

Organic Peroxyl Radical Photolysis in the Near-Infrared: Effects on Tropospheric Chemistry

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Received: May 27, 1999; In Final Form: July 30, 1999

We investigate the effects of near-infrared photolysis of organic peroxy radicals (RO_2) on tropospheric chemistry. We propose that the excitation of an RO_2 to its lowest excited electronic state with near-infrared (near-IR) light is followed by intramolecular reactions that produce hydroxyl (OH) or hydroperoxyl (HO_2) radicals. Spectra to this low-lying state have recently been obtained, but absorption cross sections for this electronic transition and yields of the resulting photoproducts have not been directly measured. We suggest a limiting range of cross sections from estimates for the same transition in HO_2 and by comparison to other allowed electronic transitions. On the basis of a thermochemical assessment, we propose that OH and an aldehyde are the principal photoproducts of near-IR photolysis of RO_2 . These photolysis reactions are included in a model of the troposphere with a standard photochemical mechanism and conditions appropriate to remote, rural, and urban locations. Inclusion of RO_2 photolysis has a small effect on any of the major tropospheric chemical constituents if lower limit estimates of the absorption cross sections are used. Midrange or upper limit cross section estimates result in significant departures from the currently accepted photochemical scheme. These studies provide a clear need for further measurements of RO_2 absorption cross sections and photoproduct yields, which are the principal uncertainties.

1. Introduction

Peroxy radicals play a central role in the chemistry of the troposphere. Because of their close coupling to the hydroxyl radical OH, they are involved in photochemical smog production, acid formation and precipitation, and the control of emitted trace species such as carbon monoxide and volatile organic compounds (VOCs).^{1–4} Organic peroxy radicals (R-O-O or RO_2 , where R is a carbon-containing chain) are generated in the atmospheric oxidation of biogenic and anthropogenic VOCs. These peroxy radicals are intimately connected to various tropospheric chemical cycles through reactions involving the radical families HO_x ($\text{OH} + \text{HO}_2$) and NO_x ($\text{NO} + \text{NO}_2$). By oxidizing NO to NO_2 , RO_2 are key reactants in the photochemical production of tropospheric ozone.

We investigate the relationship between atmospheric radicals and radiation by proposing a new photochemical reaction for organic peroxy radicals. This novel photochemistry of RO_2 requires reaction on the lowest electronic state of A' symmetry as described by Clifford et al.⁵ This excited state can be pumped by near-infrared (near-IR) solar radiation (5500 to 9000 cm^{-1}). The excited peroxy radicals can then form cyclic structures which facilitate intramolecular reactions, with possible products including either an aldehyde and OH or an alkene and HO_2 .

This photochemical reaction channel has the potential to affect the tropospheric concentrations and diurnal distribution of RO_2 , HO_x , NO_x , O_3 , and other compounds. A photochemical box model allowed us to explore the tropospheric consequences of the near-IR photolysis of peroxy radicals. The model results

underscore the complexity of tropospheric chemistry demonstrated in the three situations investigated, including a remote site with low VOC and NO_x levels, a rural location with high [VOC] and moderate [NO_x], and an urban environment with high [VOC] and [NO_x]. It has been pointed out⁶ that the nonlinear dependence between radical families makes model predictions of local HO_x concentrations and O_3 production challenging. The proposed addition of RO_2 near-IR photolysis to the currently understood photochemical mechanism amplifies these effects. Our model results illustrate the nonlinear coupling between solar radiation and radical chemistry as well as that between the different radical families in the troposphere. Recent atmospheric measurements of radical levels^{7–11} have begun to probe these complex relationships. Our model calculations suggest the sensitivities needed for observation of the proposed RO_2 photochemistry.

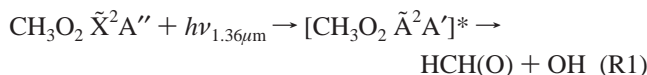
2. Proposed RO_2 Photolysis Channels in the Troposphere

The proposed tropospheric photochemical reactions involve near-IR solar pumping of RO_2 radicals to an excited electronic state in which the radical undergoes rearrangement and decomposition. The chemistry and spectroscopy of alkylperoxy radicals has been studied recently.^{1,5} All RO_2 radicals have a low-lying electronic state that is within 1 eV of the ground state. In particular the ground state of CH_3O_2 is \tilde{X}^2A'' and the first excited state is \tilde{A}^2A' with $T_e = 7375 \pm 2\text{ cm}^{-1}$ ($0.9144 \pm 0.0002\text{ eV}$, $1.3559\text{ }\mu\text{m}$).^{12,13}

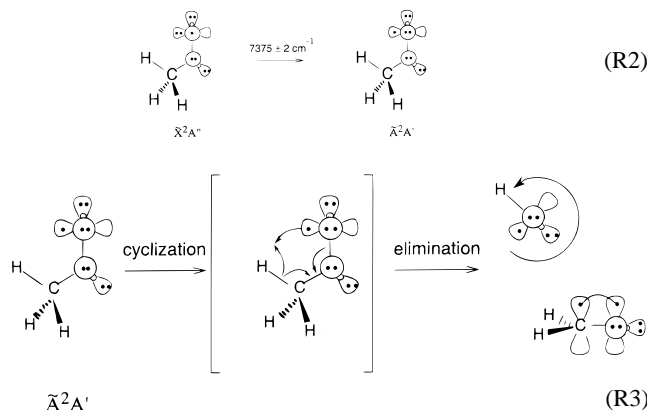
Tropospheric oxidation of methane produces CH_3 which rapidly combines with oxygen to produce CH_3O_2 \tilde{X}^2A'' .¹⁴ Solar pumping of the methylperoxy radical at 7375 cm^{-1} will

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populate the \tilde{A}^2A' state of CH_3O_2 , which will decompose to formaldehyde and OH.

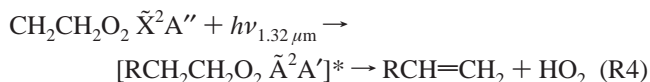


The decomposition of \tilde{A}^2A' CH_3O_2 in R1 is exothermic by $40.2 \pm 0.8 \text{ kcal mol}^{-1}$.⁵ This (1,4) fragmentation of \tilde{A}^2A' CH_3O_2 to produce HCH(O) and rotationally excited OH can be described by the GVB diagrams.¹⁵



The (1,4) cyclization barrier, estimated by Clifford et al.⁵ to be about 15 kcal mol^{-1} in the \tilde{A}^2A' state, appears to be a little over 20 kcal mol^{-1} in light of recent theoretical calculations.¹⁶ Excited vibrational levels in the \tilde{A}^2A' state would have enough energy to overcome such barriers.

In addition to (1,4) fragmentations which generate aldehydes and OH radicals, more complex alkylperoxy radicals can undergo (1,5) decompositions to yield alkenes and the hydroperoxy radical.^{1,5}



The activation energy required to close a five-member activated complex is expected to be small.⁵ Both the (1,4) and (1,5) rearrangements feature an internal abstraction of a H atom but both are unlikely to occur from the ground states of the alkylperoxy radicals, \tilde{X}^2A'' , because of poor orbital overlap. In contrast, a more "reactive" configuration of RO_2 will be \tilde{A}^2A' .

