ATMOSPHERIC CHEMISTRY OF BIOGENIC HYDROCARBONS: RELEVANCE TO THE AMAZON*

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The Amazon rainforest, one of the most productive ecosystems of Earth, plays an important role in global atmospheric chemistry. Biogenic emissions from the Amazon include isoprene, terpenes and possibly other reactive organic compounds whose photochemical reactions have a significant impact on atmospheric ozone, carbon monoxide, the hydroxyl radical, precipitation acidity and aerosol formation, among others. In this study, atmospheric oxidation mechanisms are examined for biogenic hydrocarbons that are relevant to known and probable emissions from the Amazon region. Results from recent laboratory studies are used to estimate atmospheric persistence from kinetic data, to outline reaction mechanisms that lead to oxidation products and to assess the atmospheric persistence and fate of the reaction products. Whenever possible, laboratory results are compared to data from field measurements carried out recently in the Amazon and other tropical regions. Common features of atmospheric oxidation mechanisms are outlined first, with focus on the reactions of biogenic hydrocarbons with ozone, with the hydroxyl radical, and with the nitrate radical. For the ozone reaction, formation of OH as a reaction product and its implications are examined; OH yields are given for isoprene, terpenes and other unsaturated compounds. Kinetic data for the ozone and OH reactions are compiled and are used to estimate the atmospheric half-lives of biogenic hydrocarbons under conditions relevant to the Amazon. The Amazon is a major source (13% of global emissions) of isoprene, whose atmospheric chemistry is examined next. Mechanisms are outlined for the O_3, OH and NO_3 reactions. Yields of the three major isoprene carbonyl products, formaldehyde, methacrolein (MTA) and methyl vinylketone (MVK) are given for the isoprene-OH and the isoprene-ozone reactions. Further oxidation of MVK and MTA by reactions with OH and with O_3 is discussed. In the presence of oxides of nitrogen, isoprene also leads to the two peroxyacyl nitrates ($RC(O)OONO_2$) PAN (R = CH_3) and MPAN (R = $CH_2 = C(CH_3)$-). Kinetic data, together with data for hydrocarbons in the atmosphere of the Amazon, are used to show that isoprene plays a major role in OH chemistry, accounting for 71% of OH removal (as compared to only 11% for CO and 5% for methane). Terpenes are discussed next, including monoterpenes (of which only four have been measured in the Amazon) and sesquiterpenes (for which no data exist). The nature and yields of the carbonyl products are compiled for both terpene-ozone and terpene-OH reactions. Reaction mechanisms are outlined. The contribution of terpenes to the global CO budget is compared to that of isoprene. PAN formation and aerosol production from terpenes are discussed. Unsaturated oxygenates (for which no data are available for the Amazon) are examined next. A compilation is given of unsaturated oxygenates that have been recently identified in biogenic emissions. Two categories, namely unsaturated alcohols and unsaturated carbonyls, are discussed in more detail. Reaction mechanisms are outlined; carbonyl products and their yields are listed for the ozone and OH reactions. Also discussed is the formation of peroxyacyl nitrates (PANs) including PPN (R = C_2H_5) from leaf alcohol and unsaturated PANs such as MPAN from unsaturated carbonyls. The last section of this study focuses on one important category of reaction products, the peroxyacyl nitrates. Their nature and formation yields are given for biogenic precursors including isoprene, terpenes and several unsaturated oxygenates. Atmospheric removal processes for PANs include thermal decomposition, whose rates are given for the relevant compounds studied to date. Other removal processes for PANs in the atmosphere include their reactions with OH and with ozone; reaction rates and mechanisms are discussed for the only compound studied, MPAN. The atmospheric persistence of MPAN is estimated for the three removal pathways of thermal decomposition, reaction with ozone and reaction with OH. Finally, this analysis of the atmospheric chemistry of isoprene, terpenes, unsaturated oxygenates and peroxyacyl nitrates serves as a basis for a brief list of suggestions to carry out additional field and laboratory work that may contribute to improving our understanding of the role, persistence and fate of biogenic hydrocarbons in the atmosphere of the Amazon.

Keywords: Amazon; biogenic hydrocarbons; isoprene; terpenes; unsaturated oxygenates; carbonyls; peroxyacyl nitrates; ozone; hydroxyl radical; reaction mechanisms; tropical atmosphere; global atmospheric chemistry.

INTRODUCTION

The Amazon ecosystem continues to receive considerable attention for its importance with regard to a number of global issues. These issues, which constituted major topics for discussion at the United Nations Conference on Environment and Development held in June 1992 in Rio de Janeiro[1-3], include the protection of the world's forests, biodiversity, and global climate change[1-6].

With regard to global climate change, the role of the tropical

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rainforest was poorly documented until the mid-1980's. While several exploratory studies have been carried out in Ivory Coast, Guyana, Panama and Brazil[7-18] (Table 1), little information was available on the concentrations and role of trace gases and particulate matter in the atmosphere of the continental tropics. This lack of information appears surprising since, by virtue or receiving a maximum of uv-visible radiation, the continental tropics, which are among the most productive ecosystems on Earth, are expected to play a large role in global atmospheric photochemistry. In addition, biomass burning contributes substantial amounts of trace gases and aerosols to the atmosphere, thereby greatly influencing global atmospheric chemistry[12,13]. Moreover, there has been massive deforestation in tropical regions in the last two decades: in Amazonia alone (which, with an area of 4.9×10^6 km^2, constitutes about 56% of Brazil's territory), about 9% of the rainforest, i.e. 3.9 million km^2, had been lost as of 1991[19]. The Amazon deforestation rate, estimated to be between 20×10^3 and 80×10^3 km^2 per year in the 1970's and 1980's[3], has recently decreased to 11×10^3 km^2 per year (as of 1991), due to environmental protection measures as well as to a decline in the Brazilian economy[19].

The perceived importance of the continental tropics, together with the rapid changes that are currently taking place in the tropics all over the world, have prompted in recent years several comprehensive field studies of the role of the rainforest in global atmospheric chemistry (Table 1). An exploratory study carried out in Brazil during the 1979 and 1980 dry seasons[12,13] suggested an important role for the continental tropics with respect to the distribution of trace gases in the global atmosphere. A few years later, a major field study involving several research groups from the United States and from Brazil was carried out in the Amazon region[16,17]. This study, the Amazon Boundary Layer Experiment (ABLE-2) consisted of two field campaigns, one carried out during the 1985 dry season[16] and the other carried out during the 1987 wet season[17] (ABLE-2A and ABLE-2B, respectively). During ABLE-2, measurements were made of many trace gases and particulate constituents, on the ground and aloft, in the Amazon Basin from Tatabinga to Belem. At about the same time, another major field study, DECAFE, was carried out in the African rainforest of Congo[18]. The findings of the DECAFE study in Congo and those of ABLE-2 in Amazonia clearly underline the powerful influence of the continental tropics on global atmospheric chemistry. The major role of Amazonia with respect to environmental chemistry, geochemistry, hydrochemistry and chemistry of natural products was the focus of the First International Symposium on the Chemistry of the Amazon, held in Manaus in November 1993.

At the time major field experiments including ABLE-2 and DECAFE were carried out in tropical forests, our understanding of the nature and atmospheric chemistry of biogenic hydrocarbons was somewhat limited. It has been known for many years that reactive organics emitted by vegetation include isoprene and monoterpenes[20-22]. Laboratory studies of the atmospheric chemistry of isoprene and terpenes, although initiated some time ago[23,24], have only recently yielded quantitative information on reaction products including carbonyls (RCHO), carboxylic acids (RCOOH) and peroxyacyl nitrates $(RC(O)OONO_2)$[25-32]. More recently, field studies have shown that, besides isoprene and terpenes, many other compounds are emitted by vegetation[33-40]. These compounds include sesquiterpenes as well as unsaturated oxygenates such as unsaturated alcohols, esters, and carbonyls[33-40]. For some of these compounds, a basic understanding of atmospheric oxidation processes has emerged from recent laboratory investigations including kinetic and product studies[41-45].

Table 1. Field studies of atmospheric trace constituents in the tropics.

Study	Location	Parameters measured	Comments
Lodge and Pate, 1966[7]	Panama	gases and aerosols	-
Lodge et al, 1974[8]	central and south America	gases and aerosols	-
Brinkmann and de Santos, 1974[9]	Brazil	hydrogen sulfide	-
Delmas et al, 1980[10]	Ivory Coast	hydrogen sulfide	-
Stallard and Edmond, 1981[11]	Brazil	precipitation chemistry	-
Greenberg et al, 1984[12]	Brazil	CO, hydrocarbons	focus on biomass burning
Crutzen et al, 1985[13]	Brazil	CO, ozone, NOx, N_2O, CH_4, hydrocarbons	focus dry season and biomass burning
Gregory et al, 1986[14]	Guyana	CO, ozone, isoprene, dimethyl sulfide, walter soluble aerosol	aircraft measurements above and within the boundary layer
Bruynseels et al, 1987[15]	Brazil	aerosol trace metals	- - -
ABLE-2A (Harris et al, 1988)[16](a)	Brazil	meteorology, NO, N_2O, O_3, CO, CH_4, isoprene, other HC, organo-sulfur cpds, aerosol size distribution, aerosol chemistry, dynamics of vertical exchange, biomass burning, organic acids, precipitation chemistry	dry season, 1985
ABLE-2B (Harris et al, 1990)[17](a)	Brazil	same as ABLE 2A, also NOy, CO_2, PAN	wet season, 1987
DECAFE (Fontan et al, 1992)[18](a)	congo	O_3, CH_4, CO, HC (C_2-C_5), sulfur cpds, organic acids, Aitken nuclei, rainwater chemistry	

(a) and accompanying articles in the same journal issue.

Accordingly, the major objective of this review is to examine atmospheric oxidation mechanisms for biogenic hydrocarbons that are relevant to known and likely biogenic emissions from the Amazon region. The biogenic hydrocarbons of interest are isoprene, monoterpenes (for which ambient air concentration data for Amazonia are available[46,47]), sesquiterpenes, and unsaturated oxygenates. For these biogenic hydrocarbons, results from recent laboratory studies (up to mid-1994) will be used to estimate atmospheric persistence from kinetic data, to outline reaction mechanisms leading to oxidation products in the atmosphere, and to examine the atmospheric persistence and fate of the reaction products. In turn, these results and the corresponding information gaps will serve as a basis to suggest additional field and laboratory measurements that may contribute to a better understanding of the role, persistence and fate of biogenic hydrocarbons in the atmosphere of the Amazon.

ATMOSPHERIC CHEMISTRY OF BIOGENIC HYDROCARBONS: COMMON FEATURES

The major hydrocarbons relevant to biogenic emissions in the Amazon, i.e. isoprene, monoterpenes, sesquiterpenes and unsaturated oxygenates, all contain at least one unsaturated carbon-carbon bond. The C=C bond reaction center is reactive towards electrophilic molecules and free radicals that are present in the atmosphere, i.e. ozone, the hydroxyl radical and the nitrate radical[48] (reactions with other atmospheric electrophiles, e.g. atomic oxygen and the HO_2 radical, are of negligible importance under most conditions). Therefore, unsaturated biogenic hydrocarbons exhibit common features with respect to their atmospheric chemistry. These common features are outlined in this section, which includes both kinetic and mechanistic considerations.

Kinetic data and atmospheric persistence of biogenic hydrocarbons

Once emitted into the atmosphere, unsaturated biogenic hydrocarbons are removed by reactions with O_3, OH and NO_3[48]. These three removal processes have distinctly different diurnal variations. Reaction with O_3 is important day and night. Reaction with OH, whose concentrations are maximum during the day and decrease to low levels at night, is a daytime removal process[48]. In contrast, removal of biogenic hydrocarbons by reaction with NO_3 is only important at night owing to the rapid photolysis of the nitrate radical in daylight[48].

Rate constants for the reactions of O_3 and OH with isoprene, monoterpenes, sesquiterpenes and unsaturated oxygenates, either measured or estimated from structure-reactivity relationships and linear free energy relationships[49, 50], are listed in Table 2. Using these reaction rate constants, estimates can be made of the atmospheric persistence of the biogenic hydrocarbons of interest. These estimates are listed in Table 2 using O_3 = 50 ppb (1.2 x 10^{12} molecule cm^{-3}) and OH = 1.0 x 10^6 molecule cm^{-3} as typical concentrations that are representative of the atmosphere in Amazonia [51, 52]. As the data in Table 2 clearly show, isoprene, terpenes, sesquiterpenes and unsaturated alcohols are rapidly removed from the atmosphere of the tropical rainforest, with lifetimes of only a few hours or even less for the more reactive compounds. It is therefore important to examine the corresponding reaction mechanisms and the nature, yields and atmospheric reactivity of the reaction products.
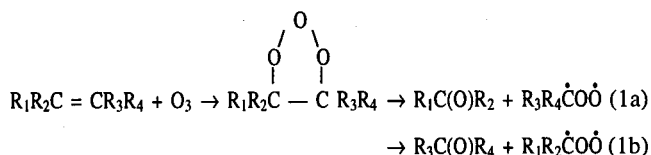
Reaction mechanism: ozone

The reaction of ozone with olefins in the gas phase involves electrophilic addition on the unsaturated carbon-carbon bond, unimolecular decomposition of the 1,2,3-trioxolane adduct, and formation of two carbonyls and two biradicals:
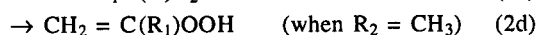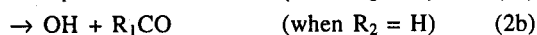
Table 2. Reaction rate constants and atmospheric persistence for biogenic hydrocarbons and their oxidation products.

