

# Atmospheric Chemistry of Biogenic Organic Compounds

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## Introduction

It was first recognized over 30 years ago that isoprene [2-methyl-1,3-butadiene;  $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$ ] is emitted into the atmosphere from plants.<sup>1,2</sup> Numerous studies carried out since ca. 1970 have shown a wide variety of volatile non-methane organic compounds (referred to hereafter as NMOCs) to be emitted from vegetation.<sup>3–15</sup> Table 1 lists a subset of the total number of NMOCs observed as plant emissions, chosen to be representative of the organic compound classes involved (see also Figure 1). In addition to emissions of NMOCs from living plants, NMOCs are also emitted into the atmosphere from wildfires,<sup>16</sup> oceans,<sup>17</sup> logging operations,<sup>18</sup> and wood-pulping operations.<sup>19</sup> It has been estimated that 1150 Tg of carbon  $\text{yr}^{-1}$  (1 Tg =  $10^{12}$  g =  $10^6$  metric tons) from biogenic NMOCs is emitted worldwide.<sup>20</sup> Although there are large uncertainties in the emission rates of total biogenic NMOCs and of individual compounds, worldwide 44% and 11% of biogenic NMOC emissions have been attributed to isoprene and monoterpenes, respectively.<sup>20</sup> A recent estimate for North America<sup>21</sup> suggests that of the 86 Tg  $\text{yr}^{-1}$  of biogenic NMOC emissions, 30% are isoprene, 30% are methanol, 20% are monoterpenes and sesquiterpenes, 8% are hexene derivatives, and 5% are 2-methyl-3-buten-2-ol, with the remainder being relatively nonreactive species.

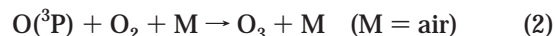
Published emission inventories of biogenic and anthropogenic NMOCs imply that on regional and global scales the emissions of biogenic NMOCs are comparable

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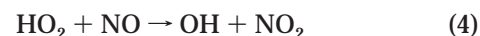
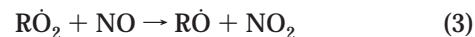
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to, or exceed, those of anthropogenic NMOCs.<sup>20,22–24</sup> Thus, on a worldwide basis biogenic NMOC emissions are estimated to be a factor of  $\sim 10$  higher than anthropogenic NMOC emissions, while for the U.S. biogenic NMOC emissions are estimated to be a factor of  $\sim 1.5$  higher than the anthropogenic NMOC emissions. Because of the higher atmospheric reactivity of most biogenic NMOCs compared to many anthropogenic NMOCs (with calculated lifetimes of biogenic NMOCs being typically a few hours or less compared to a few days for several chemical classes of anthropogenic NMOCs), biogenic NMOCs are calculated to play a dominant role in the chemistry of the lower troposphere and atmospheric boundary layer,<sup>25,26</sup> the lowest 1–2 km of the troposphere which is affected by the Earth's surface and in which we live.

In the presence of NO emitted from combustion sources (mainly anthropogenic and exemplified by vehicle exhaust in an urban area such as Los Angeles) and, to a lesser extent, from soils, atmospheric biogenic NMOC reactions lead to the formation of  $\text{O}_3$  and other manifestations of photochemical air pollution.<sup>27</sup> The only significant formation route of  $\text{O}_3$  in the troposphere is the photolysis of  $\text{NO}_2$ .<sup>27</sup>



Organic peroxy ( $\text{RO}_2$ ) radicals and  $\text{HO}_2$  radicals formed during the photooxidations of biogenic (and anthropogenic) NMOCs react with NO to form  $\text{NO}_2$



whose photolysis then leads to net  $\text{O}_3$  formation through reactions 1 and 2.<sup>27</sup>

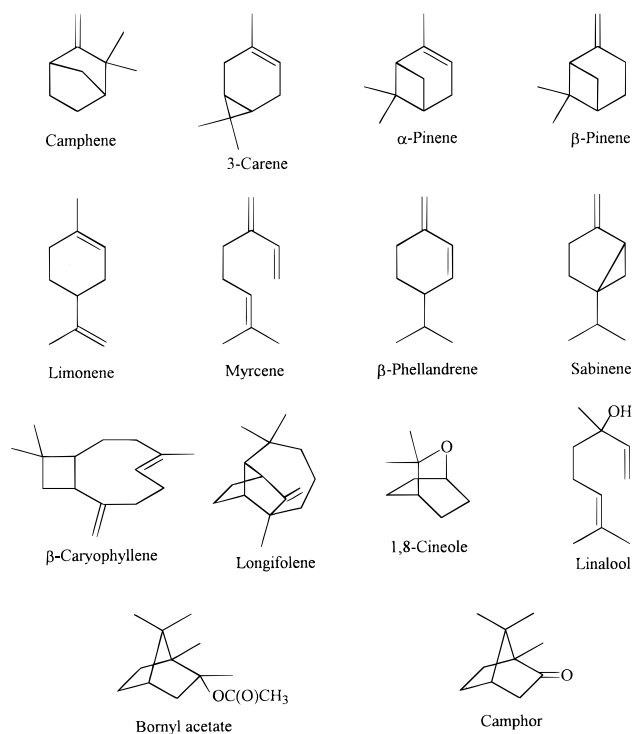
Even for such a highly urbanized area as Los Angeles, CA, the estimated summer-day biogenic NMOC emissions are 125–140 tons per day,<sup>28</sup> which, while small compared to estimated 1990 anthropogenic NMOC emissions of  $\sim 1650$  tons per day,<sup>29</sup> are a significant fraction of the 410 tons per day of NMOC emissions calculated to be the upper value allowable if the Federal National Ambient Air Quality Standard (NAAQS) for  $\text{O}_3$  is to be achieved in the Los Angeles air basin.<sup>29</sup> Biogenic NMOC emissions therefore make the attainment of the NAAQS for  $\text{O}_3$  more difficult, and likely impossible in some areas, utilizing only controls of anthropogenic NMOC emissions.<sup>30–32</sup> To meet air quality standards, it will be imperative in many parts of the U.S., and indeed in many urban areas worldwide, to place controls on anthropogenic  $\text{NO}_x$  emissions from, for example, fossil-fueled power plants and gasoline- and diesel-fueled vehicles.

