# Supplement of "Inversion of $CO$ and $NO_x$ emissions using the adjoint of the IMAGES model"

J.-F. Müller and T. Stavrakou

Belgian Institute for Space Aeronomy, Brussels, Belgium

**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.

*Correspondence to:* J.-F. Müller (jfm@aeronomie.be)

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

| **Chemical species included in the model** | | |
|---|---|---|
| *Species Category* | *Chemical Formula* | *Name* |
| Fixed | $O_2$ : 20.95% | oxygen |
| | $N_2$ : 79.05% | nitrogen |
| | $H_2O$ (from ECMWF) | water |
| | $H_2$ : 550 ppbv | hydrogen |
| | $N_2O$ : 311 ppbv | nitrous oxide |
| | $COS$ : 0.5 ppbv | carbonyl sulfide |
| Long-lived (transported) | $O_3$ | ozone |
| | $H_2O_2$ | hydrogen peroxide |
| | $HNO_3$ | nitric acid |
| | $NO_x$ ($NO + NO_2 + NO_3 + HNO_4 + 2N_2O_5$) | nitrogen oxides (family) |
| | $CH_4$ | methane |
| | $C_2H_6$ | ethane |
| | $C_2H_4$ | ethylene |
| | $C_3H_8$ | propane |
| | $C_3H_6$ | propylene |
| | ISOP ($C_5H_8$) | isoprene |
| | APIN ($C_{10}H_{16}$) | $\alpha$-pinene |
| | OTHC | other hydrocarbons |
| | $CO$ | carbon monoxide |
| | $CH_3OH$ | methanol |
| | $CH_2O$ | formaldehyde |
| | $CH_3CHO$ | acetaldehyde |
| | GLYALD ($CH_2OHCHO$) | glycolaldehyde |
| | HYDRALD ($HOCH_2C(CH_3)=CHCHO$ + $HOCH_2CH=C(CH_3)CHO$) | hydroxy carbonyls from ISOP |
| | MACR ($CH_2=CCH_3CHO$) | methylacrolein |
| | $CH_3COCH_3$ | acetone |
| | HYAC ($CH_2OHCOCH_3$) | hydroxy acetone |
| | MVK ($CH_2=CHCOCH_3$) | methylvinylketone |
| | $CH_3OOH$ | methyl peroxide |
| | $C_2H_5OOH$ | ethyl peroxide |
| | POOH ($C_3H_6OHOOH$) | peroxide from propylene |
| | $CH_3COOOH$ | peracetic acid |
| | $C_3H_7OOH$ | peroxide from propane |
| | ACETOOH ($CH_3COCH_2OOH$) | peroxide from acetone |
| | ISOPOOH ($C_5H_8OHOOH$) | peroxide from ISOP |
| | MACROOH ($CH_3COCHOOHCH_2OH$) | peroxide from MACR |

