

**Supplement of “Inversion of CO and NO<sub>x</sub> emissions  
using the adjoint of the IMAGES model”**

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## **Abstract**

This supplement contains three tables. The chemical species included in the IMAGES model are presented in Table 1. The chemical reaction mechanism of the model is described in Table 2. References for the reaction rates are also given. In Table 3 we present the photodissociations included in the model, as well as references for their cross sections, quantum yields, and products.

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**Table 1.** Chemical species included in the model.

<b>Chemical species included in the model</b>		
<i>Species Category</i>	<i>Chemical Formula</i>	<i>Name</i>
Fixed	O <sub>2</sub> : 20.95%	oxygen
	N <sub>2</sub> : 79.05%	nitrogen
	H <sub>2</sub> O (from ECMWF)	water
	H <sub>2</sub> : 550 ppbv	hydrogen
	N <sub>2</sub> O : 311 ppbv	nitrous oxide
	COS : 0.5 ppbv	carbonyl sulfide
Long-lived (transported)	O <sub>3</sub>	ozone
	H <sub>2</sub> O <sub>2</sub>	hydrogen peroxide
	HNO <sub>3</sub>	nitric acid
	NO <sub>x</sub> (NO + NO <sub>2</sub> + NO <sub>3</sub> + HNO <sub>4</sub> + 2N <sub>2</sub> O <sub>5</sub> )	nitrogen oxides (family)
	CH <sub>4</sub>	methane
	C <sub>2</sub> H <sub>6</sub>	ethane
	C <sub>2</sub> H <sub>4</sub>	ethylene
	C <sub>3</sub> H <sub>8</sub>	propane
	C <sub>3</sub> H <sub>6</sub>	propylene
	ISOP (C <sub>5</sub> H <sub>8</sub> )	isoprene
	APIN (C <sub>10</sub> H <sub>16</sub> )	α-pinene
	OTHC	other hydrocarbons
	CO	carbon monoxide
	CH <sub>3</sub> OH	methanol
	CH <sub>2</sub> O	formaldehyde
	CH <sub>3</sub> CHO	acetaldehyde
	GLYALD (CH <sub>2</sub> OHCHO)	glycolaldehyde
	HYDRALD (HOCH <sub>2</sub> C(CH <sub>3</sub> )=CHCHO + HOCH <sub>2</sub> CH=C(CH <sub>3</sub> )CHO)	hydroxy carbonyls from ISOP
	MACR (CH <sub>2</sub> =CCH <sub>3</sub> CHO)	methylacrolein
	CH <sub>3</sub> COCH <sub>3</sub>	acetone
	HYAC (CH <sub>2</sub> OHCOCH <sub>3</sub> )	hydroxy acetone
	MVK (CH <sub>2</sub> =CHCOCH <sub>3</sub> )	methylvinylketone
	CH <sub>3</sub> OOH	methyl peroxide
	C <sub>2</sub> H <sub>5</sub> OOH	ethyl peroxide
	POOH (C <sub>3</sub> H <sub>6</sub> OHOH)	peroxide from propylene
	CH <sub>3</sub> COOOH	peracetic acid
	C <sub>3</sub> H <sub>7</sub> OOH	peroxide from propane
	ACETOOH (CH <sub>3</sub> COCH <sub>2</sub> OOH)	peroxide from acetone
	ISOPOOH (C <sub>5</sub> H <sub>8</sub> OHOH)	peroxide from ISOP
	MACROOH (CH <sub>3</sub> COCHOHCH <sub>2</sub> OH)	peroxide from MACR

Chemical species included in the model (continued)		
Species Category	Chemical Formula	Name
	XOOH (HOCH <sub>2</sub> COOHCH <sub>3</sub> CH=CHOH)	peroxide from XO <sub>2</sub>
	PAN (CH <sub>3</sub> CO <sub>3</sub> NO <sub>2</sub> )	peroxy-acetyl nitrate
	MPAN (CH <sub>2</sub> =CCH <sub>3</sub> CO <sub>3</sub> NO <sub>2</sub> )	peroxymethacrylic nitrate
	ONITR (C <sub>5</sub> H <sub>8</sub> OHONO <sub>2</sub> )	substituted organic nitrate from ISOP
	SO <sub>2</sub>	sulfur dioxide
	SO <sub>4</sub> <sup>2-</sup>	non-sea-salt sulfate
	DMS (CH <sub>3</sub> SCH <sub>3</sub> )	dimethyl sulfide
	CS <sub>2</sub>	carbon disulfide
	H <sub>2</sub> S	hydrogen sulfide
Short-lived	O( <sup>1</sup> D)	oxygen atom (excited state)
	OH	hydroxyl radical
	HO <sub>2</sub>	hydroperoxyl radical
	NO	nitrogen oxide
	NO <sub>2</sub>	nitrogen dioxide
	HNO <sub>4</sub>	pernitric acid
	NO <sub>3</sub>	nitrogen trioxide
	N <sub>2</sub> O <sub>5</sub>	nitrogen hemipentoxide
	CH <sub>3</sub> COCHO	methylglyoxal
	CH <sub>3</sub> O <sub>2</sub>	methylperoxy radical
	PO <sub>2</sub> (C <sub>3</sub> H <sub>6</sub> OHO <sub>2</sub> )	peroxy radical from propylene
	ACETO <sub>2</sub> (CH <sub>3</sub> COCH <sub>2</sub> O <sub>2</sub> )	peroxy radical from acetone
	XO <sub>2</sub> (HOCH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> CH=CHOH)	peroxy radical from HYDRALD+OH and ISOPOOH+OH
	C <sub>2</sub> H <sub>5</sub> O <sub>2</sub>	ethylperoxy radical
	C <sub>3</sub> H <sub>7</sub> O <sub>2</sub>	propylperoxy radical
	ISOPO <sub>2</sub> (HOCH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> CH=CH <sub>2</sub> )	peroxy radical from ISOP
	MACRO <sub>2</sub> (CH <sub>3</sub> COCHO <sub>2</sub> CH <sub>2</sub> OH)	peroxy radical from MACR+OH
	CH <sub>3</sub> CO <sub>3</sub>	acetylperoxy radical
MCO <sub>3</sub> (CH <sub>2</sub> =CCH <sub>3</sub> CO <sub>3</sub> )	peroxymethacrylic radical	