Definitive evidence for the occurrence of biogenic NMOC reactions and their contribution to  $\text{O}_3$  formation

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**Table 1. Selected Biogenic NMOCs Emitted from Vegetation**

VOC class	VOC	chemical formula
alkanes	<i>n</i> -hexane	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>
	C <sub>10</sub> –C <sub>17</sub> alkanes	C <sub><i>n</i></sub> H <sub>2<i>n</i>+2</sub> ( <i>n</i> = 10–17)
alkenes	isoprene	CH <sub>2</sub> =C(CH <sub>3</sub> )CH=CH <sub>2</sub>
	C <sub>10</sub> H <sub>16</sub> monoterpenes C <sub>15</sub> H <sub>24</sub> sesquiterpenes	see Figure 1 see Figure 1
alcohols	methanol	CH <sub>3</sub> OH
	<i>cis</i> -3-hexen-1-ol	CH <sub>3</sub> CH <sub>2</sub> CH=CHCH <sub>2</sub> CH <sub>2</sub> OH
	2-methyl-3-buten-2-ol linalool	(CH <sub>3</sub> ) <sub>2</sub> C(OH)CH=CH <sub>2</sub> see Figure 1
aldehydes	<i>n</i> -hexanal <i>trans</i> -2-hexenal	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CHO CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH=CHCHO
ketones	acetone	CH <sub>3</sub> C(O)CH <sub>3</sub>
	6-methyl-5-hepten-2-one camphor	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> CH <sub>2</sub> C(O)CH <sub>3</sub> see Figure 1
ethers	1,8-cineole	see Figure 1
esters	3-hexenyl acetate	CH <sub>3</sub> CH <sub>2</sub> CH=CHCH <sub>2</sub> CH <sub>2</sub> OC(O)CH <sub>3</sub>
	bornyl acetate	see Figure 1

**FIGURE 1.** Structures of selected monoterpenes, sesquiterpenes, and oxygenated compounds emitted from vegetation (See Table 1).

is available from measurements of the isoprene reaction products methyl vinyl ketone, methacrolein, 3-methylfuran, and peroxyacetylnitric anhydride [MPAN; CH<sub>2</sub>=C(CH<sub>3</sub>)C(O)OONO<sub>2</sub>] in the eastern and southeastern U.S.<sup>33–35</sup> Of particular relevance are aircraft measurements of MPAN, peroxyacetyl nitrate [PAN; CH<sub>3</sub>C(O)OONO<sub>2</sub>] and peroxypropionyl nitrate [PPN; CH<sub>3</sub>CH<sub>2</sub>C(O)OONO<sub>2</sub>],<sup>35</sup> allowing the contribution of biogenic NMOCs to O<sub>3</sub> formation to be directly derived over a wide area of the central and southern U.S., with a 50–60 parts per billion (ppb) mixing ratio of O<sub>3</sub> (~75% of the measured O<sub>3</sub>) being assigned to biogenic NMOC chemistry in the presence of NO<sub>x</sub>.<sup>35</sup>

Coupled with the potential for forming secondary organic aerosol from biogenic NMOC photooxidations, as illustrated by an ~100% efficiency of secondary aerosol formation from one sesquiterpene studied,<sup>36</sup> it appears

that biogenic NMOC chemistry plays a dominant role in the chemistry of the lower troposphere over much of the U.S., and also in many other locations in the world. Worldwide the abundance of biogenic NMOCs makes them an important control on the OH radical concentration and, through this reactive radical species, on the tropospheric lifetimes of other organic compounds, including the long-lived greenhouse gas methane.

The mechanisms by which plants emit NMOCs have only relatively recently received attention.<sup>37–43</sup> Isoprene formation in leaves is linked with photosynthesis<sup>39,41–43</sup> and its emission represents a loss of fixed carbon from the plant; its production has been proposed to aid in thermal protection of the plant leaf.<sup>42,43</sup> Emissions of *cis*-3-hexen-1-ol, which provides the smell of newly cut grass, and *cis*-3-hexenyl acetate appear to occur as a result of “wounding”<sup>39,42</sup> and may attract insects as well as have antimicrobial activity.<sup>39,42</sup> Emissions of monoterpenes appear to play a role as antiherbivores,<sup>39,43</sup> while sesquiterpene emissions have been proposed to occur as a result of herbivore damage and act as an attractant for predatory insects.<sup>37,38</sup>

Because earlier studies focused on the emissions of isoprene and monoterpenes from vegetation, the environmental parameters affecting their emissions have been most studied. As noted above, isoprene emission is linked to photosynthesis with negligible amounts being stored in the leaves, and hence the isoprene emission rate reflects its formation rate. The isoprene emission rate is a function of light intensity and temperature.<sup>43–46</sup> The isoprene emission rate increases with light intensity up to a photosynthetically active radiation intensity of ~1000 μmol m<sup>-2</sup> s<sup>-1</sup> (reasonably bright sunlight), above which the emission rate becomes constant, and increases with temperature up to a value of ~40 °C, above which the emission rate is reported to decrease rapidly due to denaturing of the biosynthetic enzymes.<sup>43–46</sup> In contrast, most monoterpene-emitting plant species have a monoterpene reservoir pool and emissions then reflect the leaf-air flux, which is affected primarily by temperature.<sup>45–48</sup> For those plants with a monoterpene pool, emissions occur throughout a 24 h period, with the temperature dependence of the emission rate being similar to the

temperature dependence of the vapor pressure, increasing by a factor of  $\sim 2.5$  for a  $10^\circ\text{C}$  temperature increase.<sup>45–48</sup> However, studies in the Mediterranean region of Europe have shown that *Quercus ilex* L. (Holm Oak) emits monoterpenes (in contrast to most Oak species which are isoprene emitters) and that the monoterpene emissions from *Q. ilex* L. are both light intensity and temperature dependent and are linked to photosynthesis,<sup>49,50</sup> indicating a negligible or small reservoir pool.