| Chemical species included in the model (continued) | | |
|---|---|---|
| *Species Category* | *Chemical Formula* | *Name* |
| | $XOOH$ ($HOCH_2COOHCH_3CH{=}CHOH$) | peroxide from $XO_2$ |
| | $PAN$ ($CH_3CO_3NO_2$) | peroxy-acetyl nitrate |
| | $MPAN$ ($CH_2{=}CCH_3CO_3NO_2$) | peroxymethacrylic nitrate |
| | $ONITR$ ($C_5H_8OHONO_2$) | substituted organic nitrate from ISOP |
| | $SO_2$ | sulfur dioxide |
| | $SO_4^{2-}$ | non-sea-salt sulfate |
| | $DMS$ ($CH_3SCH_3$) | dimethyl sulfide |
| | $CS_2$ | carbon disulfide |
| | $H_2S$ | hydrogen sulfide |
| Short-lived | $O(^1D)$ | oxygen atom (excited state) |
| | $OH$ | hydroxyl radical |
| | $HO_2$ | hydroperoxyl radical |
| | $NO$ | nitrogen oxide |
| | $NO_2$ | nitrogen dioxide |
| | $HNO_4$ | pernitric acid |
| | $NO_3$ | nitrogen trioxide |
| | $N_2O_5$ | nitrogen hemipentoxide |
| | $CH_3COCHO$ | methylglyoxal |
| | $CH_3O_2$ | methylperoxy radical |
| | $PO_2$ ($C_3H_6OHO_2$) | peroxy radical from propylene |
| | $ACETO_2$ ($CH_3COCH_2O_2$) | peroxy radical from acetone |
| | $XO_2$ ($HOCH_2CO_2CH_3CH{=}CHOH$) | peroxy radical from HYDRALD+OH and ISOPOOH+OH |
| | $C_2H_5O_2$ | ethylperoxy radical |
| | $C_3H_7O_2$ | propylperoxy radical |
| | $ISOPO_2$ ($HOCH_2CO_2CH_3CH{=}CH_2$) | peroxy radical from ISOP |
| | $MACRO_2$ ($CH_3COCHO_2CH_2OH$) | peroxy radical from MACR+OH |
| | $CH_3CO_3$ | acetylperoxy radical |
| | $MCO_3$ ($CH_2{=}CCH_3CO_3$) | peroxymethacrylic radical |

