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Significance of HO_x and peroxides production due to alkene ozonolysis during fall and winter: A modeling study

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Abstract. In an attempt to identify new mechanisms for the generation of oxidants during fall and winter, we carried out a modeling investigation in which ozonolysis reactions of alkenes that were primarily anthropogenic in origin were considered. Our results indicate that the ozonolysis reactions of these molecules can be the major sources of HO_x, H_2O_2, and organic peroxides during the night and therefore especially during dark seasons. These O_3-initiated oxidation reactions produce more peroxy radicals than those initiated by HO or NO_3. This increase in RO_2 also results in an increase in HO, HO_2, and H_2O_2. The direct HO formation pathways by ozonolysis of alkenes can form more HO radicals than that from the reaction of $O(^1D) + H_2O$ during the dark seasons. This additional source of HO can augment significantly atmospheric oxidation. H_2O_2 formation by ozonolysis also appears to be the most important dark season tropospheric sources of this oxidant. Our modeling results suggest that the existence of pollutant hydrocarbons and trace amount of biogenically produced terpenes can also lead to important production of HO_x, H_2O_2, and organic peroxides. Substantially enhanced gas-phase production of H_2O_2 and organic peroxides due to ozonolysis reactions can cause significant liquid-phase oxidation of S(IV) to S(VI), and hence the role of ozonolysis reactions can be important for the sulfur conversion studies.

1. Introduction

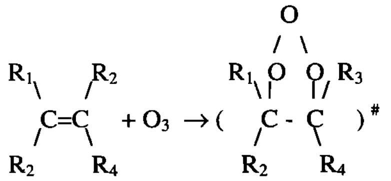
The HO_x ($HO + HO_2$) radicals, together with H_2O_2, play a major role in the oxidation reactions in the atmosphere. The most reactive member of them, the HO radical, is the primary daytime cleanser of the troposphere including destruction of hydrocarbons. It is widely believed that HO is formed as the result of photolysis of tropospheric ozone by solar radiation of wave lengths shorter than about 420 nm, producing electronically excited $O(^1D)$, which reacts with water vapor:

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \qquad (1)$$

$$O(^1D) + H_2O \rightarrow 2\,HO. \qquad (2)$$

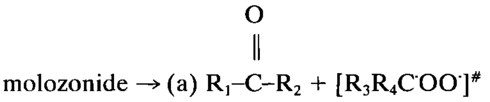
However, during the late fall and winter this and other photolysis reactions slow down.

Among various classes of organic compounds in the atmosphere, the alkenes, due to their double bonds, are unique in exhibiting significant reactivity toward ozone as well as toward the HO radical. This reaction of ozone with alkenes is called ozonolysis. Ozonolysis reactions do not require any light to be initiated, and hence they can occur all day long and through all seasons. These reactions are suggested to be competitive with the daytime HO initiated reactions and the nighttime NO_3 radical reactions as a sink for alkenes in the troposphere [*Seinfeld and Pandis*, 1998]. Numerous researchers have studied gas-phase ozonolysis reactions over the last 3 decades. The following reaction is known to be the first step of addition reaction of O_3 to the double bond:

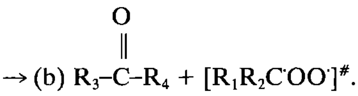


(molozonide). (3)

The primary ozonide or molozonide undergoes a decomposition reaction forming a carbonyl compound and a biradical which is called a Criegee intermediate:



$$\text{molozonide} \rightarrow \text{(a) } R_1\text{–}\overset{\displaystyle O}{\overset{\|}{C}}\text{–}R_2 + [R_3R_4C^{\cdot}OO^{\cdot}]^{\#} \qquad (4)$$



$$\rightarrow \text{(b) } R_3\text{–}\overset{\displaystyle O}{\overset{\|}{C}}\text{–}R_4 + [R_1R_2C^{\cdot}OO^{\cdot}]^{\#}. \qquad (5)$$

The two reaction pathways (a and b) are considered to be of equal importance [*Atkinson and Carter*, 1984], and this leads to one mole of carbonyl compound and one mole of biradical. However, later studies show that for asymmetric alkenes, this may be an oversimplification [e.g., *Atkinson et al.*, 1995; *Grosjean and Grosjean*, 1998]. The fate of the Criegee biradical has also been extensively studied (e.g., *Niki et al.*, 1983; *Atkinson*, 1994; *Horie and Moortgat*, 1991; *Grosjean et al.*, 1994; *Thomas et al.*, 1995; *Neeb et al.*, 1995]. The initially energetically rich Criegee radical may either be stabilized collisionally or undergo unimolecular or bimolecular dissociations. Unimolecular dissociation channels can also lead to the direct formation of HO radicals which were observed extensively in various laboratory studies [e.g., *Niki et al.*, 1983; *Hakola et al.*, 1994; *Atkinson et al.*, 1995; *Paulson and Orlando*, 1996],

$$[R_1CH_2C^{\cdot}(R_2)OO^{\cdot}]^{\#} \rightarrow [R_1CH{=}C(OOH)R_2]^{\#}$$
$$\rightarrow R_1CHC(O)R_2 + HO^{\cdot}. \qquad (6)$$

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Table 1. List of Chemical Species in This Version of MOCCA

Group	Gas Phase Species
Oxygen	O_3, O_2, O, $O(^1D)$
Hydrogen	HO, HO_2, H_2O, H_2O_2
Nitrogen	N_2, NO, NO_2, NO_3, N_2O_5, HNO_2, HNO_3, HNO_4, NH_3
Sulfur	SO_2, SO_3 (H_2SO_4)
C_1 carbon	CH_4, CH_3OO, CH_3OOH, HCHO, HCOOH, CO, CO_2
Higher hydrocarbons	Alkanes: C_2H_6, C_3H_6, n-C_4H_{10}, iso-C_4H_{10}, n-C_5H_{12}, i-C_5H_{12}, generic higher alkanes
	Alkyne: C_2H_2
	Aromatics: C_6H_6 (representing unsubstituted aromatics), C_6H_5-CH_3 (toluene, representing substituted aromatics)
	Alkenes: C_2H_4, C_3H_6, 1-C_4H_8, C_4H_6 (1,3-butadiene), i-C_4H_8, (E)-2-C_4H_8, (Z)-2-C_4H_8, 1-C_5H_{10}, (E)-2-C_5H_{10}, (Z)-2-C_5H_{10}, C_5H_{10} (2-methyl 1-butene), 1-C_6H_{12}, (E)-2-C_6H_{12}, (Z)-2-C_6H_{12}, C_5H_8 (isoprene), $C_{10}H_{16}$ (terpene), generic higher alkenes
	Others: (aldehydes/ketones, organonitrates, PAN-type molecules, hydroperoxides and peroxyhydroperoxides, and organic acids, as well as alkoxy and alkylperoxy radicals): CH_3OOOH, RCH_2O, RCH_2OO, RCH_2OOH, RC(O)OOH, RCHO, RCH_2ONO_2, $RC(O)OONO_2$

The stabilized Criegee biradicals can also react with a few atmospheric species such as H_2O, NO, NO_2, SO_2, CO, other aldehydes, or may undergo unimolecular isomerization [*Niki et al.*, 1983; *Finlayson-Pitts and Pitts*, 1986; *Seinfeld and Pandis*, 1998]. Additional to aqueous production of peroxides, H_2O_2 may also be formed in the ozonolysis of isoprene and simple alkenes under humid conditions as reported by *Becker et al.* [1990], *Simonaitis et al.* [1991], *Hewitt and Kok* [1991], *Neeb et al.* [1997], and *Sauer et al.* [1999], through reactions such as

$$R_1R_2C'OO + H_2O \rightarrow R_1R_2C(OH)OOH$$
$$\rightarrow R_1C(O)R_2 + H_2O_2. \qquad (7)$$

In search for new sources of oxidants during dark seasons, we carried out a study that uses a box model in which the so-called "traditional" reactions, as well as the gas-phase ozonolysis reactions of alkenes, have been incorporated. Many reactive hydrocarbons such as anthropogenic alkenes are found to show seasonal variations [e.g., *Penkett et al.*, 1993; *Blake et al.*, 1993], so that their highest mixing ratios are observed during winter, when the photochemistry is slowed down, while the lowest mixing ratios occur during the summertime. Thus the ozonolysis reactions of anthropogenic alkenes can be more pronounced during the wintertime. Hereby, we present results on the importance of HO_x and peroxides formation due to the ozonolysis reactions in (1) a typical urban/suburban and (2) a remote rural continental setting during the late fall/winter.

2. Model Description

In this study, we used the box model Model of Chemistry Considering Aerosols (MOCCA), which was created to investigate the chemistry of the marine boundary layer. The details of our model have been described elsewhere [*Sander and Crutzen*, 1996]. The model was adapted for the continental (urban/suburban and remote continental) boundary layer. In this paper, we concentrated on gas-phase reactions, and hence heterogeneous reactions occurring in aerosols were not considered. This version of MOCCA includes 120 gas-phase, 19 photolysis reactions, and 38 emissions and depositions. The temperature and relative humidity were set to $T = 283$ K and $\varphi_v = 76\%$, respectively. Photolysis rates were calculated at a latitude of 45°N. Model runs were initiated on Julian day (JD) 314 and lasted for 2 weeks. Photolysis rates were varied according to the solar declination and were calculated using *Brühl and Crutzen* [1989] model for a cloud-free sky and an ozone column of 300 Dobson units (DU). Both assumptions tend to overestimate the production of OH by photolysis of ozone. However, the main emphasis of this study is to show that HO_x formation in fall and winter is mainly determined by ozonolysis.

The species incorporated in the model are listed in Table 1, and the emission fluxes and depositions velocities along with initial concentrations of certain species are tabulated in Tables 2, 3 and 4, respectively. The photolysis and gas-phase reactions in the model are given in Tables 5 and 8. Figure 1 gives a schematic of gas-phase interactions of selected key reactions in our model. Here we summarize important features of our chemical scheme. The tropospheric chemistry is complex, and in this study we intended to grasp the general chemical processes by classifying molecules into groups; however, we paid particular attention to detailed information on processes involving major identified compounds and primary pollutants. With respect to hydrocarbon chemistry, four classes of mole-

Table 2. Emission Fluxes

Molecule	Urban/Suburban	Remote Area
NO	1.0×10^{11}	1.0×10^9
SO_2	5.0×10^{10}	···
NH_3	2.5×10^{10}	2.5×10^{10}

Given in units of molecules s^{-1} cm^{-2}.

Table 3. Dry Deposition Velocity v_d

Molecule	v_d, cm s^{-1}
O_3	1.0
H_2O_2	1.0
NO_2	0.6
N_2O_5	2.0
HNO_3	2.0
RCH_2OOH	0.5
CH_3OOH	0.5
HCHO	1.0
HCOOH	1.0
SO_2	1.0

cules were incorporated which were identified by *Singh and Zimmermann* [1992] as the primary anthropogenic hydrocarbons. These groups are (1) alkanes (ethane, propane, n-butane, 2-methyl butane, n-pentane, 2-methyl pentane, and a generic alkane representing those containing more than five carbons); (2) alkenes (including 16 individual mono- and di-alkenes and generic alkenes for more than five carbon atoms); (3) alkyne (grouped in one category and represented by ethyne); and (4) aromatics (unsubstituted and substituted represented by benzene and toluene, respectively). The primary reactions of these hydrocarbons were dealt with in detail. Reactions in the methane and carbon monoxide oxidation cycles were also treated in detail. However, for nonmethane hydrocarbons, their intermediates have been lumped by combining different alkyl groups into a generic R (i.e., RO and RO_2). Secondary reactions lead to formation of molecules such as aldehydes (or ketones), alcohols, carboxylic acids, peroxides and hyperoxides, organic nitrates, and peroxycarboxylic nitrates. The further reactions of these secondary products were also considered (see Table 8). The product yield for RO_2 formation as the result of NO_3-initiated reactions is assumed to be unity [*Paulson and Orlando*, 1996]. The primary reactions of hydrocarbon are summarized as follows.