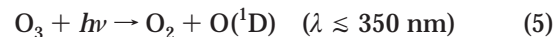
## Tropospheric Loss Processes for Biogenic NMOCs

As with other volatile organic compounds, the potential removal and transformation processes for NMOCs emitted from vegetation are wet and dry deposition, photolysis, reaction with the hydroxyl (OH) radical, reaction with the nitrate ( $\text{NO}_3$ ) radical, and reaction with ozone ( $\text{O}_3$ ).<sup>51</sup> Reaction with chlorine (Cl) atoms may also be important in certain locales during certain times of the year, as observed for anthropogenic NMOCs in the Arctic during the early springtime.<sup>52</sup> For most NMOCs, dry and wet deposition are probably of minor importance, though these physical removal processes could be important for the chemically long-lived methanol and for certain biogenic NMOC reaction products. Because of absorption of short-wavelength solar radiation by  $\text{O}_2$  and  $\text{O}_3$  in the stratosphere, photolysis in the troposphere requires the NMOC to absorb radiation of wavelengths  $\geq 290$  nm and is expected to be potentially important for aldehydes and ketones, and hence for many of the biogenic NMOC reaction products. The processes leading to the presence of  $\text{O}_3$ , OH radicals, and  $\text{NO}_3$  radicals, in the troposphere are briefly discussed below.

**Presence of  $\text{O}_3$  in the Troposphere.** Because of the presence of high mixing ratios of  $\text{O}_3$  in the stratosphere, there is net transport of  $\text{O}_3$  by eddy diffusion from the stratosphere into the troposphere.<sup>53,54</sup> In addition,  $\text{O}_3$  is formed photochemically in the troposphere from the interactions of NMOCs and oxides of nitrogen ( $\text{NO} + \text{NO}_2$ ;  $\text{NO}_x$ ) in the presence of sunlight<sup>53,54</sup> (see reactions 1–4). These sources of tropospheric  $\text{O}_3$  are balanced by in situ photochemical destruction and by dry deposition at the Earth's surface.<sup>53,54</sup> The result of these processes is the presence of ozone throughout the troposphere with mixing ratios at "clean" remote sites at ground level in the range of 10–40 ppb,<sup>53,55</sup> and with  $\text{O}_3$  mixing ratios in polluted urban areas often exceeding 100 ppb. While those biogenic NMOCs containing  $>\text{C}=\text{C}<$  bonds can react with  $\text{O}_3$ , in the presence of NO net  $\text{O}_3$  formation will result from the atmospheric reactions of NMOCs. This net  $\text{O}_3$  production occurs because  $\text{R}\dot{\text{O}}_2$  and  $\text{HO}_2$  radicals, intermediates formed from all of the important atmospheric reactions of NMOCs, convert NO to  $\text{NO}_2$  (reactions 3 and 4) and hence lead to  $\text{O}_3$  production (reactions 1 and 2).

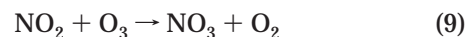
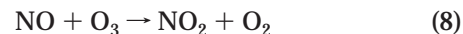
**Formation of Hydroxyl Radicals in the Troposphere.** The presence of relatively low levels of  $\text{O}_3$  in the troposphere is extremely important, because photolysis of  $\text{O}_3$

at wavelengths  $\geq 290$  nm occurs in the troposphere to form the excited oxygen,  $\text{O}(^1\text{D})$ , atom.<sup>56</sup>  $\text{O}(^1\text{D})$  atoms are either deactivated to ground-state oxygen,  $\text{O}(^3\text{P})$ , atoms or react with water vapor to generate OH radicals.<sup>56</sup>



Recent direct spectroscopic measurements of OH radical concentrations at close to ground level<sup>57–59</sup> showed peak daytime OH radical concentrations in the range  $(2–10) \times 10^6$  molecule  $\text{cm}^{-3}$  at two mid-latitude northern hemisphere sites during August and September. A diurnally, seasonally, and annually averaged global tropospheric OH radical concentration of  $1.0 \times 10^6$  molecule  $\text{cm}^{-3}$  (24 h average) has been estimated from the emissions, atmospheric concentrations, and atmospheric chemistry of methyl chloroform.<sup>60,61</sup> While the photolysis of  $\text{O}_3$  results in the formation of OH radicals only during daylight hours, it has been suggested that OH radical formation from the reactions of  $\text{O}_3$  with alkenes (including biogenic alkenes such as the monoterpenes) during both daytime and nighttime could be significant<sup>62</sup> (see the discussion below of the  $\text{O}_3$  reaction mechanisms).