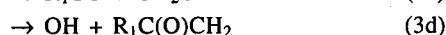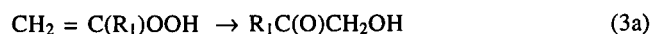|	Reaction rate constant, $cm^3 molecule^{-1} s^{-1}$(a)		Atmospheric half-life, hours	
	ozone (10^{18}x k)	hydroxyl radical (10^{11}x k)	$[O_3]$= 50 ppb	[OH]= 1.0x 10^6molecule cm^{-3}
isoprene	12.2 (b)	10.1	12.6	1.9
monoterpenes				
alpha-pinene	87 (c)	5.37	1.8	3.6
beta-pinene	15 (c)	7.89	10.2	2.4
d-limonene	210	17.0	0.7	1.1
delta-3-carene	38 (c)	8.8	4.0	2.2
sabinene	88 (c)	11.7	1.7	1.6
2-carene	240 (c)	-	0.64	-
alpha-terpinene	8,700 (c)	21	0.018	0.91
gamma-terpinene	140 (c)	17	1.1	1.1
terpinolene	1,400 (c)	-	0.11	-
alpha-phellandrene	1,900 (c)	17	0.08	1.1
beta-phellandrene	48	17.0	3.2	1.1
myrcene	490 (c)	8.9 (d)	0.31	2.1
trans-ocimene	560 (c)	-	0.27	-
camphene	0.9	5.3	170	3.6
alpha-fenchene	0.5	5.1	307	3.8
unsaturated alcohols				
allyl alcohol	14.4 (e)	2.6	10.6	7.4
3-buten-1-ol	4.9 (e)	3.1 (d)	31	6.2
1-penten-3-ol	17.9 (e)	3.2 (d)	8.6	6.0
3-buten-2-ol	16.2 (e)	3.1 (d)	9.4	6.2
2-methyl-3-buten-2-ol	10.0 (e)	2.8 (d)	15.4	6.8
cis-3-hexen-1-ol	105 (e)	6.3 (d)	1.4	3.0
2-buten-1-ol	251 (e)	5.6 (d)	0.6	3.4
cis-2-penten-1-ol	169 (e)	6.5 (d)	0.9	2.9
unsaturated esters				
vinyl acetate	2.9 (e)	2.9 (d)	53	6.0
aldehydes				
formaldehyde	slow (f)	0.98	-	19.6
acetaldehyde	slow	1.58	-	12.1
propanal	slow	1.96	-	9.8
glyoxal	slow	1.14	-	16.8
methylglyoxal	slow	1.72	-	20.9
hydroxyacetaldehyde	slow	1.0	-	19.2
acrolein	0.26 (e)	2.0	600	9.6
methacrolein	1.02 (g)	3.35	152	5.8
2-ethyl acrolein	1.07 (e)	2.3 (d)	142	8.3
ketones				
acetone	slow	0.023	-	835
2-butanone	slow	0.115	-	167
methylvinylketone	4.7 (g)	1.88	33	10.1
ethylvinylketone	6.0 (e)	3.6 (d)	26	5.5
hydroxyacetone	slow	0.3	-	64
nopinone	slow	1.5 (d)	-	12.8
4-acetyl-1-methylcyclohexene	100 (d)	10 (d)	1.5	1.9
sesquiterpenes				
alpha-cedrene	28.7 (h)	-	5.2	-
alpha-copaene	158 (h)	-	0.9	-
trans-caryophyllene	8,700 (h)	-	0.02	-
alpha-humulene	11,500 (h)	-	0.01	-

(a) from ref. 48 unless otherwise indicated; (b) from ref. 66; (c) from ref. 67; (d) estimated from structure-reactivity relationships[43,44,49,50]; (e) from ref. 43 and 44; (f) slow = negligible importance as a removal process in the atmosphere; (g) from ref. 32; (h) from ref. 82.

$$R_1R_2C = CR_3R_4 + O_3 \rightarrow R_1R_2C \overset{\overset{O}{\underset{|}{\diagdown}}\overset{O}{\underset{|}{\diagup}}}{-} C\,R_3R_4 \rightarrow R_1C(O)R_2 + R_3R_4C\dot{O}\dot{O} \quad (1a)$$

$$\rightarrow R_3C(O)R_4 + R_1R_2\dot{C}O\dot{O} \quad (1b)$$

The two biradicals formed in **1a** and **1b** may lead to carboxylic acids, carbonyls, hydroxycarbonyls, dicarbonyls and other products:

$$R_1R_2\dot{C}O\dot{O} \rightarrow R_1COOH \qquad \text{(when } R_2 = H) \qquad (2a)$$

$$\rightarrow OH + R_1CO \qquad \text{(when } R_2 = H) \qquad (2b)$$

$$\rightarrow O + R_1C(O)R_2 \qquad\qquad\qquad\quad (2c)$$

$$\rightarrow CH_2 = C(R_1)OOH \quad \text{(when } R_2 = CH_3) \quad (2d)$$

where reaction **2d** is followed by rearrangement of the unsaturated hydroperoxide:

$$CH_2 = C(R_1)OOH \rightarrow R_1C(O)CH_2OH \qquad (3a)$$

$$\rightarrow H_2 + R_1COCHO \qquad\qquad (3b)$$

$$\rightarrow R_1CO + CH_2OH \qquad\qquad (3c)$$

$$\rightarrow OH + R_1C(O)CH_2 \qquad\quad (3d)$$

Under atmospheric conditions, the hydroxymethyl radical produced in **3c** reacts rapidly with oxygen to yield formaldehyde:

$$CH_2OH + O_2 \rightarrow HCHO + HO_2 \qquad (3e)$$
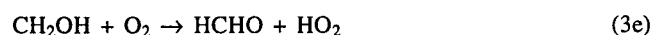
Five major features of the above reaction scheme need to be emphasized (Table 3). First, the two carbonyls formed in **1a** and **1b** always account for a large fraction, e.g. 33-88% for simple alkenes, of the total ozone-olefin reaction[53]. Second, the yields of carboxylic acids, pathway **2a**, are 13-17% for formic acid from the H_2COO biradical and are lower, 6-10%, for acetic acid from the CH_3CHOO biradical[53]. Third, unimolecular decomposition of the biradicals, pathway **3c** followed

by **3e**, accounts for a substantial fraction of their total reaction, with formaldehyde yields of 5-12% from methyl-substituted biradicals and acetaldehyde yields of 15-39% for ethyl-substituted biradicals[53]. Fourth, hydroxycarbonyl and/or dicarbonyl products, pathways **3a** and **3b**, also account for a substantial fraction of the total biradical reaction, e.g. 18-44% for simple alkenes[53]. Fifth, the hydroxyl radical is formed in the dark reaction of ozone with olefins, see pathways **2b** and **3d**. This observation, made only recently in laboratory studies of alkenes, isoprene, terpenes and unsaturated oxygenates[54,55], implies that earlier product studies of the ozone-olefin reaction may have yielded ambiguous data since the carbonyls observed were in fact products of both ozone-olefin and OH-olefin reactions. A summary of OH yields in the dark reaction of ozone with simple alkenes, isoprene and terpenes is given in Table 4. Formation of OH in the dark reaction of ozone with olefins may have important implications for the nighttime chemistry of biogenic hydrocarbons in the atmosphere of tropical rainforests including Amazonia.

Reaction mechanism: hydroxyl radical

The reaction of OH with olefins involves addition on the unsaturated carbon-carbon bond:

$$R_1R_2C = CR_3R_4 + OH \rightarrow R_1R_2\dot{C} - C(OH)R_3R_4 \qquad (4a)$$

$$\rightarrow R_1R_2C(OH)\text{-}\dot{C}\,R_3R_4 \qquad (4b)$$

The alkyl radicals formed in **4a** and **4b** react with oxygen, i.e. $R + O_2 \rightarrow RO_2$, followed by reaction of the peroxy radicals with NO:

$$RO_2 + NO \rightarrow RONO_2 \qquad (5a)$$

$$\rightarrow RO + NO_2 \qquad (5b)$$

The relative importance of **5a** vs **5b**, i.e. organic nitrate

Table 3. Yields of carbonyls and carboxylic acids from the ozone-alkene reaction with cyclohexane added to scavenge OH (a).

| alkene	primary carbonyls (b)	biradical unimolecular decomposition (c)	biradical → hydroxycarbonyl and/or dicarbonyl (d)	organic acid (e)
1-butene	propanal 0.26 formaldehyde 0.13 (total 0.39)	acetaldehyde 0.15	HAC/MEG 0.03	formic 0.16
trans-2-butene	acetaldehyde 0.71 (total 0.71)	formaldehyde 0.05	HA/glyoxal 0.18	acetic 0.10
2-methyl propene (isobutene)	formaldehyde 0.31 acetone 0.27 (total 0.58)	-	HA/MEG 0.44	formic 0.16
2-methyl-1-butene	2-butanone 0.22 formaldehyde 0.11 (total 0.33)	acetaldehyde 0.15	biacetyl 0.19	formic 0.17
2-ethyl-1-butene	formaldehyde 0.41 3-pentanone 0.18 (total 0.59)	acetaldehyde 0.39	2,3-pentadione (f)	-
2-methyl-2-butene	acetaldehyde 0.46 acetone 0.35 (total 0.81)	formaldehyde 0.07	HA/glyoxal 0.03 HAC/MEG 0.40 (total 0.43)	acetic 0.06
2,3-dimethyl-2-butene	acetone 0.88 (total 0.88)	formaldehyde 0.12	HAC/MEG 0.31	-

(a) at room temperature and 1 atm. of air; adapted from ref. 53; (b) from reactions 1a and 1b; (c) formaldehyde from methyl-substituted biradicals ($CH_3\dot{C}HO\dot{O}$) and acetaldehyde from ethyl-substituted biradicals ($CH_3CH_2\dot{C}HO\dot{O}$); (d) HA = hydroxyacetaldehyde, HAC = hydroxyacetone, MEG = methylglyoxal; (e) from reaction 2a; (f) yield not measured.

Table 4. Hydroxyl radical yield in the dark reaction of ozone with alkenes, dienes and terpenes.
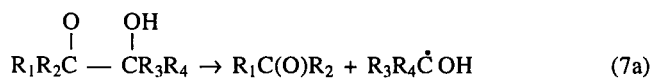
alkenes	OH yield (a)	monoterpenes	OH yield (a)
ethylene	0.12	3-carene	1.06
propene	0.33	d-limonene	0.86
1-butene	0.41	myrcene	1.15
cis-2-butene	0.41	ocimene	
trans-2-butene	0.64	(cis-and trans)	0.63
cyclohexene	0.68	alpha-pinene	0.85
2-methylpropene		terpinolene	1.03
(isobutene)	0.84	camphene	≤0.18
2-methyl-1-butene	0.83	beta-pinene	0.35
2-methyl-2-butene	0.89	sabinene	0.26
2,3-dimethyl-2		beta-phellandrene	0.14
butene	1.00		
dienes		**sesquiterpenes**	
1,3-butadiene	0.08	alpha-cedrene	0.65
isoprene	0.27	alpha-copaene	0.35
		beta-caryophyllene	0.06
		alpha-humulene	0.22

(a) at room temperature and 1 atm. of air; adapted from references 54, 55 and 82.
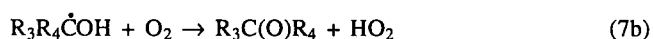
formation vs. alkoxy radical (RO) production, increases with the size of the alkyl substituent. Thus, the organic nitrate yield is essentially zero for R = CH_3 and is about 30% for C_6-C_8 radicals[56,58]. The alkoxy radicals RO formed in **5b** may undergo unimolecular decomposition or may react with oxygen:

$$RO \rightarrow carbonyl + alkyl\ radical \qquad (6a)$$

$$RO + O_2 \rightarrow carbonyl + HO_2 \qquad (6b)$$
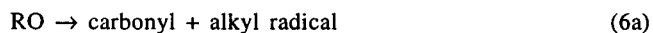
with the relative importance of **6a** and **6b** being a function of the nature and size of the alkyl substituent[59]. For the hydroxy-substituted alkoxy radicals formed in **5b** following **4a** and **4b**, unimolecular decomposition prevails over reaction with oxygen[48,59], i.e. $k_{6a} \gg k_{6b}$:

$$\overset{O}{\underset{|}{R_1R_2C}} — \overset{OH}{\underset{|}{CR_3R_4}} \rightarrow R_1C(O)R_2 + R_3R_4\dot{C}OH \qquad (7a)$$

followed by:

$$R_3R_4\dot{C}OH + O_2 \rightarrow R_3C(O)R_4 + HO_2 \qquad (7b)$$

thus leading to two carbonyl products.

Reaction mechanism: nitrate radical

The mechanism of the olefin-NO_3 reaction has received limited attention and is not completely understood at the present time[48]. The initial step involves addition of NO_3 on the unsaturated carbon-carbon bond:

$$R_1R_2C = CR_3R_4 + NO_3 \rightarrow R_1R_2C(ONO_2) — \dot{C}R_3R_4 \qquad (8a)$$

$$\rightarrow R_1R_2\dot{C} — C(ONO_2)R_3R_4 \qquad (8b)$$

Subsequent reactions of the ONO_2-substituted alkyl radicals formed in **8a** and **8b** have been assumed to involve unimolecular decomposition as a major pathway, resulting in the formation of NO_2 and of a carbonyl product[48,60-62]:

$$R_1R_2\dot{C} — C(ONO_2)R_3R_4 \rightarrow NO_2 + R_1R_2C(O)R_3R_4 \qquad (9)$$
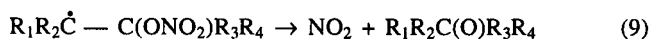
Additional laboratory studies are obviously needed to improve our understanding of the olefin-NO_3 reaction.

ATMOSPHERIC CHEMISTRY OF ISOPRENE

Importance of isoprene

Isoprene is a major component of biogenic emissions in the Amazon. Comprehensive field measurements of isoprene have been carried out as part of ABLE-2[46,47] and are summarized in Table 5. Also included in Table 5 for comparison are data for other tropical regions. Measurements made within Amazonia's forest canopy have documented strong diurnal variations in isoprene emissions, with mid-day maxima (when temperature and solar radiation are highest) and nighttime minima[46].

Table 5. Ambient concentrations of methane, carbon monoxide, isoprene and terpenes in the Amazon and in other tropical areas (units: ppb).

	methane	carbon monoxide	isoprene	terpenes (d)
Brazil, Amazon, Sept. 1980, biomass burning (a)	1830	229	2.40	0.53
Brazil, Amazon, Oct. 1984, wet season (a)	1801	167	5.45	0.35
Brazil, Amazon, July-Aug. 1985 (a, b)	1657	207	2.04	0.17
Brazil,Amazon, 1985 (b, c)	-	-	up to 3.3	-
Nigeria; 1984 (a)	1643	138	1.21	0.09
Kenya, July 1983, dry season (a)	1747	227	0.04	≤0.04
Kenya, April 1986, wet season (a)	1643	80	<0.01	≤0.04

(a) from ref. 47; (b) ABLE-2A, dry season; (c) from ref. 46; (d) alpha-pinene, beta-pinene, camphene and delta-3-carene.

These results, together with data for other ecosystems worldwide, indicate that the Amazon accounts for about 13% of the isoprene emissions into the Earth's atmosphere (Table 6). The importance of isoprene is even more clearly seen if reactivity considerations are taken into account. To illustrate this, we have compiled in Table 7, for each hydrocarbon measured in Amazonia, the product of the hydrocarbon ambient concentration and of the OH-hydrocarbon reaction rate constant. Also given in Table 7 are the resulting fractional contributions of each hydrocarbon to the total consumption of OH radicals. These calculations indicate that isoprene plays a dominant role with respect to levels of OH in the Amazon atmosphere. Unfortunately, similar calculations cannot be made for unsaturated oxygenates, sesquiterpenes or terpenes for which emissions and/or ambient concentration data are not yet available for the Amazon rainforest.

