atmospheric distributions, sources, and sinks of selected halocarbons, hydrocarbons, SF_6, and N_2O. EPA 600/3-79-107, Research Triangle Park, NC.

Singh H. B., Salas L. J. and Viezee W. (1986) Global distribution of peroxyacetyl nitrate. *Nature* **321**, 588–591.

Singh H. B. and Viezee W. (1988) Enhancement of PAN abundance in the pacific marine air upon contact with selected surfaces. *Atmospheric Environment* **22**, 419–422.

Singh H. B. and Salas L. J. (1989) Measurements of peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) at selected urban, rural and remote sites. *Atmospheric Environment* **23**, 231–238.

Spence J. W., Edney E. O. and Hanst P. L. (1978) Peroxychloroformyl nitrate: synthesis and thermal stability. *Chem. Phys. Lett.* **56**, 478–483.

Spicer C. W., Gemma J. L., Joseph D. W. and Levy A. (1975) The fate of nitrogen oxides in urban atmospheres. In *Removal of Trace Contaminants from the Air* (edited by Deitz V. R.), pp. 159–173. American Chemical Society, Washington, DC.

Spicer C. W., Holdren M. W. and Keigley G. W. (1983) The ubiquity of peroxyacetyl nitrate in the continental boundary layer. *Atmospheric Environment* **17**, 1055–1058.

Spicer C. W., Villa A., Wiebe H. A. and Heicklen J. (1973) Reactions of methylperoxy radicals with nitric oxide and nitrogen dioxide. *J. Am. Chem. Soc.* **95**, 13–20.

Steer R. P., Darnall K. R. and Pitts J. N. Jr. (1969) The base-induced decomposition of peroxyacetylnitrate. *Tet. Lett.* **43**, 3765–3767.

Steinburger R., Orlick C. A. and Schaaf V. P. (1955) Burning rates of deuterated nitrate esters. *J. Am. Chem. Soc.* **77**, 4748–4750.

Stephens E. R. (1961) The photochemical olefin–nitrogen oxides reaction. In *Chemical Reactions in the Lower and Upper Atmosphere*, pp. 51–69. Interscience, New York.

Stephens E. R. (1964) Absorptivities for infrared determination of peroxyacyl nitrates. *Analyt. Chem.* **36**, 928–929.

Stephens E. R. (1967) The formation of molecular oxygen by alkaline hydrolysis of peroxyacetyl nitrate. *Atmospheric Environment* **1**, 19–20.

Stephens E. R. (1969) The formation, reactions, and properties of peroxyacyl nitrates (PANs) in photochemical air pollution. *Adv. Envir. Sci.* **1**, 119–146.

Stephens E. R. (1987) Smog studies of the 1950's. *EOS Trans.* **68**, 89–92.

Stephens E. R., Darley E. F., Taylor O. C. and Scott W. E. (1961) Photochemical reaction products in air pollution. *Int. J. Air Water Pollut.* **4**, 79–100.

Stephens E. R., Hanst P. L., Doerr R. C. and Scott W. (1956a) Reactions of nitrogen dioxide and organic compounds in air. *Ind. Eng. Chem.* **48**, 1498–1503.

Stephens E. R., Scott W. E., Hanst P. L. and Doerr R. C. (1956b) Recent developments in the study of the organic chemistry of the atmosphere. *J. Air Pollut. Control Ass.* **6**, 159–165.

Stephens E. R. and Price M. A. (1973) Analysis of an

important air pollutant: peroxyacetyl nitrate. *J. Chem. Ed.* **50**, 351–354.

Stockwell W. R. (1986) A homogeneous gas phase mechanism for use in a regional acid deposition model. *Atmospheric Environment* **20**, 1615–1632.

Suzuki S., Koga O. and Das R. C. (1978) Analysis of ethyl nitrate by chemical ionization mass spectrometry. *Chem. Lett.* 573–574.

Takagi H., Washida N., Akimoto H. and Okuda M. (1981a) Analysis of nitrate and nitrite esters by gas chromatography/photoionization mass spectrometry. *Analyt. Chem.* **53**, 175–179.

Takagi H., Washida N., Bandow H., Akimoto H. and Okuda M. (1981b) Photooxidation of C_5–C_7 cycloalkanes in the NO–H_2O–air system. *J. Phys. Chem.* **85**, 2701–2705.

Tanner R. L., Miguel A. H., de Andrade J. B., Gaffney J. S. and Streit G. E. (1988) Atmospheric chemistry of aldehydes: Enhanced peroxyacetyl nitrate formation from ethanol-fueled vehicular emissions. *Environ. Sci. Technol.* **22**, 1026–1034.

Taylor W. D., Allston T. D., Mascato M. J., Fazekas G. B., Kozlowski R. and Takacs G. A. (1980) Atmospheric photodissociation lifetimes for nitromethane, methyl nitrite, and methyl nitrate. *Int. J. Chem. Kinet.* **12**, 231–240.

Temple P. J. and Taylor O. C. (1983a) World-wide ambient measurements of peroxyacetyl nitrate (PAN) and implications for plant injury. *Atmospheric Environment* **17**, 1583–1587.