Table 4. Initial Mixing Ratios for a Series of Compounds

Molecule[a]	Urban[b]/Suburban, nmol/mol	Remote Site, nmol/mol
O_3	2.5×10^1	2.5×10^1
NH_3	3.3	3.3
NO_2	0.2	0.2
CH_4	1.8×10^3	1.8×10^3
CO	2.0×10^2	2.0×10^2
CO_2	3.5×10^5	3.5×10^5
HCHO	0.3	0.3
C_2H_6	3.2 ± 1.7	4.2 ± 1.0
C_3H_8	2.5 ± 1.6	2.7 ± 0.8
n-C_4H_{10}	3.0 ± 5.6	1.1 ± 0.3
i-C_4H_{10} (2-methyl propane)	1.0 ± 1.6	0.4 ± 0.1
n-C_5H_{12}	0.7 ± 0.8	0.7 ± 0.8
i-C_5H_{12} (2-methyl butane)	1.2 ± 1.7	0.5 ± 0.2
Alkanes ($C > 5$)[c]	1.0	0.5
C_6H_6	0.5 ± 0.2	0.2 ± 0.01
C_6H_5-CH_3 (toluene)	2.0 ± 1.4	0.2 ± 0.1
C_2H_2	1.8 ± 0.9	0.6 ± 0.1
C_2H_4	2.0 ± 1.4	0.5 ± 0.1
C_3H_6	0.5 ± 0.4	0.1 ± 0.01
C_4H_6 (1,3-butadiene)	$(8.0 \pm 6.0) \times 10^{-2}$	$(1.0 \pm 0.1) \times 10^{-2}$
iso-C_4H_8	$(1.6 \pm 2.0) \times 10^{-1}$	$(2.0 \pm 1.0) \times 10^{-2}$
(E)-2-C_4H_8	$(8.0 \pm 1.8) \times 10^{-2}$	$(3.6 \pm 1.0) \times 10^{-3}$
(Z)-2-C_4H_8	$(1.1 \pm 3.1) \times 10^{-1}$	$(3.4 \pm 1.0) \times 10^{-3}$
1-C_4H_8	$(1.0 \pm 1.2) \times 10^{-1}$	$(2.0 \pm 0.4) \times 10^{-2}$
1-C_5H_{10}	$(4.0 \pm 5.0) \times 10^{-2}$	$(9.0 \pm 2.0) \times 10^{-3}$
(E)-2-C_5H_{10}	$(3.0 \pm 5.0) \times 10^{-2}$	$(7.0 \pm 4.0) \times 10^{-3}$
(Z)-2-C_5H_{10}	$(5.0 \pm 9.0) \times 10^{-2}$	$(4.0 \pm 1.0) \times 10^{-3}$
C_5H_{10} (2-methyl 1-butene)	$(6.0 \pm 8.0) \times 10^{-2}$	$(5.0 \pm 3.0) \times 10^{-3}$
1-C_6H_{12}	$(2.0 \pm 2.0) \times 10^{-2}$	$(8.0 \pm 2.0) \times 10^{-3}$
(E)-2-C_6H_{12}	$(1.0 \pm 1.0) \times 10^{-2}$	$(1.0 \pm 1.0) \times 10^{-2}$
(Z)-2-C_6H_{12}	$(1.0 \pm 1.0) \times 10^{-2}$	$(1.0 \pm 0.1) \times 10^{-3}$
C_5H_8 (isoprene)	$(3.0 \pm 2.0) \times 10^{-2}$	$(2.0 \pm 0.1) \times 10^{-3}$
Alkenes ($C > 5$)[c]	5.0×10^{-3}	2.0×10^{-3}

[a] Alkane and alkene mixing ratios were kept constant during modeling runs. These are the average values from field measurement, and reported uncertainties correspond to one standard deviation (1σ).

[b] For urban sites, since the air is much less homogenous than remote sites, we observe wider distribution of mixing ratios leading to larger standard deviations.

[c] Values are estimated based on traces of higher alkanes and alkenes.

Table 5. Photolysis Reactions in the Gas Phase

Reaction No.	Reaction[a]
J01	$O_3 \rightarrow O(^1D) + O_2$
J02	$O_3 \rightarrow O + O_2$
J03	$H_2O_2 \rightarrow 2\ HO$
J04	$NO_2 \rightarrow NO + O_3$
J05	$NO_3 \rightarrow NO + O_2$
J06	$NO_3 \rightarrow NO_2 + O_3$
J07	$N_2O_5 \rightarrow NO_3 + NO_2$
J08	$HNO_3 \rightarrow NO_2 + HO$
J09	$CH_3OOH \rightarrow HCHO + HO_2 + HO$
J10	$HCHO \rightarrow 2\ HO_2 + CO$
J11	$HCHO \rightarrow CO$
J12	$RCHO \rightarrow CO + CH_4$
J13	$HNO_4 \rightarrow NO_2 + HO_2$
J14	$HNO_2 \rightarrow NO + HO$
J15	$RCH_2OOH \rightarrow RCH_2O + HO$
J16	$RCHO \rightarrow CO + HO_2 + CH_3OO$
J17	$RCH_2ONO_2 \rightarrow RCH_2O + NO_2$
J18	$RC(O)O_2NO_2 \rightarrow RC(O)O_2 + NO_2$
J19	$RC(O)OOH \rightarrow HO + RO_2 + CO_2$

[a] The photolysis rates are calculated using *Brühl and Crutzen* [1989] model using reference spectra from *DeMore et al.* [1997] at 45°N and an ozone column of 300 DU.

2.1. Reactions of Alkanes

HO or NO_3-initiated reactions of alkanes were included. The latter occur at night and proceed much more slowly than HO-initiated reactions of alkanes. Both HO and NO_3 reactions involve H abstraction from C–H bond in alkanes (represented as RH), forming an alkyl (R) radical which reacts rapidly with molecular oxygen forming a peroxy radical:

$$RH + HO/NO_3(+O_2) \rightarrow RO_2 + H_2O/HNO_3. \qquad (8)$$

2.2. Reactions of Aromatics

HO or NO_3-initiated reactions of aromatics proceed via two reaction pathways: (1) H abstraction from C–H bonds from the aromatic ring or for an alkyl-substituted aromatic from the alkyl substituent group. In case of nonsubstituted aromatics the efficiency of this pathway is a minor [*Seinfeld and Pandis*, 1998]. (2) The major channel (90%) involves the addition of HO radical to the aromatic ring. The H abstraction channel for aromatic compounds is very similar to those in alkanes, forming a radical (ring/substituted) which reacts rapidly with oxygen. If HO is added to the aromatic ring, the adduct can react with O_2 or NO_2. In this study, since NO_2 mixing ratios do not

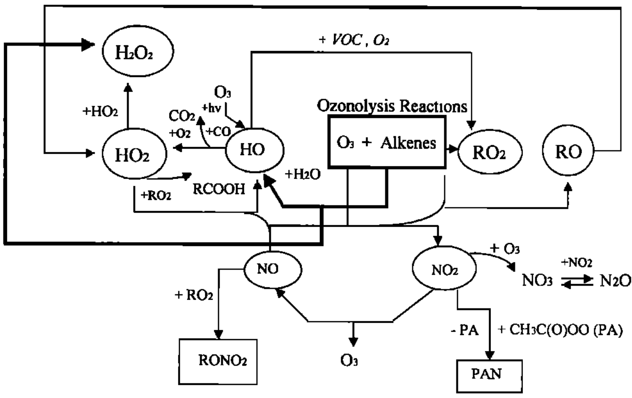

Figure 1. Simplified schematic of hydrocarbon chemistry in this model.

Table 6. Description of Modeling Runs

Run	Summary of Modeling Runs
1	base run - urban/suburban setting - no ozonolysis reactions
2	urban/suburban setting + ozonolysis reactions: $>=< + O_3 \rightarrow RCHO$
3	urban/suburban setting + ozonolysis reactions: $>=< + O_3 \rightarrow 2\ RCHO$
4	urban/suburban setting + ozonolysis reactions: $>=< + O_3 \rightarrow RCHO + RO_2$
5	urban/suburban setting + ozonolysis reactions: $>=< + O_3 \rightarrow RCHO + 2\ RO_2$
6	same as run 4, but all the ozonolysis rate constants are multiplied by 1.4
7	same as run 4, but all the ozonolysis rate constants are multiplied by 0.6
8	same as run 4, but each alkene average value was increased by one standard deviation
9	same as run 4, but each alkene average value was decreased by one standard deviation
10	urban/suburban setting + ozonolysis reactions: $>=< + O_3 \rightarrow RCHO + x \times HO$
11	urban/suburban setting + ozonolysis reactions: $>=< + O_3 \rightarrow RCHO + RO_2 + x \times HO$
12	same as run 10, but direct HO yield was increased by a factor of 2
13	same as run 10, but direct HO yield was decreased by a factor of 2
14	urban/suburban setting + ozonolysis reactions: $>=< + O_3 \rightarrow RCHO + y \times H_2O_2$
15	urban/suburban setting + ozonolysis reactions: $>=< + O_3 \rightarrow RCHO + RO_2 + y \times H_2O_2$
16	same as run 14, but H_2O_2 yields are multiplied by 2
17	same as run 14, but H_2O_2 yields are multiplied by 0.01
18	urban/suburban setting + ozonolysis reactions: $>=< + O_3 \rightarrow RCHO + RO_2 + x \times HO + y \times H_2O_2$
19	(a) urban/suburban setting + terpenes − ozonolysis reactions: $>=< + O_3 \rightarrow RCHO + 2\ RO_2 + x \times HO + y \times H_2O_2$ (b) urban/suburban setting + terpenes + ozonolysis reactions: $>=< + O_3 \rightarrow RCHO + 2\ RO_2 + x \times HO + y \times H_2O_2$
20	(a) remote setting - no ozonolysis reactions (b) remote setting + ozonolysis reactions: $>=< + O_3 \rightarrow RCHO + RO_2 + x \times HO + y \times H_2O_2$

exceed 10 nmol/mol, the NO_2 addition reaction to adduct was neglected. Hence it is assumed that through the HO addition reactions to the ring, both H abstraction and addition channels lead to formation of a peroxy group (RO_2):

$$\text{aromatic} + HO/NO_3(+O_2) \rightarrow RO_2 + H_2O/HNO_3. \qquad (9)$$

2.3. Reactions of Alkenes

Owing to the presence of the double bond in alkenes, the addition of an oxidant such as HO, NO_3, or O_3 to the double bond is the preferred reaction pathway leading to a complex reaction scheme starting with the formation of a peroxy radical:

$$>C{=}C< + HO/NO_3/O_3 \rightarrow RO_2. \qquad (10)$$

For NO_3 reactions, as pointed out by *Atkinson* [1991], a nitroperoxy radical can be formed. Being a peroxy radical, this was treated as a normal RO_2. Ozonolysis reactions, the focus of this study, will be dealt with in detail in the discussion section. To avoid potential complications due to detailed treatment of dienes, we treated all alkenes as mono-alkenes.

2.4. Reactions of Alkynes

$$-C{\equiv}C- + HO/NO_3 \rightarrow RO_2. \qquad (11)$$

The addition of HO and NO_3 is thought to be the major reaction pathway [*Atkinson*, 1991]. From the rapid addition of O_2, we considered RO_2 as the primary product of these reactions.

For brevity, we describe only some important secondary reactions involving peroxy radicals, the reactions of peroxy radicals with NO and HO_2, as well as their reactions with themselves (i.e., self-reactions).

$$RCH_2OO + NO \rightarrow RCH_2O + NO_2 \qquad (12a)$$

$$\rightarrow RCH_2ONO_2 \text{ (organic nitrates)} \qquad (12b)$$

$$RCH_2OO + HO_2 \rightarrow RCH_2OOH + O_2 \qquad (13)$$

$$RCH_2OO + RCH_2OO \rightarrow 2\ RCH_2O + O_2. \qquad (14)$$

The two pathways considered of the RCH_2O radicals are

$$RCH_2O + O_2 \rightarrow RCHO + HO_2 \qquad (15)$$

$$RCH_2O + O_2 \rightarrow CH_2O + RCH_2OO \qquad (16)$$

$$RCHO + HO/NO_3(+O_2) \rightarrow RC(O)O_2 + H_2O/HNO_3. \qquad (17)$$

Photolysis reactions of aldehydes were also included (see Table 5). $RC(O)O_2$ can react with NO, HO_2, and NO_2 or go through self-reactions. Addition of NO_2 forms a peroxy carboxylic nitrate (PAN-type compound):

$$RC(O)O_2 + NO_2 \leftrightarrow RC(O)OONO_2. \qquad (18)$$

This molecule in turn reacts with HO or can photodissociate. The detailed reaction scheme for secondary reactions is given in Table 8.

3. Results and Discussion

The purpose of our study was to examine the impact of ozonolysis reactions of alkenes on the chemistry of the continental boundary layer. For this we compared chemistry occurring in our box model with and without ozonolysis reactions (pathways indicated by thicker lines in Figure 1). Hydrocarbon mixing ratios were based on field data obtained during late fall and early winter in urban/suburban and remote continental regions and thus represent average hydrocarbon concentrations. We kept hydrocarbons and ozone constant at values as given in Table 4. Emission fluxes for NO, SO_2, and NH_3 were chosen to represent measured values of these compounds in the field and/or calculated values through modeling studies [*Seila et al.*, 1989; *Shim and Carmicheal*, 1991; *Chameides et al.*, 1992; *Sander and Crutzen*, 1996; B. Kieser and J. Rudolph, personal communication, 1996; D. Plummer, personal communication, 1996]. We carried out the modeling runs for 2 weeks in order to let the system reach a steady state so that the results would not have been affected by the choice of initial concentrations of various species. Table 6 summarizes the major modeling runs presented in this paper.

3.1. Base Run

The base run (run 1) includes all gas-phase reactions given in Tables 5 and 8 with the exception of the ozonolysis of alkenes, and reactions involving sulfur-containing compounds and terpenes. The time series for selected molecules during this run are shown in Figure 2. It is noteworthy that RO_2 radicals are produced mainly at night through reactions of alkenes with NO_3 leading to a peak. Secondary reactions of RO_2 produce more HO_2 at night than photochemistry during the day.