**Formation of Nitrate Radicals in the Troposphere.** The presence of NO in the troposphere from natural and anthropogenic sources is followed by the reactions<sup>56</sup>



leading to the formation of the  $\text{NO}_3$  radical. Because the  $\text{NO}_3$  radical photolyzes rapidly, with a lifetime due to photolysis of  $\sim 5$  s for overhead sun, and reacts rapidly with NO,<sup>56</sup>  $\text{NO}_3$  radical concentrations remain low during daylight hours but can increase to measurable levels during nighttime. Measurements made over the past  $\sim 20$  years show nighttime  $\text{NO}_3$  radical concentrations at or near ground level over continental areas ranging up to  $1 \times 10^{10}$  molecule  $\text{cm}^{-3}$  [a mixing ratio of 430 parts per trillion (ppt)].<sup>63–65</sup> A 12 h average nighttime concentration of  $5 \times 10^8$  molecule  $\text{cm}^{-3}$  (20 ppt mixing ratio) has been proposed as a reasonable value for lifetime calculations.<sup>66</sup>

## Lifetimes of Biogenic Organic Compounds in the Troposphere

Rate constants for the gas-phase reactions of many of the NMOCs emitted from vegetation with OH radicals,  $\text{NO}_3$  radicals, and  $\text{O}_3$  have been measured,<sup>66–75</sup> and the measured rate constants can be combined with assumed ambient tropospheric concentrations of OH radicals,  $\text{NO}_3$  radicals, and  $\text{O}_3$  to calculate the lifetimes of the NMOCs with respect to each of these loss processes (as shown in Table 2 for selected biogenic NMOCs). The data shown

**Table 2. Calculated Tropospheric Lifetimes for Selected Biogenic NMOCs with Respect to Gas-Phase Reaction with OH Radicals, NO<sub>3</sub> Radicals, and O<sub>3</sub>**

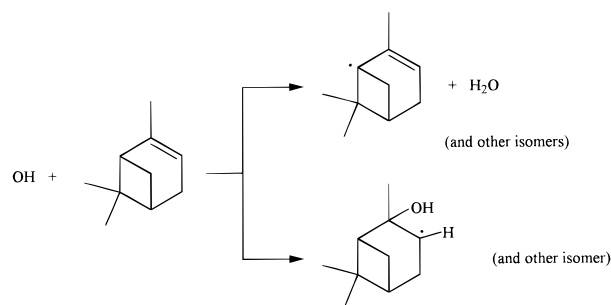
biogenic VOC	lifetime <sup>a</sup> for reaction with		
	OH	NO <sub>3</sub>	O <sub>3</sub>
isoprene	1.4 h	1.6 h	1.3 days
camphene	2.6 h	1.7 h	18 days
3-carene	1.6 h	7 min	11 h
limonene	50 min	5 min	2.0 h
myrcene	40 min	6 min	50 min
$\beta$ -phellandrene	50 min	8 min	8 h
$\alpha$ -pinene	2.6 h	11 min	4.6 h
$\beta$ -pinene	1.8 h	25 min	1.1 day
sabinene	1.2 h	7 min	4.6 h
$\beta$ -caryophyllene	40 min	4 min	2 min
longifolene	3.0 h	1.6 h	>33 days
methanol	12 days	~1 yr	>4.5 yr
2-methyl-3-buten-2-ol	2.1 h	8 days	1.7 day
<i>cis</i> -3-hexen-1-ol	1.3 h	4.1 h	6 h
linalool	50 min	6 min	55 min
1,8-cineole	1.0 days	1.5 yr	>4.5 yr
<i>cis</i> -3-hexenyl acetate	1.8 h	4.5 h	7 h
6-methyl-5-hepten-2-one	55 min	9 min	1.0 h

<sup>a</sup> Time for decay of compound to 1/e of its initial concentration, assuming concentrations (molecule cm<sup>-3</sup>) of OH, 12 h daytime average of  $2.0 \times 10^6$ , NO<sub>3</sub>, 12 h nighttime average of  $5 \times 10^8$ , and O<sub>3</sub>, 24 h average of  $7 \times 10^{11}$ .

in Table 2 indicate that many of the NMOCs emitted from biogenic sources (including isoprene, monoterpenes, sesquiterpenes, hexene derivatives, linalool, and 6-methyl-5-hepten-2-one) are highly reactive in the troposphere, with calculated lifetimes of a few hours or less. Also noteworthy is that for two of the sesquiterpenes for which data are available ( $\beta$ -caryophyllene and  $\alpha$ -humulene)<sup>75</sup> the reactions with O<sub>3</sub> result in lifetimes of ~2 min at a 30 ppb mixing ratio of O<sub>3</sub>, meaning that if these two sesquiterpenes are emitted from vegetation, they will be rapidly removed by reaction and be present at very low concentrations in the atmosphere. The highly reactive nature of many of the biogenic NMOCs explains the difficulties encountered in reconciling biogenic NMOC emission inventories calculated from measured emission rates with the observed ambient concentrations of these compounds.

In addition to the data shown in Table 2, rate constants (and hence tropospheric lifetimes) are available for certain of the products of the tropospheric degradation reactions of biogenic NMOCs, and specifically for methyl vinyl ketone, methacrolein, and 3-methylfuran (products formed from isoprene) and for camphenilone, caronaldehyde, 4-acetyl-1-methylcyclohexene, pinonaldehyde, nopinone, and sabinaketone (products formed from camphene, 3-carene, limonene,  $\alpha$ -pinene,  $\beta$ -pinene, and sabinene, respectively).<sup>67,68,72,76–81</sup> It must be recognized that the ambient atmospheric concentrations of OH radicals, NO<sub>3</sub> radicals, and O<sub>3</sub> are variable, and those of OH and NO<sub>3</sub> radicals have pronounced diurnal profiles. The lifetimes given in Table 2 are inversely proportional to the OH radical, NO<sub>3</sub> radical, and O<sub>3</sub> concentrations used in the calculations and should be considered as only approximations, useful, for example, in ranking the reactivity of the various biogenic NMOCs.