Temple P. J. and Taylor O. C. (1983b) Assessment of crop loss due to peroxyacetyl nitrate (PAN). EPA Report CR807554010, Corvallis, OR.

Thompson C. R., Kats G. and Lennox R. W. (1979) Phytotoxicity of air pollutants formed by high explosive production. *Envir. Sci. Technol.* **13**, 1263–1268.

Tolbert M. A., Rossi M. J., Malhotra R. and Golden D. M. (1987) Reaction of chlorine nitrate with hydrogen chloride and water at Antarctic stratospheric temperatures. *Science* **238**, 1258–1260.

Troe J. (1979) Predictive possibilities of unimolecular rate theory. *J. Phys. Chem.* **83**, 114–125.

Tsalkani N., Perros P. and Toupance G. (1987) High PAN concentrations during nonsummer periods: A study of two episodes in Creteil (Paris), France. *J. atmos. Chem.* **5**, 291–299.

Tsalkani N., Mellouki A., Poulet G., Toupance G., and Le Bras (1988) Rate constant measurement for the reactions of OH and Cl with peroxyacetyl nitrate at 298 K. *J. atmos. Chem.* **7**, 409–419.

Tsani-Bazaca E., Glavas S. and Güsten H. (1988) Peroxyacetyl nitrate (PAN) concentrations in Athens, Greece. *Atmospheric Environment* **22**, 2283–2286.

Tuazon E. C., Graham R. A., Winer A. M., Easton R. R., Pitts J. N. Jr. and Hanst P. L. (1978) A kilometer pathlength Fourier-transform infrared system for the study of trace pollutants in ambient and synthetic atmospheres. *Atmospheric Environment* **12**, 865–875.

Van Swieten A. P., Louw R., Arnoldy P. (1978) Chemistry of peroxyacyl nitrates. I. Thermal decomposition in cyclohexane solution; effect of added nitric oxide and nitrogen dioxide. *Recl. Trav. Chim. Pays-Bas* **97**, 61–90.

Varetti E. L. and Pimentel G. C. (1974) The infrared spectrum of ^{15}N-labeled peroxyacetyl-nitrate (PAN) in an oxygen matrix. *Spectrochim. Acta* **30A**, 1069–1072.

Vierkorn-Rudolph B., Rudolph J. and Diederich S. (1985) Determination of peroxyacetylnitrate (PAN) in unpolluted areas. *Int. J. Envir. Analyt. Chem.* **20**, 131–148.

Vogel A. I. (1948) Physical properties and chemical constitution. Part XXIII. *J. Chem. Soc.* 1833–1855.

Wallington T. J., Atkinson R. and Winer A. M. (1984) Rate constants for the gas-phase reaction of OH radicals with peroxyacetyl nitrate (PAN) at 273 and 297 K. *Geophys. Res. Lett.* **11**, 861–864.

Wantuck P. J., Olenburg R. C., Baughcum S. L. and Winn K. R. (1987) Removal rate constant measurements for CH_3O by O_2 over the 298–973 K range. *J. phys. Chem.* **91**, 4653–4655.

Watanabe I. and Stephens E. R. (1978) Reexamination of moisture anomaly in analysis of peroxyacetyl nitrate. *Envir. Sci. Technol.* **12**, 222–223.

Westberg H., Allwine E. and Robinson E. (1978) Measurement of light hydro-carbon and oxidant transport: Houston study 1976. EPA 600/3-78-662, Research Triangle Park, NC.

Williams E. J., Buhr M. P., Parrish D. D., Norton R. B., Shimshock J. P., Curran C. M., Fehsenfeld F. C., Shetter J. D., Walega J. G., Ellsworth C. M., Ridley B. A., Allwine E. J., Farmer J. C. and Westberg H. H. (1987) Relation between odd-nitrogen species partitioning and non-methane hydrocarbon concentrations at two rural continental sites. Presented at the American Geophysical Union 1987 Fall Meeting, San Francisco, CA, 7–11 December.

Williams I. H. (1965) Gas chromatographic techniques for the identification of low concentrations of atmospheric pollutants. *Analyt. Chem.* **37**, 1723–1732.

Winer A. M., Peters J. W., Smith J. P. and Pitts J. N. Jr. (1974) Response of commercial chemiluminescent $NO-NO_2$ analyzers to other nitrogen-containing compounds. *Envir. Sci. Technol.* **8**, 1118–1121.

Winer A. M., Atkinson R. and Pitts J. N. Jr. (1984) Gaseous nitrate radical: Possible night-time sink for biogenic organic compounds. *Science* **224**, 156–159.

Witanowski M. and Webb G. A. (1973) *Nitrogen NMR.* Plenum Press, London.

Zabarnick S. and Heicklen J. (1985a) The reactions of alkoxy radicals with O_2. I. C_2H_5O radicals. *Int. J. Chem. Kinet.* **17**, 455–476.

Zabarnick S. and Heicklen J. (1985b) The reactions of alkoxy radicals with O_2. II. n-C_3H_7O radicals. *Int. J. Chem. Kinet.* **17**, 477–501.

Zabarnick S. and Heicklen J. (1985c) The reactions of alkoxy radicals with O_2. III. i-C_4H_9O radicals. *Int. J. Chem. Kinet.* **17**, 503–524.