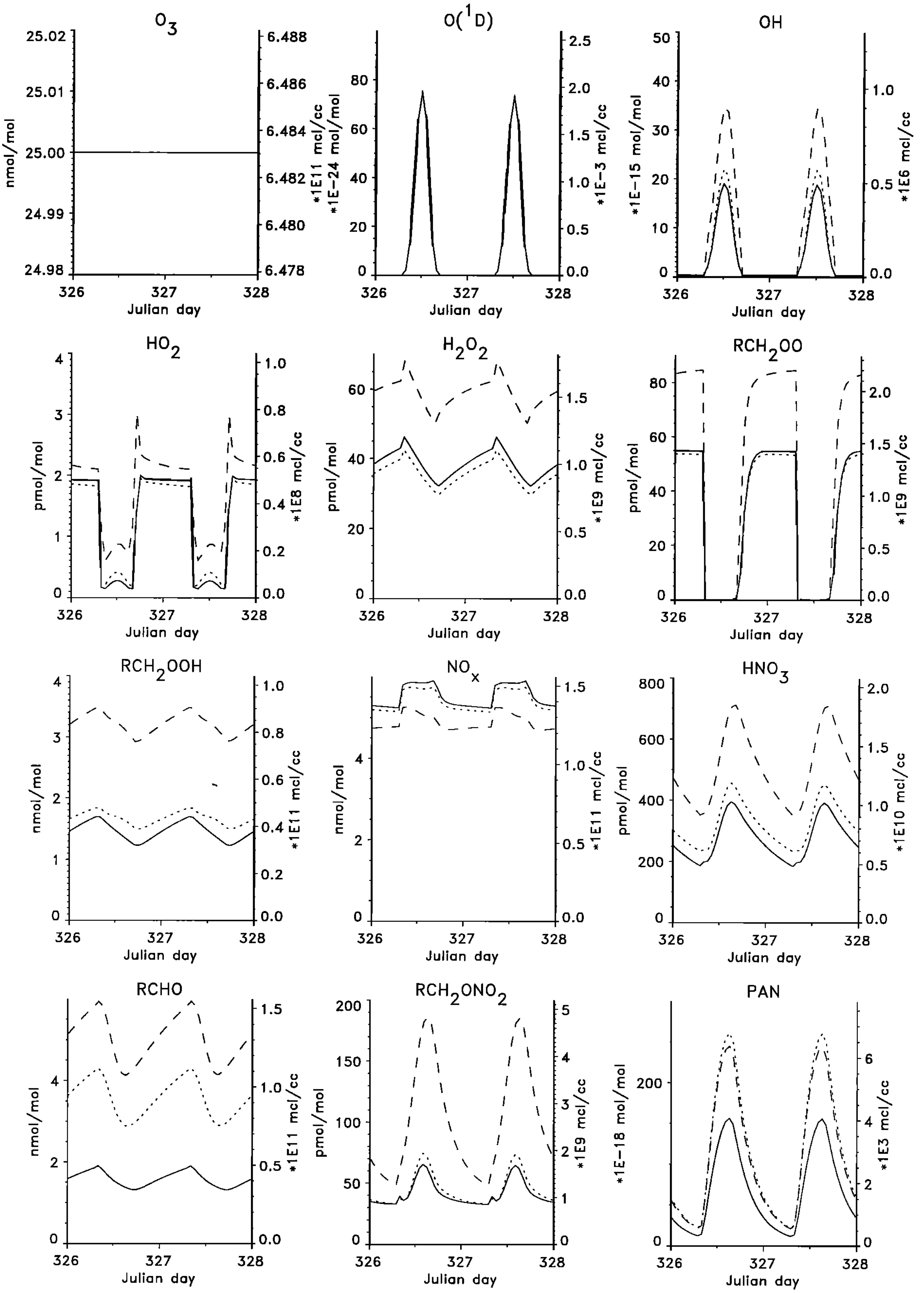

Figure 2. Selected species in run 2 (dotted line) and run 4 (dashed line) compared to the base run (solid line) during the last 2 days of 14-day modeling runs.

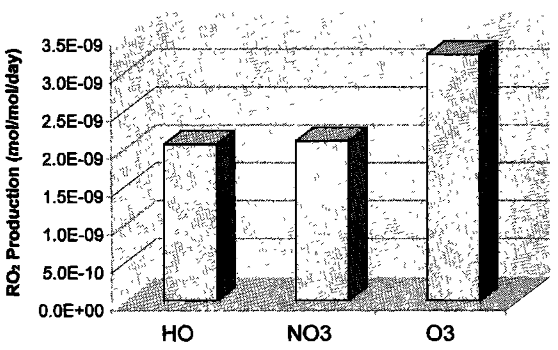

Figure 3. Comparison in RO_2 formation due to O_3, HO, and NO_3 reactions.

3.2. Additional Formation of Carbonyl and RO_2 Compounds

3.2.1. Run 2: $>=< + O_3 \rightarrow R_1R_2C{=}O$. Laboratory studies have generally confirmed the production of one mol of carbonyl per mol of O_3 and alkene reacted. In run 2 we included ozonolysis reactions of alkenes producing only one mol of a carbonyl compound ($>=< + O_3 \rightarrow R_1R_2C{=}O$). From this point on, it is assumed to be an aldehyde. Figure 2 compares selected results from run 2 with the base run. As a steady state ozone mixing ratio was assumed (Table 4), no difference in $O(^1D)$ concentration was observed among the base run and sensitivity runs herein and after (Figure 2). Our results indicate that additional aldehyde reaction with HO radicals forming peroxy and acyl peroxy (R–C(O)OO) radicals that will have an enhanced indirect effect on the formation of HO. An HO increase of about 20% is obtained as depicted in Figure 2. The NO_x ($NO + NO_2$) mixing ratio also decreases due to the secondary reaction of peroxy and acyl peroxy radicals with NO and NO_2, leading to the formation of organonitrates and peroxyacetyl nitrates, respectively. Moreover, additional hydroperoxides (ROOH) are formed via $RC(O)OO + HO_2$ reaction. RO_2 and HO_2 reaction forming ROOH is more enhanced leading to higher concentration of ROOH in run 2, whereas RO_2 and HO_2 are slightly lower in run 2 compared to run 1.

3.2.2. Run 3: $>=< + O_3 \rightarrow 2\ R_1R_2C{=}O$. In addition to one mol of carbonyl compound, the formation of one mol of the Criegee biradical was generally confirmed experimentally. Its ultimate fate, particularly for the larger alkenes, is yet to be investigated. Up to now, literature laboratory results on ozonolysis of simple alkenes suggest that there are several possible reaction pathways, including stabilization of the energetic Criegee radial and formation of organic peroxy radicals, in the presence of oxygen. The reaction channel efficiency for these pathways is different for different alkenes. The stabilized Criegee can react further with atmospheric water, NO, NO_2, SO_2, and CO leading to the formation of aldehydes (major product), ketones, and organic acids [*Seinfeld and Pandis*, 1998]. In this study, we did not consider ketones and organic acids due to the secondary reactions of stabilized Criegee, and only concentrated on aldehydes, the major commonly observed products. In run 3 we considered that the Criegee radical leads to the ultimate formation of an additional carbonyl compound. Run 3 demonstrates even more enhanced impact of additional aldehyde formation, compared to run 2, consistent with the chemistry described above.

3.2.3. Run 4: $>=< + O_3 \rightarrow R_1R_2C{=}O + RO_2$. We herein considered that the excited Criegee radical leads to the formation of RO_2 radicals (run 4). We assumed a molar efficiency of unity for this reaction, a reasonable assumption considering that many transient products may undergo secondary reactions leading to the formation of additional peroxy radicals. The results of this run for selected compounds are depicted in Figure 2 and are compared to the base run. We note an increase in HO concentration by up to a factor of 2. This is due to secondary reactions of peroxy radicals leading to a major increase in the formation rates of HO and HO_2 (see Tables 5 and 8). This leads to a notable increase by 10% in H_2O_2. The additional RO_2 will also react with NO decreasing NO_x concentration and leading to the formation of $RONO_2$ and PAN-type compounds. As secondary reactions may lead to the formation of more than one mol of RO_2 (with smaller R groups than the parent compound), we carried out run 5, in which the ozonolysis reaction was assumed to produce two mols of RO_2 (run 5: $>=< + O_3 \rightarrow R_1R_2C{=}O + 2\ RO_2$). These results are also shown in Figure 2 indicating that secondary RO_2 formation can enhance significantly the HO_x formation.

3.2.3.1. Comparison among RO_2 production from HO, NO_3, and O_3 reactions: Figure 3 compares the accumulated daily RO_2 production formed as the result of ozonolysis reactions with those formed by HO- as well as NO_3-initiated reactions for run 4. Note that we assumed 100% RO_2 formation as the result of NO_3-initiated reactions of all hydrocarbons. In many studies, RO_2 was not formed from NO_3 reaction of hydrocarbons hence the RO_2 due to NO_3 reactions reported here is an upper bound on RO_2 production resulting from NO_3-initiated reactions. The amount of RO_2 formation per day due to ozonolysis is significantly more than that due to HO and NO_3 reactions.

3.2.3.2. Sensitivity studies on rate constants: To take into account the uncertainties associated with rate constant measurements of ozonolysis reactions, we varied all these rate constants in runs 6 and 7 by a factor of 0.6 and 1.4, respectively. The results of these runs, shown in Figure 4a, indicate a high degree of sensitivity to the values of rate constants over the range of values reported in various laboratory studies. At the same time, we note that, even in run 6, we can observe a clear increase in HO_x formation relative to the base run. Thus our results revealing the importance of ozonolysis reactions hold up despite the uncertainties in rate constants.

3.2.3.3. Sensitivity studies on the mixing ratios of alkenes: In this study, we used the average measurements for two consecutive years of alkenes on York University campus, Toronto (B. Kieser, personal communication, 1996). To avoid any influence of outliers biasing the mean values, we excluded all data outside 3 σ range. We carried out a series of sensitivity runs in which the average mixing ratios for each given alkene was varied by $\pm 1\ \sigma$. The values of standard deviations for each compound are given in Table 4. Figure 4b shows the results of runs 8 and 9 in which the mixing ratios were increased and decreased by one standard deviation for each compound, respectively. Even in the lower limit of range of mixing ratios, contribution of alkenes to an increase of HO_x is quite significant.

3.3. HO Formation

Laboratory studies suggest from alkene ozonolysis that HO can be formed as the result of secondary reactions of Criegee radicals [e.g., *Niki et al.*, 1983; *Donahue et al.*, 1998], via reac-

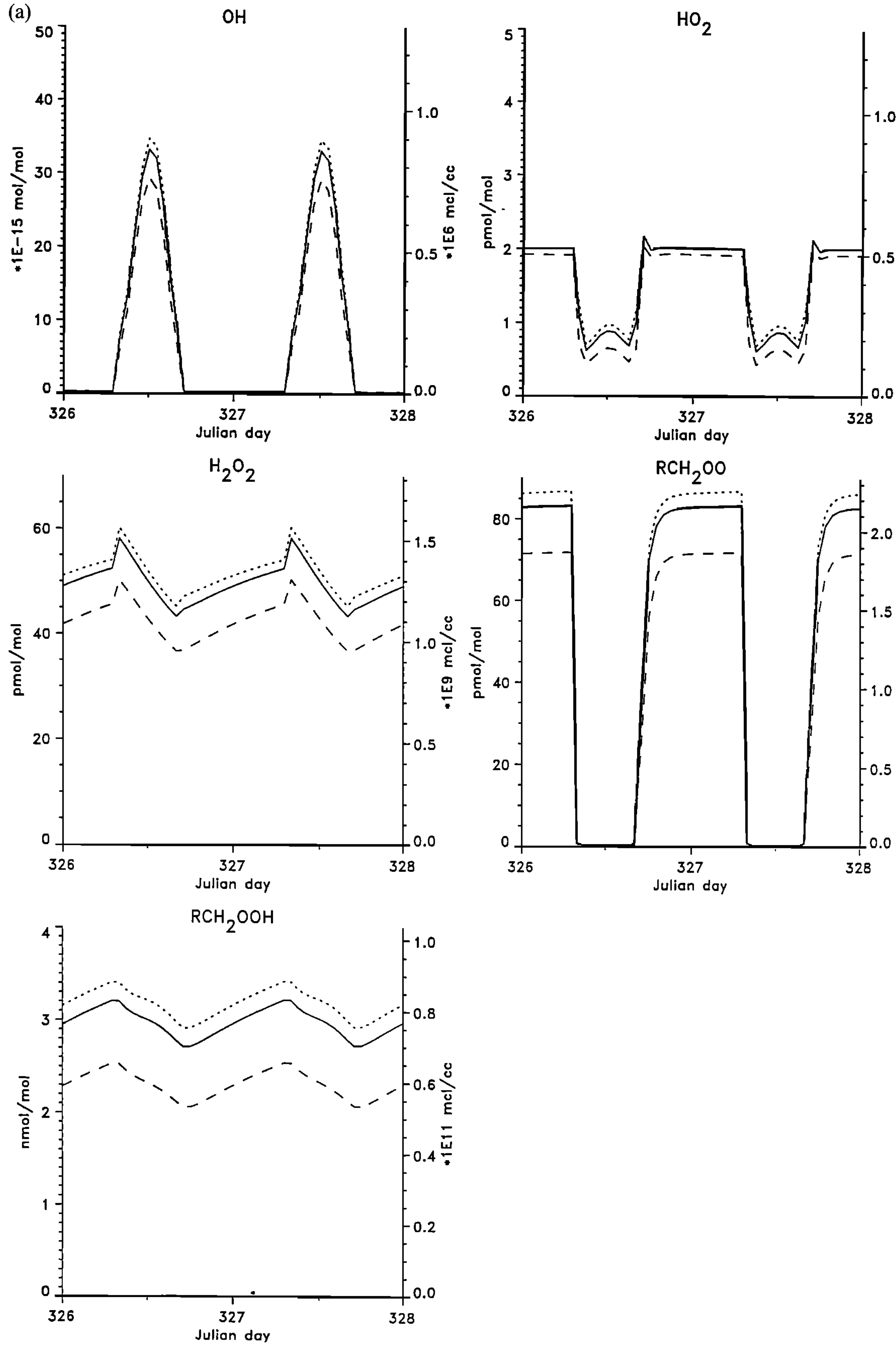

Figure 4. (a) Sensitivity studies on the rate constant of ozonolysis reactions: run 6 (dotted line) and run 7 (dashed line) are compared with run 4 (solid line). (b) Sensitivity studies on the mixing ratios of alkenes: run 8 (dotted line) and run 9 (dashed line) compared to run 4 (solid line).