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

| **Chemical reaction mechanism and kinetic rates** | | |
|---|---|---|
| *Reaction* | *Rate* | *Ref.* |
| $O(^1D) + N_2 \rightarrow O_3 + N_2$ | $2.14(-11)\exp(110/T)$ | 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 |
| $OH + OH + M \rightarrow H_2O_2 + M$ | $k_0 = 6.2(-31)(300/T)^{1.0}$<br>$k_\infty = 2.6(-11)$<br>$Fc = 0.6$ | 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 |
| $NO_2 + OH + M \rightarrow HNO_3 + M$ | $k_0 = 2.4(-30)(300/T)^{3.1}$<br>$k_\infty = 1.7(-11)(300/T)^{2.1}$<br>$Fc = 0.6$ | 2 |
| $HNO_3 + OH \rightarrow H_2O + NO_3$ | $k = k_0 + k_3[M]/(1 + k_3[M]/k_2)$<br>$k_0 = 2.4(-14)\exp(460/T)$<br>$k_2 = 2.7(-17)\exp(2199/T)$<br>$k_3 = 6.5(-34)\exp(1335/T)$ | 2 |
| $NO_2 + HO_2 + M \rightarrow HO_2NO_2 + M$ | $k_0 = 1.8(-31)(300/T)^{3.2}$<br>$k_\infty = 4.7(-12)(300/T)^{1.4}$<br>$Fc = 0.6$ | 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.* |
| $NO_3 + OH \rightarrow HO_2 + NO_2$ | $2.2(-11)$ | 1 |
| $NO + NO_3 \rightarrow 2NO_2$ | $1.5(-11)\exp(170/T)$ | 1 |
| $NO_2 + NO_3 + M \rightarrow N_2O_5 + M$ | $k_0 = 2.0(-30)(300/T)^{4.4}$ | 2 |
| | $k_\infty = 1.4(-12)(300/T)^{0.7}$ | |
| | $Fc = 0.6$ | |
| $N_2O_5 + M \rightarrow NO_2 + NO_3 + M$ | $K_{eq} = 3.0(-27)\exp(10991/T)$ | 2 |
| $OH + CH_4 \rightarrow CH_3O_2 + H_2O$ | $2.45(-12)\exp(-1775/T)$ | 1 |
| $CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$ | $4.1(-13)\exp(750/T)$ | 3 |
| $CH_3O_2 + NO \rightarrow CH_2O + NO_2 + HO_2$ | $2.8(-12)\exp(300/T)$ | 3 |
| $CH_3O_2 + NO_3 \rightarrow CH_2O + HO_2 + NO_2$ | $1.1(-12)$ | 8 |
| $CH_3O_2 + CH_3O_2 \rightarrow 2CH_2O + 2HO_2$ | $5.0(-13)\exp(-424/T)$ | 5 |
| $CH_3O_2 + CH_3O_2 \rightarrow CH_2O + CH_3OH$ | $1.9(-14)\exp(706/T)$ | 5 |
| $CH_3O_2 + O_3 \rightarrow CH_2O + HO_2$ | $3.0(-16)\exp(-1000/T)$ | 3 |
| $OH + CH_3OOH \rightarrow 0.3(CH_2O + OH) + 0.7CH_3O_2$ | $3.8(-12)\exp(200/T)$ | 1 |
| $OH + CH_2O \rightarrow H_2O + CO + HO_2$ | $1.0(-11)$ | 1 |
| $NO_3 + CH_2O \rightarrow CO + HO_2 + HNO_3$ | $6.0(-13)\exp(-2058/T)$ | 5 |
| $OH + CO \rightarrow CO_2 + HO_2$ | $1.5(-13)(1 + 0.6P_{atm})$ | 1 |
| $OH + C_2H_6 \rightarrow H_2O + C_2H_5O_2$ | $7.8(-12)\exp(-1025/T)$ | 4 |
| $C_2H_5O_2 + NO \rightarrow CH_3CHO + HO_2 + NO_2$ | $2.7(-12)\exp(350/T)$ | 3 |
| $C_2H_5O_2 + NO_3 \rightarrow CH_3CHO + HO_2 + NO_2$ | $2.5(-12)$ | 8 |
| $C_2H_5O_2 + HO_2 \rightarrow C_2H_5OOH + O_2$ | $7.4(-13)\exp(700/T)$ | 3 |
| $C_2H_5O_2 + CH_3O_2 \rightarrow 0.7CH_2O$ | $2.0(-13)$ | 5 |
| $+0.8CH_3CHO + HO_2$ | | |
| $+0.3CH_3OH + 0.2C_2H_5OH$ | | |
| $C_2H_5O_2 + C_2H_5O_2 \rightarrow 1.2HO_2$ | $6.8(-14)$ | 1 |
| $+1.6CH_3CHO + 0.4C_2H_5OH$ | | |
| $C_2H_5OOH + OH \rightarrow 0.5C_2H_5O_2$ | $3.8(-12)\exp(200/T)$ | 6 |
| $+0.5CH_3CHO + 0.5OH$ | | |
| $OH + C_3H_8 \rightarrow C_3H_7O_2 + H_2O$ | $8.0(-12)\exp(-590/T)$ | 4 |
| $C_3H_7O_2 + NO \rightarrow 0.82CH_3COCH_3$ | $2.7(-12)\exp(350/T)$ | 5,*a* |
| $+0.27CH_3CHO + NO_2 + HO_2$ | | |
| $C_3H_7O_2 + HO_2 \rightarrow C_3H_7OOH + O_2$ | $1.51(-13)\exp(1300/T)$ | 8 |
| $C_3H_7O_2 + CH_3O_2 \rightarrow 0.82CH_3COCH_3$ | $3.75(-13)\exp(-40/T)$ | 7 |
| $+CH_2O + HO_2$ | | |
| $C_3H_7OOH + OH \rightarrow H_2O + C_3H_7O_2$ | $3.8(-12)\exp(200/T)$ | 7 |
| $OH + CH_3COCH_3 \rightarrow ACETO_2 + H_2O$ | $1.1(-12)\exp(-520/T)$ | 4 |
| $ACETO_2 + NO \rightarrow NO_2 + CH_2O + CH_3CO_3$ | $2.8(-12)\exp(300/T)$ | 3 |
| $ACETO_2 + HO_2 \rightarrow ACETOOH + O_2$ | $8.6(-13)\exp(700/T)$ | 3 |
| $ACETO_2 + CH_3O_2 \rightarrow 0.3(CH_3CO_3 + CH_2O + HO_2)$ | $7.5(-13)\exp(500/T)$ | 3 |