The purpose of this paper is to demonstrate some of the atmospheric implications of RO_2 near-IR photolysis, which requires knowledge of the rates of the two possible reaction channels illustrated by R1 and R4. Theoretical and experimental studies of thermal reactions of alkyl radicals and O_2 , in which alkylperoxy radicals are intermediates, suggest that the various products result from coupling between two potential energy surfaces of $^2A''$ and $^2A'$ symmetry.¹⁷⁻²² There are still many unanswered questions about the reactivity on the excited $^2A'$ surface, and direct experimental studies will be needed to resolve uncertainties in the photochemistry we propose here. In the absence of the necessary rates for this excited state chemistry, we have done the following. We first describe the known tropospheric chemistry of peroxy radicals in section 3. In section 4 we outline thermochemical calculations of the proposed reaction channels for various RO_2 species and eliminate photoproducts not thermodynamically accessible by near-IR excitation. Absorption cross sections and quantum yields for

TABLE 1: Key Tropospheric Photochemical Reactions

no. of reaction	reaction
R5	$\text{O}_3 + h\nu \rightarrow \text{O}(^1\text{D}) + \text{O}_2$
R6 ^a	$\text{O}(^1\text{D}) + \text{M} \rightarrow \text{O}(^3\text{P}) + \text{M}$
R7	$\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}$
R8	$\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$
R9	$\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$
R10	$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$
R11	$\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$
R12	$\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M}$
R13 ^b	$\text{RH} + \text{OH} \rightarrow \text{R} + \text{H}_2\text{O}$
R14	$\text{R} + \text{O}_2 + \text{M} \rightarrow \text{RO}_2 + \text{M}$
R15	$\text{R}=\text{R}' + \text{OH} + \text{M} \rightarrow \text{HORR}' + \text{M}$
R16	$\text{HORR}' + \text{O}_2 + \text{M} \rightarrow \text{HORR}'\text{O}_2 + \text{M}$
R17	$\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$
R18	$\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$
R19	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$
R20	$\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2$
R21	$\text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{OOH} + \text{O}_2$
R22a	$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow 2\text{CH}_3\text{O} + \text{O}_2$
R22b	$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{HCH(O)} + \text{CH}_3\text{OH} + \text{O}_2$
R23	$\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCH(O)} + \text{HO}_2$
R24	$\text{RH}_2\text{CO}_2 + \text{NO} \rightarrow \text{RH}_2\text{CO} + \text{NO}_2$
R25	$\text{RH}_2\text{CO} + \text{O}_2 \rightarrow \text{RCH(O)} + \text{HO}_2$
R26	$\text{RO}_2 + \text{HO}_2 \rightarrow \text{ROOH} + \text{O}_2$
R27	$\text{H}_2\text{O}_2 + h\nu \rightarrow \text{OH} + \text{OH}$
R28	$\text{CH}_3\text{OOH} + h\nu \rightarrow \text{CH}_3\text{O} + \text{OH}$
R29	$\text{RH}_2\text{COOH} + h\nu \rightarrow \text{RH}_2\text{CO} + \text{OH}$
R30	$\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$
R31a	$\text{OH} + \text{CH}_3\text{OOH} \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O}$
R31b	$\text{OH} + \text{CH}_3\text{OOH} \rightarrow \text{HCH(O)} + \text{OH} + \text{H}_2\text{O}$
R32	$\text{OH} + \text{ROOH} \rightarrow \text{RO}_2 + \text{H}_2\text{O}$
R33a	$\text{HCH(O)} + h\nu \rightarrow \text{H}_2 + \text{CO}$
R33b	$\text{HCH(O)} + h\nu \rightarrow \text{HCO} + \text{H}$
R34	$\text{RCH(O)} + h\nu \rightarrow \text{R} + \text{HCO}$
R35	$\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$
R36	$\text{OH} + \text{HCH(O)} \rightarrow \text{HCO} + \text{H}_2\text{O}$
R37	$\text{OH} + \text{RCH(O)} \rightarrow \text{RC(O)} + \text{H}_2\text{O}$
R38	$\text{RC(O)} + \text{O}_2 + \text{M} \rightarrow \text{RC(O)}\text{O}_2 + \text{M}$
R39	$\text{RC(O)}\text{O}_2 + \text{NO}_2 + \text{M} \rightarrow \text{RC(O)}\text{O}_2\text{NO}_2 + \text{M}$
R40	$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$
R41	$\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$
R42	$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}(^3\text{P})$
R43	$\text{O}(^3\text{P}) + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$

^a M = any air molecule, predominantly N_2 and O_2 . ^b R = organic chain.

the two possible reaction channels have yet to be determined experimentally. In section 5 we therefore estimate the rate of photolysis of peroxy radicals in the near-IR. We assume that the overall rate is limited by the near-IR excitation and that the thermodynamically allowed excited state photoproducts will subsequently form with unit efficiency.

3. Current Tropospheric RO_2 Photochemical Mechanism

To establish how the proposed peroxy radical photolysis will affect tropospheric chemistry, we must consider the current understanding of peroxy radical sources and sinks and their connection to other chemical families.^{1,4} Table 1 is a list of the key chemical reactions in the troposphere, which we briefly outline here.

This chemistry is initiated by the photolysis of ozone at wavelengths shorter than about 340 nm (R5). Any $\text{O}(^1\text{D})$ from R5 not quenched in R6 can react with H_2O to produce OH (R7). Peroxy radicals are generated by OH reactions with reduced species such as H_2 , CO, alkanes, and alkenes (R8, R9, R11, R13, R15) followed by barrierless reactions of H or R radicals with O_2 (R10, R12, R14, R16). HO_2 is destroyed by reactions with NO (R17) and O_3 (R18), which recycle the original OH, and by reacting with another HO_2 to produce hydrogen peroxide

(R19). The main losses of organic peroxy radicals are reactions with NO to produce an aldehyde and HO₂ (R20 followed by R23, R24 followed by R25) and with HO₂ to form a peroxide (R21, R26). RO₂ + RO₂ reactions, such as R22, are generally less important RO₂ loss channels.

The products of these RO₂ loss reactions can themselves be secondary radical sources. H₂O₂ photolysis produces OH radicals (R27), while photolysis of the organic peroxides produces OH, HO₂, and an aldehyde (R28, 29). OH oxidation of peroxides (R30, 31, 32) liberates the parent RO₂ but not the parent HO₂. Photolysis of aldehydes generally produces HO₂ and an RO₂ with one less carbon than the parent (R33b followed by R35 and R10, R34 followed by R35 and R14), though formaldehyde photolysis also has an important channel with only molecular products (R33a). Reaction of aldehydes with OH produces CO and HO₂ in the case of HCH(O) (R36 followed by R35) and an acyl peroxy radical in the case of larger aldehydes (R37 followed by R38). Acyl peroxy radicals (such as CH₃C(O)O₂, peroxy acetyl (PA)) can combine with NO₂ to produce peroxy acyl nitrates (e.g., CH₃C(O)O₂NO₂, peroxy acetyl nitrate (PAN)). At higher temperatures these nitrates rapidly undergo thermal decomposition, but at lower temperatures they represent a reservoir for both radicals and NO₂ (R39). Other radical termination processes include peroxide formation (R19, R21, R26) followed by OH reaction (R30, R31, R32), R40, R41, and heterogeneous losses of peroxides and aldehydes.

An important consequence of the radical chemistry described above is ozone formation. NO₂ produced from reactions of HO₂ or RO₂ with NO (R17, R20, and R24) is rapidly photolyzed in the visible (R42), and the resulting O(³P) combines with O₂ to form O₃ (R43). This is the predominant photochemical source of tropospheric ozone and is generally limited by the rates of the HO₂ + NO (R17) and RO₂ + NO (R20, R24) reactions. When [NO] is greater than a few parts per trillion by volume (pptv), ozone production is faster than its losses (R5 followed by R7, R18).