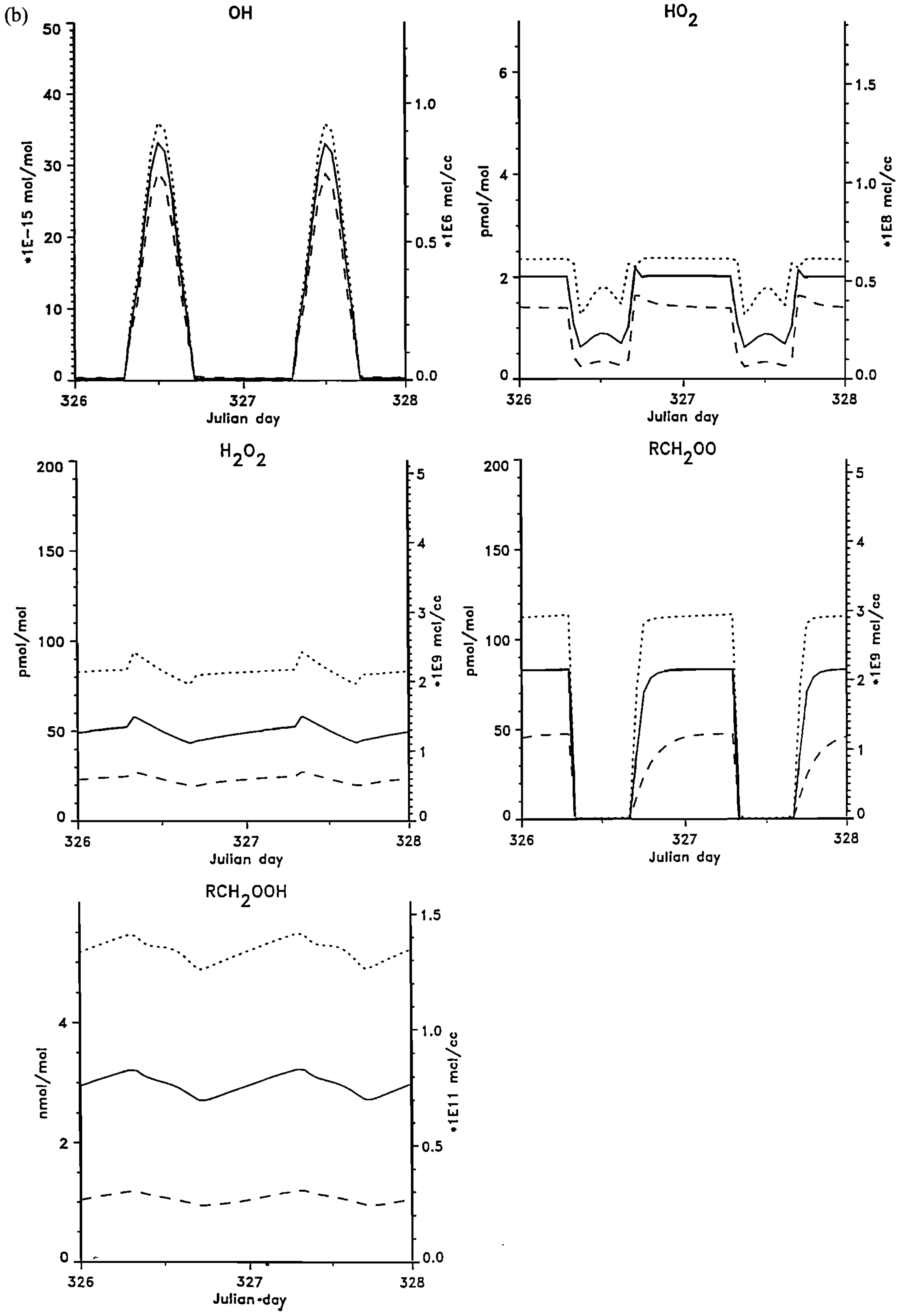

Figure 4. (continued)

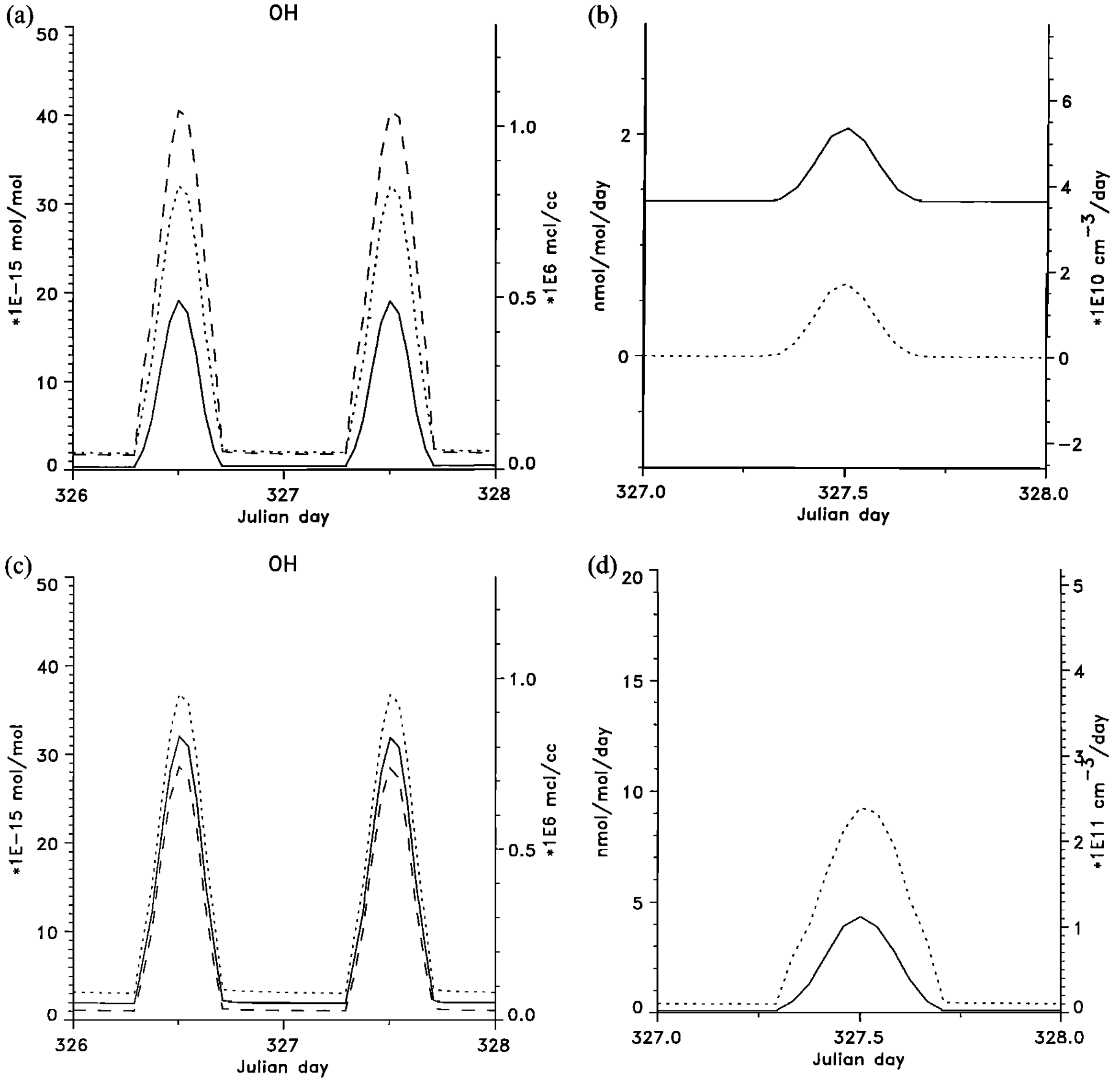

Figure 5. (a) HO concentration calculated from run 10 (dotted line) and run 11 (dashed line) are compared with run 1 (solid line). (b) Comparison of rate of HO production channels in runs 10 and 1: The area between solid line (run 1) represents the rate of HO formation due to the reaction of $O(^1D)$ with water ($d[HO]/dt = 2 \times k_{G207} \times [O(^1D)] \times H_2O$). The area between the dashed line and the axis (run 10) represents the sum of HO production due to the ozonolysis and the reaction of $O(^1D)$ with water ($d[HO]/dt = 2 \times k_{G207} \times [O(^1D)] \times H_2O + \Sigma((\text{HO yield}) \times [\text{alkene}] \times [O_3])$). (c) Sensitivity studies on HO yield due to ozonolysis reactions: run 12 (dotted line) and run 13 (dashed line) are compared with the run 10 (solid line). (d) Effect of additional direct HO formation channels on further depletion of hydrocarbons. Hydrocarbon loss equal to $\Sigma k_{HO} \times [HO] \times [\text{hydrocarbon}]$ is shown for run 11 and compared to the base run. (e) Relative contribution of individual alkenes to HO production.

tions such as (6). Despite the large body of supporting evidence for HO formation channels as the result of ozonolysis reactions, the existence of this reaction pathway was also questioned in the literature by some researchers [*Schafer et al.*, 1997]. However, the majority of the recent ozonolysis studies confirm the existence of HO radicals [*Atkinson*, 1998]. We have carried out several simulations in which the impact of direct HO formation channels under various conditions was evaluated. Here we only focus on two runs (10 and 11). In Run 10, ozonolysis reactions result in the production of HO (run 10: $>=< + O_3 \rightarrow R_1R_2C{=}O + x \times HO$; where $0 < x < 1$ and x is the product yield of HO). Run 11 considers ozonolysis reactions that produce HO as well as one mol of carbonyl compound and one mol of peroxy radicals (run 11: $>=< + O_3 \rightarrow R_1R_2C{=}O + RO_2 + x \times HO$). The results of runs 10 and 11 are depicted in Figure 5a and are compared to the base run. This suggests that HO concentration can be enhanced up to three times (run 11) due to this direct HO production channel, compared to the base run. Low concentration of HO was observed at night in these runs in contrast to the complete absence of nocturnal HO in the base run. The concentration of nocturnal HO reaches values up to 5×10^4 molecule cm^{-3} in run 11.