Scheme 1

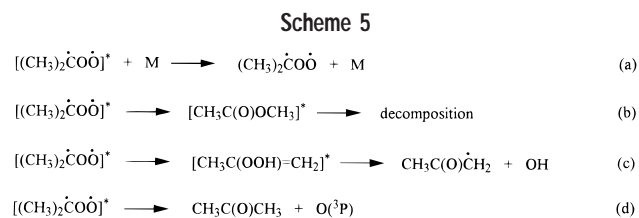
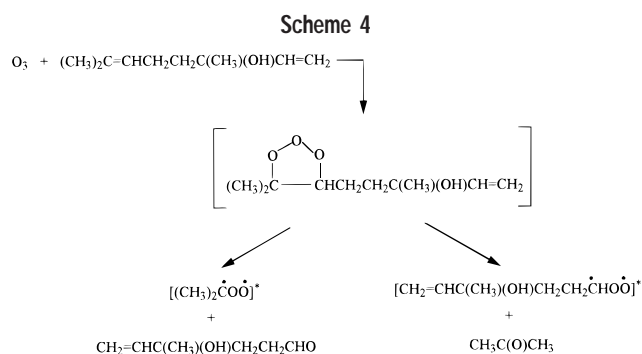
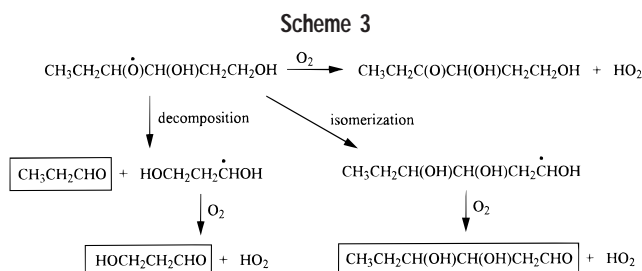
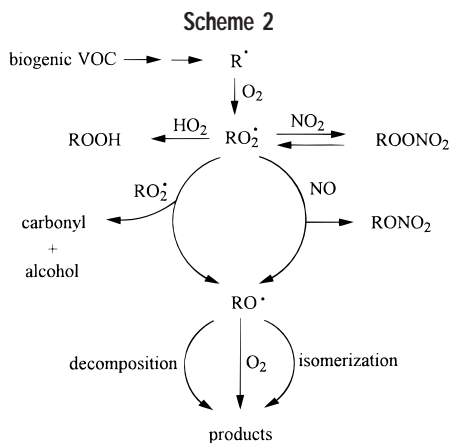


## Reaction Mechanisms and Products

The initial reactions of OH radicals, NO<sub>3</sub> radicals, and O<sub>3</sub> with NMOCs (including NMOCs of biogenic origin) have been elucidated over the past two decades,<sup>66,68,75</sup> and for biogenic NMOCs there are two general reaction mechanisms: (1) H atom abstraction by OH radicals and NO<sub>3</sub> radicals and (2) addition to carbon-carbon double bonds by OH radicals, NO<sub>3</sub> radicals, and O<sub>3</sub>. Hydrogen atom abstraction by OH radicals and NO<sub>3</sub> radicals occurs from the various C-H bonds in alkanes, ethers, alcohols, carbonyls, and esters. This reaction pathway is of minor importance for isoprene, monoterpenes, and sesquiterpenes, and for alcohols, ethers, esters, and ketones containing >C=C< bonds, but is expected to be important for aldehydes containing >C=C< bonds.<sup>66,68,75</sup> These H atom abstraction reactions lead to the formation of alkyl or substituted alkyl ( $\dot{R}$ ) radicals. The second general reaction mechanism involves addition of OH radicals, NO<sub>3</sub> radicals, or O<sub>3</sub> to >C=C< bonds in alkenes (for example, isoprene, monoterpenes, and sesquiterpenes), unsaturated alcohols (for example, *cis*-3-hexen-1-ol, linalool, and 2-methyl-3-buten-2-ol), esters (for example, *cis*-3-hexenyl acetate), and carbonyls (for example, methacrolein, methyl vinyl ketone, and 6-methyl-5-hepten-2-one). As an example of these two reaction pathways, Scheme 1 shows the reaction of the OH radical with  $\alpha$ -pinene proceeding by both H atom abstraction and initial addition to the >C=C< bond at the 2-position (note that H atom abstraction can occur from the other C-H bonds as well, and that OH radical addition can also occur at the 3-position on the >C=C< bond).

The reactions of the alkyl or substituted alkyl radicals formed after H atom abstraction from C-H bonds or after OH or NO<sub>3</sub> radical addition to >C=C< bonds are shown schematically in Scheme 2, with the reactions proceeding through the intermediary of organic peroxy ( $\dot{R}O_2$ ) and alkoxy ( $\dot{R}O$ ) radicals.<sup>68,75</sup> In the atmosphere, alkoxy radicals can decompose by C-C bond scission, isomerize by a 1,5-H shift through a six-membered transition state, and react with O<sub>2</sub>.<sup>68,75</sup> and these reactions are illustrated in Scheme 3 for the CH<sub>3</sub>CH<sub>2</sub>CH( $\dot{O}$ )CH(OH)CH<sub>2</sub>CH<sub>2</sub>OH alkoxy radical formed after OH radical addition to the carbon atom at the 3-position in *cis*-3-hexen-1-ol (the products shown in boxes have been identified and quantified or tentatively identified).<sup>82</sup>

The reactions of O<sub>3</sub> with biogenic alkenes and with other classes of NMOCs containing >C=C< bonds (for



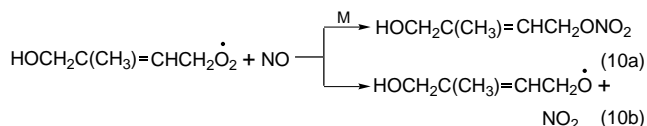
example, *cis*-3-hexen-1-ol, 2-methyl-3-buten-2-ol, and linalool) also proceed by initial  $O_3$  addition to the  $>C=C<$  bond, in this case to form a primary ozonide which rapidly decomposes to, in general, two sets of a carbonyl plus a biradical,<sup>68,75</sup> as shown in Scheme 4 for linalool,<sup>83</sup> a fragrant NMOC which contributes, for example, to the scent of orange blossoms.<sup>10</sup>