**Table 2.** Chemical reaction mechanism and kinetic rates.

<b>Chemical reaction mechanism and kinetic rates</b>		
<i>Reaction</i>	<i>Rate</i>	<i>Ref.</i>
$O(^1D) + N_2 \rightarrow O_3 + N_2$	$2.14(-11) \exp(110/T)$	1,11
$O(^1D) + O_2 \rightarrow O_3 + O_2$	$3.2(-11) \exp(70/T)$	1
$O(^1D) + H_2O \rightarrow OH + OH$	$2.2(-10)$	2
$O(^1D) + N_2O \rightarrow N_2 + O_2$	$4.9(-11)$	2
$O(^1D) + N_2O \rightarrow NO + NO$	$6.7(-11)$	2
$O(^1D) + CH_4 \rightarrow 0.75(OH + CH_3O_2)$ $+0.2(CH_2O + HO_2) + 0.05(CH_2O + H_2)$	$1.5(-10)$	1
$O(^1D) + H_2 \rightarrow OH + HO_2$	$1.1(-10)$	1
$OH + HO_2 \rightarrow H_2O + O_2$	$4.8(-11) \exp(250/T)$	1
$OH + OH + M \rightarrow H_2O_2 + M$	$k_0 = 6.2(-31)(300/T)^{1.0}$ $k_\infty = 2.6(-11)$ $Fc = 0.6$	1
$OH + OH \rightarrow O_3 + H_2O$	$4.2(-12) \exp(-240/T)$	1
$OH + O_3 \rightarrow HO_2 + O_2$	$1.5(-12) \exp(-880/T)$	2
$HO_2 + O_3 \rightarrow OH + 2O_2$	$2.0(-14) \exp(-680/T)$	2
$OH + H_2O_2 \rightarrow H_2O + HO_2$	$2.9(-12) \exp(-160/T)$	1
$OH + H_2 \rightarrow H_2O + HO_2$	$5.5(-12) \exp(-2000/T)$	1
$HO_2 + HO_2 \rightarrow H_2O_2$	$2.30(-13) \exp(600/T)$	1
$HO_2 + HO_2 + M \rightarrow H_2O_2 + M$	$1.70(-33) \exp(1000/T)$	1
$HO_2 + HO_2 + H_2O \rightarrow H_2O_2 + H_2O$	$3.22(-34) \exp(2800/T)$	1
$HO_2 + HO_2 + H_2O + M \rightarrow H_2O_2 + H_2O + M$	$2.38(-54) \exp(3200/T)$	1
$NO + O_3 \rightarrow NO_2 + O_2$	$3.0(-12) \exp(-1500/T)$	2
$NO + HO_2 \rightarrow NO_2 + OH$	$3.5(-12) \exp(250/T)$	1
$NO_2 + OH + M \rightarrow HNO_3 + M$	$k_0 = 2.4(-30)(300/T)^{3.1}$ $k_\infty = 1.7(-11)(300/T)^{2.1}$ $Fc = 0.6$	2
$HNO_3 + OH \rightarrow H_2O + NO_3$	$k = k_0 + k_3[M]/(1 + k_3[M]/k_2)$ $k_0 = 2.4(-14) \exp(460/T)$ $k_2 = 2.7(-17) \exp(2199/T)$ $k_3 = 6.5(-34) \exp(1335/T)$	2
$NO_2 + HO_2 + M \rightarrow HO_2NO_2 + M$	$k_0 = 1.8(-31)(300/T)^{3.2}$ $k_\infty = 4.7(-12)(300/T)^{1.4}$ $Fc = 0.6$	1
$HO_2NO_2 + M \rightarrow HO_2 + NO_2 + M$	$K_{eq} = 2.1(-27) \exp(10900/T)$	1
$HO_2NO_2 + OH \rightarrow H_2O + NO_2 + O_2$	$1.3(-12) \exp(380/T)$	1
$NO_2 + O_3 \rightarrow NO_3 + O_2$	$1.2(-13) \exp(-2450/T)$	1
$NO_3 + HO_2 \rightarrow OH + NO_2$	$3.5(-12)$	1