3.3.1. Comparison of rates for the HO production channels. Figure 5b compares HO concentration for run 10 with the base run. The integrated rate of HO formation as the result

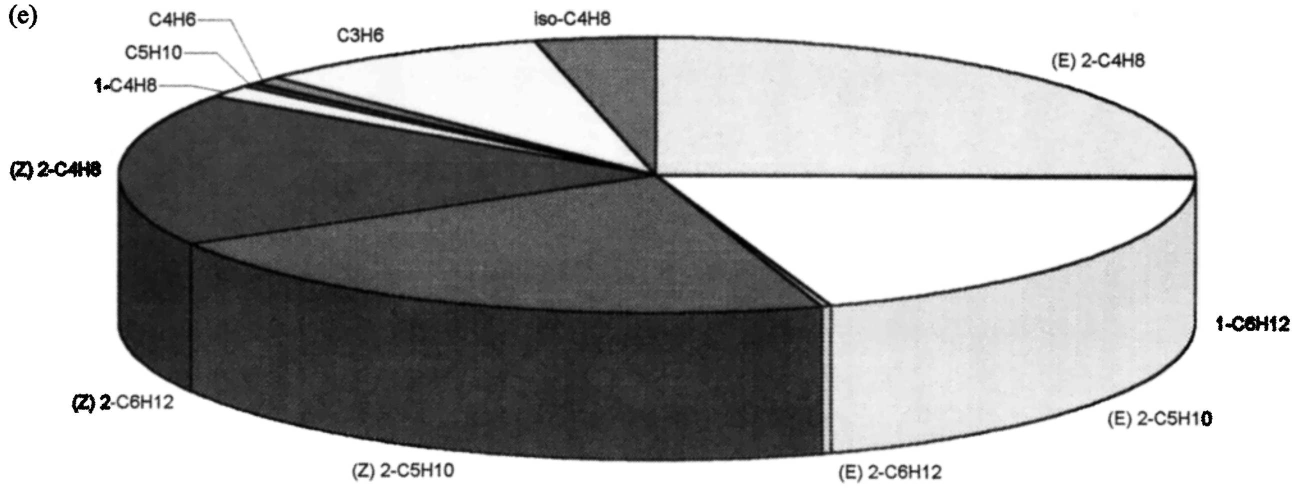

Figure 5. (continued)

of the reaction of $O(^1D) + H_2O$ (reaction G201 in Table 8) is compared to those in which asides from G201, the direct HO formation from ozonolysis reactions, were also included. Figure 6b clearly shows that the HO formed as the result of ozonolysis is a much greater source of HO than the reaction of $O(^1D) + H_2O$. This is in addition to the extra HO obtained as the result of extra RO_2 formed in the course of ozonolysis reactions (see Table 8).

3.3.2. Sensitivity runs for HO yields. It is commonly accepted in the literature that HO is formed as the result of ozonolysis reaction of alkenes; however, there are still differences in the reported values of HO yields. Recently, *Atkinson* [1990] provided a review on this subject. To verify how differences reported in HO yield affect our results, we carried out a series of sensitivity runs in which HO yields (x) reported in Table 7 were varied by a factor of 2. Maximum branching ratio was set equal to unity. Figure 5c shows the results of runs 12 and 13 compared to run 1. This indicates that even when we decreased the HO yield by a factor of 2, we still observed an additional 40% increase in HO concentration compared to the base run, and a nocturnal HO concentrations up to 2×10^4 cm^{-3}. Hence our major conclusions regarding the importance of the ozone-alkene chemistry is valid even when the effects of reasonable uncertainties in the input data of HO yields are considered.

3.3.3. Impact of the direct HO formation channel on further oxidation of hydrocarbons. Figure 5d illustrates the impact of the additional HO formation channel due to the ozonolysis of alkenes on the oxidation of hydrocarbons comparing the accumulated product of HO-initiated reaction rate of hydrocarbons (k_{HO}) and hydrocarbon mixing ratios (i.e., $k_{HO} \times$ [hydrocarbon]) in run 11 and the base run. The daily accumulated impact of primary HO-initiated hydrocarbon degradation channel is significantly enhanced by a factor of 2.7 in run 11 relative to the base run. The ozonolysis reactions thus appear to not only play an important role in the destruction of alkenes, but also may influence substantially further HO-initiated destruction of all tropospheric hydrocarbons including species containing oxygen, nitrogen, halogens, and sulfur.

3.3.4. Individual contributions of alkenes to HO production. Figure 5e shows the results of the accumulated daily production of HO due to each individual alkene considered in this study. Our results suggest that (E) and (Z) 2-butene and (E) and (Z) 2-pentene are the major contributors to direct hydroxyl radical formation, even though their atmospheric mixing ratios are determined to be much less abundant than those of smaller alkenes (see Table 8). This is due to the faster ozonolysis reaction rate constant of internal alkenes, as electron-donating groups (such as the methyl group) tend to enhance ozonolysis rate constants. It is noteworthy that our conclusions for the dark seasons agree well with *Paulson and Orlando*'s [1996] studies where they simulated HO_x (defined as "$HO + RO_2 + HO_2$") formation capability of alkene ozonolysis under summer conditions.

3.4. H_2O_2 Production Channels

The formation of hydrogen peroxide as the result of ozonolysis reactions was reported by several researchers [e.g., *Becker et al.*, 1990; *Hewitt and Kok*, 1991; *Simonaitis et al.*, 1991; *Sauer et al.*, 1999]. Upon the addition of water vapor in many ozonolysis reactions of alkenes, the formation of molecules such as hydrogen peroxides, formic acid, and hydroperoxides were observed [e.g., *Neeb et al.*, 1997; *Sauer et al.*, 1999]. The yields of H_2O_2 in ozonolysis reaction systems were less extensively studied compared to those of HO, and the agreement between the existing results is poor. For instance, *Simonaitis et al.* [1991] reported H_2O_2 yield in the reactions of ozone with trans-2-butene and isoprene of 0.16 and 0.09, respectively, whereas *Becker et al.* [1990] obtained yields of 0.005 and 0.001 for these reactions. For those reactions where the H_2O_2 yields were not published, estimated values were used (G. Moortgat et al., personal communication, 1996). Table 7 depicts the used product yields.

We conducted two runs (runs 14 and 15): run 14: ($>=< + O_3 \rightarrow R_1R_2C{=}O + y \times H_2O_2$), and run 15: ($>=< + O_3 \rightarrow R_1R_2C{=}O + RO_2 + y \times H_2O_2$), where $0 < y < 1$ and y is the product yield of H_2O_2 formation due to the ozonolysis reaction of a given alkene. The results of these simulations are reported in Figure 6a and are compared to the base run. The increase in hydrogen peroxide in this case is conclusively due to ozonolysis, which is the major gas-phase source of H_2O_2. Our calculated hydrogen peroxide mixing ratios due to ozonolysis reactions agree with the winter measurement of gaseous H_2O_2 (<0.1 to 1.0 nmol/mol) over the south central United States by *Van Valin* [1987]. They are also within agreement with winter measurement of gaseous hydrogen peroxide (<2.4 nmol/mol and generally <1 nmol/mol) in the east coast of the United States [*Barth*, 1989]. Figure 6b shows the integrated rate of H_2O_2 formation as the result of the reaction G206 (base run) compared to those in which asides from this reaction, the direct H_2O_2 formation from ozonolysis reactions (run 14) were also included. This figure illustrates the importance of ozonolysis reactions in the formation of hydrogen peroxide.

Since there exists a large discrepancy in the reported H_2O_2 yields, we carried out two runs (runs 16 and 17) in which the H_2O_2 yield given in Table 7 was varied by a factor of 2 and 0.01. The latter represents the lowest values of H_2O_2 production ever reported for any ozonolysis reaction. Results of these runs compared to the base run indicate that even the smallest reported H_2O_2 yields from ozonolysis can increase the atmospheric mixing ratio of H_2O_2 by ~20%.

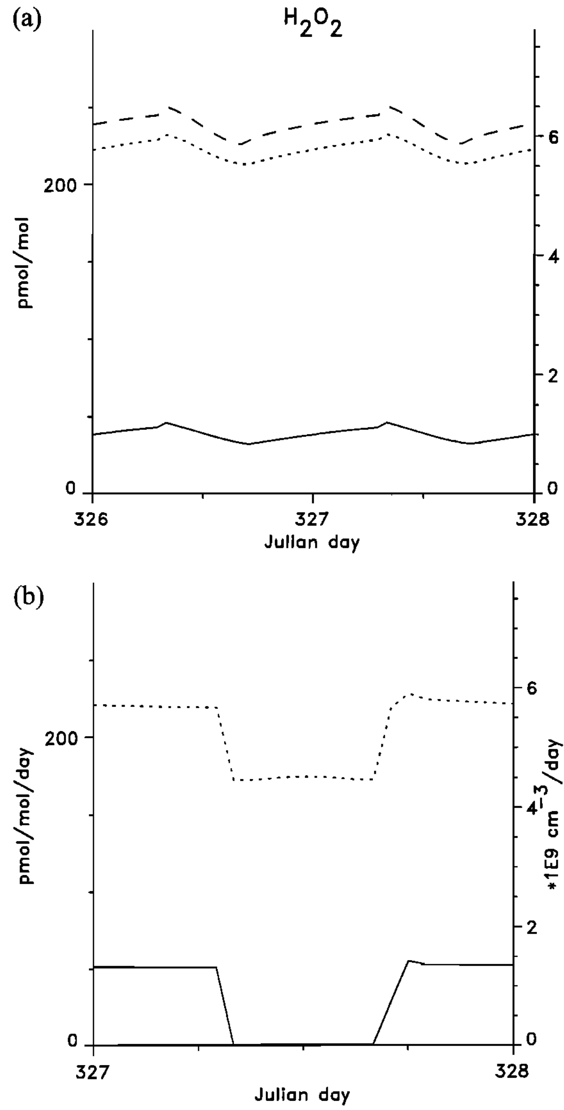

Figure 6. (a) H_2O_2 concentration for run 14 (dotted line) and run 15 (dashed line) are compared to run 1 (solid line). (b) Comparison of H_2O_2 production in run 14 (area between dashed line and the axis, and $d[H_2O_2]/dt = (k_{G206} \times [HO_2] \times [HO_2] + \Sigma((H_2O_2 \text{ yield}) \times [\text{alkene}] \times [O_3]))$, to the base run (the hatched area between the solid line and the axis, and $d[H_2O_2]/dt = k_{G206} \times HO_2 \times HO_2$).

Table 7. HO and H_2O_2 Yield in Alkene + O_3 System

Alkene	HO Yield,[a] %	H_2O_2 Yield, %
C_2H_4	0.12	0.00[b]
C_3H_6	0.33	0.02[b]
1-C_4H_8	0.41	0.06[c]
iso-C_4H_8	0.84	0.06[c]
(E) 2-C_4H_8	0.41	0.06[d]
(Z) 2-C_4H_8	0.64	0.09[e]
C_4H_6 (1,3-butadiene)	0.08	0.06[c]
1-C_5H_{10}	0.37	0.06[c]
(E) 2-C_5H_{10}	0.41	0.06[c]
(Z) 2-C_5H_{10}	0.64	0.06[c]
C_5H_{10} (2-methyl 1-butene)	0.7	0.06[c]
C_5H_8 (isoprene)	0.27	0.09[e]
1-C_6H_{12}	0.32	0.06[c]
(E) 2-C_6H_{12}	0.37	0.06[c]
(Z) 2-C_6H_{12}	0.32	0.06[c]
$C_{10}H_{16}$ (terpene)	0.54	0.09[e]

[a] *Atkinson* [1998].
[b] *Becker et al.* [1993].
[c] G. Moortgat et al. (personal communication, 1996).
[d] *Hewitt and Kok* [1991].
[e] *Simonaitis et al.* [1991].

3.5. Concurrent Formation of HO and H_2O_2

Existing laboratory studies have mostly been targeted to measure either HO or H_2O_2 yields individually, as laboratory studies suggest that the HO and H_2O_2 formation pathways may be different (reactions (6) and (7)). The former is generated via the excited Criegee biradical, and the latter is generated through the stabilized Criegee biradical reactions. A modeling run was designed to investigate the importance of simultaneous HO and H_2O_2 along with RO_2 formation in the ozonolysis reaction. As such, the reaction for each alkene was written (see Table 4, run 18): $>=< + O_3 \rightarrow R_1R_2C{=}O + RO_2 + x \times HO + y \times H_2O_2$, where as shown in Table 7, x and y are HO and H_2O_2 product yields. Results of this run are given in Figure 7 and are compared to the base run indicating that during winter, ozonolysis reactions are the major sources of HO_x, RO_2, and organic peroxides. For instance, H_2O_2 mixing ratios are increased by a factor 6 in run 18 compared to the base run, peaking to a value of ~240 pmol/mol in run 18.