The reaction of isoprene with ozone

It is only recently that the reaction of isoprene with ozone, in which OH is formed as a product (see Table 4), has been studied under conditions that minimize "interferences" from the OH-isoprene reaction[29,32]. The major carbonyl products are formaldehyde and the two unsaturated carbonyls methacrolein (MTA) and methylvinylketone (MVK). Ozone adds on both unsaturated carbon-carbon bonds:
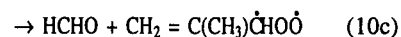
$$O_3 + CH_2 = C(CH_3)CH = CH_2 \rightarrow HCHO + CH_2 = CH\dot{C}(CH_3)O\dot{O} \qquad (10a)$$

$$\rightarrow H_2\dot{C}O\dot{O} + CH_2 = CHCOCH_3\ (MVK) \qquad (10b)$$

$$\rightarrow HCHO + CH_2 = C(CH_3)\dot{C}HO\dot{O} \qquad (10c)$$

$$\rightarrow H_2\dot{C}O\dot{O} + CH_2 = C(CH_3)CHO\ (MTA) \qquad (10d)$$

Table 6. Net isoprene production for major ecosystems of the world.

Ecosystem (a)	Area $10^6 km^2$	Leaf surface area, $10^6 km^2$	Isoprene emitters, %	Effective area, $10^6 km^2$	Rate of emission, $10^{10} g\ h^{-1}$	Duration of emission, hours x days	Total isoprene, $Tg\ yr^{-1}$
Amazon rainforest	5	40	50	20	4.41	12 x 365	60
Other tropical rainforest	12	96	50	48	4.41	12 x 365	140
Tropical seasonal forest	7.5	38	50	19	1.23	12 x 270	20
Temperate forest:							
Evergreen	5.0	60	40	24	1.55	14 x 200	40
Deciduous	7.0	35	50	18	1.17	14 x 200	30
Boreal forest	12.0	144	60	86	5.57	18 x 110	100
Woodland and shrubland	8.5	34	30	10	6.48	12 x 270	20
Savanna	15.0	60	10	6	3.89	12 x 270	10
Cultivated land	14.0	56	10	5.6	3.63	14 x 200	10
Total continental (b)	**149**	**644**		**251**		**13.5 x 220.4**	**450**

(a) adapted from ref. 46; ecosystems that contribute less than 10 Tg/year of isoprene are not listed for clarity (temperate grassland, tundra, alpine, desert and semidesert scrub, desert (rock, sand, ice), swamp, marsh, lake and stream); (b) marine production of isoprene makes a negligible contribution to isoprene's global budget, set ref. 68 and 69.

Table 7. Reactivity ranking of hydrocarbons present in Amazonia air.

Compound	A = median concentration, ppbv (a)	B = OH reaction rate constant (b)	A x B	Compound	A = median concentration, ppbv (a)	B = OH reaction rate constant (b)	A x B
methane	1657	8.36×10^{-3}	13.9	n-hexane	0.02	5.61	0.11
CO	207	0.15 (c)	31.0	benzene	0.08	1.23	0.10
ethane	0.98	0.27	0.26	1-heptene	0.01	40.0	0.40
ethylene	0.97	8.52	8.26	n-heptane	0.03	7.15	0.21
acetylene	0.30	0.83 (a)	0.25	toluene	0.74	6.0	4.4
propane	0.37	1.15	0.42	n-octane	0.02	8.68	0.17
propene	0.31	26.3	8.15	ethylbenzene	0.07	7.1	0.50
iso-butane	0.08	2.34	0.19	p-xylene	0.05	14.3	0.71
n-butane	0.09	2.54	0.23	m-xylene	-	23.6	-
1-butene	<0.01	31.4	<0.31	o-xylene	0.04	13.7	0.55
iso-pentane	0.13	3.9	0.51	n-nonane	0.02	10.2	0.20
neo-pentane	0.11	0.85	0.09	n-decane	0.02	11.6	0.23
n-pentane	0.07	3.94	0.27	alpha-pinene	0.10	53.7	5.37
isoprene	2.04	101	206.0	camphene	0.03	53	1.59
1-hexene	0.01	37.0	0.37	beta-pinene	0.03	78.9	2.37
				delta-3-carene	0.01	88.0	0.88

Contribution to removal of OH:

	ranking	A x B	percent of total OH removal
isoprene	1	206.0	71.5
CO	2	31.0	10.8
all alkenes	3	17.5	6.1
methane	4	13.9	4.8
terpenes (c)	5	10.2	3.5
all aromatics	6	6.3	2.2
all alkanes	7	2.9	1.0
total		288	99.9

(a) from ref. 47; (b) units: $10^{-12} cm^3 molecule^{-1} s^{-1}$; (c) contribution of terpenes is underestimated since only four terpenes were measured (see Table 5).

The biradical $H_2 C\overset{\bullet}{O}\overset{\bullet}{O}$ produced in **10b** and **10d** leads to CO, CO_2, OH and other products[48]. As discussed in more detail elsewhere[32], the unsaturated biradicals formed in **10a** and **10c** yield formaldehyde, MVK, MTA and other products. Overall, the measured formaldehyde, MVK and MTA yields are ≥ 0.9, 0.44 and 0.17, respectively (Table 8), and the MVK/MTA ratio is 2.44 - 2.59, with good agreement among recent studies of the isoprene-ozone reaction[29,32].

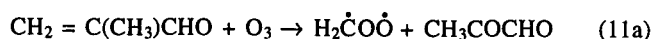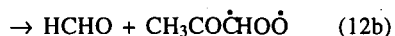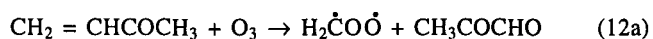In turn, the unsaturated carbonyls MVK and MTA react with ozone as is shown below for MTA:

$$CH_2 = C(CH_3)CHO + O_3 \rightarrow H_2\overset{\bullet}{C}O\overset{\bullet}{O} + CH_3COCHO \qquad (11a)$$

Table 8. Carbonyl products of the isoprene-ozone, methacrolein-ozone and methylvinyl ketone-ozone reactions.

	isoprene			methacrolein	methylvinylketone
	ref. 32	ref. 29	ref. 24	ref. 32	ref. 32
OH scavenger added	yes	yes	no	yes	yes
carbonyl products (yield in parentheses):					
formaldehyde	0.90 ± 0.04	0.80 (estimated)	0.96	0.12	0.05
methacrolein (MTA)	0.44 ± 0.02	0.39 ± 0.03	0.42	-	-
methylvinylketone (MVK)	0.17 ± 0.01	0.16 ± 0.01	0.18	-	-
methylglyoxal	0.03 ± 0.01	-	-	0.58	0.87
pyruvic acid	0.02 ± 0.01	-	-	0.0	0.05
MTA/MVK yield ratio:	2.59	2.44	2.28	-	-

$$CH_2 = C(CH_3)CHO + O_3 \rightarrow HCHO + HCO\dot{C}(CH_3)O\dot{O} \quad (11b)$$

and similarly for MVK:

$$CH_2 = CHCOCH_3 + O_3 \rightarrow H_2\dot{C}O\dot{O} + CH_3COCHO \quad (12a)$$

$$\rightarrow HCHO + CH_3CO\dot{C}HO\dot{O} \quad (12b)$$

thus leading to methylglyoxal and formaldehyde as major products (Table 8). Pyruvic acid was also observed as a product of the MVK-ozone reaction[32] and may form from the biradical produced in **12b**:

$$CH_3CO\dot{C}HO\dot{O} \rightarrow CH_3COCOOH \quad (12c)$$

Pyruvic acid, along with formic acid and acetic acid, has been measured in rainwater samples collected in the Amazon[63]. These organic acids have been shown to play a role in the acidity of precipitation in the tropical rainforest[63-65].

The reaction of isoprene with OH

The hydroxyl radical reacts with isoprene by addition on the two unsaturated carbon-carbon bonds:

$$CH_2 = C(CH_3)CH = CH_2 + OH \rightarrow CH_2OH\text{-}\dot{C}(CH_3)CH = CH_2 \quad (13a)$$

$$\rightarrow \dot{C}H_2\underset{|}{C}(CH_3)CH = CH_2 \quad (13b)$$
$$OH$$

$$\rightarrow CH_2 = C(CH_3)CHOH\dot{C}H_2 \quad (13c)$$

$$\rightarrow CH_2 = C(CH_3)\dot{C}HCH_2OH \quad (13d)$$
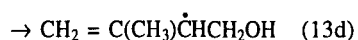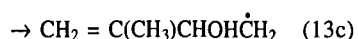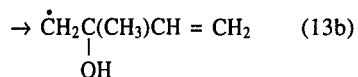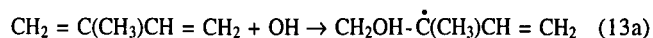
The four alkyl radicals formed in **13** undergo the $R + O_2 \rightarrow RO_2$, $RO_2 + NO \rightarrow NO_2 + RO$ reaction sequence followed by unimolecular decomposition of the alkoxy radicals, (see reactions **4-7** in preceding section), thus leading to formaldehyde, methacrolein, methylvinylketone and other products. This is shown below for the alkoxy radicals formed after **13a** and **13d**:
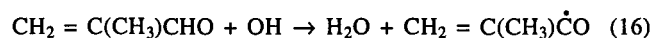
$$CH_2OHC(\dot{O})(CH_3)CH = CH_2 \rightarrow \dot{C}H_2OH +$$
$$CH_2 = CHCOCH_3 \text{ (MVK)} \quad (14a)$$

$$CH_2 = C(CH_3)CH(\dot{O})CH_2OH \rightarrow \dot{C}H_2OH +$$
$$CH_2 = C(CH_3)CHO \text{ (MTA)} \quad (14d)$$
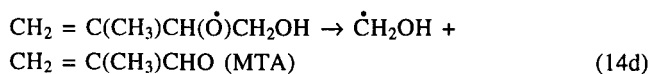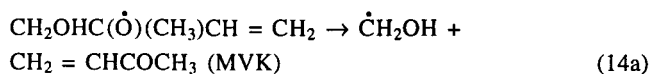
followed in both cases by $\dot{C}H_2OH + O_2 \rightarrow HCHO + HO_2$.
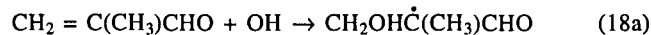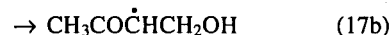
Consistent with reactions **13** and **14** above, Tuazon and Atkinson[28] and Grosjean et al[32] have identified formaldehyde, MVK and MTA as the major products of the OH-isoprene reaction (Table 9). The MVK/MTA yield ratio for the OH-

isoprene reaction is $1.4^{28,32}$. This compares to a MVK/MTA yield ratio of 0.4 for the ozone-isoprene reaction.

In turn, formaldehyde, MVK and MTA react with OH. The two aldehydes, formaldehyde and MTA, react with OH by H-atom abstraction from the carbonyl carbon[28,32,48,71,72]:
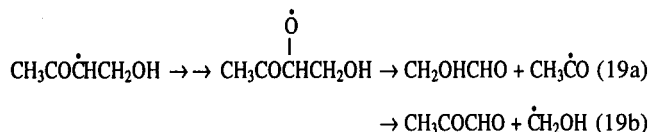
$$HCHO + OH \rightarrow H_2O + H\dot{C}O \quad (15a)$$

$$H\dot{C}O + O_2 \rightarrow HO_2 + CO \quad (15b)$$

$$CH_2 = C(CH_3)CHO + OH \rightarrow H_2O + CH_2 = C(CH_3)\dot{C}O \quad (16)$$

The two unsaturated carbonyls MVK and MTA react with OH by addition on the C = C bond:

$$CH_3COCH = CH_2 + OH \rightarrow CH_3COCHOH\dot{C}H_2 \quad (17a)$$

$$\rightarrow CH_3CO\dot{C}HCH_2OH \quad (17b)$$

$$CH_2 = C(CH_3)CHO + OH \rightarrow CH_2OH\dot{C}(CH_3)CHO \quad (18a)$$

$$\rightarrow \dot{C}H_2C(OH)(CH_3)CHO \quad (18b)$$

Table 9. Products of the OH-isoprene, OH-MTA and OH-MVK reactions.

	product	yield	
		ref. 28	ref. 32
isoprene	formaldehyde	0.50	0.50
	methylvinylketone (MVK)	0.29 ±0.07	0.31
	methacrolein (MTA)	0.21 ±0.05	0.22
	other carbonyls	0.25 (a)	0.22 (b)
	3-methyl furan	0.04 ±0.01	
	alkyl nitrates	0.12 (a)	
		ref. 72	ref. 32
MVK	hydroxyacetaldehyde	0.72	0.60
	methylglyoxal	0.28	0.32
	formaldehyde	0.28	0.28
		ref. 71	ref. 32
MTA	CH = C(CH₃)CHO (c)	0.50	-
	hydroxyacetone	0.41	0.30
	methylglyoxal	0.09	0.07
	formaldehyde	0.09	0.07

(a) estimated; (b) sum of methylglyoxal (yield = 0.06), hydroxyacetaldehyde (0.08) and hydroxyacetone (0.08); (c) abstraction pathway, leads to the unsaturated peroxyacyl nitrate MPAN, see text.

The reaction of formaldehyde with OH leads to CO (pathway **15b**). The importance of isoprene to the global budget of CO will be compared to that of terpenes in the next section. The reaction of MVK with OH leads to hydroxyacetaldehyde, methylglyoxal and formaldehyde[32,72,] e.g. **17b** followed by (alkyl → peroxy → alkoxy radical sequence simplified for clarity):

$$CH_3CO\overset{\bullet}{C}HCH_2OH \to \to CH_3COCHCH_2OH \to CH_2OHCHO + CH_3\overset{\bullet}{C}O \quad (19a)$$

$$\to CH_3COCHO + \overset{\bullet}{C}H_2OH \quad (19b)$$

The reaction of MTA with OH involves both abstraction (pathway **16**) and addition (pathway **18**). These two pathways are roughly of equal importance under atmospheric conditions[32,71]. The addition pathway leads to hydroxyacetone, e.g. **18a** followed by:

$$CH_2OH\overset{\bullet}{C}(CH_3)CHO \to \to CH_2OHC(CH_3)CHO \to$$

$$CH_2OHCOCH_3 + HCO \quad (20)$$
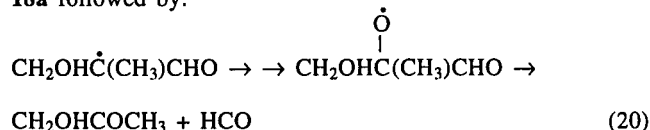
The abstraction pathway **16** leads to the $CH_2 = C(CH_3)CO_3$ radical:

$$CH_2 = C(CH_3)CO + O_2 \to CH_2 = C(CH_3)CO_3 \quad (21)$$
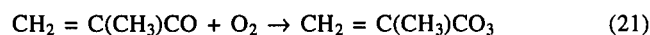
When NO_2 is present in the atmosphere, as is often the case, the abstraction pathway of the OH-MTA reaction leads to an unsaturated peroxyacyl nitrate:

$$CH_2 = C(CH_3)CO_3 + NO_2 \rightleftharpoons CH_2 = C(CH_3)\underset{\underset{O}{\|}}{C}OONO_2 \text{ (MPAN)} \quad (22)$$
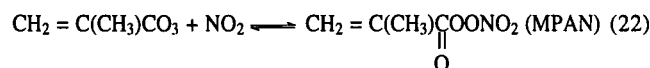
In the same way, the acetyl radical produced in the MVK-OH reaction, e.g. pathway **19a**, leads to peroxyacetyl nitrate:

$$CH_3CO + O_2 \to CH_3CO_3 \quad (23)$$

$$CH_3CO_3 + NO_2 \rightleftharpoons CH_3\underset{\underset{O}{\|}}{C}OONO_2 \text{ (PAN)} \quad (24)$$
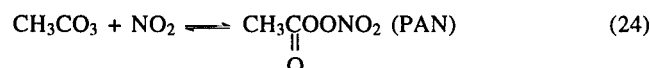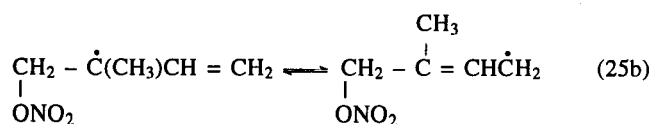
Since MVK and MTA are products of the isoprene-OH and isoprene-O_3 reactions, both PAN and MPAN are expected to form by photooxidation of isoprene in the presence of oxides of nitrogen, i.e. under atmospheric conditions. This is indeed the case, see Figure 1. The atmospheric importance and fate of PAN and MPAN will be discussed in a subsequent section.