4. Thermochemistry of RO₂ Near-IR Photolysis

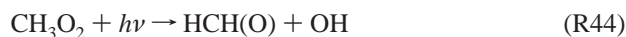
We carried out thermochemical calculations for various RO₂ species to understand the photoproducts resulting from near-IR excitation from the ground \tilde{X}^2A'' state to the excited \tilde{A}^2A' state (Table 2). The enthalpy of reaction ($\Delta_{\text{rxn}}H_{298}$) for this process is the sum of the enthalpies of formation (Δ_fH_{298}) for the photoproducts minus the sum of Δ_fH_{298} for RO₂(\tilde{X}) and the near-IR photon energy. We assumed the photon energy was just enough to excite RO₂ from its lowest rovibrational level in the \tilde{X} state to the lowest rovibrational level in the \tilde{A} state.¹² A particular photolysis channel is energetically accessible in the near-IR if $\Delta_{\text{rxn}}H_{298} \leq 0$. This approach allows us to narrow down the new reactions we must include in the photochemical scheme, though it does not indicate the rate or branching ratios of the photoproduct channels.

Table 2 summarizes the calculations for HO₂, CH₃O₂, CH₃-CH₂O₂, CH₃C(O)O₂, HOCH₂CH₂O₂, and HOCH₂C(O)O₂, which are the peroxy radicals produced from the oxidation of CO, methane, ethane, and ethene. We did not consider RO₂ derived from VOCs with more than 2 carbon atoms given the lack of information about their spectra and thermochemistry. For completeness we show other possible reaction products in Table 2 besides those of the (1,4) and (1,5) rearrangement, though none of these other channels are thermodynamically allowed for a near-IR excitation. HO₂ cannot be photolyzed in the near-IR, since both channels are substantially endothermic; an excitation to the ultraviolet \tilde{B}^2A'' state is required. CH₃O₂ near-

IR photolysis results in only one allowed product channel: OH + formaldehyde. For CH₃CH₂O₂, an analogous set of products (OH and acetaldehyde) is obtained with high exothermicity, while the HO₂ + ethene channel is thermoneutral within the uncertainties of the thermochemical data. Peroxyl acetyl radical, CH₃C(O)O₂, cannot photolyze in the near-IR. All investigated photolysis channels of HOCH₂CH₂O₂ are exothermic with near-IR excitation. The only exothermic route for HOCH₂C(O)O₂ photolysis produces HCH(O), CO₂, and OH. These calculations relied on Δ_fH_{298} values for HOCH₂CH₂O₂, HOCH₂CH(O), and HOCH₂C(O)O₂ which have not been directly measured. The values used here were estimated from model calculations and from enthalpies for analogous species and reactions using Hess' law (see Table 2 footnotes). Experimental measurements of these enthalpies would be useful.

These thermochemical calculations suggest that the principal near-IR photolytic channel for organic peroxy radicals produces OH and an aldehyde. Consequently, out of all of the possible near-IR photolysis reactions, four were added to the model chemical scheme:

methane oxidation



ethane oxidation



ethene oxidation



In the case of HOCH₂CH₂O₂ photolysis (R46), it seems reasonable to conclude that the most exothermic channel, HOCH₂CH(O) + OH, will predominate. R46 produces hydroxyacetaldehyde (HAC), HOCH₂CH(O), which is not otherwise formed in the chemical mechanism when oxidation of VOCs with two or fewer carbon atoms is considered. Its fate is either photolysis (R34) or reaction with OH (R37). The HOCH₂ radical formed from photolysis rapidly reacts with O₂ to form HCH(O) and HO₂. R37 followed by R38 leads to HOCH₂C(O)O₂ (hydroxyl peroxy acetyl, or HPA), which also does not appear in the reference chemical mechanism. As with other acyl peroxy radicals, R35 will produce HOCH₂C(O)O₂NO₂ (HPAN), a third species only appearing in the mechanism when RO₂ photolysis is included.

5. RO₂ Near-IR Photolysis Rate Coefficients

The photolysis rate coefficient, or *j* value, of a species (units of s⁻¹) is given by

$$j = \int \sigma(\lambda)\phi(\lambda)I(\lambda)d\lambda \quad (1)$$

where λ is wavelength, $\sigma(\lambda)$ is the absorption cross section (units of cm²), $\phi(\lambda)$ is the photolysis quantum yield, and $I(\lambda)$ is the actinic (solar) flux (units of photons cm⁻² s⁻¹).⁴ In the following calculations we assumed $\phi(\lambda)$ was 1, and $I(\lambda)$ was obtained from the Madronich radiative transfer model.²³

Cross sections for the near-IR transitions have not been directly measured. Hunziker and Wendt²⁴ estimated that the σ_{max} of the HO₂ $\tilde{A}^2A' \leftarrow \tilde{X}^2A''$ (0,0) transition (where (*n,m*) indicates the excitation is from the lower electronic state with

TABLE 2: Thermochemistry of Peroxyl Radical Near-IR Photolysis Reactions^a

RO ₂ and Δ _f H ₂₉₈	+	photon ^b	→	products and Δ _f H ₂₉₈	Δ _{rxn} H ₂₉₈			
HO ₂ 2.8	+	<i>hν</i> 20.1	→	H 52.1	+	O ₂ 0		29.2
			→	OH 9.3	+	O(³ P) 59.57		45.97
CH ₃ O ₂ 4	+	<i>hν</i> 21.1	→	HCH(O) -26	+	OH 9.3		-41.8
			→	CH ₃ 35	+	O ₂ 0		
			→	CH ₃ O 4	+	O(³ P) 59.57		38.47
			→	CH ₂ 93	+	HO ₂ 2.8		70.7
CH ₃ CH ₂ O ₂ -6	+	<i>hν</i> 21.7	→	CH ₃ CH(O) -39.7	+	OH 9.3		-46.1
			→	H ₂ C=CH ₂ 12.45	+	HO ₂ 2.8		-0.45
			→	CH ₃ CH ₂ 28.4	+	O ₂ 0		12.7
			→	CH ₃ CH ₂ O -4.1	+	O(³ P) 59.57		39.77
CH ₃ C(O)O ₂ -41	+	<i>hν</i> 15.9	→	H ₂ C=C(O) -11	+	HO ₂ 2.8		16.9
			→	CH ₃ C(O) -2.4	+	O ₂ 0		22.7
			→	CH ₃ 35	+	CO ₂ -94.07	+	O(³ P) 59.57
			→	CH ₂ 93	+	CO ₂ -94.07	+	OH 9.3
			→	CH ₃ 35	+	CO -26.42	+	O ₂ 0
			→	CH ₃ C(O)O -49.6	+	O(³ P) 59.57		35.07
			→	CH ₂ 93	+	CO -26.42	+	HO ₂ 2.8
HOCH ₂ CH ₂ O ₂ -42.4 ^c	+	<i>hν</i> 21.7 ^d	→	HOCH ₂ CH(O) -86.7 ^e	+	OH 9.3		-56.7
			→	HCH(O) -26	+	HCH(O) -26	+	OH 9.3
			→	HOCH=CH ₂ -30 ^f	+	HO ₂ 2.8		-6.5
HOCH ₂ C(O)O ₂ -88 ^g	+	<i>hν</i> 15.9 ^h	→	HCH(O) -26	+	CO ₂ -94.07	+	OH 9.3
			→	HCH(O) -26	+	CO -26.42	+	HO ₂ 2.8