The initially energy-rich biradicals react by a number of routes (Scheme 5),<sup>75</sup> including (a) collisional stabilization to a thermalized biradical, (b) rearrangement to a "hot" ester followed by decomposition (including to  $CO_2 + RCH_3$  for biradicals of structure  $[RCH_2\dot{C}HOO]^*$ ), (c) rearrangement to a "hot" hydroperoxide followed by decomposition to an OH radical plus a substituted alkyl radical, and (d) potentially elimination of an  $O(^3P)$  atom,

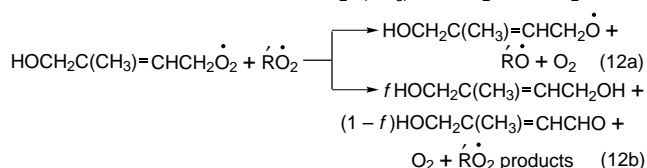
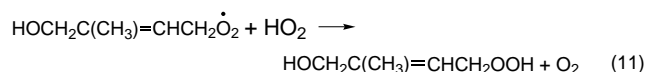
although this reaction pathway has not been observed to date from NMOCs other than from *trans*-1,2-dichloroethene.<sup>75</sup>

Two recent studies<sup>84,85</sup> have confirmed earlier reports<sup>75</sup> that OH radicals are formed from the reactions of  $O_3$  with alkenes (including alkenes of biogenic origin), and the formation of OH radicals (molar yields given in parentheses) from the reactions of  $O_3$  with isoprene (0.27), monoterpenes ( $\leq 0.18$ –1.15), sesquiterpenes (0.06–0.67), *cis*-3-hexen-1-ol (0.26), *cis*-3-hexenyl acetate (0.16), linalool (0.72), and 6-methyl-5-hepten-2-one (0.75) have been measured.<sup>70,74,75,86–88</sup> Therefore, in laboratory product studies, unless OH radicals are scavenged, the  $O_3$ -alkene reaction systems involve both OH radicals and  $O_3$ , and the products observed and quantified are not applicable solely to the  $O_3$  reaction. The measured OH radical formation yields are close to unity for several of these biogenic NMOCs, generally including those NMOCs containing tri- or tetraalkyl-substituted  $>C=C<$  bonds. The reactions of  $O_3$  with alkenes and other NMOCs containing  $>C=C<$  bonds are therefore an additional source of OH radicals in the troposphere, including during nighttime,<sup>62</sup> with the importance of a particular biogenic NMOC to OH radical production depending on its ambient concentration, its OH radical formation yield, the rate constant for its reaction with  $O_3$ , and the  $O_3$  concentration.

To date, product and mechanistic studies of the atmospherically important reactions of isoprene,<sup>75,77,86,89–103</sup> several monoterpenes<sup>75,86,88,91,95,104–113</sup> (and in particular for  $\alpha$ - and  $\beta$ -pinene), sesquiterpenes including  $\beta$ -caryophyllene,<sup>87,109,114</sup> *cis*-3-hexen-1-ol,<sup>70,82,115,116</sup> linalool,<sup>70,83,117,118</sup> and 6-methyl-5-hepten-2-one<sup>73,74</sup> have been carried out at room temperature and atmospheric pressure of air. As evident from Scheme 2, the products of these reactions will depend on whether the intermediate organic peroxy ( $RO_2$ ) radicals react with NO, as shown for example for the  $HOCH_2C(CH_3)=CHCH_2\dot{O}_2$  formed after OH radical addition to the 1-position in isoprene



or react with  $HO_2$  radicals and, in laboratory situations, with organic peroxy radicals.



On the basis of the rate constants for reactions 10 and 11 and the estimated concentrations of NO and  $HO_2$  radicals in the troposphere, the reactions of  $RO_2$  radicals with NO

**Table 3. Products Observed from the Atmospheric Reactions of Isoprene**<sup>75,77,86,89,90,92,96–100,102</sup>

product	yield (%)
OH Radical Reaction (in the Presence of NO)	
methyl vinyl ketone + HCHO <sup>a</sup>	32
methacrolein + HCHO <sup>a</sup>	23
3-methylfuran	4–5
HOCH <sub>2</sub> C(CH <sub>3</sub> )=CHCHO and/or HOCH <sub>2</sub> CH=C(CH <sub>3</sub> )CHO	observed
CH <sub>2</sub> =C(CH <sub>2</sub> OH)CHO	observed
organic nitrates	~8–14
NO <sub>3</sub> Radical Reaction	
methyl vinyl ketone	3.5
methacrolein	3.5
HCHO	11
O <sub>2</sub> NOCH <sub>2</sub> C(CH <sub>3</sub> )=CHCHO and isomers	observed
O <sub>2</sub> NOCH <sub>2</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> OH and isomers	observed
O <sub>2</sub> NOCH <sub>2</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> OOH and isomers	observed
HOCH <sub>2</sub> C(CH <sub>3</sub> )=CHCHO and isomers	observed
O <sub>3</sub> Reaction	
methyl vinyl ketone	16
methacrolein	39
HCHO	90
epoxides	5
OH	27
O( <sup>3</sup> P)	<10

<sup>a</sup> These products are formed as coproducts (see the text and Scheme 6).

dominate for NO mixing ratios >10–30 ppt,<sup>53</sup> with reactions with HO<sub>2</sub> radicals dominating at lower NO mixing ratios.