The reaction of isoprene with NO_3

There have been only a few laboratory studies of the isoprene-NO_3 reaction, and our knowledge of the reaction products and of the corresponding mechanisms is limited[60-62]. The initial step involves addition on the C=C bonds, preferentially at the 1-carbon[61]:

$$CH_2 = C(CH_3)CH = CH_2 + NO_3 \to \underset{\underset{ONO_2}{|}}{\overset{\bullet}{C}H_2} - \overset{\bullet}{C}(CH_3)CH = CH_2 \quad (25a)$$
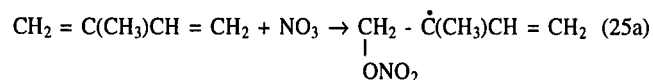
the unsaturated (allylic) alkyl radical formed in **25a** may isomerize:

$$\underset{\underset{ONO_2}{|}}{\overset{\bullet}{C}H_2} - \overset{\bullet}{C}(CH_3)CH = CH_2 \rightleftharpoons \underset{\underset{ONO_2}{|}}{CH_2} - \overset{\overset{CH_3}{|}}{C} = CH\overset{\bullet}{C}H_2 \quad (25b)$$

followed by the usual $R + O_2 \to RO_2$, $RO_2 + NO \to NO_2 +$
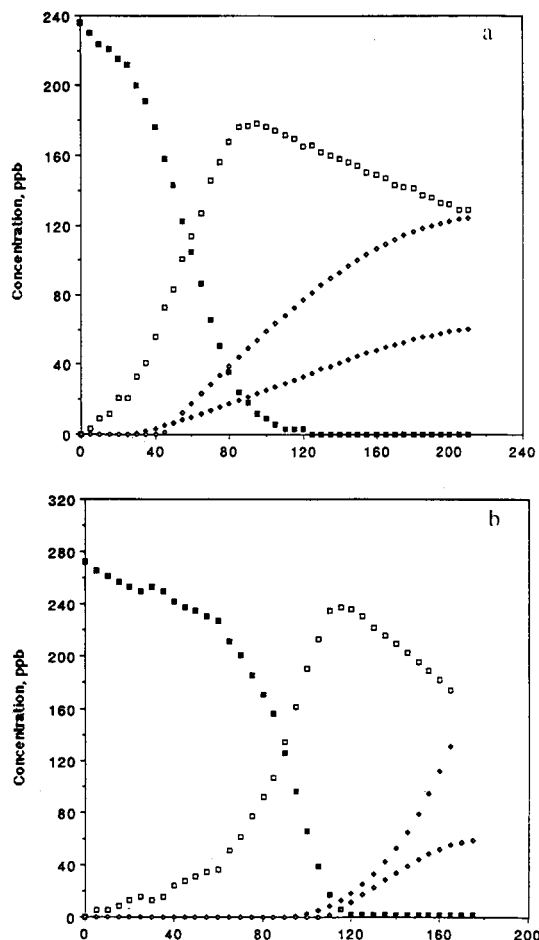

Figure 1. Concentration (ppb) vs time (min.) for NO (dark squares), NO_2 (open squares), PAN (dark diamonds) and MPAN (open diamonds) in sunlight irradiations of methacrolein-NO (Figure 1a) and isoprene-NO (Figure 1b) in pure air. Concentrations of PAN and MPAN multiplied by 3 (1a) and by 5 (1b) for clarity. Adapted from reference 32.

RO reaction sequence and by reaction of the alkoxy radical with oxygen:

$$CH_2(ONO_2)C(CH_3) = CHCH_2\overset{\bullet}{O} + O_2 \to HO_2 +$$

$$CH_2(ONO_2)C(CH_3) = CHCHO \quad (26)$$
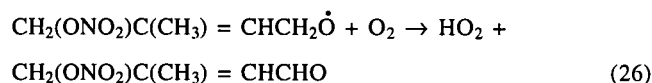
Indeed, the unsaturated carbonyl nitrate produced in **26** (3-methyl-4-nitroxy-2-butenal) has been identified as a major product of the isoprene-NO_3 reaction[61]. Other unsaturated carbonyl nitrates and/or hydroxyl nitrates have been tentatively identified[61]. In addition, epoxide formation, while perhaps important at low pressure, was shown to be negligible for isoprene at atmospheric pressure[61]. More information on the products of the isoprene-NO_3 reaction is obviously needed.

ATMOSPHERIC CHEMISTRY OF TERPENES

Importance of terpenes

Terpenes are major components of biogenic emissions and play an important role in global atmospheric chemistry. Like isoprene, they react rapidly with ozone, the hydroxyl radical and the nitrate radical (see kinetic data and atmospheric lifetimes in Table 2). These reactions lead to carbonyls, carbon monoxide and peroxyacetyl nitrate, among others. Terpenes are major contributors, along with methane and isoprene, to the global atmospheric CO budget[25,73] (Table 10). Space shuttle

measurements have shown that CO concentrations are highest over the Amazon and central African rainforests[74]. Unlike isoprene, terpenes contribute substantially to aerosol formation since their oxidation leads to low volatility, high molecular weight oxygenated products[75-80]. In turn, aerosols formed from terpenes emitted by biogenic sources may have an impact on the atmosphere's radiative budget and therefore on global climate.

Table 10. Contribution of terpenes and isoprene to the global CO budget (a).

	contribution to global CO	
	Tg CO/year	percent of total
oxidation of methane (b)	607	25
oxidation of fossil fuels	443	18
terpenes oxidation:		
ozone reaction	172	7
OH reaction	50	2
isoprene oxidation (c)	360	15

(a) adapted from ref. 25; (b) by reaction with OH, leading to formaldehyde whose oxidation leads to CO; (c) by reactions with ozone and with OH.

Terpenes emitted by vegetation include monoterpenes (C_{10}) and sesquiterpenes (C_{15}). These two sub-groups will be discussed together in this section, largely because information on sesquiterpenes is at the present time limited to a few field measurements[81] and laboratory studies[31,45]. There are no data for emissions or ambient concentrations of sesquiterpenes in the Amazon forest. Even for monoterpenes, only four compounds have been measured in the atmosphere of the Amazon (see Table 5) and this as part of only one field study carried out during the 1985 dry season[47].

Mechanisms for the O_3-terpene and OH-terpene reactions are similar to those described earlier for isoprene and are briefly outlined below. While the oxidation products of isoprene are now well characterized, those of terpenes have received less attention. For the terpene-ozone and terpene-hydroxyl radical reactions, a few reaction products have been recently identified. For the terpene-NO_3 reaction, kinetic data are available[48] but very little is known about reaction products[60]. Thus, only a brief speculative discussion of the NO_3-terpene reaction mechanism is given below.

Reaction of terpenes with ozone

The reaction of terpenes with ozone involves addition on the C=C bonds followed by reactions **1-3**. Thus, terpenes that are 1-alkenes (e.g. β-pinene, camphene, sabinene) yield formaldehyde and a C_9 ketone, as is shown in Figure 2a for β-pinene. In the same way, terpenes that contain an internal C=C bond yield C_{10} dicarbonyl products, as is shown in Figure 2b for α-pinene. Terpenes that contain several C=C bonds, e.g. d-limonene[31], yield both monofunctional and difunctional carbonyls. A summary of the carbonyl products of the ozone-terpene reaction and of the corresponding yields is given in Table 11 for the ten compounds (nine monoterpenes and one sesquiterpene) that have been studied to date[27,31,82].

Reaction of terpenes with OH

The reaction of OH with terpenes involves addition on the C=C bonds, reactions **4-7**, leading to carbonyls and other products. This is illustrated in Figure 3 for the only sesquiterpene studied, trans-caryophyllene[30]. Carbonyl products of the OH-terpene reaction and their yields[26,27,30,82] are listed in Table 11
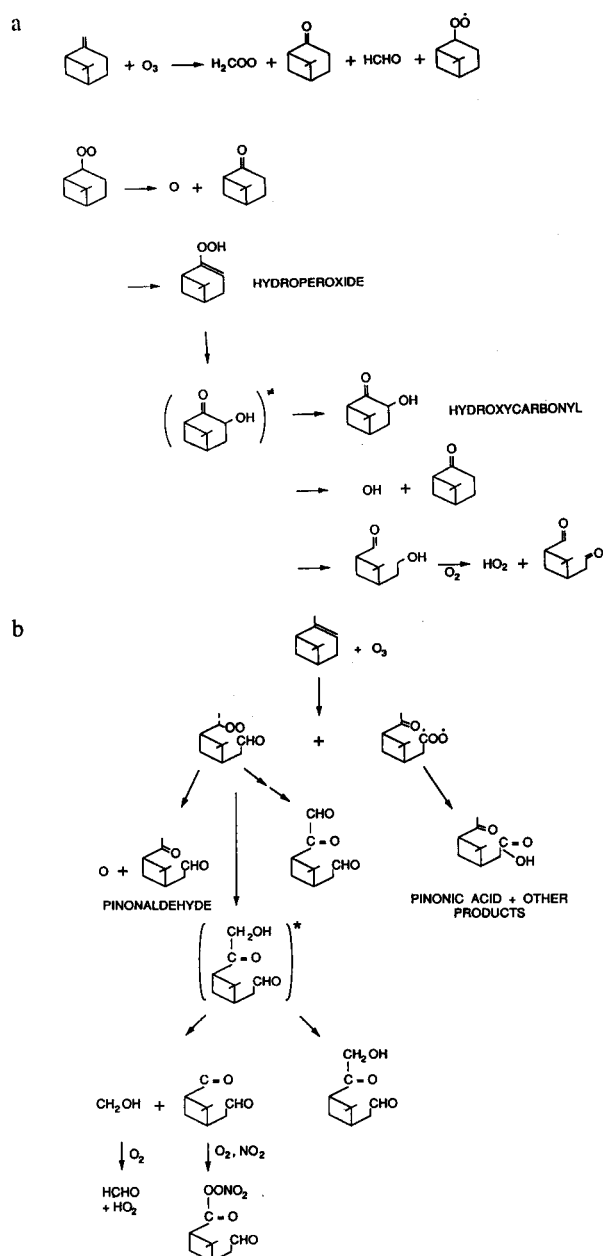

Figure 2. Ozone-terpene reaction mechanism: β-pinene (Figure 2a) and α-pinene (Figure 2b). From references 30 and 31.

together with those of the terpene-ozone reaction. Terpenes that contain two or more C=C bonds lead to unsaturated carbonyls, e.g. 4-acetyl-1-methyl-cyclohexene from d-limonene. In turn, these unsaturated carbonyls may react with OH according to reactions **4-7**. Thus, 4-acetyl-1-methyl-cyclohexene reacts with OH to yield carbonyls and, in the presence of oxides of nitrogen, peroxyacetyl nitrate[30].

Reaction of terpenes with NO_3

In the absence of data, it is assumed that the reaction of NO_3 with terpenes involves, as for simple alkenes[48], addition on the C=C bonds. A speculative reaction sequence is illustrated in Figure 4a for β-pinene and in Figure 4b for d-limonene. For both terpenes, the ONO_2-substituted alkyl radicals are assumed to undergo the R → RO_2 → RO reaction sequence followed by unimolecular decomposition of the alkoxy radicals. The reaction sequence predicts the formation

Table 11. Gas phase carbonyl products of the terpene-ozone and terpene-hydroxyl radical reactions.

Terpene	Carbonyl product	Yield (a)	
		OH reaction	ozone reaction (b)
Camphene	camphelinone	< 0.02	0.36
	ketone, MW = 154		0.2
delta-3-carene	dicarbonyl, MW = 168	0.34	≤ 0.08
d-limonene	4-acetyl-1-methylcyclohexene	0.20, + (c)	≤ 0.04, 0.02 (c)
	dicarbonyl, MW = 168	0.29, + (c)	+ (c) (d)
	formaldehyde	+ (c)	0.10 (c)
beta-phellandrene	4-isopropyl-2-cyclohexen-1-one	0.29	0.29
alpha-pinene	pinonaldehyde	0.28	0.19
	dicarbonyl, MW = 168	+ (c)	+ (c)
	formaldehyde	+ (c)	+ (c)
beta-pinene	nopinone	0.27	0.23, 0.22 (c)
	formaldehyde	+ (c)	0.42 (c)
sabinene	ketone, MW = 138	0.17	0.50
terpinolene	4-methyl-3-cyclohexen-1-one	0.26	0.40
	unsaturated dicarbonyl, MW = 168	0.08	≤ 0.02
trans-caryophyllene	formaldehyde	+ (c)	0.08 (c)
	C14 ketone, MW = 206	+ (c)	+ (c)

(a) from ref. 82 unless otherwise indicated; (b) with cyclohexane added to scavenge OH; (c) ref. 30 and 31; (d) +: identified, yield not measured.
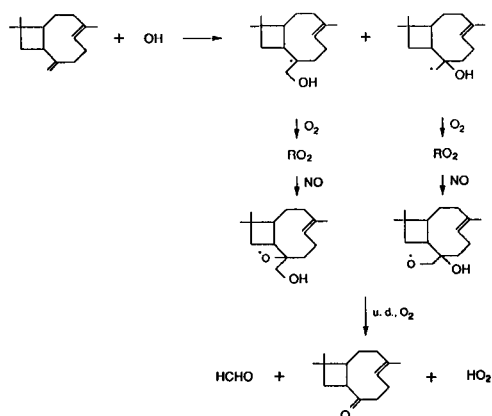
Figure 3. Hydroxyl radical-sesquiterpene reaction mechanism: OH reaction with trans-caryophyllene. RO_2 = peroxy radical (not drawn for clarity); u.d. = unimolecular decomposition. From reference 31.

of carbonyls and carbonyl nitrates as major products. Experimental confirmation of reaction products and measurements of their yields are needed for the terpene-NO_3 reaction.