| Chemical reaction mechanism and kinetic rates (continued) | | |
|---|---|---|
| *Reaction* | *Rate* | *Ref.* |
| $+0.2(\mathrm{HYAC} + \mathrm{CH_2O})$ | | |
| $+0.5(\mathrm{CH_3COCHO} + \mathrm{CH_3OH})$ | | |
| $\mathrm{ACETOOH} + \mathrm{OH} \rightarrow \mathrm{ACETO_2} + \mathrm{H_2O}$ | $3.8(-12)\exp(200/T)$ | 7 |
| $\mathrm{OH} + \mathrm{C_3H_6} + \mathrm{M} \rightarrow \mathrm{PO_2} + \mathrm{M}$ | $k_0 = 8.(-27)(300/T)^{3.5}$ | 4 |
| | $k_\infty = 3.0(-11)$ | |
| | $Fc = 0.5$ | |
| $\mathrm{O_3} + \mathrm{C_3H_6} \rightarrow 0.54\mathrm{CH_2O} + 0.19\mathrm{HO_2} + 0.33\mathrm{OH}$ | $6.5(-15)\exp(-1900/T)$ | 1 |
| $+0.08\mathrm{CH_4} + 0.56\mathrm{CO} + 0.5\mathrm{CH_3CHO}$ | | |
| $+0.31\mathrm{CH_3O_2} + 0.25\mathrm{CH_3COOH}$ | | |
| $\mathrm{OH} + \mathrm{C_2H_4} + \mathrm{M} \rightarrow \mathrm{M} + \mathrm{PO_2}$ | $k_0 = 7.(-29)(300/T)^{3.1}$ | 4 |
| | $k_\infty = 9.(-12)$ | |
| | $Fc = 0.48$ | |
| $\mathrm{O_3} + \mathrm{C_2H_4} \rightarrow \mathrm{CH_2O} + 0.5\mathrm{CO} + 0.12\mathrm{HO_2}$ | $1.2(-14)\exp(-2630/T)$ | 5 |
| $+0.12\mathrm{OH} + 0.32\mathrm{CH_3COOH}$ | | |
| $\mathrm{PO_2} + \mathrm{NO} \rightarrow \mathrm{CH_3CHO} + \mathrm{CH_2O} + \mathrm{HO_2} + \mathrm{NO_2}$ | $2.7(-12)\exp(350/T)$ | 5,*a* |
| $\mathrm{PO_2} + \mathrm{NO_3} \rightarrow \mathrm{CH_3CHO} + \mathrm{CH_2O} + \mathrm{HO_2} + \mathrm{NO_2}$ | $2.5(-12)$ | 8 |
| $\mathrm{PO_2} + \mathrm{HO_2} \rightarrow \mathrm{POOH} + \mathrm{O_2}$ | $7.5(-13)\exp(700/T)$ | 5 |
| $\mathrm{POOH} + \mathrm{OH} \rightarrow 0.5\mathrm{PO_2} + 0.5\mathrm{OH} + 0.5\mathrm{HYAC} + \mathrm{H_2O}$ | $3.8(-12)\exp(200/T)$ | 5 |
| $\mathrm{CH_3CHO} + \mathrm{OH} \rightarrow \mathrm{CH_3CO_3} + \mathrm{H_2O}$ | $5.6(-12)\exp(310/T)$ | 4 |
| $\mathrm{CH_3CHO} + \mathrm{NO_3} \rightarrow \mathrm{CH_3CO_3} + \mathrm{HNO_3}$ | $1.4(-12)\exp(-1860/T)$ | 4 |