The products observed from the reactions of OH radicals, NO<sub>3</sub> radicals, and O<sub>3</sub> with biogenic NMOCs are generally consistent with the reaction schemes presented above, and the individual studies should be consulted for details of the experimental methods and results obtained. The identification and, especially, quantification of many of the products observed or anticipated to be formed from these reactions (in particular, hydroxycarbonyls, dihydroxycarbonyls, hydroxynitrates and carbonylnitrates) has been and continues to be a challenging problem. During the past few years significant advances in analytical methods have enabled many of these multifunctional products to be identified, even if not yet quantified.<sup>77,82,83,101,102,111–113</sup> Analytical methods employed in these product studies, mostly carried out in large-volume (several hundred to several thousand liters) reaction chambers under static conditions at room temperature and atmospheric pressure of air, include gas chromatography (with flame ionization, mass spectrometric, and Fourier transform infrared (FTIR) detection),<sup>110</sup> in situ long-path-length FTIR spectroscopy,<sup>90,94,105,111</sup> and in situ atmospheric pressure ionization mass spectrometry.<sup>77,82,83,102,112,113</sup> Derivatization techniques have been used to identify multifunctional products (including hydroxycarbonyls) which are otherwise not amenable to gas chromatography.<sup>82,83,101</sup>

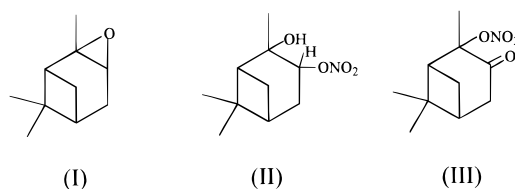
Because of space limitations, only a brief summary of the results obtained to date can be given here. Tables 3 and 4 summarize the products observed and their yields (when measured) for the reactions of OH radicals, NO<sub>3</sub> radicals, and O<sub>3</sub> with isoprene<sup>75,77,86,89,90,92,94,96–100,102</sup> (Table 3), *cis*-3-hexen-1-ol<sup>70,82</sup> (Table 4), linalool<sup>70,83</sup> (Table 4), and 6-methyl-5-hepten-2-one<sup>74</sup> (Table 4). As an example of the reactions leading to observed products

from the reaction of isoprene with the OH radical in the presence of NO, Scheme 6 shows the reactions initiated by addition of the OH radical to the 1-position, leading to formation of methyl vinyl ketone plus formaldehyde and the hydroxycarbonyls, 4-hydroxy-2-methyl-2-butenal, and/or 4-hydroxy-3-methyl-2-butenal (hydroxynitrate formation from the peroxy radical plus NO reactions has been omitted in this reaction scheme for clarity).

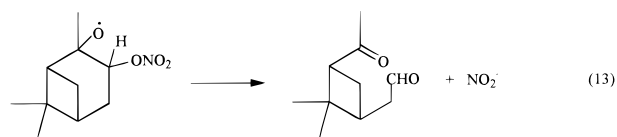
Addition of the OH radical at the 2-, 3-, and 4- positions in isoprene also occurs, leading to the formation of methyl vinyl ketone + HCHO and methacrolein + HCHO after addition at the 2- and 3-positions, respectively, and addition at the 4-position leads to methacrolein + HCHO, HOCH<sub>2</sub>C(CH<sub>3</sub>)=CHCHO, and/or HC(O)C(CH<sub>3</sub>)=CHCH<sub>2</sub>-OH, each through reaction sequences analogous to those shown in Scheme 6. Additional reactions lead to the formation of 3-methylfuran and, possibly, CH<sub>2</sub>=C(CH<sub>2</sub>-OH)CHO.<sup>75,89,92,119</sup>

The products and mechanisms of the atmospherically important reactions of the monoterpenes are not well understood,<sup>75,105–108,110–113</sup> at least in part because of the complexity of the products and the attendant difficulties in their analyses and the lack of readily available standards of the potential products. However, progress is being made.<sup>75,111–113</sup> Scheme 7 shows reactions after OH radical addition at the 2-position on  $\alpha$ -pinene (see Scheme 1) leading to products (shown in boxes) which have been either identified and quantified (pinonaldehyde) by gas chromatographic analyses<sup>106,110</sup> and in situ FTIR spectroscopy<sup>107</sup> or tentatively identified by in situ atmospheric pressure ionization tandem mass spectrometry.<sup>113</sup>

In situ FTIR spectroscopy has been used<sup>111</sup> to investigate the products formed from the reaction of the NO<sub>3</sub> radical with  $\alpha$ -pinene, and pinonaldehyde was observed as the major product together with lesser amounts of  $\alpha$ -pinene oxide (I), 2-hydroxypinan-3-nitrate (II), and 3-oxopinane-2-nitrate (III). The formation of pinonalde-