Chemical reaction mechanism and kinetic rates (continued)		
Reaction	Rate	Ref.
$\text{NO}_3 + \text{OH} \rightarrow \text{HO}_2 + \text{NO}_2$	$2.2(-11)$	1
$\text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2$	$1.5(-11) \exp(170/T)$	1
$\text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}$	$k_0 = 2.0(-30)(300/T)^{4.4}$ $k_\infty = 1.4(-12)(300/T)^{0.7}$ $Fc = 0.6$	2
$\text{N}_2\text{O}_5 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_3 + \text{M}$	$K_{eq} = 3.0(-27) \exp(10991/T)$	2
$\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O}$	$2.45(-12) \exp(-1775/T)$	1
$\text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{OOH} + \text{O}_2$	$4.1(-13) \exp(750/T)$	3
$\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_2\text{O} + \text{NO}_2 + \text{HO}_2$	$2.8(-12) \exp(300/T)$	3
$\text{CH}_3\text{O}_2 + \text{NO}_3 \rightarrow \text{CH}_2\text{O} + \text{HO}_2 + \text{NO}_2$	$1.1(-12)$	8
$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow 2\text{CH}_2\text{O} + 2\text{HO}_2$	$5.0(-13) \exp(-424/T)$	5
$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{CH}_3\text{OH}$	$1.9(-14) \exp(706/T)$	5
$\text{CH}_3\text{O}_2 + \text{O}_3 \rightarrow \text{CH}_2\text{O} + \text{HO}_2$	$3.0(-16) \exp(-1000/T)$	3
$\text{OH} + \text{CH}_3\text{OOH} \rightarrow 0.3(\text{CH}_2\text{O} + \text{OH}) + 0.7\text{CH}_3\text{O}_2$	$3.8(-12) \exp(200/T)$	1
$\text{OH} + \text{CH}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{CO} + \text{HO}_2$	$1.0(-11)$	1
$\text{NO}_3 + \text{CH}_2\text{O} \rightarrow \text{CO} + \text{HO}_2 + \text{HNO}_3$	$6.0(-13) \exp(-2058/T)$	5
$\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{HO}_2$	$1.5(-13)(1 + 0.6P_{atm})$	1
$\text{OH} + \text{C}_2\text{H}_6 \rightarrow \text{H}_2\text{O} + \text{C}_2\text{H}_5\text{O}_2$	$7.8(-12) \exp(-1025/T)$	4
$\text{C}_2\text{H}_5\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2 + \text{NO}_2$	$2.7(-12) \exp(350/T)$	3
$\text{C}_2\text{H}_5\text{O}_2 + \text{NO}_3 \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2 + \text{NO}_2$	$2.5(-12)$	8
$\text{C}_2\text{H}_5\text{O}_2 + \text{HO}_2 \rightarrow \text{C}_2\text{H}_5\text{OOH} + \text{O}_2$	$7.4(-13) \exp(700/T)$	3
$\text{C}_2\text{H}_5\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow 0.7\text{CH}_2\text{O}$ $+ 0.8\text{CH}_3\text{CHO} + \text{HO}_2$ $+ 0.3\text{CH}_3\text{OH} + 0.2\text{C}_2\text{H}_5\text{OH}$	$2.0(-13)$	5
$\text{C}_2\text{H}_5\text{O}_2 + \text{C}_2\text{H}_5\text{O}_2 \rightarrow 1.2\text{HO}_2$ $+ 1.6\text{CH}_3\text{CHO} + 0.4\text{C}_2\text{H}_5\text{OH}$	$6.8(-14)$	1
$\text{C}_2\text{H}_5\text{OOH} + \text{OH} \rightarrow 0.5\text{C}_2\text{H}_5\text{O}_2$ $+ 0.5\text{CH}_3\text{CHO} + 0.5\text{OH}$	$3.8(-12) \exp(200/T)$	6
$\text{OH} + \text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_7\text{O}_2 + \text{H}_2\text{O}$	$8.0(-12) \exp(-590/T)$	4
$\text{C}_3\text{H}_7\text{O}_2 + \text{NO} \rightarrow 0.82\text{CH}_3\text{COCH}_3$ $+ 0.27\text{CH}_3\text{CHO} + \text{NO}_2 + \text{HO}_2$	$2.7(-12) \exp(350/T)$	5,a
$\text{C}_3\text{H}_7\text{O}_2 + \text{HO}_2 \rightarrow \text{C}_3\text{H}_7\text{OOH} + \text{O}_2$	$1.51(-13) \exp(1300/T)$	8
$\text{C}_3\text{H}_7\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow 0.82\text{CH}_3\text{COCH}_3$ $+ \text{CH}_2\text{O} + \text{HO}_2$	$3.75(-13) \exp(-40/T)$	7
$\text{C}_3\text{H}_7\text{OOH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{C}_3\text{H}_7\text{O}_2$	$3.8(-12) \exp(200/T)$	7
$\text{OH} + \text{CH}_3\text{COCH}_3 \rightarrow \text{ACETO}_2 + \text{H}_2\text{O}$	$1.1(-12) \exp(-520/T)$	4
$\text{ACETO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{CH}_2\text{O} + \text{CH}_3\text{CO}_3$	$2.8(-12) \exp(300/T)$	3
$\text{ACETO}_2 + \text{HO}_2 \rightarrow \text{ACETO}_2\text{OH} + \text{O}_2$	$8.6(-13) \exp(700/T)$	3
$\text{ACETO}_2 + \text{CH}_3\text{O}_2 \rightarrow 0.3(\text{CH}_3\text{CO}_3 + \text{CH}_2\text{O} + \text{HO}_2)$	$7.5(-13) \exp(500/T)$	3