| $\mathrm{CH_3CO_3} + \mathrm{NO} \rightarrow \mathrm{CH_3O_2} + \mathrm{NO_2} + \mathrm{CO_2}$ | $8.1(-12)\exp(270/T)$ | 3 |
| $\mathrm{CH_3CO_3} + \mathrm{NO_3} \rightarrow \mathrm{CH_3O_2} + \mathrm{NO_2} + \mathrm{CO_2}$ | $4.1(-12)$ | 8 |
| $\mathrm{CH_3CO_3} + \mathrm{NO_2} + \mathrm{M} \rightarrow \mathrm{PAN} + \mathrm{M}$ | $k_0 = 8.5(-29)(300/T)^{6.5}$ | 3 |
| | $k_\infty = 1.1(-11)(300/T)^{1.0}$ | |
| | $Fc = 0.6$ | |
| $\mathrm{PAN} + \mathrm{M} \rightarrow \mathrm{CH_3CO_3} + \mathrm{NO_2} + \mathrm{M}$ | $K_{eq} = 9.0(-29)\exp(14000/T)$ | 5 |
| $\mathrm{CH_3CO_3} + \mathrm{HO_2} \rightarrow 0.3\mathrm{O_3} + 0.7\mathrm{O_2}$ | $4.3(-13)\exp(1040/T)$ | 3 |
| $+0.7\mathrm{CH_3COOOH} + 0.3\mathrm{CH_3COOH}$ | | |
| $\mathrm{CH_3CO_3} + \mathrm{CH_3CO_3} \rightarrow 2\mathrm{CH_3O_2} + 2\mathrm{CO_2}$ | $2.5(-12)\exp(500/T)$ | 3 |
| $\mathrm{CH_3O_2} + \mathrm{CH_3CO_3} \rightarrow \mathrm{CH_2O} + 0.9\mathrm{CH_3O_2}$ | $2.0(-12)\exp(500/T)$ | 3 |
| $+0.9\mathrm{HO_2} + 0.9\mathrm{CO_2} + 0.1\mathrm{CH_3COOH}$ | | |
| $\mathrm{CH_3COOOH} + \mathrm{OH} \rightarrow 0.5\mathrm{CH_3CO_3} + \mathrm{H_2O}$ | $3.8(-12)\exp(200/T)$ | 5,*b* |
| $+0.5\mathrm{CH_2O} + 0.5\mathrm{CO_2}$ | | |
| $\mathrm{ISOP} + \mathrm{OH} \rightarrow \mathrm{ISOPO_2}$ | $2.54(-11)\exp(410/T)$ | 5 |
| $\mathrm{ISOP} + \mathrm{O_3} \rightarrow 0.4\mathrm{MACR} + 0.2\mathrm{MVK} + 0.1\mathrm{O_3} + 0.27\mathrm{OH}$ | $1.05(-14)\exp(-2000/T)$ | 5 |
| $+0.07\mathrm{C_3H_6} + 0.6\mathrm{CH_2O} + 0.3\mathrm{CO}$ | | |
| $+0.2\mathrm{MCO_3} + 0.06\mathrm{HO_2} + 0.2\mathrm{CH_3COOH}$ | | |
| $\mathrm{ISOP} + \mathrm{NO_3} \rightarrow 0.794\mathrm{ONITR} + 0.206\mathrm{NO_2} + 0.039\mathrm{MVK}$ | $3.03(-12)\exp(-446/T)$ | 5*c* |
| $+0.167\mathrm{MACR} + 0.072\mathrm{CH_2O} + 0.794\mathrm{HO_2}$ | | |