ATMOSPHERIC CHEMISTRY OF UNSATURATED OXYGENATES

Importance of unsaturated oxygenates

Biogenic emissions include, besides isoprene and terpenes, a wide variety of oxygenated compounds such as alcohols, aldehydes, ketones, esters and ethers (Table 13). Several of these compounds have been long known to be associated with plant metabolism. For example, the unsaturated alcohol cis-3-hexen-1-ol, $CH_3CH_2CH = CHCH_2CH_2OH$, has long been known by flavor and flagrance chemists as "leaf alcohol"[41,42]. Of the many oxygenated compounds that have been identified in biogenic emissions[33-40], the unsaturated ones, by virtue of their higher reactivity towards ozone, the hydroxyl radical and the nitrate radical (see kinetic data in Table 2), are likely to be of

Table 12. Aerosol formation in atmospheric oxidation of terpenes.

	aerosol formed, percent of initial terpene concentration, carbon basis	aerosol nitrogen/ carbon ratio
alpha-pinene-NO (b)	1.3	0.10
beta-pinene-NO (b)	0.90	0.17
d-limonene-O_3 (c)	1.8	0
trans-caryophyllene-NO (b)	2.2	<0.10
trans-caryophyllene-O_3 (c)	1.7	0

(a) adapted from ref. 80; (b) sunlight irradiation of terpene-NO mixture; (c) reaction of terpene with ozone in the dark.

greater importance with respect to atmospheric chemistry.

While unsaturated oxygenates have been identified in biogenic emissions from a variety of plant species, there are to our knowledge no reports of unsaturated oxygenate emissions or ambient concentrations from the Amazon rainforest. Thus, until this much-needed information becomes available, the reaction mechanisms reviewed below can only serve as a guide to assess the role of unsaturated oxygenates in the atmospheric chemistry of the Amazon region.

Atmospheric chemistry of unsaturated alcohols

The atmospheric chemistry of unsaturated alcohols involves the addition of O_3, OH or NO_3 on the C = C bond. Reaction rate constants have been measured for the ozone reaction[42,43] (see Table 2). The results indicate that the reactivity of unsaturated alcohols towards ozone is about the same as that of their alkene homologues[42,43]. For the hydroxyl radical reaction, rate constants have been estimated from structure-reactivity relationships[42,43,49,50] (see Table 2) and have been measured only for the simplest unsaturated alcohol, i.e. allyl alcohol[48]. No kinetic data or reaction product studies are available for the unsaturated alcohol-NO_3 reaction.

For the ozone-unsaturated alcohol reaction, carbonyl products have been identified and their yields measured (Table

a

$CH_3CH_2CH = CHCH_2CH_2OH + O_3 \rightarrow$
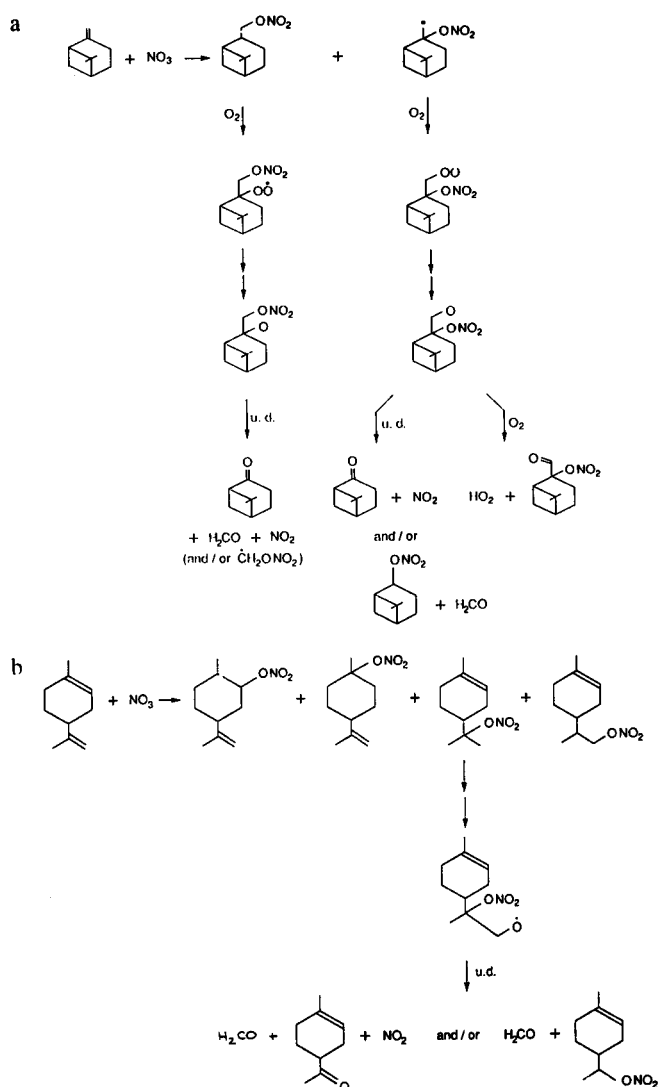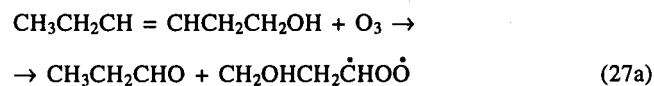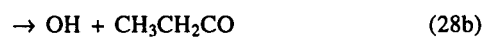
+ H₂CO + NO₂
(nnd / or CH₂ONO₂)

and / or

Figure 4. Nitrate radical-terpene reaction mechanism: NO₃ reaction with β-pinene (Figure 4a) and with d-limonene (Figure 4b). Adapted from Grosjean, et al., unpublished results, DGA, Inc., Ventura, CA, 1993.

b

$14)^{42,86}$. Using leaf alcohol (cis-3-hexen-1-ol) as an example, the reaction mechanism can be outlined as follows[42,86]:

$$CH_3CH_2CH = CHCH_2CH_2OH + O_3 \rightarrow$$

$$\rightarrow CH_3CH_2CHO + CH_2OHCH_2\dot{C}HO\dot{O} \qquad (27a)$$

$$\rightarrow CH_2OHCH_2CHO + CH_3CH_2\dot{C}HO\dot{O} \qquad (27b)$$

Propanal (pathway 27a) has been identified as a major reaction product[42] but hydroxypropanal (pathway 27b) has yet to be positively identified. The ethyl-substituted biradical $CH_3CH_2\dot{C}HO\dot{O}$ formed in 27b evolves as follows:

$$CH_3CH_2\dot{C}HO\dot{O} \rightarrow CH_3CH_2COOH \qquad (28a)$$

$$\rightarrow OH + CH_3CH_2CO \qquad (28b)$$

$$\rightarrow CH_3CH = C(H)OOH \qquad (28c)$$

The carboxylic acid propionic acid is expected to form in 28a. The hydroperoxide formed in 28c leads to carbonyl products:

$$CH_3CH = C(H)OOH \rightarrow (CH_3CHOHCHO)^* \rightarrow CH_3CHOHCHO \qquad (29a)$$

Table 13. Oxygenated compounds of biogenic origin.

Functionality	Saturated	Unsaturated
alcohols	methanol (a, b) ethanol (a)	2-methyl-3-buten-2-ol (c) 3-hexen-1-ol (a, d, e)
aldehydes	propanal (a) i-butanal (a) n-butanal (a) n-hexanal (a, d) n-C₄ to n-C₁₀ (f) n-C₄ to n-C₁₁ (g)	crotonaldehyde (a) isobutenal (a) 2-hexenal (d, h) hydroxy mono-unsaturated C₆ (h) di-unsaturated C₆ (h)
ketones	acetone (a) 2-butanone (a) 2-pentanone (a) 3-pentanone (a) methyl-i-propylketone(a) 2-heptanone (d) 3-octanone (a)	methylvinyl ketone (a) 1-octen-3-one (a) diethylcyclopentenone (a) verbenone (d) pinocarvone (d) 2-methyl-6-methylene- 1,7-octadien-3-one (d) 6-methyl-5-hepten-2-one (f)
ethers	diethyl ether (a) 1,8-cineole (d)	estragole (d)
esters	ethyl acetate (a) butyl acetate (d) methyl butyrate (a) methyl caprylate (a) bornyl acetate (d)	3-hexenyl acetate (a, d)
furans		furan (a) 2-methylfuran (a) 3-methylfuran (a) vinyl furan (a) hexenyl furan (a)

(a) ref. 33; (b) ref. 85; (c) ref. 39; (d) references 34 and 35; (e) ref. 36; (f) ref. 40; (g) ref. 83; (h) ref. 84.

Table 14. Carbonyl products of the ozone-unsaturated alcohol reaction.

unsaturated alcohol	carbonyl product (a)	yield (a)
monosubstituted		
allyl alcohol $CH_2 = CHCH_2OH$	formaldehyde hydroxyacetaldehyde	0.50 0.30
2-methyl-3-buten-2-ol $(CH_3)_2C(OH)CH = CH_2$	formaldehyde 2-hydroxypropanal acetaldehyde glyoxal	0.44 0.30 0.19 0.03
disubstituted		
2-buten-1,4-diol $CH_2OHCH = CHCH_2OH$	hydroxyacetaldehyde formaldehyde	0.29 0.18
cis-3-hexen-1-ol $CH_3CH_2CH = CHCH_2CH_2OH$	propanal methylglyoxal acetaldehyde	0.59 0.17 0.13

(a) with cyclohexane added to scavenge OH, adapted from references 42 and 86.

$$\rightarrow CH_3COCHO + H_2 \qquad (29b)$$

$$\rightarrow HCO + CH_3\dot{C}HOH \qquad (29c)$$

$$\rightarrow OH + CH_3\dot{C}HCHO \qquad (29d)$$
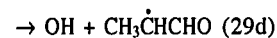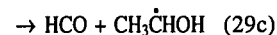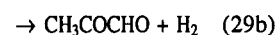
followed by $CH_3\dot{C}HOH + O_2 \rightarrow HO_2 + CH_3CHO$. The measured acetaldehyde yield indicates that unimolecular decomposition, pathway 29c, accounts for 13 ± 2% of the overall reaction

of the $CH_3CH_2\overset{\bullet}{C}HO\overset{\bullet}{O}$ biradical. The $CH_3\overset{\bullet}{C}HCHO$ radical formed in **29d** leads to methylglyoxal and other products.
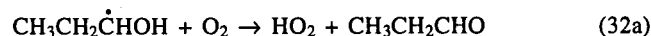
The reaction of OH with unsaturated alcohols has been studied for only three compounds, of which one, leaf alcohol, is a major component of biogenic emissions. The OH-unsaturated alcohol reaction is initiated by OH addition on the C = C bond, see reactions **4-7**. Thus, using leaf alcohol as an example:
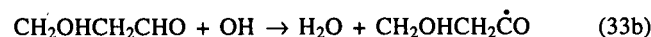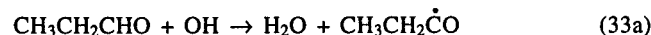
$$CH_3CH_2CH = CHCH_2CH_2OH + OH \rightarrow CH_3CH_2CHOH\overset{\bullet}{C}HCH_2CH_2OH \quad (30a)$$

$$\rightarrow CH_3CH_2\overset{\bullet}{C}HCHOHCH_2CH_2OH \quad (30b)$$
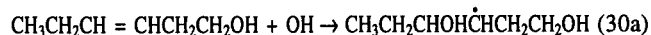
The corresponding β-hydroxyalkoxy radicals undergo unimolecular decomposition:

$$\overset{\overset{\overset{\bullet}{O}}{|}}{CH_3CH_2CHOHCHCH_2CH_2OH} \rightarrow CH_3CH_2\overset{\bullet}{C}HOH + CH_2OHCH_2CHO \quad (31a)$$

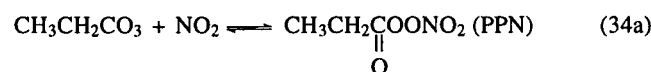$$\overset{\overset{\overset{\bullet}{O}}{|}}{CH_3CH_2CHCHOHCH_2CH_2OH} \rightarrow CH_3CH_2CHO + \overset{\bullet}{C}HOHCH_2CH_2OH \quad (31b)$$
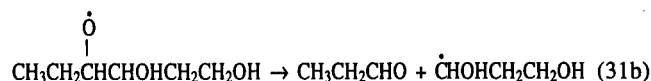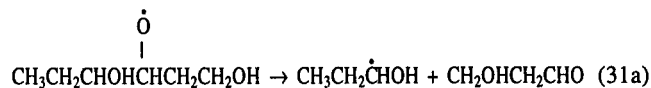
and the α-hydroxy alkyl radicals formed in **31** react with oxygen by H-atom abstraction:

$$CH_3CH_2\overset{\bullet}{C}HOH + O_2 \rightarrow HO_2 + CH_3CH_2CHO \quad (32a)$$

$$\overset{\bullet}{C}HOHCH_2CH_2OH + O_2 \rightarrow HO_2 + CH_2OHCH_2CHO \quad (32b)$$

The major products of the reaction are therefore propanal (pathways **31b** and **32a**) and hydroxypropanal (pathways **31a** and **32b**). In turn, these aldehydes react rapidly with OH:

$$CH_3CH_2CHO + OH \rightarrow H_2O + CH_3CH_2\overset{\bullet}{C}O \quad (33a)$$

$$CH_2OHCH_2CHO + OH \rightarrow H_2O + CH_2OHCH_2\overset{\bullet}{C}O \quad (33b)$$

The RCO radicals formed in **33** react rapidly with oxygen to form RCO_3 radicals. In the presence of oxides of nitrogen, the RCO_3 radicals will lead to peroxyacylnitrates, namely peroxypropionyl nitrate (PPN) and peroxyhydroxypropionyl nitrate ("hydroxy-PPN"):

$$CH_3CH_2CO_3 + NO_2 \rightleftharpoons CH_3CH_2\overset{\overset{O}{\|}}{C}OONO_2 \text{ (PPN)} \quad (34a)$$

$$CH_2OHCH_2CO_3 + NO_2 \rightleftharpoons CH_2OHCH_2\overset{\overset{O}{\|}}{C}OONO_2 \\ \text{("hydroxy-PPN")} \quad (34b)$$
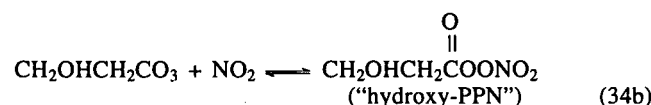
Indeed, sunlight irradiation of leaf alcohol with NO in air results in the formation of ozone, propanal and PPN as major products[41], consistent with reactions **30-34** above (Figure 5). The formation of hydroxy-substituted peroxyacyl nitrates, e.g. $CH_2OHCH_2C(O)OONO_2$ which is predicted to form in the reaction sequence **30-34**, still awaits experimental confirmation[41,42].