Chemical reaction mechanism and kinetic rates (continued)		
Reaction	Rate	Ref.
+0.2(HYAC + CH <sub>2</sub> O)		
+0.5(CH <sub>3</sub> COCHO + CH <sub>3</sub> OH)		
ACETOOH + OH → ACETO <sub>2</sub> + H <sub>2</sub> O	3.8(-12) exp(200/T)	7
OH + C <sub>3</sub> H <sub>6</sub> + M → PO <sub>2</sub> + M	$k_0 = 8.(-27)(300/T)^{3.5}$ $k_\infty = 3.0(-11)$ $Fc = 0.5$	4
O <sub>3</sub> + C <sub>3</sub> H <sub>6</sub> → 0.54CH <sub>2</sub> O + 0.19HO <sub>2</sub> + 0.33OH +0.08CH <sub>4</sub> + 0.56CO + 0.5CH <sub>3</sub> CHO +0.31CH <sub>3</sub> O <sub>2</sub> + 0.25CH <sub>3</sub> COOH	6.5(-15) exp(-1900/T)	1
OH + C <sub>2</sub> H <sub>4</sub> + M → M + PO <sub>2</sub>	$k_0 = 7.(-29)(300/T)^{3.1}$ $k_\infty = 9.(-12)$ $Fc = 0.48$	4
O <sub>3</sub> + C <sub>2</sub> H <sub>4</sub> → CH <sub>2</sub> O + 0.5CO + 0.12HO <sub>2</sub> +0.12OH + 0.32CH <sub>3</sub> COOH	1.2(-14) exp(-2630/T)	5
PO <sub>2</sub> + NO → CH <sub>3</sub> CHO + CH <sub>2</sub> O + HO <sub>2</sub> + NO <sub>2</sub>	2.7(-12) exp(350/T)	5,a
PO <sub>2</sub> + NO <sub>3</sub> → CH <sub>3</sub> CHO + CH <sub>2</sub> O + HO <sub>2</sub> + NO <sub>2</sub>	2.5(-12)	8
PO <sub>2</sub> + HO <sub>2</sub> → POOH + O <sub>2</sub>	7.5(-13) exp(700/T)	5
POOH + OH → 0.5PO <sub>2</sub> + 0.5OH + 0.5HYAC + H <sub>2</sub> O	3.8(-12) exp(200/T)	5
CH <sub>3</sub> CHO + OH → CH <sub>3</sub> CO <sub>3</sub> + H <sub>2</sub> O	5.6(-12) exp(310/T)	4
CH <sub>3</sub> CHO + NO <sub>3</sub> → CH <sub>3</sub> CO <sub>3</sub> + HNO <sub>3</sub>	1.4(-12) exp(-1860/T)	4
CH <sub>3</sub> CO <sub>3</sub> + NO → CH <sub>3</sub> O <sub>2</sub> + NO <sub>2</sub> + CO <sub>2</sub>	8.1(-12) exp(270/T)	3
CH <sub>3</sub> CO <sub>3</sub> + NO <sub>3</sub> → CH <sub>3</sub> O <sub>2</sub> + NO <sub>2</sub> + CO <sub>2</sub>	4.1(-12)	8
CH <sub>3</sub> CO <sub>3</sub> + NO <sub>2</sub> + M → PAN + M	$k_0 = 8.5(-29)(300/T)^{6.5}$ $k_\infty = 1.1(-11)(300/T)^{1.0}$ $Fc = 0.6$	3
PAN + M → CH <sub>3</sub> CO <sub>3</sub> + NO <sub>2</sub> + M	$K_{eq} = 9.0(-29) \exp(14000/T)$	5
CH <sub>3</sub> CO <sub>3</sub> + HO <sub>2</sub> → 0.3O <sub>3</sub> + 0.7O <sub>2</sub> +0.7CH <sub>3</sub> COOOH + 0.3CH <sub>3</sub> COOH	4.3(-13) exp(1040/T)	3
CH <sub>3</sub> CO <sub>3</sub> + CH <sub>3</sub> CO <sub>3</sub> → 2CH <sub>3</sub> O <sub>2</sub> + 2CO <sub>2</sub>	2.5(-12) exp(500/T)	3
CH <sub>3</sub> O <sub>2</sub> + CH <sub>3</sub> CO <sub>3</sub> → CH <sub>2</sub> O + 0.9CH <sub>3</sub> O <sub>2</sub> +0.9HO <sub>2</sub> + 0.9CO <sub>2</sub> + 0.1CH <sub>3</sub> COOH	2.0(-12) exp(500/T)	3
CH <sub>3</sub> COOOH + OH → 0.5CH <sub>3</sub> CO <sub>3</sub> + H <sub>2</sub> O +0.5CH <sub>2</sub> O + 0.5CO <sub>2</sub>	3.8(-12) exp(200/T)	5,b
ISOP + OH → ISOPO <sub>2</sub>	2.54(-11) exp(410/T)	5
ISOP + O <sub>3</sub> → 0.4MACR + 0.2MVK + 0.1O <sub>3</sub> + 0.27OH +0.07C <sub>3</sub> H <sub>6</sub> + 0.6CH <sub>2</sub> O + 0.3CO +0.2MCO <sub>3</sub> + 0.06HO <sub>2</sub> + 0.2CH <sub>3</sub> COOH	1.05(-14) exp(-2000/T)	5
ISOP + NO <sub>3</sub> → 0.794ONITR + 0.206NO <sub>2</sub> + 0.039MVK +0.167MACR + 0.072CH <sub>2</sub> O + 0.794HO <sub>2</sub>	3.03(-12) exp(-446/T)	5 <sup>c</sup>