^a All enthalpies given in kcal mol⁻¹. Δ_fH₂₉₈ taken from DeMore et al.²⁸ except where noted. ^b For excitation of the given RO₂ from the ground rovibrational level of the \tilde{X} state to the ground rovibrational level of the \tilde{A} state.¹² ^c Derived by assuming that Δ_{rxn}H₂₉₈ of HOCH₂CH₂O₂ → HOCH₂CH₂ + O₂ equals Δ_{rxn}H₂₉₈ of CH₃CH₂O₂ → CH₃CH₂ + O₂ (34.4 kcal mol⁻¹) and then subtracting this Δ_{rxn}H₂₉₈ from the sum of Δ_fH₂₉₈ for HOCH₂CH₂ and O₂. ^d HOCH₂CH₂O₂ assumed to have same spectrum as CH₃CH₂O₂. ^e From semiempirical calculations of Chen et al.³² ^f Average of Δ_fH₂₉₈ from Turecek and Havlas³³ and Holmes and Lossing.³⁴ ^g We assumed that Δ_{rxn}H₂₉₈[HOCH₂C(O)O₂ → OH + CH₂C(O)O₂] = Δ_{rxn}H₂₉₈[HOCH₂CH(O) → OH + CH₂CH(O)] and Δ_{rxn}H₂₉₈[CH₃C(O)O₂ → H + CH₂C(O)O₂] = Δ_{rxn}H₂₉₈[CH₃CH(O) → H + CH₂CH(O)]. We calculated Δ_{rxn}H₂₉₈ for the aldehyde reactions using Δ_{rxn}H₂₉₈[CH₂CH(O)] from Rossi and Golden.³⁵ Then Δ_fH₂₉₈[HOCH₂C(O)O₂] = Δ_{rxn}H₂₉₈[CH₃C(O)O₂ → H + CH₂C(O)O₂] - Δ_{rxn}H₂₉₈[HOCH₂C(O)O₂ → OH + CH₂C(O)O₂] - Δ_fH₂₉₈[H] + Δ_fH₂₉₈[CH₃C(O)O₂] + Δ_fH₂₉₈[OH]. ^h HOCH₂C(O)O₂ assumed to have same spectrum as CH₃C(O)O₂.

m quanta in the active vibrational mode to the upper electronic state with *n* quanta in this vibrational mode) was on the order of 10 L mol⁻¹ cm⁻¹ (equivalent to 3.8 × 10⁻²⁰ cm²) by comparison of the intensities of this transition with those of the ultraviolet $\tilde{B}^2A'' \leftarrow \tilde{X}^2A''$ transition. From the spectra in Hunziker and Wendt¹² we see that the HO₂ $\tilde{A} \leftarrow \tilde{X}(1,0)$ σ_{max} is about twice that of σ_{max}(0,0). The strongest transition in the $\tilde{A} \leftarrow \tilde{X}$ spectra of all other RO₂ in Hunziker and Wendt¹² is the (0,0). We made the assumption that the σ_{max}(0,0) for all other RO₂ are approximately the same as σ_{max}(1,0) for HO₂, or about 8 × 10⁻²⁰ cm². The Hunziker and Wendt¹² spectra were then used to scale the RO₂ σ_{max}(*n*,0) where *n* > 0. We also assumed that the HOC₂H₄O₂ cross sections were the same as those of C₂H₅O₂ and that the cross sections of HOCH₂C(O)O₂ were equal to those of CH₃C(O)O₂, since the spectra of the hydroxylated RO₂ species have not been measured.

The *j* values could then be derived by using eq 1. The version of the Madronich radiative transfer model²³ we used did not

give accurate actinic flux predictions in the near-IR because the absorptions due to H₂O, CO₂, and O₄ were not included. We obtained the actinic flux for overhead sun including these absorptions from another radiative transfer model.²⁵ Using this actinic flux, the above estimated cross sections, and an assumed quantum yield of 1, we derived the following for overhead sun:

$$j(\text{CH}_3\text{O}_2) = 2.5 \times 10^{-4} \text{ s}^{-1} \approx 10^{-3} j(\text{NO}_3) \quad (2)$$

$$j(\text{C}_2\text{H}_5\text{O}_2) = 6 \times 10^{-4} \text{ s}^{-1} \approx 2.4 \times 10^{-3} j(\text{NO}_3) \quad (3)$$

$$j(\text{CH}_3\text{COO}_2) = 5 \times 10^{-4} \text{ s}^{-1} \approx 2 \times 10^{-3} j(\text{NO}_3) \quad (4)$$

Actinic flux in the wavelength regions of NO₃ and RO₂ absorptions should vary in approximately the same manner with solar zenith angle (angle of Sun from normal with respect to Earth's surface). We therefore used the zenith angle dependence of *j*(NO₃) as a surrogate for that of *j*(RO₂). We scaled *j*(NO₃)

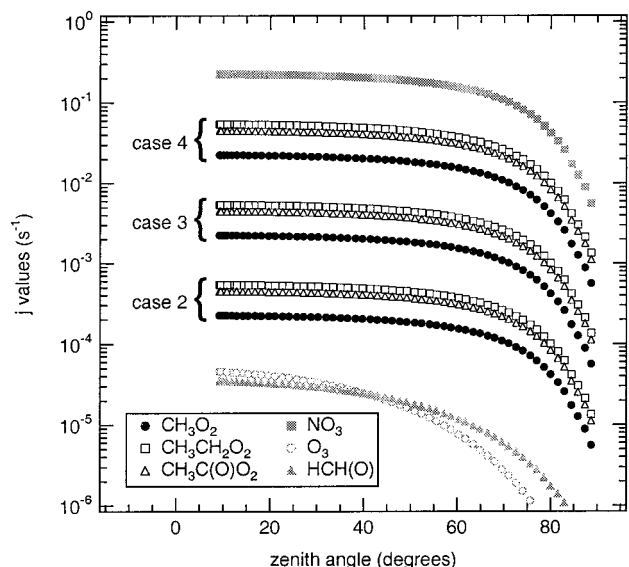


Figure 1. Estimated j values for RO_2 species whose near-IR spectra have been measured, as a function of zenith angle at the rural location. J values of NO_3 , $\text{O}_3 \rightarrow \text{O}(^1\text{D})$, and the $\text{HCH}(\text{O})$ radical channel are also shown for comparison. Box model cases 2, 3, and 4 included RO_2 photolysis with the indicated j values.

calculated by the Madronich radiative transfer model²³ according to eqs 2–4 to obtain each $j(\text{RO}_2)$ as a function of zenith angle.

The cross sections estimated above for the $\text{RO}_2 \tilde{\text{A}} \leftarrow \tilde{\text{X}}$ spectra are rather small for allowed electronic molecular transitions, which can exceed 10^{-17} cm^2 .²⁶ Ultraviolet transitions to the $\text{RO}_2 \tilde{\text{B}} \leftarrow \tilde{\text{A}}''$ state have peak cross sections in the range¹ of 3×10^{-18} to $1 \times 10^{-17} \text{ cm}^2$, which is 40–125 times larger than the Hunziker and Wendt¹² estimate for the $\tilde{\text{A}} \leftarrow \tilde{\text{X}}$ transition. We cannot assume the cross sections of the $\tilde{\text{A}} \leftarrow \tilde{\text{X}}$ and $\tilde{\text{B}} \leftarrow \tilde{\text{X}}$ transitions will be the same because the two excited states have different symmetries. However, it is likely that the above cross section estimates for the $\tilde{\text{A}} \leftarrow \tilde{\text{X}}$ transition represent a lower limit to the true values and therefore may cause us to underestimate the near-IR RO_2 photolysis rates. In the box model runs described below, we investigated the sensitivity to RO_2 photolysis by increasing $\sigma(\lambda)$ to span the range for allowed electronic transitions. Four different cases were examined for the RO_2 near-IR cross sections:

$$j(\text{RO}_2) = 0 \text{ (no } \text{RO}_2 \text{ photolysis included)} \quad (1)$$

$$\sigma_{\text{max}}[\text{RO}_2 \tilde{\text{A}} \leftarrow \tilde{\text{X}}(0,0)] = 8 \times 10^{-20} \text{ cm}^2 \text{ and } j(\text{RO}_2) \approx 10^{-3} j(\text{NO}_3) \quad (2)$$

$$\sigma_{\text{max}}[\text{RO}_2 \tilde{\text{A}} \leftarrow \tilde{\text{X}}(0,0)] = 8 \times 10^{-19} \text{ cm}^2 \text{ and } j(\text{RO}_2) \approx 10^{-2} j(\text{NO}_3) \quad (3)$$

$$\sigma_{\text{max}}[\text{RO}_2 \tilde{\text{A}} \leftarrow \tilde{\text{X}}(0,0)] = 8 \times 10^{-18} \text{ cm}^2 \text{ and } j(\text{RO}_2) \approx 10^{-1} j(\text{NO}_3) \quad (4)$$

The $\text{RO}_2 j$ values in case 2 are probably a lower limit and those of case 4, an upper limit, to the true values. The j values for the above cases as a function of zenith angle at one of the model locations are shown in Figure 1.

6. Photochemical Box Model Description

The photochemical box model was similar to one described previously²⁷ with a few modifications. Each chemical species

in the model with the exception of those discussed below was allowed to vary with time. The time-dependent concentrations of shorter lived species (OH , RO_2 , and most of the reactive nitrogen compounds) were assumed to be controlled by only photochemical reactions. The levels of longer lived species can be significantly affected by photochemistry and physical or transport processes such as emission from the surface, surface deposition, and advection. The time-dependent concentrations of longer lived compounds were therefore calculated from the photochemistry but were additionally constrained by a “virtual” source or sink term to reach a specified value at local noon. These “virtual” sources and sinks were expressed simply as additional first-order production and loss rates in the chemical continuity equations. There was no explicit atmospheric transport included in the box model. Rate constants were obtained from DeMore et al.²⁸ J values were precalculated for a fixed set of zenith angles and for various locations using the Madronich radiative transfer model²³ and then interpolated by the box model for the appropriate zenith angle at each time step. We kept $[\text{H}_2\text{O}]$, $[\text{CH}_4]$, $[\text{M}]$, temperature, pressure and altitude fixed at all times. To limit the number of new RO_2 photolysis reactions carried in the mechanism, we lumped alkanes with two or more carbons as “ethane” and alkenes as “ethene”:

$$[\text{“ethane”}] = \frac{k_{\text{OH}+\text{C}_2\text{H}_6}[\text{C}_2\text{H}_6] + k_{\text{OH}+\text{C}_3\text{H}_8}[\text{C}_3\text{H}_8] + \dots}{k_{\text{OH}+\text{C}_2\text{H}_6}} \quad (5)$$

$$[\text{“ethene”}] = \frac{k_{\text{OH}+\text{C}_2\text{H}_4}[\text{C}_2\text{H}_4] + k_{\text{OH}+\text{C}_3\text{H}_6}[\text{C}_3\text{H}_6] + \dots}{k_{\text{OH}+\text{C}_2\text{H}_4}} \quad (6)$$

The chemical mechanism included reactions R5–R43 for VOCs containing one to two carbon atoms and, in cases two to four, the RO_2 near-IR photolysis reactions R44–R47.

We considered three sets of chemical environments, chosen to represent remote, rural, and urban locations (see Table 3). We chose these locations in order to understand the effects of the RO_2 photolysis channels for different NO_x and VOC levels. As mentioned above, four cases were run at each location (start time was just before local noon). Integration was carried out until a constant diurnal cycle was achieved in all time-varying concentrations. In the base case (case 1), no RO_2 photolysis was considered. In this case, “virtual” sources and sinks for the longer lived species were adjusted so that their noon time concentrations maintained their initialized values at local noon. In cases 2–4, these “virtual” sources and sinks were kept the same as in the base case. Cases 2–4 included RO_2 photolysis with the above-mentioned j values. After a constant diurnal cycle was achieved in cases 2–4, we compared the change in the concentrations of all time-varying species from their case 1 final values. A relatively constant diurnal cycle was achieved in cases 2–4 after approximately 100 days of integration; we report the comparisons for the 198th day of the simulation. Model conditions and results from case 1 at solar noon for this day at each location are shown in Table 3.

7. Box Model Results and Discussion

The effects of including near-IR peroxy radical photolysis on all species in the chemical mechanism depend on the competition between photolysis and the other two primary loss processes for RO_2 , the reactions with NO and HO_2 . We explored this competition by varying both the j values for RO_2 photolysis in cases 2–4 and by changing the chemical environment from remote to rural to urban. Figure 2 compares the diurnally

TABLE 3: Selected Box Model Conditions and Results from Case 1^a

quantity	location		
	remote	rural	urban
site ^b	off SW coast of Tasmania (45°S, 144°E)	Kinterbish, Alabama (32°N, 88°W)	downtown Atlanta (34°N, 84°W)
date ^b	7 December	1 July	1 July
[M], molecule cm ⁻³ ^b	2.6 × 10 ¹⁹	2.4 × 10 ¹⁹	2.4 × 10 ¹⁹
[H ₂ O], % ^b	0.9	2.6	2.3
[CH ₄], ppmv ^b	1.68	1.7	1.75
[OH], molecule cm ⁻³ ^c	3.5 × 10 ⁶	3.2 × 10 ⁶	1.5 × 10 ⁷
[HO ₂], pptv ^c	12	38	52
[CH ₃ O ₂], pptv ^c	10	3	8
[CH ₃ CH ₂ O ₂], pptv ^c	0.06	0.6	10
[HOCH ₂ CH ₂ O ₂], pptv ^c	0.02	36	9
[CH ₃ C(O)O ₂], pptv ^c	0.007	0.4	2
[HOCH ₂ C(O)O ₂], pptv ^{c,d}	0	0	0
[RO ₂], pptv ^c	10	40	29
[HO ₂]+[RO ₂], pptv ^c	22	78	81
[H ₂ O ₂], ppbv ^e	0.44	0.8	3.9
[CH ₃ OOH], ppbv ^e	0.22	0.04	0.3
[ROOH], ppbv ^e	0.003	1.1	1.0
[HCH(O)], ppbv ^e	0.12	5.7	33
[CH ₃ CH(O)], ppbv ^e	0.002	1.1	12
[HOCH ₂ CH(O)], ppbv ^{d,e}	0	0	0
[NO], ppbv ^e	0.006	0.2	1
[NO ₂], ppbv ^c	0.008	0.9	16
[HNO ₃], ppbv ^e	0.006	0.9	23
[CH ₃ C(O)O ₂ NO ₂], ppbv ^c	0.0002	0.07	7
[HOCH ₂ C(O)O ₂ NO ₂], ppbv ^{c,d}	0	0	0
[NO _y], ppbv ^e	0.020	2.1	47
[O ₃], ppbv ^e	21	48	198
[CO], ppbv ^e	62	149	209
[“ethane”], ppbv ^{e,f}	0.36	39	733
[“ethene”], ppbv ^{e,f}	0.004	74	20