3.6. Impact of Ozonolysis of Terpenes

Mono terpenes ($C_{10}H_{16}$) such as α- and β-pinene, myrcene, camphene, 2- or 3-sabinene, 3-carene, limonene, and α-terpinene are primarily produced via coniferous trees. As many biogenic activities slow down during winter, many biogenic hydrocarbon emissions such as those of terpenes decrease as well, but some production continues even during fall and winter. This occurs only if the branch temperature gets high enough, a condition that may be observed under sunny and low wind condition (B. Kieser, personal communication, 1996). Hence under specific conditions, terpene emissions can indeed occur in the wintertime, though much less than during summer. To our knowledge, there is no data set of terpene measurements during wintertime in midlatitude. According to the Global Emission Inventory Activity (GEIA) data set, a mall amount of terpene emission was reported during a few months in fall and winter at midlatitude locations ~45°N (e.g., eastern and western coastal regions of Canada and the United States). A mixing ratio of 30 pmol/mol (where 1 pmol/mol = 1×10^{-12} mol/mol) was used, which is similar to measured mixing ratio

Table 8. Gas-Phase Rate Constant for Added Reactions in This Version of MOCCA

Reaction No.	Reaction	n	$k^{\varnothing}$ $(\mathrm{cm}^{-3})^{1-n}$ $\mathrm{s}^{-1\mathrm{a}}$	$-E_a/R$, K	Reference
G101	$O(^1D) + N_2(+O_2) \rightarrow O_3 + N_2$	2	2.6×10^{-11}	110	*DeMore et al.* [1997]
G102	$O(^1D) + O_2(+O_2) \rightarrow O_3 + O_2$	2	4.0×10^{-11}	70	*DeMore et al.* [1997]
G201	$H_2O + O(^1D) \rightarrow 2\,HO$	2	2.2×10^{-10}	0	*DeMore et al.* [1997]
G202	$O_3 + HO \rightarrow HO_2 + O_2$	2	6.8×10^{-14}	−940	*DeMore et al.* [1997]
G203	$O_3 + HO_2 \rightarrow HO + 2O_2$	2	2.0×10^{-15}	−500	*DeMore et al.* [1997]
G204	$HO + HO_2 \rightarrow H_2O + O_2$	2	1.1×10^{-10}	250	*DeMore et al.* [1997]
G205	$H_2O_2 + HO \rightarrow HO_2 + H_2O$	2	1.7×10^{-12}	−160	*DeMore et al.* [1997]
G206	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	2	6.8×10^{-12}	note 1$^{\mathrm{b}}$	*DeMore et al.* [1997]
G301	$O_3 + NO \rightarrow NO_2 + O_2$	2	1.8×10^{-14}	−1400	*DeMore et al.* [1997]
G302	$HO_2 + NO \rightarrow NO_2 + HO$	2	8.1×10^{-12}	250	*DeMore et al.* [1997]
G303	$O_3 + NO_2 \rightarrow NO_3 + O_2$	2	3.2×10^{-17}	−2450	*DeMore et al.* [1997]
G304	$NO + NO_3 \rightarrow 2NO_2$	2	2.6×10^{-11}	170	*DeMore et al.* [1997]
G305	$NO_2 + NO_3(+M) \rightarrow N_2O_5$	3	1.3×10^{-12}	note 1	*DeMore et al.* [1997]
G306	$N_2O_5 \rightarrow NO_3 + NO_2$	1	4.3×10^{-02}	note 1	*DeMore et al.* [1997]
G307	$NO_2 + HO(+M) \rightarrow HNO_3$	2	8.8×10^{-12}	note 1	*DeMore et al.* [1997]
G395	$HNO_2 + HO \rightarrow NO_2 + H_2O$	2	4.5×10^{-12}	−390	*DeMore et al.* [1997]
G396	$HO_2 + NO_2(+M) \rightarrow HNO_4$	2	1.4×10^{-12}	note 1	*DeMore et al.* [1997]
G397	$HNO_4 \rightarrow HO_2 + NO_2$	1	3.4×10^{-01}	−10900	*Atkinson et al.* [1992]
G398	$HNO_4 + HO \rightarrow H_2O + NO_2 + O_2$	2	4.6×10^{-12}	380	*DeMore et al.* [1997]
G399	$OH + NO(+M) \rightarrow HNO_2$	2	7.4×10^{-12}	note 1	*DeMore et al.* [1997]
G401	$HCHO + HO(+O_2) \rightarrow HO_2 + CO + H_2O$	2	1.0×10^{-11}	0	*DeMore et al.* [1997]
G402	$CH_3OOH + HO \rightarrow HCHO + HO + H_2O$	2	2.2×10^{-12}	200	*DeMore et al.* [1997]
G403	$CH_3OOH + HO \rightarrow CH_3OO + H_2O$	2	5.2×10^{-12}	200	*DeMore et al.* [1997]
G404	$CO + HO(+O_2) \rightarrow HO_2 + CO_2$	2	2.4×10^{-13}	0	*DeMore et al.* [1997]
G405	$CH_3OO + CH_3OO(+O_2) \rightarrow 2HCHO + 2HO_2$	2	4.7×10^{-13}	190	*DeMore et al.* [1997]
G406	$HCHO + NO_3(+O_2) \rightarrow HNO_3 + HO_2 + CO$	2	5.8×10^{-16}	note 1	*DeMore et al.* [1997]
G407	$HCOOH + HO(+O_2) \rightarrow H_2O + HO_2 + CO_2$	2	4.0×10^{-13}	0	*DeMore et al.* [1997]
G408	$CH_4 + HO(+O_2) \rightarrow CH_3OO + H_2O$	2	6.3×10^{-15}	−1775	*DeMore et al.* [1997]
G409	$CH_3OO + NO(+O_2) \rightarrow HCHO + HO_2 + NO_2$	2	7.7×10^{-12}	280	*DeMore et al.* [1997]
G410	$CH_3OO + HO_2 \rightarrow CH_3OOH + O_2$	2	5.6×10^{-12}	800	*DeMore et al.* [1997]
G706	$SO_2 + HO(+M+O_2) \rightarrow HO_2 + H_2SO_4$	2	8.9×10^{-13}	note 1	*DeMore et al.* [1997]
G901	$C_2H_6 + HO(+O_2) \rightarrow RCH_2OO + H_2O$	2	2.4×10^{-13}	−1070	*DeMore et al.* [1997]
G903	$C_3H_8 + HO(+O_2) \rightarrow RCH_2OO + H_2O$	2	1.1×10^{-12}	−660	*DeMore et al.* [1997]
G905	n-C_4H_{10} + HO $(+O_2) \rightarrow RCH_2OO + H_2O$	2	2.5×10^{-12}	−540	*Atkinson* [1985]
G907	iso-C_4H_{10} + HO $(+O_2) \rightarrow RCH_2OO + H_2O$	2	2.4×10^{-12}	note 1	*Atkinson* [1985]
G909	n-C_5H_{12} + HO $(+O_2) \rightarrow RCH_2OO + H_2O$	2	4.1×10^{-12}	−500	*Atkinson* [1985]
G911	iso-$C_5H_{12} + HO(+O_2) \rightarrow RCH_2OO + H_2O$	2	3.9×10^{-12}	note 1	*Atkinson* [1985]
G411	alkanes + $HO(+O_2) \rightarrow RCH_2OO + H_2O$	2	7.2×10^{-12}	note 1	*Atkinson* [1986] for alkane = n-heptane
G925	C_2H_2 + HO $(+M+O_2) \rightarrow HCHO + CO + HO_2$	2	7.5×10^{-13}	note 1	*DeMore et al.* [1997]
G928	$C_6H_6 + HO \rightarrow RCH_2OO$	2	1.3×10^{-12}	−529	*Atkinson* [1985]
G977	$C_5H_6CH_3$ (toluene) + HO $(+O_2) \rightarrow RCH_2OO + H_2O$		5.0×10^{-12}	note 1	*Perry et al.* [1977]
G921	C_2H_4 + HO $(+M+O_2) \rightarrow RCH_2OO$	2	8.2×10^{-12}	note 1	*DeMore et al.* [1997]
G930	C_3H_6 + HO $(+M+O_2) \rightarrow RCH_2OO$	2	4.9×10^{-12}	−504	*Tsang* [1991]
G932	1-C_4H_8 + HO $(+M+O_2) \rightarrow RCH_2OO$	2	6.59×10^{-12}	−468	*Atkinson* [1986]
G934	iso-C_4H_8 + HO $(+M+O_2) \rightarrow RCH_2OO$	2	9.5×10^{-12}	−503	*Atkinson* [1986]
G012	(E) 2-C_4H_8 + HO $(+M+O_2) \rightarrow RCH_2OO$	2	1.09×10^{-11}	−549	*Atkinson* [1986]
G013	(Z) 2-C_4H_8 + HO $(+M+O_2) \rightarrow RCH_2OO$	2	1.1×10^{-11}	−488	*Atkinson* [1986]
G938	C_4H_6(1,3-butadiene) + $HO(+M+O_2) \rightarrow RCH_2OO$	2	1.4×10^{-11}	−468	*Atkinson* [1986]
G010	1-C_5H_{10} + HO $(+M+O_2) \rightarrow RCH_2OO$	2	3.1×10^{-11}	note 1	*Atkinson and Aschmann* [1984]
G020	(E) 2-C_5H_{10} + HO $(+M+O_2) \rightarrow RCH_2OO$	2	6.9×10^{-11}	note 1	*Ohta* [1983]
G021	(Z) 2-C_5H_{10} + HO $(+M+O_2) \rightarrow RCH_2OO$	2	6.4×10^{-11}	note 1	*Ohta* [1984]
G936	C_5H_{10} (2-methyl 1-butene) + HO $(+M+O_2) \rightarrow RCH_2OO$	2	6.5×10^{-11}	note 1	*Ohta* [1984]
G989	C_5H_8 (isoprene) + HO $(+M+O_2) \rightarrow RCH_2OO$	2	2.6×10^{-11}	−409	*Atkinson* [1986]
G015	1-C_6H_{12} + HO $(+M+O_2) \rightarrow RCH_2OO$	2	3.7×10^{-11}	note 1	*Atkinson and Aschmann* [1984]
G022	(E) 2-C_6H_{12} + HO $(+M+O_2) \rightarrow RCH_2OO$	2	same as G020	note 1	assumed
G023	(Z) 2-C_6H_{12} + HO $(+M+O_2) \rightarrow RCH_2OO$	2	same as G020	note 1	assumed
G896	$C_{10}H_{16}$ (terpene) + HO $(+M+O_2) \rightarrow RCH_2OO$	2	1.3×10^{-10}	note 1	calculated, see the text
G412	alkenes + HO $(+O_2) \rightarrow RCH_2OO$	2	3.7×10^{-11}	note 1	*Atkinson and Aschmann* [1984] for alkene = 1-hexene
G924	$C_2H_4 + O_3\ (+O_2) \rightarrow RCHO + RCH_2OO + 0.12\ HO$	2	1.7×10^{-18}	−2630	*DeMore et al.* [1997]
G931	$C_3H_6 + O_3\ (+O_2) \rightarrow RCHO + RCH_2OO + 0.02\ H_2O_2 + 0.33\ HO$	2	6.5×10^{-15}	1880	*Atkinson et al.* [1992]
G933	1-$C_4H_8 + O_3\ (+O_2) \rightarrow RCHO + RCH_2OO + 0.06\ H_2O_2 + 0.41\ HO$	2	3.5×10^{-15}	1801	*Treacy et al.* [1992]
G935	iso-$C_4H_8 + O_3\ (+O_2) \rightarrow RCHO + RCH_2OO + 0.06\ H_2O_2 + 0.84\ HO$		2.5×10^{-15}	1592	*Treacy et al.* [1992]
G001	(E) 2-$C_4H_8 + O_3\ (+O_2) \rightarrow RCHO + RCH_2OO + 0.06\ H_2O_2 + 0.41\ HO$	2	6.7×10^{-15}	1066	*Treacy et al.* [1992]
G002	(Z) 2-$C_4H_8 + O_3\ (+O_2) \rightarrow RCHO + RCH_2OO + 0.09\ H_2O_2 + 0.64\ HO$	2	3.4×10^{-15}	978	*Treacy et al.* [1992]
G939	C_4H_6 (1,3-butadiene) + $O_3\ (+O_2) \rightarrow RCHO + RCH_2OO + 0.06\ H_2O_2 + 0.08\ HO$	2	8.2×10^{-15}	2135	*Treacy et al.* [1992]
G003	1-$C_5H_{10} + O_3\ (+O_2) \rightarrow RCHO + RCH_2OO + 0.06\ H_2O_2 + 0.37\ HO + CO$		1.1×10^{-15}	1603	*Treacy et al.* [1992]

Table 8. (continued)