Chemical reaction mechanism and kinetic rates (continued)		
Reaction	Rate	Ref.
$\text{OH} + \text{OTHC} \rightarrow 0.8\text{ISOPO}_2$	$6.(-11) \exp(-540/T)$	<i>g</i>
$\text{ISOPO}_2 + \text{NO} \rightarrow 0.23\text{MACR} + 0.32\text{MVK} + 0.08\text{ONITR}$ $+ 0.92\text{NO}_2 + \text{HO}_2 + 0.51\text{CH}_2\text{O} + 0.37\text{HYDRALD}$	$2.7(-12) \exp(350/T)$	5, <i>a</i>
$\text{ISOPO}_2 + \text{NO}_3 \rightarrow \text{HO}_2 + \text{NO}_2 + 0.6\text{CH}_2\text{O}$ $+ 0.25\text{MACR} + 0.35\text{MVK} + 0.4\text{HYDRALD}$	$2.5(-12)$	5,8
$\text{ISOPO}_2 + \text{HO}_2 \rightarrow \text{ISOPOOH}$	$2.06(-13) \exp(1300/T)$	5,8
$\text{ISOPO}_2 + \text{CH}_3\text{O}_2 \rightarrow 0.25\text{CH}_3\text{OH} + \text{HO}_2 + 1.2\text{CH}_2\text{O}$ $+ 0.19\text{MACR} + 0.26\text{MVK} + 0.3\text{HYDRALD}$	$5.0(-13) \exp(400/T)$	5
$\text{ISOPO}_2 + \text{CH}_3\text{CO}_3 \rightarrow \text{CH}_3\text{O}_2 + \text{HO}_2 + 0.6\text{CH}_2\text{O}$ $+ 0.25\text{MACR} + 0.35\text{MVK} + 0.4\text{HYDRALD}$	$1.4(-11)$	5
$\text{MACR} + \text{OH} \rightarrow 0.5\text{MACRO}_2 + 0.5\text{H}_2\text{O} + 0.5\text{MCO}_3$	$1.86(-11) \exp(175/T)$	5
$\text{MACR} + \text{O}_3 \rightarrow 0.8\text{CH}_3\text{COCHO} + 0.275\text{HO}_2$ $+ 0.2\text{CO} + 0.2\text{O}_3 + 0.7\text{CH}_2\text{O} + 0.215\text{OH}$	$4.4(-15) \exp(-2500/T)$	5
$\text{MVK} + \text{OH} \rightarrow \text{MACRO}_2$	$4.13(-12) \exp(452/T)$	5
$\text{MVK} + \text{O}_3 \rightarrow 0.8\text{CH}_2\text{O} + 0.95\text{CH}_3\text{COCHO} + 0.08\text{OH}$ $+ 0.06\text{HO}_2 + 0.05\text{CO} + 0.04\text{CH}_3\text{CHO} + 0.2\text{O}_3$	$7.52(-16) \exp(-1521/T)$	5
$\text{MACRO}_2 + \text{NO} \rightarrow \text{NO}_2 + 0.47\text{HO}_2 + 0.22(\text{CO} + \text{HYAC})$ $+ 0.53(\text{CH}_3\text{CO}_3 + \text{GLYALD})$ $+ 0.25(\text{CH}_2\text{O} + \text{CH}_3\text{COCHO})$	$2.7(-12) \exp(350/T)$	5, <i>a</i>
$\text{MACRO}_2 + \text{NO} \rightarrow \text{ONITR}$	$1.3(-13) \exp(350/T)$	5
$\text{MACRO}_2 + \text{NO}_3 \rightarrow \text{NO}_2 + 0.47\text{HO}_2 + 0.22(\text{CO} + \text{HYAC})$ $+ 0.53(\text{CH}_3\text{CO}_3 + \text{GLYALD})$ $+ 0.25(\text{CH}_2\text{O} + \text{CH}_3\text{COCHO})$	$2.5(-12)$	5,8
$\text{MACRO}_2 + \text{HO}_2 \rightarrow \text{MACROOH}$	$1.82(-13) \exp(1300/T)$	5,8
$\text{MACRO}_2 + \text{CH}_3\text{O}_2 \rightarrow 0.73\text{HO}_2 + 0.88\text{CH}_2\text{O} + 0.11\text{CO}$ $+ 0.24\text{CH}_3\text{COCHO} + 0.25\text{CH}_3\text{OH} + 0.26\text{GLYALD}$ $+ 0.23\text{HYAC} + 0.26\text{CH}_3\text{CO}_3$	$5.0(-13) \exp(400/T)$	5
$\text{MACRO}_2 + \text{CH}_3\text{CO}_3 \rightarrow 0.53\text{GLYALD} + \text{CH}_3\text{O}_2$ $+ 0.22\text{CO} + 0.47\text{HO}_2 + 0.25\text{CH}_3\text{COCHO}$ $+ 0.22\text{HYAC} + 0.53\text{CH}_3\text{CO}_3 + 0.25\text{CH}_2\text{O}$	$1.4(-11)$	5
$\text{MACROOH} + \text{OH} \rightarrow 0.5\text{MCO}_3 + 0.2\text{MACRO}_2$ $+ 0.1\text{OH} + 0.2\text{HO}_2$	$2.3(-11) \exp(200/T)$	5
$\text{MCO}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{CH}_2\text{O} + \text{CH}_3\text{CO}_3$	$8.1(-12) \exp(270/T)$	5, <i>d</i>
$\text{MCO}_3 + \text{NO}_3 \rightarrow \text{NO}_2 + \text{CH}_2\text{O} + \text{CH}_3\text{CO}_3$	$4.1(-12)$	5,8
$\text{MCO}_3 + \text{HO}_2 \rightarrow 0.3\text{O}_3 + 0.3\text{CH}_3\text{COOH}$ $+ 0.7\text{CH}_3\text{COOOH} + 0.7\text{O}_2$	$4.3(-13) \exp(1040/T)$	5
$\text{MCO}_3 + \text{CH}_3\text{O}_2 \rightarrow 2\text{CH}_2\text{O} + \text{HO}_2 + \text{CH}_3\text{CO}_3 + \text{CO}_2$	$2.0(-12) \exp(500/T)$	5, <i>d</i>
$\text{MCO}_3 + \text{CH}_3\text{CO}_3 \rightarrow 2\text{CO}_2 + \text{CH}_3\text{O}_2 + \text{CH}_2\text{O} + \text{CH}_3\text{CO}_3$	$5.0(-12) \exp(500/T)$	5, <i>d</i>
$\text{MCO}_3 + \text{MCO}_3 \rightarrow 2\text{CO}_2 + 2\text{CH}_2\text{O} + 2\text{CH}_3\text{CO}_3$	$2.5(-12) \exp(500/T)$	5, <i>d</i>