Atmospheric chemistry of unsaturated carbonyls

The atmospheric chemistry of unsaturated aldehydes and unsaturated ketones has received limited attention. Two compounds, methylvinylketone (MVK, $CH_2 = CHCOCH_3$) and methacrolein (MTA, $CH_2 = C(CH_3)CHO$), have been studied in some detail[71,72] because of their importance as major oxidation products of isoprene, see section on isoprene and references therein. Two other unsaturated carbonyls have been studied, the simplest unsaturated aldehyde acrolein ($CH_2 = CHCHO$) and its higher molecular weight homologue 2-ethylacrolein ($CH_2 = C(C_2H_5)CHO$)[87,88]. Rate constants have been
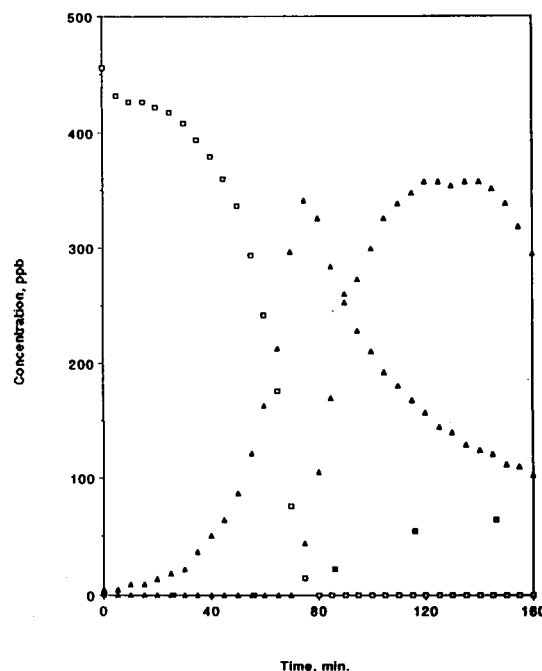
measured for the unsaturated carbonyl-ozone and unsaturated carbonyl-OH reactions, see Table 2.

The reaction of unsaturated carbonyls with ozone involves addition at the C = C bond as described earlier for MVK and MTA. Thus, the reaction of ozone with acrolein (with cyclohexane added to scavenge OH) yields glyoxal, formaldehyde and glyoxylic acid[87]. In the same way, the reaction of ozone with 2-ethylacrolein yields formaldehyde, acetaldehyde and the dicarbonyl ethylglyoxal, CH_3CH_2COCHO[88].

As seen earlier for MTA, the reaction of unsaturated aldehydes with OH involves both addition and abstraction[28,32,48]. The addition pathway leads to carbonyls, e.g. for acrolein[87]:
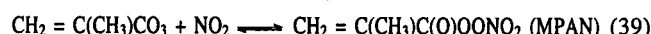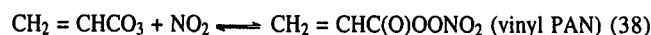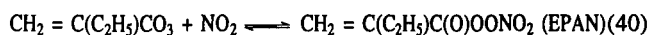
$$CH_2 = CHCHO + OH \rightarrow CH_2OH\overset{\bullet}{C}HCHO \quad (35)$$

$$CH_2OH\overset{\bullet}{C}HCHO \rightarrow\rightarrow \overset{\overset{\overset{\bullet}{O}}{|}}{CH_2OHCHCHO} \rightarrow CHOCHO + \overset{\bullet}{C}H_2OH \quad (36a)$$

$$\rightarrow CH_2OHCHO + HCO \quad (36b)$$
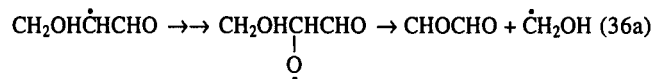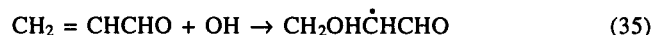
leading to glyoxal (**36a**), formaldehyde (**36a** followed by $\overset{\bullet}{C}H_2OH + O_2 \rightarrow HCHO + HO_2$) and hydroxyacetaldehyde (**36b**). Similarly, the OH addition pathway for 2-ethylacrolein yields formaldehyde, acetaldehyde and ethylglyoxal[88].

The OH abstraction pathway leads to unsaturated peroxyacyl nitrates, i.e. "vinyl-PAN" from acrolein[87], MPAN from methacrolein[32] as discussed above in the section on isoprene, and "EPAN" from 2-ethylacrolein[88]:

$$RCHO + OH \rightarrow H_2O + RCO \quad (37a)$$

$$RCO + O_2 \rightarrow RCO_3 \quad (37b)$$

with R = CH_2=CH - (acrolein), $CH_2 = C(CH_3)$ - (MTA) and $CH_2 = C(C_2H_5)$ - (2-ethyl acrolein) followed by:

$$CH_2 = CHCO_3 + NO_2 \rightleftharpoons CH_2 = CHC(O)OONO_2 \text{ (vinyl PAN)} \quad (38)$$

$$CH_2 = C(CH_3)CO_3 + NO_2 \rightleftharpoons CH_2 = C(CH_3)C(O)OONO_2 \text{ (MPAN)} \quad (39)$$

$$CH_2 = C(C_2H_5)CO_3 + NO_2 \rightleftharpoons CH_2 = C(C_2H_5)C(O)OONO_2 \ (EPAN)(40)$$

These unsaturated peroxyacyl nitrates have been identified and characterized only recently. Their atmospheric chemistry is outlined in the next section along with that of other peroxyacyl ntirates.

ATMOSPHERIC CHEMISTRY OF PEROXYACYL NITRATES

Importance of peroxyacyl nitrates

Peroxyacyl nitrates, $RC(O)OONO_2$, are of major importance in atmospheric chemistry[89]. Formed *in situ* by photochemical reactions involving hydrocarbons and oxides of nitrogen, they serve as reservoirs for the transport of reactive nitrogen on regional and global scales[90]. Peroxyacyl nitrates are phytotoxic[91]; their adverse effects on natural vegetation and agricultural crops have been studied in some detail[89,91]. They are also mutagenic[92] and eye irritants[89]. Their thermal decomposition (see below) leads to aldehydes and free radicals[93], thus "fueling" photochemicals reactions in the atmosphere.

Information on peroxyacyl nitrates in the atmosphere of the Amazon is very limited. Only one compound, peroxyacetyl nitrate, has been measured[94]. As part of the ABLE-2 1987 wet season study (no measurements of PAN were made during the 1985 dry season), aircraft measurements were made of PAN over the Amazon basin[94]. Concentrations of PAN were 5-125 ppt (1 ppt = 10^{-3} ppb) and increased with altitude, i.e. median

PAN concentrations were 12, 20 and 48 ppt at 0-2, 2-4 and 4-6 km, respectively[94]. Concentrations of PAN were highest over the Amazon (Manaus) and decreased towards the Atlantic coast (Belem).

While no other study of PAN has been made in the Amazon, high concentrations of PAN have been recently observed over west Africa[95] as a result of biomass burning. In the same study, which included flights over northeast Brazil (Salvador-Fortaleza-Recife area) but not in the Amazon region, high levels of PAN were observed over Lima, Peru and Rio de Janeiro, Brazil. Back trajectory analysis suggested contributions of biomass burning in the Amazon and the Matto Grosso regions, respectively[95].

The atmospheric reactions that lead to peroxyacyl nitrates have been outlined in the preceding sections, which have included examples relevant to the Amazon forest (PAN and MPAN from isoprene, PAN from several terpenes, PPN from leaf alcohol, etc). Once formed in the atmosphere, peroxyacyl nitrates are removed by three chemical pathways: thermal decomposition, reaction with OH, and reaction with ozone (removal by photolysis may become important at higher altitude). Reaction with OH is negligibly slow for PAN[48], slow for the other saturated compounds, and may be important for unsaturated compounds such as MPAN. Reactions with ozone is negligibly slow for saturated compounds and may be important for unsaturated compounds such as MPAN. The OH-MPAN and ozone-MPAN reactions for which some kinetic and product data are available[96,97], are briefly outlined below. Thermal decomposition, which is an important removal process for all peroxyacyl nitrates[89,99-104], will be outlined first.
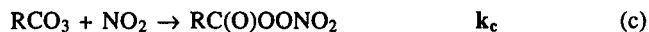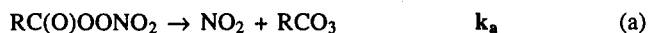
Table 15. Peroxyacyl nitrate yields in biogenic hydrocarbon-NO sunlight irradiation experiments.

biogenic hydrocarbon	initial concentrations, ppm		initial HC/NO ratio, ppmC/ppm	peroxyacyl nitrate, percent of initial NO (f)	
	hydrocarbon	NO		PAN	other peroxyacyl nitrate
isoprene (a)	1.0	0.27	18.5	>7.4	MPAN 4.4
	1.0	0.27	18.5	>11.8	MPAN 5.5
methacrolein (a)	1.0	0.24	16.7	8.75	MPAN 17.5
	1.0	0.23	17.4	>6.1	MPAN >14.3
acrolein (b)	1.0	0.40	7.5	-	vinyl PAN 5.3
	1.0	0.20	15.0	-	vinyl PAN 2.5
	1.0	0.20	15.0	-	vinyl PAN 7.0
	10.0	1.4	21.4	-	vinyl PAN 1.5
	2.0	0.58	10.3	-	vinyl PAN 2.6
	8.0	0.56	43.0	-	vinyl PAN 10.9
2-ethylacrolein (c)	2.0	0.40	25.0	1.3	PPN 6.0, EPAN 0.5
	2.0	0.39	25.6	6.9	PPN 13.3, EPAN 1.3
methyvinyl ketone (a)	1.0	0.35	11.4	>8.6	-
	1.0	0.32	12.5	>10.0	-
cis-3-hexen-1-ol (d)	1.0	0.22	27	6.8	PPN 19.5
	2.0	0.46	26	4.6	PPN 13.9
alpha-pinene (e)	1.8	0.225	80.0	>8.9	-
	1.6	0.260	61.5	4.6	-
	10.1	1.10	91.8	>3.3	-
beta-pinene (e)	1.8	0.165	109	1.8	-
	10.1	1.08	93.5	0.3	-
d-limonene (e)	1.7	0.25	68.0	13.2	-
	1.7	0.20	85.0	14.5	-
nopinone (e)	2.0	0.18	100	<0.3	-
4-acetyl-1-methylcyclohexene (e)	1.9	0.215	79.5	18.6	-

(a) from ref. 32; (b) from ref. 87; (c) from ref. 88; (d) from ref. 41; (e) from ref. 30; (f) as measured, i. e. not corrected upwards to account for loss by thermal decomposition, reaction with OH and/or reaction with ozone.

Thermal decomposition of peroxyacyl nitrates

The reactions relevant to the thermal stability of peroxyacyl nitrates include their formation/decomposition equilibrium, (reactions **a** and **c** below) and the rapid reaction of the RCO_3 radicals with nitric oxide (reaction **b**):

$$RC(O)OONO_2 \rightarrow NO_2 + RCO_3 \qquad \mathbf{k_a} \qquad (a)$$

$$RCO_3 + NO \rightarrow R + CO_2 + NO_2 \qquad \mathbf{k_b} \qquad (b)$$

$$RCO_3 + NO_2 \rightarrow RC(O)OONO_2 \qquad \mathbf{k_c} \qquad (c)$$

At a given temperature and pressure, the peroxyacyl nitrate concentration is a function of [NO] and [NO_2], i.e.:

$$-d(\ln [PAN])/dt = \frac{k_a k_b [NO]}{k_b [NO] + k_c [NO_2]} \qquad (Eq.1)$$

The rate constant k_a for the decomposition step can be readily measured by adding excess NO since, with [NO] >> [NO_2], Equation 1 simplifies to:

$$-d(\ln [PAN])/dt = k_a \qquad (Eq. 2)$$

$$\ln([PAN]_o/[PAN]_t) = k_a t \qquad (Eq. 3)$$

where $[PAN]_o$ is the initial peroxyacyl nitrate concentration and $[PAN]_t$ is the concentration at time t. Using Equation 3, k_a has been measured at ambient temperature and one atm. of air for a number of peroxyacyl nitrates[98-104]. The results, compiled in Table 16, indicate that all peroxyacyl nitrates studied to date have comparable thermal decomposition rates, i.e. the nature of the substituent R does not appear to have a strong influence on the strength of the O-N bond.

The decomposition of peroxyacyl nitrates according to **a-c** has been studied over a range of temperatures and pressures relevant to the atmosphere[98-102]. The results, given in Table 17 in Arrhenius form, indicate that the thermal stability of peroxyacyl nitrates decrease rapidly with increasing temperature.

While the kinetics of peroxyacyl nitrate decomposition has been the object of several studies, less is known about the reaction products. The alkyl radical product of $RCO_3 + NO \rightarrow R + CO_2 + NO_2$ is expected to yield the corresponding alkoxy radical ($R + O_2 \rightarrow RO_2$, $RO_2 + NO \rightarrow NO_2 + RO$) which

Table 16. Rate constants for the thermal decomposition of peroxyacyl nitrates at ambient temperature and one atm. of air.
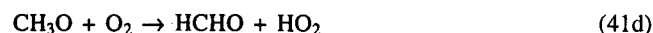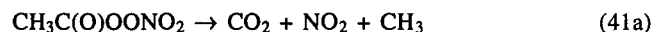
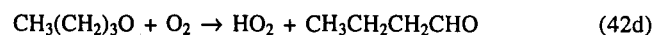| Peroxyacyl nitrate, $RC(O)OONO_2$		k_a, 10^{-4} s^{-1} (a)	reference
acronym	R =		
PAN	CH_3	4.3	98
		5.3	99
		4.2	100
		3.7	101
		3.0	102
PPN	C_2H_5	3.4	102
vinyl PAN	$CH_2 = CH-$	3.0	102
PnBN	$n-C_3H_7$	2.7	105
MPAN	$CH_2 = C(CH_3)-$	2.3	103
		3.5	101
nC_5 -PAN	$n-C_4H_9$	1.8	104
iC_5 -PAN	$iso-C_4H_9$	2.4	104
EPAN	$CH_2 = C(C_2H_5)-$	2.0	88

(a) at 298K and 1 atm. of air.

Table 17. Arrhenius parameters for the thermal decomposition of PAN and MPAN.