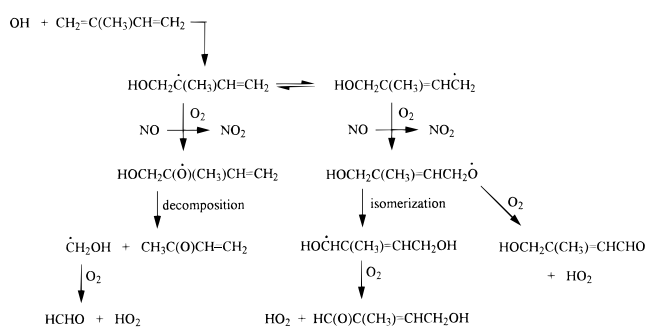
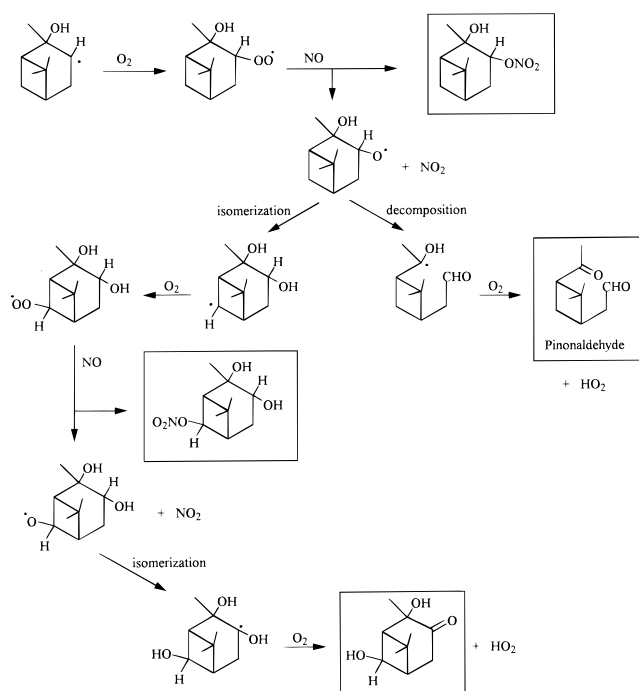
hyde, 2-hydroxypinan-3-nitrate, and 3-oxopinane-2-nitrate can be rationalized through peroxy radical + peroxy radical reactions [analogous to reactions 12a and 12b] of the intermediate nitrooxyalkyl peroxy radicals, with the nitrooxyalkoxy radical formed in the reaction analogous to reaction 12a decomposing to yield pinonaldehyde plus NO<sub>2</sub>.<sup>111</sup>



It is important to note that when NO<sub>3</sub> radicals are present at significant concentrations, NO concentrations will be

**Table 4. Products Observed and Their Molar Yields from the Gas-phase Reaction of OH Radicals, NO<sub>3</sub> Radicals, and O<sub>3</sub> with Selected Biogenic NMOCs<sup>70,74,82,83</sup>**

product	yield (%) from reaction with		
	OH	NO <sub>3</sub>	O <sub>3</sub>
<i>cis</i> -3-Hexen-1-ol			
propanal	75		49
3-hydroxypropanal	~48		~33
CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CH <sub>2</sub> CH <sub>2</sub> OH or isomer	observed		
CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH(OH)CH <sub>2</sub> CHO	observed		
OH			26
Linalool			
acetone	51	23	21
CH <sub>2</sub> =CHC(CH <sub>3</sub> )(OH)CH <sub>2</sub> CH <sub>2</sub> CHO	46	19	85
6-methyl-5-hepten-2-one	7		
(CH <sub>3</sub> ) <sub>2</sub> C(ONO <sub>2</sub> )C(O)CH <sub>2</sub> CH <sub>2</sub> C(CH <sub>3</sub> )(OH)CH=CH <sub>2</sub>		observed	
5-ethenyldihydro-5-methyl-2(3 <i>H</i> )-furanone			13
HCHO			36
OH			72
6-Methyl-5-hepten-2-one			
acetone	71		30
CH <sub>3</sub> C(O)CH <sub>2</sub> CH <sub>2</sub> CHO	59		82
OH			75

**Scheme 6****Scheme 7**

very low and organic peroxy radicals will react with HO<sub>2</sub> radicals and/or organic peroxy radicals,<sup>66</sup> and that while organic peroxy + organic peroxy radicals appear to dominate in laboratory NO<sub>3</sub> radical reaction systems,<sup>111</sup>

the reactions of organic peroxy radicals with HO<sub>2</sub> radicals to form hydroperoxides may dominate in the atmosphere.<sup>66</sup>

Concurrently with studies of the atmospheric chemistry of the biogenic NMOCs emitted into the atmosphere, kinetic and product studies have been carried out for a few of the atmospheric reaction products of isoprene and monoterpenes (methyl vinyl ketone,<sup>67,68,72,77,96,120,121</sup> methacrolein,<sup>67,68,72,77,96,120,122</sup> 3-methylfuran,<sup>76,78,89</sup> camphenilone,<sup>123</sup> caronaldehyde,<sup>79–81</sup> 4-acetyl-1-methylcyclohexene,<sup>123</sup> pinonaldehyde,<sup>79–81</sup> nopinone,<sup>123</sup> and sabinaketone<sup>81</sup>), and these references should be consulted for details.

## Conclusions

Emissions of non-methane organic compounds from vegetation and other biogenic sources are to a large extent comprised of compounds containing unsaturated carbon-carbon double bonds. Biogenic NMOCs react with OH radicals, and many of them also react rapidly with NO<sub>3</sub> radicals and O<sub>3</sub> and have calculated lifetimes in the troposphere of a few hours or less. While the kinetics of the gas-phase reactions of biogenic NMOCs with OH radicals, NO<sub>3</sub> radicals, and O<sub>3</sub> appear to be reasonably well understood, the products formed from these reactions and the detailed reaction mechanisms are less well-known. In large part, this is because of the lack of analytical methods for the identification and quantification of labile multifunctional products formed from these reactions.

However, substantial progress has been made during the past few years, and additional progress is expected soon. As mentioned above, studies of the atmospheric chemistry of first-generation products of isoprene and monoterpenes have been carried out, and at least for isoprene, a reasonably complete detailed reaction mechanism describing its atmospheric chemistry is available.<sup>119</sup> Ambient measurements of isoprene and of its first- and second-generation products have been made,<sup>33–35</sup> and these show consistency with the laboratory kinetic and

product data. Laboratory and ambient air data obtained over the past few years have not altered earlier conclusions that biogenic NMOC emissions play an important role in the chemistry of the planetary boundary layer<sup>25,26</sup> and contribute to the formation of ozone in urban<sup>30</sup> and rural<sup>25</sup> areas. Furthermore, recent studies indicate that several biogenic NMOCs (monoterpenes and sesquiterpenes) can contribute significantly to secondary organic aerosol formation through gas/particle partitioning of their tropospheric reaction products.<sup>36</sup>

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