Chemical reaction mechanism and kinetic rates (continued)		
<i>Reaction</i>	<i>Rate</i>	<i>Ref.</i>
MCO <sub>3</sub> + NO <sub>2</sub> → MPAN	1.1(-11)(300/T) <sup>1.0</sup>	5
MPAN → MCO <sub>3</sub> + NO <sub>2</sub>	$K_{eq} = 9.0(-29) \exp(14000/T)$	5
CH <sub>3</sub> COCHO + OH → CH <sub>3</sub> CO <sub>3</sub> + CO + H <sub>2</sub> O	8.4(-13) exp(830/T)	5
CH <sub>3</sub> COCHO + NO <sub>3</sub> → HNO <sub>3</sub> + CO + CH <sub>3</sub> CO <sub>3</sub>	1.4(-12) exp(-1860/T)	5
APIN + OH → 1.7ISOPO <sub>2</sub>	1.2(-11) exp(444/T)	f,7
APIN + O <sub>3</sub> → 0.68MACR + 0.34MVK +0.17O <sub>3</sub> + 0.459OH + 0.119C <sub>3</sub> H <sub>6</sub> +1.02CH <sub>2</sub> O + 0.51CO + 0.102HO <sub>2</sub> +0.34MCO <sub>3</sub> + 0.34CH <sub>3</sub> COOH	1.01(-15) exp(-732/T)	f,12
APIN + NO <sub>3</sub> → 1.7ISOPO <sub>2</sub> + NO <sub>2</sub>	9.3(-13) exp(565/T)	5,13
ONITR + OH → HNO <sub>3</sub> + 0.5CO + HO <sub>2</sub> +HYDRALD + 0.5CH <sub>2</sub> O	1.5(-11)	5,e
ONITR + NO <sub>3</sub> → HO <sub>2</sub> + NO <sub>2</sub> + HYDRALD	1.4(-12) exp(-1860/T)	5
OH + HYDRALD → XO <sub>2</sub>	1.86(-11) exp(175/T)	5
XO <sub>2</sub> + NO → NO <sub>2</sub> + 1.5HO <sub>2</sub> + CO +0.25(HYAC + CH <sub>3</sub> COCHO + GLYALD)	2.7(-12) exp(350/T)	5
XO <sub>2</sub> + NO <sub>3</sub> → NO <sub>2</sub> + 1.5HO <sub>2</sub> + CO +0.25(HYAC + CH <sub>3</sub> COCHO + GLYALD)	2.5(-12)	5,8
XO <sub>2</sub> + HO <sub>2</sub> → XOOH	1.82(-13) exp(1300/T)	8
XO <sub>2</sub> + CH <sub>3</sub> O <sub>2</sub> → 0.3CH <sub>3</sub> OH + HO <sub>2</sub> +0.7CH <sub>2</sub> O + 0.4CO +0.1(HYAC + CH <sub>3</sub> COCHO + GLYALD)	5.0(-13) exp(400/T)	5
XO <sub>2</sub> + CH <sub>3</sub> CO <sub>3</sub> → CO + CH <sub>3</sub> O <sub>2</sub> + 1.5HO <sub>2</sub> +0.25(HYAC + CH <sub>3</sub> COCHO + GLYALD)	1.3(-12) exp(640/T)	5
XOOH + OH → H <sub>2</sub> O + XO <sub>2</sub>	1.9(-12) exp(190/T)	9
XOOH + OH → H <sub>2</sub> O + OH	7.69(-17) exp(253/T)T <sup>2</sup>	9
ISOPOOH + OH → 0.5XO <sub>2</sub> + 0.5ISOPO <sub>2</sub>	3.8(-12) exp(200/T)	5
CH <sub>3</sub> OH + OH → HO <sub>2</sub> + CH <sub>2</sub> O	6.7(-12) exp(-600/T)	1
MPAN + OH + M → 0.5(HYAC + NO <sub>3</sub> +CH <sub>2</sub> O + HO <sub>2</sub> ) + M	$k_0 = 8.(-27)(300/T)^{3.5}$ $k_\infty = 3.0(-11)$ $Fc = 0.5$	5
PAN + OH → CH <sub>2</sub> O + NO <sub>3</sub>	4.0(-14)	1
OH + HYAC → CH <sub>3</sub> COCHO + HO <sub>2</sub>	3.0(-12)	5
OH + GLYALD → 0.8CH <sub>3</sub> CO <sub>3</sub> + 0.4CO + 0.6HO <sub>2</sub>	1.0(-11)	5
OH + H <sub>2</sub> S → HO <sub>2</sub> + SO <sub>2</sub>	6.(-12) exp(-75/T)	1
OH + COS → HO <sub>2</sub> + SO <sub>2</sub>	1.1(-13) exp(-1200/T)	1,10
OH + DMS → SO <sub>2</sub> + 2CH <sub>2</sub> O	1.2(-11) exp(-260/T)	1,10
OH + DMS → 0.6SO <sub>2</sub> + 1.2CH <sub>2</sub> O +0.4(0.6SO <sub>2</sub> + 0.4SO <sub>4</sub> + 1.5CH <sub>2</sub> O)	3.04(-12) exp(350/T)(α/(1+α)) α = 1.159(-31) exp(7460/T)[M]	1