^a Fixed and constrained quantities are average or typical values for remote (First Aerosol Characterization Experiment³⁶), rural (Rural Oxidants in the Southern Environment program²⁷), and urban³⁷ locations. ppmv = parts per million by volume, ppbv = parts per billion by volume, pptv = parts per trillion by volume. ^b Fixed. ^c Calculated value at local noon based on photochemistry only. ^d Not produced in the case 1 chemical mechanism; formed when the RO₂ photolysis reactions are allowed to occur. ^e Calculated based on photochemistry but constrained by “virtual” sources or sinks to reach this value at local noon. ^f Lumped concentration of all nonmethane alkanes or alkenes.

averaged rates of RO₂ loss via the 3 main channels at each of the locations. In any particular chemical environment, increasing the RO₂ *j* value between cases 2 and 4 dramatically changes the competition between the three loss reactions. In the rural location, HO₂ and NO reactions are more important loss terms than photolysis at the lowest RO₂ *j* values (case 2), while RO₂ photolysis predominates for the upper limit *j* values (case 4). With the increased [NO] of the rural and urban locations (Table 3), photolysis becomes less important relative to NO reaction for each individual RO₂ species. At the rural location, only the largest *j* values (case 4) give photolysis rates comparable to those of NO loss, while in the urban location, NO reaction is always the dominant loss term. However, since VOCs also increase drastically in rural and urban areas relative to remote ones (Table 3), the overall participation of larger RO₂ increases. As Figure 2 shows, the rural and urban loss rates of CH₃CH₂O₂, HOCH₂CH₂O₂ and HOCH₂C(O)O₂ radicals are similar to or larger than those of CH₃O₂ and much larger than their values in the remote case. This is a result of the much larger concentrations of these radicals because of higher VOC levels in the rural and urban environments (Table 3). We thus have two opposing effects in changing the chemical environment from remote to urban: photolysis of each individual RO₂ becomes less important with higher [NO] but the overall level of RO₂ increases with higher [VOCs] and somewhat offsets the effects of increasing [NO_x].

Figure 3 shows the percentage change in the diurnally averaged concentrations of a number of chemical species for each of the *j* value cases at each location. Using the lower limit RO₂ *j* values (case 2) at any of the locations, there is no significant effect of including the RO₂ photolysis reactions in

the standard chemical mechanism. Methane is the major VOC in the remote environment. The levels of larger RO₂, aldehydes larger than HCH(O), and organic nitrate species are extremely small there (Table 3), so changes of a factor of 2 in their concentrations at the remote site are not significant to the overall chemistry. On the other hand, cases 3 and 4, representing midrange and upper limit RO₂ *j* values, demonstrate that RO₂ photolysis can have significant effects on some of the major species for each of the locations. In the rest of this discussion we focus on the specific changes caused by RO₂ photolysis in a few of the compounds.

[OH] increases in all chemical environments studied when peroxy radical photolysis is included in the chemical mechanism, because [OH] is a direct product of RO₂ photolysis (R44–R47). The largest effect on diurnally averaged OH levels is seen at the rural location. Despite having higher [NO] than the remote site, the rural area’s much higher VOC levels (mostly from biogenic VOCs such as isoprene) produce the highest [RO₂] and thus the greatest direct impact of the photolysis reactions of the 3 locations chosen.

HO₂ levels respond differently to RO₂ photolysis in the different locations because the controlling chemistry changes. In the remote environment, OH + CO (R9–R10) is the main source of HO₂ so that HO₂ follows the behavior of OH. In rural and urban environments, the larger VOC levels provide other sources of HO₂, such as RO₂ + NO (R20 and R23, R24–R25) and photolysis of aldehydes (R33–R34), so that HO₂ levels respond more to changes in these other species than to [OH] changes.

The levels of RO₂ species which can photolyze in the near-IR, such as CH₃O₂, CH₃CH₂O₂, and HOCH₂CH₂O₂, generally

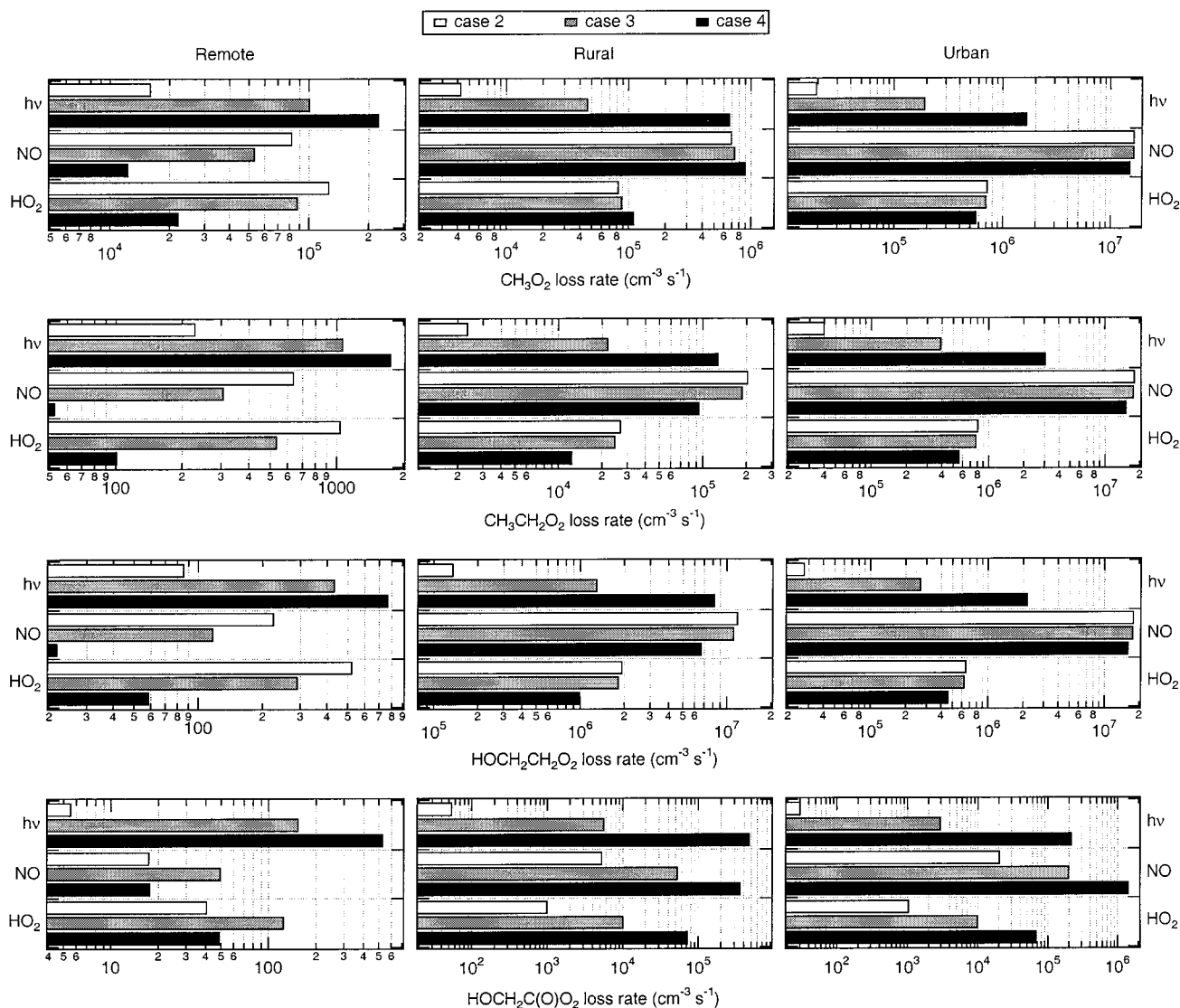


Figure 2. Diurnally averaged loss rates of selected RO₂ radicals via near-IR photolysis and reactions with NO and HO₂ for the different model locations.

decrease when this photolysis is included in the chemical mechanism because it represents an additional loss channel. Decreases in these RO₂ from the additional photolysis loss are mitigated in rural and urban areas by higher production from OH + VOCs (R11–R16). The increase in [CH₃O₂] at the rural site is also due to higher [CH₃C(O)O₂], which produces CH₃O₂ through self-reaction and reaction with NO.