Reaction No.	Reaction	n	$k^{\varnothing}$ $(\mathrm{cm}^{-3})^{1-n}$ s^{-1}[a]	$-E_a/R$, K	Reference
G016	(E) $2\text{-}C_5H_{10} + O_3\ (+O_2) \rightarrow RCHO + RCH_2OO + 0.06\ H_2O_2 + 0.41\ HO$	2	3.2×10^{-16}	note 1	*Cox and Penkett* [1972]
G017	(Z) $2\text{-}C_5H_{10} + O_3\ (+O_2) \rightarrow RCHO + RCH_2OO + 0.06\ H_2O_2 + 0.64\ HO$	2	2.1×10^{-16}	note 1	*Cox and Penkett* [1972]
G937	C_5H_{10} (2-methyl 1-butene) + $O_3\ (+O_2) \rightarrow RCHO + RCH_2OO + 0.06\ H_2O_2 + 0.7\ HO$	2	calculated to be $1.03 \times k_{O3}$ of $1\text{-}C_4H_8$		*Vrabski and Cventanovic* [1960]
G989	C_5H_8 (isoprene) + $O_3\ (+O_2) \rightarrow RCHO + RCH_2OO + 0.09\ H_2O_2 + 0.27\ HO$	2	1.4×10^{-14}	2153	*Atkinson et al.* [1982]
G004	$1\text{-}C_6H_{12} + O_3\ (+O_2) \rightarrow RCHO + RCH_2OO + 0.06\ H_2O_2 + 0.32\ HO$	2	1.4×10^{-15}	1478	*Treacy et al.* [1992]
G018	(E) $2\text{-}C_6H_{12} + O_3\ (+O_2) \rightarrow RCHO + RCH_2OO + 0.06\ H_2O_2 + 0.37\ HO$	2	same as G004	note 1	assumed
G019	(Z) $2\text{-}C_6H_{12} + O_3\ (+O_2) \rightarrow RCHO + RCH_2OO + 0.06\ H_2O_2 + 0.32\ HO$	2	same as G004	note 1	assumed
G897	$C_{10}H_{16}$ (terpene) + $O_3\ (+O_2) \rightarrow RCHO + RCH_2OO + 0.09\ H_2O_2 + 0.54\ HO$	2	8.6×10^{-16}	note 1	calculated, see text
G415	alkenes + $O_3 \rightarrow RCHO + RCH_2OO$	2	1.4×10^{-15}	1478	*Treacy et al.* [1992] for alkene = 1-hexene
G988	$C_2H_6 + NO_3\ (+O_2) \rightarrow RCH_2OO + HNO_3$	2	1.1×10^{-17}	note 1	*Boyd et al.* [1991]
G987	$n\text{-}C_3H_8 + NO_3\ (+O_2) \rightarrow RCH_2OO + HNO_3$	2	2.2×10^{-17}	note 1	*Boyd et al.* [1991]
G986	$n\text{-}C_4H_{10} + NO_3\ (+O_2) \rightarrow RCH_2OO + HNO_3$	2	6.6×10^{-17}[c]	note 1	*Atkinson* [1991]
G985	$iso\text{-}C_4H_{10} + NO_3\ (+O_2) \rightarrow RCH_2OO + HNO_3$	2	9.8×10^{-17}	note 1	*Atkinson* [1991]
G984	$n\text{-}C_5H_{12} + NO_3\ (+O_2) \rightarrow RCH_2OO + HNO_3$	2	8.1×10^{-17}	note 1	*Atkinson* [1991]
G983	$iso\text{-}C_5H_{12} + NO_3\ (+O_2) \rightarrow RCH_2OO + HNO_3$	2	3.1×10^{-12}	2941	*Bagley et al.* [1990]
G413	alkanes + $NO_3\ (+O_2) \rightarrow RCH_2OO + HNO_3$	2	1.4×10^{-16}	note 1	*Atkinson* [1991] for alkane = n-heptane
G035	$C_2H_2 + NO_3\ (+O_2) \rightarrow RCH_2OO$	2	5.0×10^{-17}[c]	note 1	*Atkinson* [1991]
G981	$C_6H_6 + NO_3\ (+O_2) \rightarrow RCH_2OO + HNO_3$	2	3.0×10^{-17}[c]	note 1	*Atkinson* [1991]
G982	$C_5H_6CH_3$ (toluene) + $NO_3\ (+O_2) \rightarrow RCH_2OO + HNO_3$	2	6.8×10^{-17}	note 1	*Atkinson* [1991]
G979	$C_2H_4 + NO_3\ (+O_2) \rightarrow HCHO + CO + HO_2$	2	3.3×10^{-12}	2880	*Atkinson et al.* [1992]
G005	$C_3H_6 + NO_3\ (+O_2) \rightarrow RCH_2OO$	2	9.5×10^{-15}	note 1	*Atkinson* [1991]
G006	$1\text{-}C_4H_8 + NO_3\ (+O_2) \rightarrow RCH_2OO$	2	1.3×10^{-14}	note 1	*Atkinson* [1991]
G009	$iso\text{-}C_4H_8 + NO_3\ (+O_2) \rightarrow RCH_2OO$	2	3.3×10^{-13}	note 1	*Atkinson* [1991]
G007	(E) $2\text{-}C_4H_8 + NO_3\ (+O_2) \rightarrow RCH_2OO$	2	3.9×10^{-13}	note 1	*Atkinson* [1991]
G008	(Z) $2\text{-}C_4H_8 + NO_3\ (+O_2) \rightarrow RCH_2OO$	2	3.5×10^{-13}	note 1	*Atkinson* [1991]
G961	C_4H_6 (1,3-butadiene) + $NO_3\ (+O_2) \rightarrow RCH_2OO$	2	1.0×10^{-13}	note 1	*Atkinson* [1991]
G010	$1\text{-}C_5H_{10} + NO_3\ (+O_2) \rightarrow RCH_2OO$	2	1.6×10^{-14}	note 1	*Aird et al.* [1992]
G029	(E) $2\text{-}C_5H_{10} + NO_3\ (+O_2) \rightarrow RCH_2OO$	2	1.6×10^{-14}	note 1	*Aird et al.* [1992]
G030	(Z) $2\text{-}C_5H_{10} + NO_3\ (+O_2) \rightarrow RCH_2OO + NO_2$	2	1.6×10^{-14}	note 1	*Aird et al.* [1992]
G033	C_5H_{10} (2-methyl 1-butene) + $NO_3\ (+O_2) \rightarrow RCH_2OO$	2	4.4×10^{-13}	note 1	*Aird et al.* [1992]
G980	C_5H_8 (isoprene) + $NO_3\ (+O_2) \rightarrow RCH_2OO$	2	3.0×10^{-12}	446	*Atkinson* [1991]
G011	$1\text{-}C_6H_{12} + NO_3\ (+O_2) \rightarrow RCH_2OO$	2	2.1×10^{-14}	note 1	*Aird et al.* [1992]
G031	(E) $2\text{-}C_6H_{12} + NO_3\ (+O_2) \rightarrow RCH_2OO$	2	2.1×10^{-14}	note 1	*Aird et al.* [1992]
G032	(Z) $2\text{-}C_6H_{12} + NO_3\ (+O_2) \rightarrow RCH_2OO$	2	2.1×10^{-14}	note 1	*Aird et al.* [1992]
G036	$C_{10}H_{16}$ (terpene) + $NO_3\ (+O_2) \rightarrow RCH_2OO$	2	2.4×10^{-11}	note 1	calculated (see the text)
G414	alkenes + $NO_3\ (+O_2) \rightarrow RCH_2OO$	2	2.1×10^{-14}	note 1	*Aird et al.* [1992] for alkene = 1-hexene
G961	$RCH_2OO + RCH_2OO \rightarrow 2RCH_2O + O_2$	2	6.8×10^{-14}	note 1	*DeMore et al.* [1997]
G963	$RCH_2OO + HO_2 \rightarrow RCH_2OOH$	2	8.0×10^{-12}	700	*DeMore et al.* [1997]
G964	$RCH_2OO + NO \rightarrow RCH_2O + NO_2$	2	8.7×10^{-12}	365	*DeMore et al.* [1997]
G965	$RCH_2OOH + OH \rightarrow RCH_2OO + H_2O$	2	G402 + G403	note 1	*DeMore et al.* [1997]
G968	$RCHO + HO\ (+O_2) \rightarrow H_2O + CH_3OO + CO$	2	1.4×10^{-11}	270	*DeMore et al.* [1997]
G971	$RCH_2O + O_2 \rightarrow RCHO + HO_2$	2	9.9×10^{-15}	−550	*DeMore et al.* [1997]
G972	$RCH_2O + O_2 \rightarrow RCH_2OO + HCHO$	2	1.0×10^{-16}	−550	*DeMore et al.* [1997]
G973	$RCH_2OO + NO \rightarrow RCH_2ONO_2$	2	0.1 × G964	note 1	*Sander et al.* [1997]
G974	$RCH_2ONO_2 \rightarrow RCH_2OO + NO$	1			assumed to be the same as G995
G975	$RCH_2ONO_2 + OH \rightarrow H_2O + NO_2$	2	1.0×10^{-12}	note 1	*Sander et al.* [1997]
G992	$RCHO + NO_3 \rightarrow RC(O)O_2 + HNO_3$	2	1.4×10^{-12}	1863	*Atkinson* [1991], RCHO = CH_3CHO
G993	$RCHO + HO\ (+O_2) \rightarrow RC(O)O_2 + H_2O$	2	5.6×10^{-12}	−310	*Atkinson et al.* [1992], RCHO = CH_3CHO
G994	$RC(O)O_2 + NO_2 \rightarrow RC(O)OONO_2$	2	$1.2 \times 10^{-11} \times (T/298)^{-0.9}$	note 1	*Atkinson et al.* [1992], $RC(O)O_2 = CH_3C(O)O_2$
G995	$RC(O)OONO_2 \rightarrow RC(O)OO + NO_2$	1	4.0×10^{16}	13600	*Atkinson et al.* [1992], $RC(O)O_2 = CH_3C(O)O_2$
G025	$RC(O)O_2 + NO\ (+O_2) \rightarrow RCH_2OO + CO_2 + NO_2$	2	2.0×10^{-11}	note 1	*Atkinson et al.* [1992]
G026	$RC(O)O_2 + RC(O)O_2 \rightarrow RCH_2OO\ (+O_2)$	2	2.8×10^{-12}	−530	*Atkinson et al.* [1992]
G027	$HO + RC(O)OONO_2 \rightarrow HCHO + CO_2 + NO_2 + H_2O$	2	5.1×10^{-14}	650	*Atkinson et al.* [1992]
G024	$RC(O)O_2 + HO_2 \rightarrow RCH_2OOH + O_3$	2	3.0×10^{-3}	−1040	*Atkinson et al.* [1992]
G028	$RC(O)O_2 + HO_2 \rightarrow RC(O)OOH + O_2$	2	1.3×10^{-3}	−1040	*Atkinson et al.* [1992]

Note 1: For those reactions where the temperature dependency was not measured, the room temperature rate constants are given. In the case of ozonolysis reaction for the low temperature studies, the temperature dependencies of similar analogous molecules were adopted, as described in the text. The air pressure (1013 hPa) has been included into the three-body reactions (X + Y (+M) → Z) to obtain a pseudo second-order rate coefficient. The complex temperature dependence was calculated using the formula of *DeMore et al.* [1997].

[a] The temperature dependence is $k = k^{\varnothing} \times \exp\left(-E_a/R\ (1/T - 1/T^{\varnothing})\right)$.

[b] Includes H_2O as third-body as well.

[c] These are upper limits for the rate constants, and these values are used in the model.

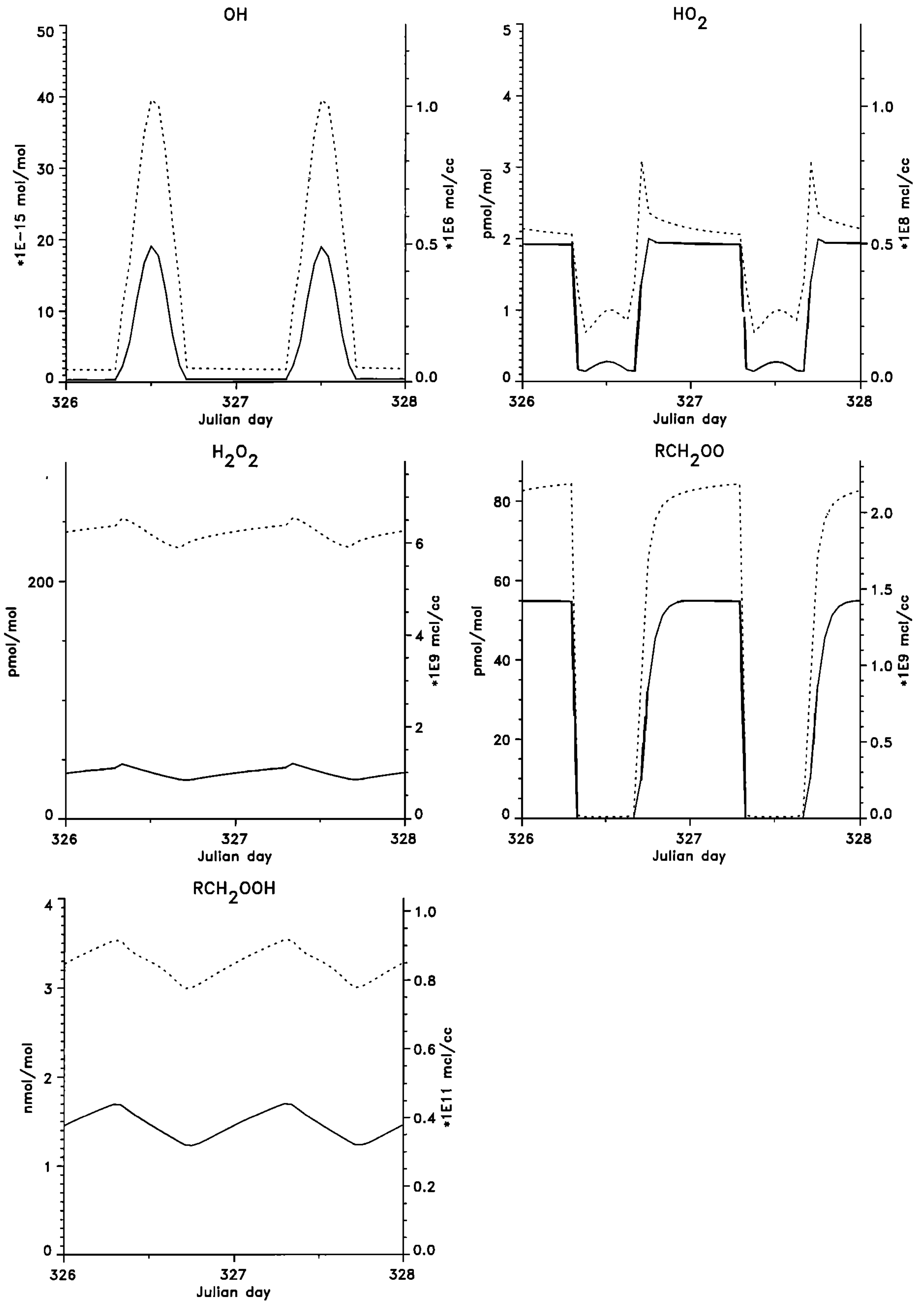

Figure 7. Concurrent HO and H_2O_2 production: selected results of run 18 (dashed line) are compared with run 1 (solid line).