**Chemical reaction mechanism and kinetic rates (continued)**

<i>Reaction</i>	<i>Rate</i>	<i>Ref.</i>
$\text{NO}_3 + \text{DMS} \rightarrow \text{HNO}_3 + \text{SO}_2 + 2\text{CH}_2\text{O}$	$1.9(-13) \exp(500/T)$	1,10
$\text{OH} + \text{CS}_2 \rightarrow \text{COS} + \text{SO}_2 + \text{HO}_2$	$8.8(-16) \exp(2300/T)$	10
$\text{OH} + \text{SO}_2 + \text{M} \rightarrow \text{SO}_4 + \text{HO}_2 + \text{M}$	$k_0 = 3(-31)(300/T)^{3.3}$ $k_\infty = 1.5(-12)$ $F_c = 0.6$	1
$\text{SO}_2 \rightarrow \text{SO}_4$	in-cloud $\text{SO}_2$	10
$\text{N}_2\text{O}_5 + \text{SO}_4^{2-} \rightarrow 2\text{HNO}_3 + \text{SO}_4^{2-}$	$\gamma = 0.1$	14, <i>h</i>
$\text{NO}_3 + \text{SO}_4^{2-} \rightarrow \text{HNO}_3 + \text{SO}_4^{2-}$	$\gamma = 0.001$	14, <i>h</i>
$\text{HO}_2 + \text{SO}_4^{2-} \rightarrow 0.5\text{H}_2\text{O}_2 + \text{SO}_4^{2-}$	$\gamma = 0.2$	14, <i>h</i>

Read  $2.14(-11)$  as  $2.14 \cdot 10^{-11}$ ;  $T$ =temperature (K);  $[M]$  is the air density (molecule  $\text{cm}^{-3}$ );  $P_{atm}$  is the atmospheric pressure (atm);  $\gamma$  is the reaction probability on aerosols. Units for first-, second-, and third-order reactions are  $\text{sec}^{-1}$ ,  $\text{cm}^3\text{molecule}^{-1}\text{sec}^{-1}$  and  $\text{cm}^6\text{molecule}^{-2}\text{sec}^{-1}$  respectively. Three-body reaction rates are calculated with  $k = \frac{k_0[M]}{1+k_0[M]/k_\infty} F_c^{\{1+[\log_{10}(k_0[M]/k_\infty)]^2\}^{-1}}$ . Rates for equilibrium reactions calculated as  $k = k_f/K_{eq}$ , where  $k_f$  is the rate of the formation reaction and  $K_{eq}$  is the equilibrium constant.

**References:** 1, DeMore et al. (1997); 2, Sander et al. (2000); 3, Tyndall et al. (2001); 4, Atkinson et al. (1999); 5, Horowitz et al. (2003); 6, Müller and Brasseur (1995); 7, Brasseur et al. (1998); 8, Saunders et al. (2003); 9, Brocheton (1999); 10, Pham et al. (1995); 11, Ravishankara et al. (2002); 12, Atkinson (1994); 13, Martinez et al. (1999); 14, Jacob (2000).

**Notes.**

- a.* Rate assumed equal to the rate of the corresponding reaction of  $\text{C}_2\text{H}_5\text{O}_2$ .
- b.* Rate assumed equal to the rate of the corresponding reaction of  $\text{CH}_3\text{OOH}$ .
- c.* Based on Horowitz et al. (2003) assuming that the peroxy radical produced in this reaction reacts with NO. The conversion of NO to  $\text{NO}_2$  is neglected.
- d.* Rate assumed equal to the rate of the corresponding reaction of  $\text{CH}_3\text{CO}_3$ .
- e.* Products as in Horowitz et al. (2003), except that  $\text{NO}_2$  is replaced by  $\text{HNO}_3$ , a more likely product in the OH-addition pathway of alkyl nitrates (Atkinson, 1994).
- f.* Adapted from Brasseur et al. (1998).
- g.* OTHC represents all non-methane VOCs (NMVOCs) non explicitly included in the mechanism. See article for details.
- h.* The heterogenous reaction of a gas on sulphate aerosols is represented as a pseudosecond-order reaction between the gas and particulate sulphate.