Peroxyacyl nitrate, $RC(O)OONO_2$		T (K)	$\log_{10}$ A (s^{-1})	E_a (Kcal/mol)	ref.
acronym	R=				
PAN	CH_3	294-328	14.9 ± 0.6	24.9 ± 0.8	98
		248-393	16.6	27.1 ± 0.7	99
		283-313	16.4 ± 0.2	27.0 ± 0.6	100
		298-313	16.3 ± 0.6	26.9 ± 0.9	101
		288-298	16.2 ± 1.6	26.9 ± 2.1	102
MPAN	$CH_2=C(CH_3)-$	298-313	16.2 ± 0.7	26.8 ± 1.0	101

undergoes decomposition or reacts with oxygen[59]. For example, PAN leads to formaldehyde as follows:

$$CH_3C(O)OONO_2 \rightarrow CO_2 + NO_2 + CH_3 \qquad (41a)$$

$$CH_3 + O_2 \rightarrow CH_3O_2 \qquad (41b)$$

$$CH_3O_2 + NO \rightarrow NO_2 + CH_3O \qquad (41c)$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2 \qquad (41d)$$

and, similarly, the aliphatic $n-C_5$ peroxyacyl nitrate leads to n-butanal [104]:

$$CH_3CH_2CH_2CH_2C(O)OONO_2 \rightarrow CO_2 + NO_2 + CH_3(CH_2)_3 \qquad (42a)$$

$$CH_3(CH_2)_3 + O_2 \rightarrow CH_3(CH_2)_3O_2 \qquad (42b)$$

$$CH_3(CH_2)_3O_2 + NO \rightarrow CH_3(CH_2)_3O \qquad (42c)$$

$$CH_3(CH_2)_3O + O_2 \rightarrow HO_2 + CH_3CH_2CH_2CHO \qquad (42d)$$
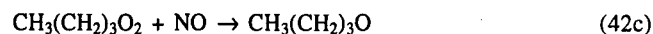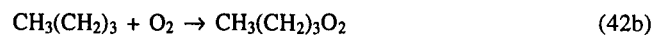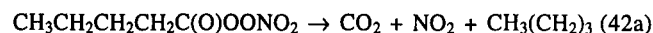
A list of the carbonyls that have been identified as major products of the thermal decomposition of peroxyacyl nitrates is given in Table 18. In turn, these carbonyls react rapidly with OH, leading to free radicals and to lower molecular weight carbonyls and peroxyacyl nitrates.

Reaction of peroxyacyl nitrates with OH

Peroxyacyl nitrates that bear saturated substituents may react with OH by H-atom abstraction from the alkyl groups. The OH reaction rate constant has been measured for only one compound, PAN. The OH-PAN reaction is slow and is negligible as a removal process for PAN in the atmosphere. No kinetic data are available for the higher saturated homologues. Structure-reactivity considerations suggest that, because of the electron-withdrawing CO_3NO_2 group, these compounds react with OH more slowly than the corresponding alkanes, i.e., k (OH + PPN) < k (OH + propane), k (OH + n-propyl $C(O)OONO_2$) < k (OH + n-butane), and so on. Thus, reaction with OH, for which kinetic data are obviously needed, may contribute to the atmospheric removal of saturated peroxyacyl nitrates other than PAN.

Peroxyacyl nitrates that bear unsaturated substituents are expected to react with OH by addition on the C = C bond. Kinetic and product data are available for only one compound, MPAN[96] (Table 19) and suggest a half-life of about 2 days for MPAN against removal by OH. The major carbonyl products of the MPAN-OH reaction are hydroxyacetone (yield 0.59) and formaldehyde[96], consistent with OH addition:
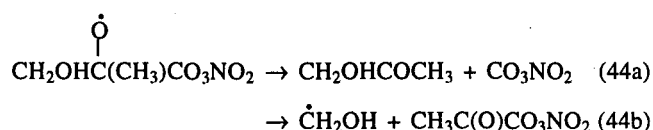
$$CH_2 = C(CH_3)C(O)OONO_2 + OH \rightarrow CH_2OH\overset{\bullet}{C}(CH_3)C(O)OONO_2 \qquad (43)$$
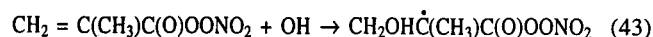
followed by the alkyl $\rightarrow$ peroxy $\rightarrow$ alkoxy sequence and by unimolecular decomposition of the alkoxy radical:

Table 18. Carbonyl products of the thermal decomposition of peroxyacyl nitrates.

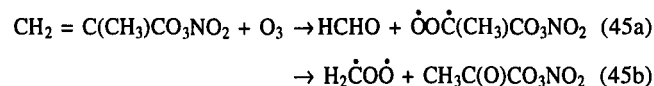| Peroxyacyl nitrate $RC(O)OONO_2$		Alkoxy radical RO	Carbonyl products		Alkoxy + O_2 percent of total alkoxy radical reaction (c)
acronym	R=		Alkoxy + O_2 (a)	Alkoxy decomposition (b)	
PAN	CH_3	CH_3O	formaldehyde	-	>99
PPN	C_2H_5	CH_3CH_2O	acetaldehyde	formaldehyde	>99
PnBN	n-C_3H_7	$CH_3CH_2CH_2O$	propanal	formaldehyde + acetaldehyde	≥89
PiBN	iso-C_3H_7	$(CH_3)_2CHO$	acetone	formaldehyde + acetaldehyde	≥96
nC_5-PAN	n-C_4H_9	$CH_3(CH_2)_2CH_2O$	n-butanal	formaldehyde + propanal	≥94
iC_5-PAN	iso-C_4H_9	$(CH_3)_2CHCH_2O$	isobutanal	formaldehyde + acetone	≥96

(a) reaction with oxygen, RO + $O_2 \rightarrow HO_2$ + carbonyl with same number of carbon atoms as the alkoxy radical; (b) unimolecular decomposition, RO $\rightarrow$ smaller carbonyl + smaller radical, e. g. $CH_3CH_2O \rightarrow HCHO + CH_3$; (c) adapted from Grosjean et al[102-106].

$$CH_2OHC(CH_3)CO_3NO_2 \overset{\overset{\bullet}{O}}{\rightarrow} CH_2OHCOCH_3 + CO_3NO_2 \quad (44a)$$

$$\rightarrow \overset{\bullet}{C}H_2OH + CH_3C(O)CO_3NO_2 \quad (44b)$$

followed by $\overset{\bullet}{C}H_2OH + O_2 \rightarrow HCHO + HO_2$.

Reactions of peroxyacyl nitrates with ozone

For saturated peroxyacyl nitrates, this reaction is too slow to be important in the atmosphere. In contrast, unsaturated peroxyacyl nitrates are expected to react with ozone (by addition on the C = C bond) at rates that would result in rapid removal under atmospheric conditions. Kinetic and product data are available for only one compound, MPAN[97] (Table 19) and suggest half-lives of only 9-18 h for MPAN when $[O_3]$ = 50-100 ppb. Formaldehyde (yield = 0.6) is a major product of the ozone-MPAN reaction[97]:

$$CH_2 = C(CH_3)CO_3NO_2 + O_3 \rightarrow HCHO + \overset{\bullet}{O}O\overset{\bullet}{C}(CH_3)CO_3NO_2 \quad (45a)$$

$$\rightarrow H_2\overset{\bullet}{C}O\overset{\bullet}{O} + CH_3C(O)CO_3NO_2 \quad (45b)$$

with the biradical formed in **45a** possibly leading to more formaldehyde (via the $\overset{\bullet}{O}H_2OH$ radical) as discussed earlier for the reaction of ozone with isoprene, terpenes and unsaturated oxygenates. The acetyl-substituted peroxyacyl nitrate postulated to form in **45b** (if stable at all; it may decompose to, e.g., CO + PAN) remains to be identified.

CONCLUDING COMMENTS AND SUGGESTIONS FOR FUTURE RESEARCH

In this article, we have attempted to underline the major role of the Amazon with regard to global atmospheric chemistry and to outline, on the basis of the most recent kinetic and

product studies, the reaction mechanisms that are involved in the atmospheric oxidation of biogenic hydrocarbons that are relevant to emissions from the Amazon rainforest. Much progress has been made in recent years in developing a better understanding of the complex chemistry of the atmosphere of the Amazon region. However, it is evident from the review of available data presented in this article that uncertainties and large "information gaps" still exist and that additional research is needed. Listed below are several suggestions for additional field measurements and laboratory investigations.

Field measurements: biogenic emissions

There is no information on emissions of unsaturated oxygenates (e.g. alcohols, aldehydes, esters) from the Amazon rainforest. Yet, these oxygenated compounds, which have been shown to be important in other ecosystems, may play an important, and perhaps dominant, role in the atmospheric chemistry of the Amazon region. As is shown in Table 20, reactivity ranking calculations of the type given in Table 7 indicate that only 2 ppb of unsaturated alcohol (e.g. leaf alcohol) + 1 ppb unsaturated aldehyde would make unsaturated oxygenates as important as isoprene for removal of OH in the Amazon atmosphere. Information on terpenes, of which only four compounds have been identified in the Amazon region, needs to be expanded especially for sesquiterpenes for which no data exist. Additional information on isoprene, for which much data are available for the Amazon rainforest, would still be useful in the form of simultaneous measurements of isoprene, terpenes and oxygenates in order to better delineate the relative importance of each category of biogenic emissions. Dry season versus wet season measurements would be useful, as would additional measurements aimed at a better characterization of the impact of biomass burning.

Table 19. Atmospheric removal of MPAN.

Reaction	Rate constant at 298K and 1 atm. of air	MPAN half-life	Reaction products
thermal decomposition[103]	$2.3 \times 10^{-4} s^{-1}$	from 1-2 hours when NO > NO_2 to very long when NO_2 > NO	formaldehyde, methylglyoxal
reaction with ozone[97]	$(8.2 \pm 2.0) \times 10^{-18}$ cm^3 molecule^{-1}s^{-1}	18 hours when $[O_3]$ = 50 ppb	formaldehyde
reaction with OH[96]	$(3.6 \pm 0.4) \times 10^{-12}$ cm^3 molecule^{-1}s^{-1}	2.2 days when [OH] = 1.0 x 10^6 molecule cm^3	hydroxyacetone, formaldehyde

Table 20. Hypothetical reactivity ranking of carbonyls and unsaturated oxygenates.

	A = Ambiet concentration, ppbv	B = rate constant for OH reaction, 10^{12}x cm^3 molecule^{-1}s^{-1}	A x B	Percent of total OH removal scenario#1	scenario#2
isoprene			206.0 (a)	44.5	58.8
CO			31.0 (a)	6.7	8.8
methane			13.9 (a)		
alkanes + alkenes + aromatics			26.7 (a)		
terpenes			10.2 (a)		
scenario #1:unsaturated oxygenates (b)					
leaf alcohol	2.0	72	144	31.2	-
2-hexen-al	1.0	30	30	6.5	-
subtotal, unsat. oxygenates	**3.0**	-	**174**	**37.7**	-
scenario #2: carbonyls (c)					
formaldehyde	2.0	9.77	19.5	-	5.6
methacrolein (MTA)	0.5	33.5	16.7	-	
methylvinylketone (MVK)	0.5	18.8	9.4	-	
methylglyoxal	0.5	17.2	8.6	-	
acetaldehyde	0.5	15.8	7.9	-	
subtotal, carbonyls	**4.0**	-	**62.1**	-	**17.7**

(a) from Table 7; (b) adding 2.0 ppb unsaturated alcohol (leaf alcohol) and 1.0 ppb unsaturated aldehyde (2-hexen-al) to the biogenic hydrocarbons listed in Table 7; (c) adding 2.0 ppb formaldehyde and 0.5 ppb each of acetaldehyde, MVK, MTA and methylglyoxal to the biogenic hydrocarbons listed in Table 7.

Field measurements: reaction products

The laboratory studies reviewed in this article underline the critical importance of carbonyl products. Yet, there are to our knowledge no data for ambient levels of carbonyls in the Amazon region, not even for the three major carbonyl products of isoprene, i.e. formaldehyde, methacrolein and methyl vinylketone. The critical importance of carbonyl measurements is illustrated in Table 20, where the reactivity ranking data given in Table 7 are compared to a hypothetical situation in which 2.0 ppb formaldehyde and 0.5 ppb each of acetaldehyde, MVK, MTA and methylglyoxal are added to the hydrocarbon ambient concentration data available for the Amazon forest. This simple scenario clearly shows the potential importance of carbonyls with respect to control of OH in the Amazon region (a similar impact is expected with respect to levels of ozone and carbon monoxide, among others).

In the same way, more data are needed for peroxyacyl nitrates. PAN has been measured in only one field study carried out in the Amazon about ten years ago. There are no data for MPAN, which, along with PAN, is produced from isoprene. As is the case for biogenic emissions, data for carbonyls and for peroxyacyl nitrates should include dry season versus wet season measurements as well as measurements that focus on biomass burning.

Laboratory studies

Reliable kinetic data are available for isoprene, the terpenes and, to some extent, for unsaturated oxygenates including alcohols and carbonyls. With respect to studies of reaction products, the atmospheric chemistry of isoprene is reasonably well understood but more studies are needed for terpenes (especially sesquiterpenes) and for unsaturated oxygenates. For example, the formation of hydroxycarbonyls and of hydroxy-substituted peroxyacyl nitrates from leaf alcohol and other unsaturated alcohols needs to be investigated. The nature and yields of carboxylic acids from the ozone-unsaturated biogenic compound reaction need further study, i.e. methacrylic acid and pyruvic acid from isoprene, formic acid and high molecular weight acids from terpenes (such as pinonic acid from α-pinene) and hydroxyacids from unsaturated alcohols. The nighttime

chemistry of biogenic emissions is poorly understood; this include reactions with the nitrate radical and with OH which is formed in the reaction of unsaturated biogenic compounds with ozone in the dark.

With the exception of PAN, which has been well characterized, much information is needed regarding atmospheric formation and removal processes for peroxyacyl nitrates. This include formation yields from isoprene (PAN and MPAN), terpenes (PAN and possibly high molecular weight PAN's) and unsaturated oxygenates (e.g. hydroxyalkyl PAN's from unsaturated alcohols). Removal processes, i.e. thermal decomposition, reaction with OH and, for unsaturated PAN's, reaction with ozone also need further study. In addition, information on aerosol yields and aerosol molecular composition is needed for many terpenes.

The research topics suggested above would contribute to a better understanding of the importance, persistence and fate of biogenic hydrocarbons in the atmosphere of the Amazon and of the role of the Amazon in global atmospheric chemistry.

ACKNOWLEDGEMENTS

REFERENCES

1. Speth, J. G.; *Environ. Sci. Technol.* (1992), **26**, 1075.
2. Hilerman, B.; *Chem. Eng. News* (1992), July 6, 7.
3. Miller, S.; *Environ. Sci. Technol.* (1991), **25**, 1345.
4. Reid, W. V.; *Environ. Sci. Technol.* (1992), **26**, 1090.
5. Zentilli, B.; *Environ. Sci. Technol.* (1992), **26**, 1096.
6. Batalha, B. H. L.; *Ambiente* (1992), **6**, 12 (CETESB, São Paulo, SP).