An exception to this RO₂ behavior is HPA. Its parent molecule, HAC, is not produced in the simplified chemical mechanism considering only ethane and ethene oxidation (case 1), but only through photolysis of HOCH₂CH₂O₂ (R46). HAC reaches levels of up to 2 parts per billion (ppbv) for the rural and urban locations, its concentration increasing with increasing HOCH₂CH₂O₂ *j* value. Since HPA comes only from HAC oxidation by OH, [HPA] increases with increasing HOCH₂CH₂O₂ *j* value even though the *j* value of HPA (and thus its loss rate) is also increasing. The concentration of HPAN also increases with increasing *j* value because of its connection to HPA through R39. Since neither HAC, HPA, or HPAN are produced in the case 1 mechanism, we cannot show their percentage changes relative to case 1 directly. Instead in Figure 3 we have grouped each of these species with its unhydroxylated cousin: HAC with CH₃CH(O), represented as ΣRCH(O); HPA with PA, denoted ΣRPA; and HPAN with PAN, given by

ΣRPAN. The difference between changes in these combined categories and the changes in the unhydroxylated species represent the changes in the hydroxylated compound. The increases in the ΣRPA, ΣRCH(O), and ΣRPAN categories relative to PA, CH₃CH(O), and PAN show that predicted concentrations of the hydroxylated species HAC, HPA, and HPAN are significant compared with those of their unhydroxylated analogues.

Diurnally averaged concentrations of total organic peroxy radicals, RO₂, and total peroxy radicals, HO₂ + RO₂, decrease at all locations with the inclusion of RO₂ photolysis into the mechanism. In the remote environment the decrease in [RO₂] is just the change in [CH₃O₂] since the concentrations of other RO₂ are so small (Table 3). Decreases in [RO₂] at the rural and urban locations are controlled by the decreases in [CH₃CH₂O₂] and [HOCH₂CH₂O₂], which represent the bulk of RO₂ at these sites.

Significant effects of RO₂ photolysis are seen on the levels of longer-lived compounds including peroxides, aldehydes, organic nitrates, O₃, CO, and VOCs. Changes in peroxide levels follow the behavior of [HO₂] and [RO₂], the peroxide precursors in R19, R21, and R26. Aldehyde concentrations at the remote location increase because they are products of RO₂ photolysis (R44–R47). At the rural and remote sites, this additional source

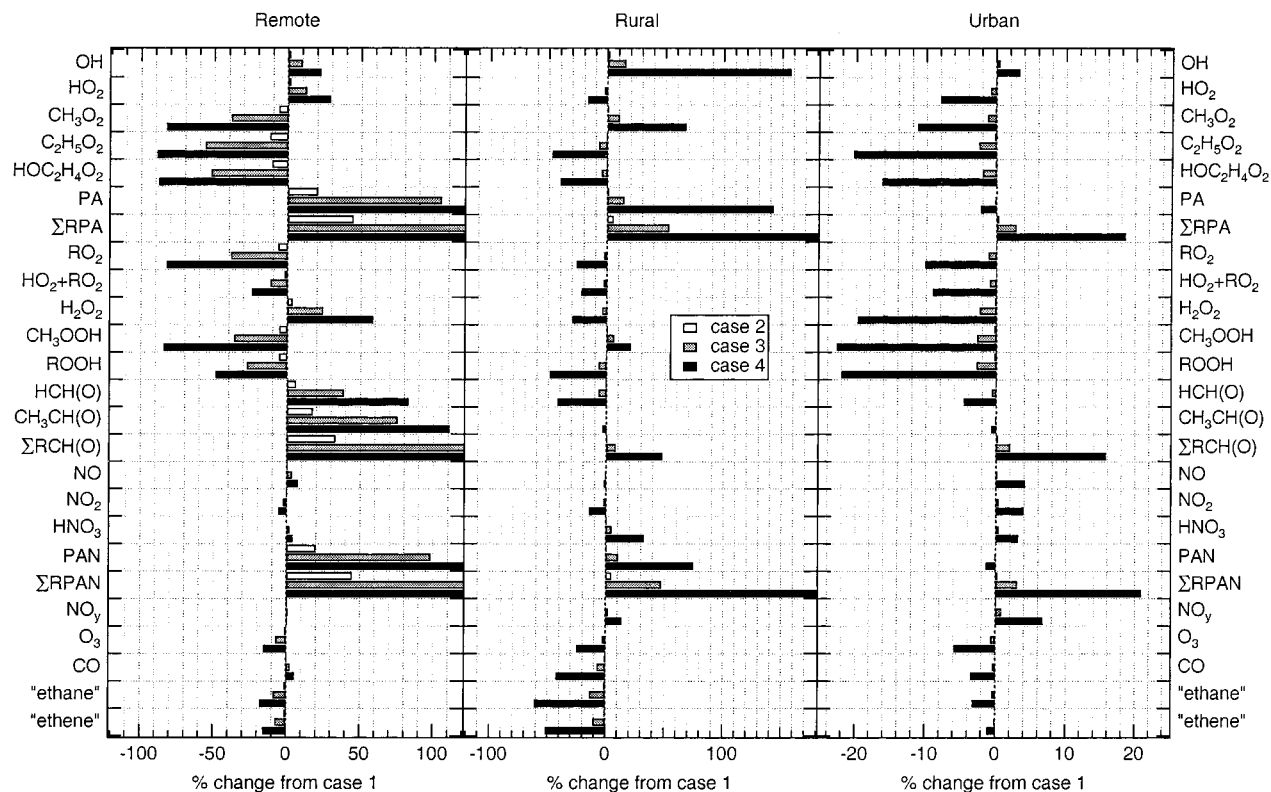


Figure 3. Percent changes in the diurnally averaged concentrations of the important model-calculated constituents when the near-IR RO_2 photolysis reactions are included.

of $\text{HCH}(\text{O})$ and $\text{CH}_3\text{CH}(\text{O})$ is balanced or surpassed by increased loss due to higher $[\text{OH}]$ (R36–R37). RO_2 photolysis changes the diurnally averaged concentrations of peroxides and aldehydes by as much as a factor of 2. Changes in the acyl peroxy nitrates reflect changes in $[\text{PA}]$ and $[\text{HPA}]$. $[\text{O}_3]$ decreases at all locations, with up to a 25% diurnally averaged decrease in the rural environment. The O_3 production rate is essentially limited by the rates of HO_2 or RO_2 reactions with NO (R17, R20, R24), and changes in $[\text{NO}]$ because of RO_2 photolysis are quite small, so that decreases in the predicted $[\text{O}_3]$ are similar to those in $[\text{HO}_2] + [\text{RO}_2]$. $[\text{CO}]$ changes are a balance between increased sinks with OH by R9 and changing production from photolysis of $\text{HCH}(\text{O})$ and other aldehydes (R33–R35). At the remote site, large increases in $[\text{HCH}(\text{O})]$ and subsequent CO production from its photolysis dominate the small increase in $[\text{OH}]$. For the rural and urban locations, increases in the OH sink and decreases in the aldehyde sources work in tandem to decrease $[\text{CO}]$ by up to 40% (case 4, rural site). VOC concentrations always decrease in the simulations carried out here because of the increasing $[\text{OH}]$, with the largest reductions seen at the rural location.