**Table 3.** Photodissociations included in the model.

<b>Photodissociations</b>			
<i>Reaction</i>	<i>Cross section</i>	<i>Quantum yield</i>	<i>Products</i>
$O_2 + h\nu \rightarrow O_3 + O_3$	$1^a, 14^b$	$2^c$	$1^d$
$NO_2 + h\nu \rightarrow NO + O_3$	2	2	$1^d$
$O_3 + h\nu \rightarrow O(^1D) + O_2$	3	4	$1^d$
$NO_3 + h\nu \rightarrow NO + O_2$	2	5	1
$NO_3 + h\nu \rightarrow NO_2 + O_3$	2	5	$1^d$
$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$	2	2	1
$HNO_3 + h\nu \rightarrow OH + NO_2$	1	$2^c$	1
$HNO_4 + h\nu \rightarrow HO_2 + NO_2$	$2^e, 6^f, 7^g$	$c$	16
$H_2O_2 + h\nu \rightarrow OH + OH$	4	$2^c$	1
$CH_2O + h\nu \rightarrow CO + 2HO_2$	8	2	$1^d$
$CH_2O + h\nu \rightarrow H_2 + CO$	8	2	1
$CH_3CHO + h\nu \rightarrow CH_3O_2 + CO + HO_2$	11	2	16
$GLYALD + h\nu \rightarrow CH_2O + CO + 2HO_2$	13	$13^h$	16
$CH_3COCH_3 + h\nu \rightarrow CH_3CO_3 + CH_3O_2$	12	15	16
$CH_3COCHO + h\nu \rightarrow CH_3CO_3 + CO + HO_2$	2	2	16
$CH_3OOH + h\nu \rightarrow CH_2O + HO_2 + OH$	4	$2^c$	$1^d$
$MACR + h\nu \rightarrow 0.33(MCO_3 + OH)$ $+0.67(CH_3CO_3 + CO + HO_2 + CH_2O)$	9	$9^j$	16
$MVK + h\nu \rightarrow 0.7C_3H_6 + 0.7CO$ $+0.3CH_3O_2 + 0.3CH_3CO_3$	9	2	16
$PAN + h\nu \rightarrow 0.6(CH_3CO_3 + NO_2)$ $+0.4(CH_3O_2 + NO_3 + CO_2)$	4	$2^c$	16
$ONITR + h\nu \rightarrow HO_2 + CO + NO_2 + CH_2O$	$10^i$	$2^c$	16
$POOH + h\nu \rightarrow CH_3CHO + CH_2O$ $+HO_2 + OH$	$k$	$k$	16
$C_2H_5OOH + h\nu \rightarrow CH_3CHO + HO_2 + OH$	$k$	$k$	16
$C_3H_7OOH + h\nu \rightarrow 0.82CH_3COCH_3$ $+OH + HO_2$	$k$	$k$	16
$ACETOOH + h\nu \rightarrow CH_2O + CH_3CO_3 + OH$	$k$	$k$	16
$XOOH + h\nu \rightarrow OH$	$k$	$k$	16
$CH_3COOOH + h\nu \rightarrow CH_3O_2 + OH + CO_2$	$m$	$m$	16
$MACROOH + h\nu \rightarrow OH + 0.84CO$ $+0.16CH_2O + HO_2 + CH_3COCHO$	$k$	$k$	17
$MACROOH + h\nu \rightarrow 1.16HO_2 + CO$ $+0.84OH + 0.84CH_3COCHO$ $+0.16ACETOOH$	$l$	$l$	17
$MPAN + h\nu \rightarrow MCO_3 + NO_2$	$n$	$n$	16

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**Photodissociations (continued)**

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<i>Reaction</i>	<i>Cross section</i>	<i>Quantum yield</i>	<i>Products</i>
<p><b>References:</b> 1, DeMore et al. (1997); 2, Atkinson et al. (2002); 3, Molina and Molina (1986); 4, Sander et al. (2000); 5, Johnston et al. (1996); 6, Knight et al. (2002); 7, Roehl et al. (2002); 8, Meller et al. (2000); 9, Raber and Moortgat (1996); 10, Atkinson et al. (1999); 11, Martinez et al. (1992); 12, Gierczak et al. (1998); 13, Bacher et al. (2001); 14, Kockarts (1994); 15, Warneck (2001); 16, Horowitz et al. (2003); 17, Brocheton (1999).</p>			
<p><b>Notes:</b> <i>a</i>) Hertzberg continuum (205-240 nm) <i>b</i>) Schumann-Runge bands (175-205 nm) <i>c</i>) Quantum yield is taken equal to 1. <i>d</i>) Oxygen and hydrogen atoms as well as HCO and CH<sub>3</sub>O radicals produced in the mechanism are assumed to react instantly with O<sub>2</sub>, an excellent approximation in the troposphere. <i>e</i>) 190-280 nm temperature-independent cross sections <i>f</i>) 280-350 nm temperature-dependent cross sections <i>g</i>) The contribution of near-IR radiation to the photolysis of HNO<sub>4</sub> is about 10<sup>-5</sup> s<sup>-1</sup> during daytime throughout the atmosphere (Roehl et al., 2002; Salawitch et al., 2002). <i>h</i>) Use the corresponding CH<sub>3</sub>CHO photolysis quantum yield increased by a factor of 1.6 (Bacher et al., 2001). <i>i</i>) ONITR is assumed to photolyse as <i>n</i>-C<sub>4</sub>H<sub>9</sub>ONO<sub>2</sub>. <i>j</i>) Constant value of 0.05 (upper limit) <i>k</i>) J=J(CH<sub>3</sub>OOH) <i>l</i>) J=J(CH<sub>3</sub>CHO) <i>m</i>) J=0.28 * J(H<sub>2</sub>O<sub>2</sub>) <i>n</i>) J=J(PAN)</p>			

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