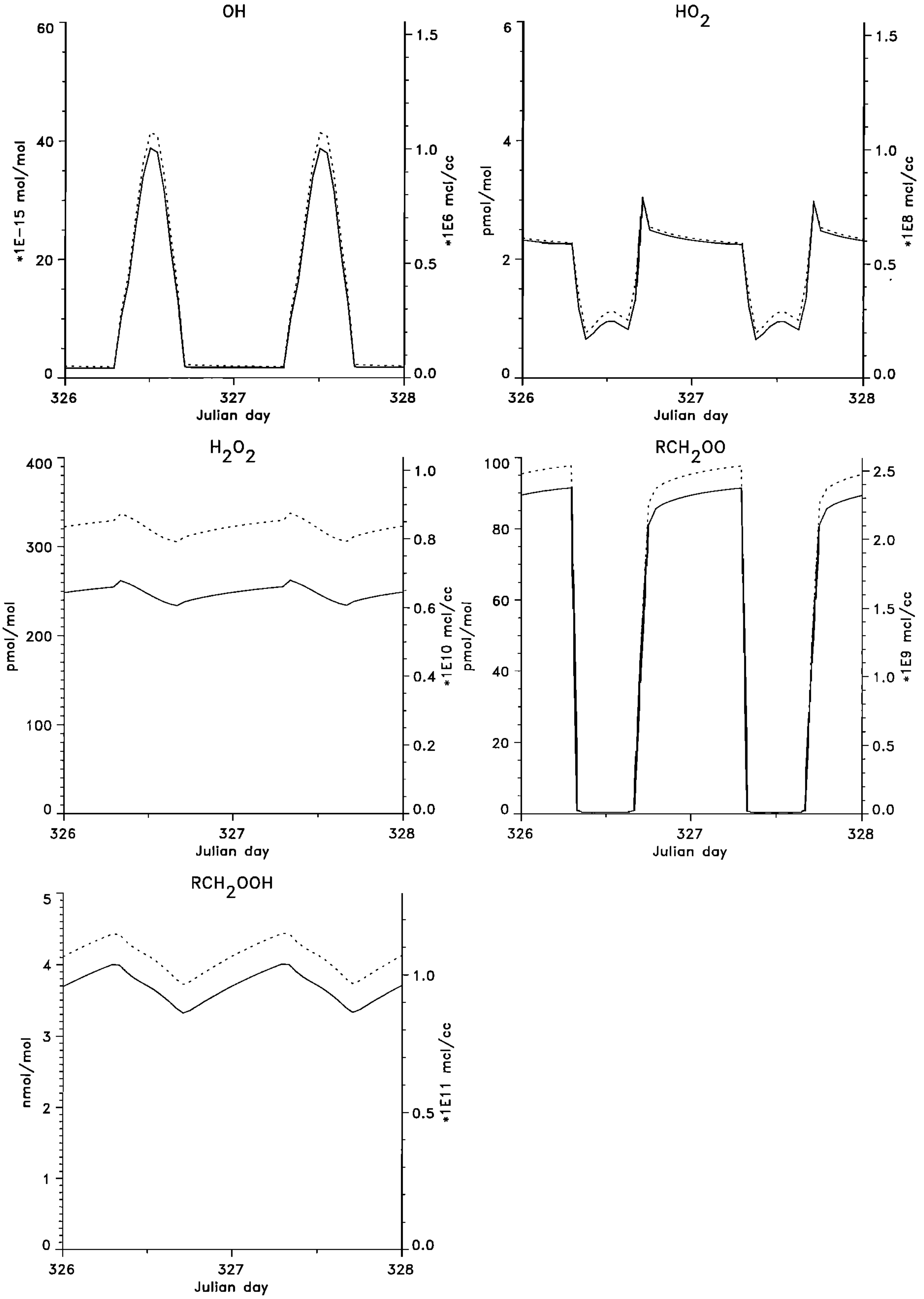

Figure 8. Impact of terpenes in enhancing HO_x production: run 19b (dashed line) are compared with the run 19a (solid line).

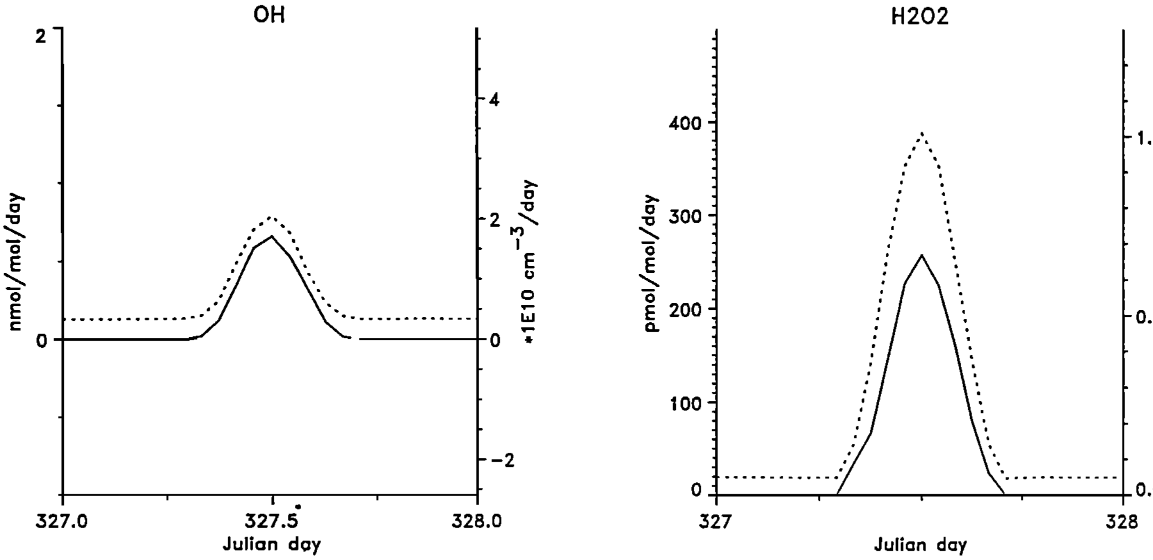

Figure 9. Impact of ozonolysis reaction on HO_x production in a remote site: run 20b (dashed line) are compared with run 20a (solid line). In base run 20a: $d[HO]/dt = (2 \times k_{G201} \times [O(^1D)] \times [H_2O])$ and $d[H_2O_2]/dt = (k_{G207} \times [HO_2] \times [HO_2])$; in ozonolysis run 20b: $d[HO]/dt = (2 \times k_{G201} \times [O(^1D)] \times [H_2O]) + \Sigma((HO \text{ yield}) \times [\text{alkene}] \times [O_3])$ and $d[H_2O_2]/dt = (k_{G207} \times [HO_2] \times [HO_2]) + \Sigma((H_2O_2 \text{ yield}) \times [\text{alkene}] \times [O_3])$.

of isoprene in suburban eastern continental regions of North America (Table 4).

We chose a mixture of five monoterpenes (with composition α-pinene: 24%; β-pinene: 9%; myrcene: 10%; α-terpinene: 9%; and sabinene mixture: 48%) as representative of terpenes. These five terpenes were the major components of terpenes measured in boreal forest in the summertime (up to ~80% of total identified terpenes) for which there is also kinetic information available. Unfortunately, the temperature dependence of the rate constants for each terpene constituent of this hypothetical mixture is not known, and hence we assumed that all the five components followed similar temperature dependences as α-pinene [*Atkinson et al.*, 1982]. The rate constant for this hypothetical terpene is assumed to be

$$k_A(\text{terpene}) = \Sigma(k_{i,A} \times n_i) \qquad (19)$$

where A = HO, O_3, or NO_3; $i \equiv$ a particular terpene in the mixture; n_i is given above, and $\Sigma n_i = 100\%$ as described above.

Figure 8 shows the results of runs 19a and 19b for a total terpene mixing ratio of 30 pmol/mol. These runs indicate that terpenes can contribute significantly to HO_x formation and particularly to the generation of H_2O_2. It is worth reiterating that several assumptions have been made in this run, regarding (1) the existence of trace concentrations of terpenes in the suburban area, (2) composition of the mixture, and (3) temperature dependence of the rate constants. Hence this exercise is only intended to provide a very preliminary consideration of the potential importance of terpene chemistry in the wintertime.

3.7. HO_x Formation in Remote Area

During winter the urban plume is being transported to more remote land sites by atmospheric processes. During this transport, hydrocarbons such as alkenes react with atmospheric oxidants such as HO and ozone. Hence, as we go from a city toward a remote continental site, the mixing ratios of anthropogenic alkenes decrease with the more reactive hydrocarbons exhibiting more reduction relative to the less reactive ones. Table 4 shows the average mixing ratios for hydrocarbons measured in a remote North American continental site during the late fall/winter time (J. Rudolph and B. Kieser, personal communication, 1996) along with some other atmospherically interesting molecules. No terpenes were considered in this exercise. Two modeling runs were carried out, with and without ozonolysis reactions. Figure 9 depicts some results, which demonstrate that even very low level of alkenes with anthropogenic origin may influence the HO_x production, notably in remote continental sites, and the impact of ozonolysis reactions even in the remote continental site should not be neglected.

4. Summary and Concluding Remarks

We have shown that the ozonolysis reactions of alkenes are major sources of oxidants (HO_x, RO_2, H_2O_2, and RO_2H) during dark seasons, under the conditions used in this modeling study. There are a number of studies suggesting that small alkenes can be produced in canisters [e.g., *Jobson*, 1994], so that the mixing ratios adopted in this study may be upper limits. In addition, there are discrepancies between laboratory studies, particularly in the direct yields of HO and H_2O_2. To shine more light on the mechanism of HO and H_2O_2 production pathways, it is interesting to measure HO and H_2O_2 yields simultaneously, to investigate the feedback between these two channels, if there is any. Hence we strongly suggest further studies on these important topics.

Our results suggest that anthropogenic alkenes both in urban and in remote areas can provide a major source for HO_x which can be much greater than the $O(^1D)$ and water vapor reaction which is traditionally thought to be the most important HO_x formation pathway in the troposphere. Nocturnal

HO and H_2O_2 formation due to ozonolysis reactions are also significant. Trace alkenes (excluding ethene and propene, the major identified alkenes) were found to be responsible for the production of HO_x. We have shown that primary RO_2 production by ozonolysis of alkenes is greater than the contributions by HO or NO_3-initiated reactions. Our modeling results suggest that direct HO and H_2O_2 production by ozonolysis of alkenes may indeed serve as the major tropospheric source of these oxidants. The additional source of HO can significantly increase hydrocarbon oxidation and contribute to the oxidizing efficiency of the mid- to high-latitude continents under fall-winter conditions. The sulfur (IV) to sulfur (VI) conversion mechanism is a long-standing subject of interest where among the various suggested mechanisms, aqueous phase oxidation by O_3 and H_2O_2 are assumed to be the major oxidants. Interestingly, already almost 30 years ago, it was established that SO_2 can be efficiently oxidized to S (VI) in presence of alkenes and ozone [*Cox and Penkett*, 1971a, b, 1972] under conditions in which neither alkenes nor ozone alone could oxidize S (IV) to S (VI). Much H_2O_2 and organic peroxides are formed as a result of ozonolysis that can be transferred to liquid form. Consequently, S(IV) to S(VI) oxidation can be much more enhanced in the liquid phase. Further large-scale modeling is needed to establish whether the ozonolysis reactions play an important role in the oxidation of SO_2 especially during fall and winter.

Although not considered in this study, there is an additional significant source of HO in pollution-affected regions, the photolysis of HNO_2, which is produced by heterogeneous reactions on aerosols [e.g., *Pitts et al.*, 1984]. Thus, contrary to traditional chemistry, the oxidation power in the dark seasons of the year may be larger than so far discussed.

We encourage the laboratory kinetics and mechanistic studies of ozonolysis reactions of biogenic and anthropogenic alkenes over sufficient wide ranges in temperature and humidity so that the results can be applied to tropospheric conditions. Terpene oxidation reactions can be important contributors to HO_x and H_2O_2, and we therefore strongly recommend their measurement including during fall and winter.

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