7. Lodge Jr, J. P.; Pate, J. B.; *Science* (1966), **153**, 408.
8. Lodge Jr, J. P.; Machado, P. A.; Pate, J. B.; Sheesley, D. C.; Wartburg, A. F.; *Tellus* (1974), **26**, 250.
9. Brinkmann, W. L. F.; Santos, U. M.; *Tellus* (1974), **26**, 261.
10. Delmas, R.; Boudet, J.; Servant, J.; Baziard, Y.; *J. Geophys. Res.* (1980), **85**, 4468.
11. Stallard, R. F.; Edmond, J. M.; *J. Geophys. Res.* (1981), **86**, 9844.
12. Greenberg, J. P.; Zimmerman, P. R.; Heidt, L.; Pollack, W.; *J. Geophys. Res.* (1984), **89**, 1350.
13. Crutzen, P. J. *et al.*; *J. Atmos. Chem.* (1985), **2**, 233.
14. Gregory, G. L. *et al.*, *J. Geophys. Res.* (1986), **91**, 8603.
15. Bruynseels, F. J.; Artaxo, P.; Storms, H. M.; Van Grieken, R. E.; LAMMA study aerosol samples collected in the Amazon basin, In Microbeam Analysis, Geiss, R. H., editor, San Francisco Press, San Francisco, CA, pp. 356-358 (1987).
16. Harris, R. C. *et al.*; *J. Geophys. Res.* (1988), **93**, 1351.
17. Harris, R. C. *et al.*, *J. Geophys. Res.* (1990), **95**, 16721.
18. Fontan, J.; Druilhet, A.; Benech, B.; Lyra, R.; Cros, B.; *J. Geophys. Res.* (1992), **97**, 6123.
19. DeSousa, E. M.; *Envirom. Sci. Technol.* (1992), **26**, 1071.
20. Rasmussen, R. A.; *J. Air Pollut. Control Assoc.* (1972); **22**, 537.
21. Lamb, B.; Westberg, H.; Allwine, G.; *J. Geophys. Res.* (1985), **90**, 2390.
22. Lamb, B.; Guenther, A.; Gray, D.; Westberg, H.; *Atmos. Environ.* (1987), **21**, 1695.
23. Grimsrud, E. P.; Westburg, H. H.; Rasmussen, R. A.; *Int. J. Chem. Kinetics, Symp. 1*, 183 (1975).
24. Kamens, R. M.; Jerry, M. W.; Jeffries, H. E.; Jackson, M.; Cole, E. I.; *Inter. J. Chem. Kinetics* (1982), **14**, 955.
25. Hatakeyama, S.; Izumi, K.; Fukuyama, T.; Akimoto, H.; Washida, N.; *J. Geophys. Res* (1991), **96**, 947.
26. Arey, J.; Atkinson, R.; Aschmann, S. M.; *J. Geophys. Res* (1990), **95**, 18539.
27. Hakola, H.; Shorees, B.; Arey, J.; Atkinson, R.; *Environ. Sci. Technol.* (1993), **27**, 278.
28. Tuazon, E. C.; Atkinson, R.; *Int. J. Chem. Kinetics* (1990), **22**, 1221.
29. Aschmann, S. M.; Atkinson, R.; *Environ. Sci. Technol.* (1994), submitted.
30. Grosjean, D.; Williams II, E. L.; Seinfeld, J. H.; *Environ. Sci. Technol.* (1992), **26**, 1526.
31. Grosjean, D.; Williams II, E. L.; Grosjean, E.; Andino, J. M.; Seinfeld, J. H.; *Environ. Sci. Technol.* (1993), **27**, 2754.
32. Grosjean, D.; Williams II, E. L.; Grosjean, E.; *Environ. Sci. Technol.* (1993), **27**, 830.
33. Isidorov, V. A.; Zenkevich, I. G.; Ioffe, B. V.; *Atmos. Environ.* (1985), **19**, 1.
34. Arey, J.; Winer, A. M.; Atkinson, R.; Aschmann, S. M.; Long, W. D.; Morrison, C. L.; *Atmos. Environ.* (1991), **25A**, 1063.
35. Arey, J.; Corchnoy, S. B.; Atkinson, R.; *Atmos. Environ.* (1991), **25A**, 1377.
36. Ohta, K.; *Geochem J.* (1984), **18**, 135.
37. Winer, A. M.; Arey, J.; Atkinson, R.; Aschmann, S. M.; Long, W. D.; Morrison, C. L.; Olszyk, D. M.; *Atmos. Environ.* (1992), **26A**, 2649.
38. Graedel, T. E.; Chemical compounds in the atmosphere, Academic Press, New York, NY (1978).
39. Goldan, P. D.; Kuster, W. C.; Fehsenfeld, F. C.; *Geophys. Res. Letters* (1993), **20**, 1039.
40. Ciccioli, P. *et al.*; *Atmos. Environ.* (1993), **27A**, 1891.
41. Grosjean, D.; Williams II, E. L.; Grosjean, E.; *Environ. Sci. Technol.* (1993), **27**, 979.
42. Grosjean, D.; Grosjean, E.; Williams II, E. L.; *Environ.*

43. Grosjean, D.; Grosjean, E.; Williams II, E. L.; *Int. J. Chem. Kinetics* (1993), **25**, 783.
44. Grosjean, E.; Grosjean, D.; *Int. J. Chem. Kinetics* (1994), in press.
45. Shu, Y.; Atkinson, R.; *Int. J. Chem. Kinetics* (1994), in press.
46. Rasmussen, R. A.; Khalil, M. A. K.; *J. Geophys Res.* (1988), **93**, 1417.
47. Zimmerman, P. R.; Greenberg, J. P.; Westberg, C. E.; *J. Geophys. Res.* (1988), **93**, 1407.
48. Atkinson, R.; *Atmos. Environ.* (1990), **24A**, 1.
49. Grosjean, D.; *J. Air Waste Manag. Assoc.* (1990), **40**, 1397.
50. Grosjean, D.; Williams II, E. L.; *Atmos. Environ.* (1992), **26A**, 1395.
51. Kirchhoff, V. W. J. H.; *J. Geophys. Res.* (1988), **93**, 1469.
52. Kirchhoff, V. W. J. H.; Silva, I. M. O. da; Browell, E. V.; *J. Geophys. Res.* (1990), **95**, 16913.
53. Grosjean, D.; Grosjean, E.; Williams II, E. L.; *Environ. Sci. Technol.* (1994), **28**, 186.
54. Atkinson, R.; Aschmann, S. M.; Arey, J.; Shorees, B.; *J. Geophys. Res.* (1992), **97**, 6065.
55. Atkinson, R.; Aschmann, S. M.; *Environ. Sci. Technol.* (1993), **27**, 1357.
56. Atkinson, R.; Aschmann, S. M.; Carter, W. P. L.; Winer, A. M.; Pitts Jr, J. N.; *J. Phys. Chem.* (1982), **86**, 4563.
57. Atkinson, R.; Aschmann, S. M.; Winer, A. M.; *J. Atmos. Chem.* (1987), **5**, 91.
58. Carter, W. P. L.; Atkinson, R.; *J. Atmos. Chem.* (1989), **8**, 165.
59. Atkinson, R.; Carter, W. P. L.; *J. Atmos. Chem.* (1991), **13**, 195.
60. Barnes, I.; Bastian, V.; Becker, K. H.; Tong, Z.; *J. Phys Chem.* (1990), **94**, 2413.
61. Skov, H.; Hjorth, J.; Lohse, C.; Jensen, N. R.; Restelli, G.; *Atmos. Environ.* (1992), **26A**, 2771.
62. Wayne, R.; Barnes, I.; Biggs, P.;Burrows, J. P.; Canosa-Mas, C. E.; Hjorth, J.; LeBras, G.; Moortgat, G. K.; Perner, D.; Poulet, G.; Restelli, G.; Sidebotton, H.; *Atmos. Environ.* (1991), **25A**, 1
63. Andreae, M. O.; Talbot, R. W.; Andreae, T. W.; Harriss, R. C.; *J. Geophys. Res.* (1988), **93**, 1616.
64. Talbot, R. W.; Andreae, M. O.; Berrensheim, H.; Jacob, D. J.; Becker, K. M.; *J. Geophys. Res.* (1990), **95**, 16799.
65. Helas, G.; Bingemer, H.; Andreae, M. O.; *J. Geophys. Res.* (1992), **97**, 6187.
66. Greene, C. R.; Atkinson, R.; *Int. J. Chem. Kinetics* (1992), **24**, 803
67. Atkinson, R.; Hasegawa,. D.; Aschmann, S. M.; *Int. J. Chem. Kinetics.* (1990), **22**, 871.
68. Bonsang, B.; Polle, C.; Lambert, G.; *Geophys. Res. Letters* (1992), **19**, 1129.
69. Riemer, D. D.; Milne, P. J.; Zika, R. G.; Brand, L. E.; Observations of marine isoprene production. Paper ENVR 186, 207th Nat. Meeting of the Amer. Chem. Soc., San Diego, CA, March 13-18, 1994.
70. Skov, H.; Benter, Th.; Schindler, R. N.; Hjorth, J.; Restelli, G.; *Atmos. Environ.* (1994), **28**, 1583.
71. Tuazon, E.; Atkinson, R.; *Int. J. Chem. Kinetics* (1990), **22**, 591.
72. Tuazon, E.; Atkinson, R.; *Int. J. Chem. Kinetics* (1989), **21**, 1141.
73. Zimmerman, P. R.; Chatfield, R. B.; Fishman, J.; Crutzen, P. J.; Hanst, P. L.; *Geophys. Res. Letters* (1978), **5**, 679
74. Reichle Jr, H. G.; Connors, V. S.; Holland, J. A.; Hypes, W. D.; Wallio, H. A.; Casas, J. C.; Gormsen, B. B.; Saylor, M. S.; Hesketh, W. D.; *J. Geophys. Res.* (1986), **91**, 10865.

Sci. Technol. (1993), **27**, 2478.

75. Schuetzle, D.; Rasmussen, R. A.; *J. Air Pollut. Control Assoc.* (1978), **28**, 236.
76. Yokouchi, Y.; Ambe, Y.; *Atmos. Envirom.* (1985), **19**, 1271.
77. Hatakeyama, S.; Izumi, K.; Fukuyama, T.; Akimoto, H.; *J. Geophys. Res.* (1989), **94**, 13013.
78. Zhang, S. H.; Shaw, M.; Seinfeld, J. H.; Flagan, R. C.; *J. Geophys. Res.* (1992), **97**, 20717.
79. Grosjean, D.; Seinfeld, J. H.; *Atmos. Environ.* (1989), **23**, 1733.
80. Grosjean, D.; Williams II, E. L.; Grosjean, E.; Novakov, T.; *Aerosol Sci. Technol.* (1994), in press.
81. Arey, J.; Winer, A. M.; Atkinson, R.; Aschmann, S. M.; Long, W. D.; Morrison, C. L.; Olszyk, D. M.; *J. Geophys. Res.* (1991), **96**, 9329.
82. Hakola, H.; Arey, J.; Aschmann, S. M.; Atkinson, R.; *J. Atmos. Chem.* (1994), **18**, 75.
83. Yokouchi, Y.; Mukai, H.; Nakajima, K.; Ambe, Y.; *Atmos. Environ.* (1990), **24A**, 439.
84. Nondek, L.; Rodier, D. R.; Birks, J. W.; *Environ. Sci. Technol.* (1992), **26**, 1174.
85. MacDonald, R. C.; Fall, R.; *Atmos. Environ.* (1993), **27A**, 1709.
86. Grosjean, D.; Grosjean, E.; Ozone formation from biogenic hydrocarbons: atmospheric chemistry of unsaturated alcohols. Paper FM7-1B-1, International Conference on Regional Photochemical Measurements and Modeling Studies, San Diego, CA, Nov. 7-12, 1993.
87. Grosjean, E.; Williams II, E. L.; Grosjean, D.; *Sci. Total Environ.*, in press.
88. Grosjean, D.; Grosjean, E.; Williams II, E. L.; *Israel J. Chem.* (1994), in press.
89. Stephens, E. R.; *Adv. Environ. Sci. Technol.* (1969), **1**, 119.
90. Singh, H. B.; Hanst, P. L.; *Geophys. Res. Letters* (1981), **8**, 941
91. Taylor, O. C.; *J. Air Pollut. Control Assoc.* (1969), **19**, 347.
92. Peak, M. J.; Belser, W. L.; *Atmos. Environ.* (1969), **3**, 385.
93. Carter, W. P. L.; Winer, A. M.; Pitts Jr, J. N.; *Environ. Sci. Technol.* (1981), **15**, 831.
94. Singh, H. B.; Herlth, D.; O'Hara, D.; Salas, L.; Torres, A. L.; Gregory, G. L.; Sachse, G. W.; Kasting, J. F.; *J. Geophys. Res.* (1990), **95**, 16945.
95. Perros, P. E.; *J. Geophys. Res.* (1994), **99**, 8269.
96. Grosjean, D.; Williams II, E. L.; Grosjean, E.; *Int. J. Chem. Kinetics* (1993), **25**, 921
97. Cox, R. A.; Roffey, M. J.; *Environ. Sci. Technol.* (1977), **11**, 900.
98. Grosjean, D.; Grosjean, E.; Williams II, E. L.; *Environ. Sci. Technol.* (1993), **27**, 2548.
99. Bridier, I.; Caralp, F.; Loirat, H.; Lesclaux, R.; Veyret, B.; Becker, K. H.; Reimer, A.; Zabel, F.; *J. Phys. Chem.* (1991), **95**, 3594.
100. Tuazon, E. C.; Carter, W. P. L.; Atkinson, R.; *J. Phys. Chem.* (1991), **95**, 2434.
101. Roberts, J. M.; Bertman, S. B.; *Int. J. Chem. Kinetics* (1992), **24**, 297.
102. Grosjean, D.; Grosjean, E.; Williams II, E. L.; *J. Air. Waste Manag. Assoc.* (1994), **44**, 391.
103. Grosjean, D.; Grosjean, E.; Williams II, E. L.; *Res. Chem. Intermediates* (1994), **20**, 447.
104. Grosjean, D.; Grosjean, E.; Williams II, E. L.; *Environ. Sci. Technol.* (1994), **28**, 1099.
105. Grosjean, D.; Williams II, E. L.; Grosjean, E.; *Int. J. Chem. Kinetics* (1994), **26**, 381.
106. Grosjean, D.; Grosjean, E.; Williams II, E. L.; Formation and thermal decomposition of peroxyacyl nitrates. Paper ENVR 248, 207th National Meeting, Amer. Chem. Soc., San Diego, CA, March 13-18, 1994.
107. Grosjean, D.; Grosjean, E.; Williams II, E. L.; Atmospheric chemistry and fate of C2-C5 peroxyacyl nitrates. Conference on Measurement of Toxic and Related Air Pollutants, Durham, NC, May 3-6, 1994.
108. Grosjean, D.; Grosjean, E.; Williams II, E. L.; Atmospheric removal of MPAN. Paper ENVR 187, 207th National Meeting, *Amer. Chem. Soc.*, San Diego, CA, March 13-18, 1994.