The model response of each chemical species to RO_2 photolysis throughout the day is complex, particularly in the rural and urban cases with their more complicated chemistry. As an example, the rural location's $[\text{OH}]$, $[\text{HOCH}_2\text{CH}_2\text{O}_2]$ (the most important RO_2 species at this location), $[\text{NO}]$, and $[\text{O}_3]$ for cases 2–4 and their changes from case 1 as a function of time are shown in Figure 4. RO_2 photolysis changes the time response of these species somewhat, particularly for the highest j values (case 4). RO_2 photolysis has less of a zenith angle dependence than photolysis of $\text{O}_3 \rightarrow \text{O}(^1\text{D})$ (R5) or $\text{HCH}(\text{O})$ (R33b) (Figure 1), because near-IR and visible wavelengths are less attenuated than ultraviolet ones in the troposphere as the zenith angle increases. Since R5 followed by R7 and R33b followed by R35 and R10 are major radical sources, we expect

the greatest effect of RO_2 photolysis to occur at the largest zenith angles. $[\text{OH}]$ shows the largest increases near sunrise and sunset, and throughout the day increases by up to 100–200% for the highest $\text{RO}_2 j$ values. Diurnal averages of $[\text{OH}]$ in Figure 3 show less of an increase because of the nearly negligible $[\text{OH}]$ at night. $[\text{HOCH}_2\text{CH}_2\text{O}_2]$ decreases throughout the day and even at night although photolysis is no longer occurring, because higher nighttime $[\text{NO}]$ results in greater $\text{HOCH}_2\text{CH}_2\text{O}_2$ loss via R24. During afternoon $[\text{NO}]$ decreases because of faster $[\text{NO}_x]$ removal by R41. O_3 is longer lived than these other species, so the effects of RO_2 photolysis persist throughout the diurnal cycle. Decreased daytime O_3 production due to lower $[\text{RO}_2]$ causes lower $[\text{O}_3]$ throughout the entire day, including at night when no O_3 production is actually occurring.

8. Conclusions

We have investigated the tropospheric effects of a novel set of peroxy radical photolysis reactions involving excitation from the ground electronic state to the first excited electronic state in the near-IR and subsequent rearrangement to form OH and an aldehyde. The estimated j values presume absorption cross sections which are small for an allowed electronic transition. Using cross sections more typical for such transitions, we see significant effects from these photolysis reactions on a number of species. In particular, relative to the standard chemical mechanism, we predict enhancements in OH levels, decreases in peroxy radical levels, changes in the concentrations of the photochemical products of CO and VOC oxidation, and decreased O_3 , CO , and VOC levels, with some diurnally averaged concentrations changing by as much as a factor of 2. If lower limit estimates of the near-IR j values of RO_2 are indeed correct, the diurnally averaged effects of peroxy radical photolysis in the troposphere are probably small. Nevertheless, the chemistry described could still affect the diurnal distribution of atmospheric radicals.

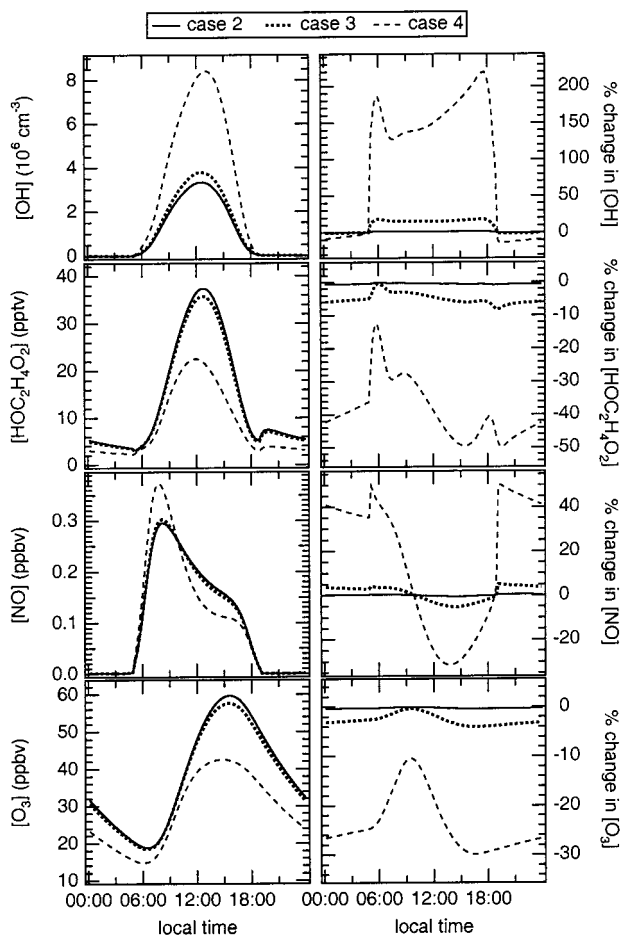


Figure 4. Concentrations of selected species for model cases 2–4 and the percent changes relative to case 1 as a function of time of day at the rural location. Case 1 concentrations of these species are indistinguishable from those of case 2 on this scale.

The presence of near-IR RO₂ photolysis in the atmosphere could be detected by looking for relationships between species which are signatures of this particular chemistry. For example, we predict that a correlation between OH and aldehyde levels should be observed at very high zenith angles as a result of RO₂ photolysis. Alternatively, one could investigate the agreement between observed levels of various chemical species and predictions from models using both the standard chemical mechanism and including RO₂ photolysis, though such an approach has its drawbacks. Model-measurement [OH] discrepancies of a factor of 2 should be detectable if the concentrations of all precursors and reactants, particularly VOCs, are measured.^{7–10,29} Radical measurements are relatively new and have yet to be tested in many environments where the other necessary observations are also made. Longer-lived gases such as O₃ and CO could be measured with enough confidence^{30,31} to distinguish differences of 30–50% from model predictions if chemistry were the only factor controlling their abundance. However, long tropospheric lifetimes for ozone and CO (on the order of days to months) require a three-dimensional chemical-transport model to simulate all of the various physical processes besides chemistry that have a major effect on their concentrations. The large uncertainties associated with these simulations could obscure the effects of any changes to the chemical mechanism.

The limiting uncertainties in these calculations are the absorption cross sections for the near-IR $\tilde{A} \leftarrow \tilde{X}$ transition and the yields and identities of the photoproducts. Our *j* value cases

span the range of absorption cross sections for allowed electronic transitions but show drastically different results depending on the order of magnitude of these cross sections. We have used thermochemical arguments to constrain the photoproducts which are energetically accessible with near-IR excitation. Thermochemistry alone does not indicate the activation barriers or rates of various reaction paths, which must either be calculated by quantum chemical methods or, ultimately, measured in the laboratory. Experimental measurements of the absorption cross sections and photoproducts are crucial to any further understanding of the effects of the proposed chemistry. The impetus for such laboratory work is clear based on the calculations we have carried out here.

Acknowledgment. We thank the investigators from the First Aerosol Characterization Experiment for making their data available. We are indebted to Bob Portmann for his radiative transfer model results. We thank Michael Trainer and Susan Solomon for insightful discussions of this work. G.B.E. is supported by a grant from the Chemical Physics Program, United States Department of Energy (Grant DE-FG02-87ER17695). V.V. thanks the University of Colorado for a Faculty Fellowship and the National Science Foundation for continuing support.

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