| Chemical reaction mechanism and kinetic rates (continued) | | |
|---|---|---|
| *Reaction* | *Rate* | *Ref.* |
| $OH + OTHC \rightarrow 0.8ISOPO_2$ | $6.(-11)\exp(-540/T)$ | *g* |
| $ISOPO_2 + NO \rightarrow 0.23MACR + 0.32MVK + 0.08ONITR$ $+0.92NO_2 + HO_2 + 0.51CH_2O + 0.37HYDRALD$ | $2.7(-12)\exp(350/T)$ | 5,*a* |
| $ISOPO_2 + NO_3 \rightarrow HO_2 + NO_2 + 0.6CH_2O$ $+0.25MACR + 0.35MVK + 0.4HYDRALD$ | $2.5(-12)$ | 5,8 |
| $ISOPO_2 + HO_2 \rightarrow ISOPOOH$ | $2.06(-13)\exp(1300/T)$ | 5,8 |
| $ISOPO_2 + CH_3O_2 \rightarrow 0.25CH_3OH + HO_2 + 1.2CH_2O$ $+0.19MACR + 0.26MVK + 0.3HYDRALD$ | $5.0(-13)\exp(400/T)$ | 5 |
| $ISOPO_2 + CH_3CO_3 \rightarrow CH_3O_2 + HO_2 + 0.6CH_2O$ $+0.25MACR + 0.35MVK + 0.4HYDRALD$ | $1.4(-11)$ | 5 |
| $MACR + OH \rightarrow 0.5MACRO_2 + 0.5H_2O + 0.5MCO_3$ | $1.86(-11)\exp(175/T)$ | 5 |
| $MACR + O_3 \rightarrow 0.8CH_3COCHO + 0.275HO_2$ $+0.2CO + 0.2O_3 + 0.7CH_2O + 0.215OH$ | $4.4(-15)\exp(-2500/T)$ | 5 |
| $MVK + OH \rightarrow MACRO_2$ | $4.13(-12)\exp(452/T)$ | 5 |
| $MVK + O_3 \rightarrow 0.8CH_2O + 0.95CH_3COCHO + 0.08OH$ $+0.06HO_2 + 0.05CO + 0.04CH_3CHO + 0.2O_3$ | $7.52(-16)\exp(-1521/T)$ | 5 |
| $MACRO_2 + NO \rightarrow NO_2 + 0.47HO_2 + 0.22(CO + HYAC)$ $+0.53(CH_3CO_3 + GLYALD)$ $+0.25(CH_2O + CH_3COCHO)$ | $2.7(-12)\exp(350/T)$ | 5,*a* |
| $MACRO_2 + NO \rightarrow ONITR$ | $1.3(-13)\exp(350/T)$ | 5 |
| $MACRO_2 + NO_3 \rightarrow NO_2 + 0.47HO_2 + 0.22(CO + HYAC)$ $+0.53(CH_3CO_3 + GLYALD)$ $+0.25(CH_2O + CH_3COCHO)$ | $2.5(-12)$ | 5,8 |
| $MACRO_2 + HO_2 \rightarrow MACROOH$ | $1.82(-13)\exp(1300/T)$ | 5,8 |
| $MACRO_2 + CH_3O_2 \rightarrow 0.73HO_2 + 0.88CH_2O + 0.11CO$ $+0.24CH_3COCHO + 0.25CH_3OH + 0.26GLYALD$ $+0.23HYAC + 0.26CH_3CO_3$ | $5.0(-13)\exp(400/T)$ | 5 |
| $MACRO_2 + CH_3CO_3 \rightarrow 0.53GLYALD + CH_3O_2$ $+0.22CO + 0.47HO_2 + 0.25CH_3COCHO$ $+0.22HYAC + 0.53CH_3CO_3 + 0.25CH_2O$ | $1.4(-11)$ | 5 |
| $MACROOH + OH \rightarrow 0.5MCO_3 + 0.2MACRO_2$ $+0.1OH + 0.2HO_2$ | $2.3(-11)\exp(200/T)$ | 5 |
| $MCO_3 + NO \rightarrow NO_2 + CH_2O + CH_3CO_3$ | $8.1(-12)\exp(270/T)$ | 5,*d* |
| $MCO_3 + NO_3 \rightarrow NO_2 + CH_2O + CH_3CO_3$ | $4.1(-12)$ | 5,8 |
| $MCO_3 + HO_2 \rightarrow 0.3O_3 + 0.3CH_3COOH$ $+0.7CH_3COOOH + 0.7O_2$ | $4.3(-13)\exp(1040/T)$ | 5 |
| $MCO_3 + CH_3O_2 \rightarrow 2CH_2O + HO_2 + CH_3CO_3 + CO_2$ | $2.0(-12)\exp(500/T)$ | 5,*d* |
| $MCO_3 + CH_3CO_3 \rightarrow 2CO_2 + CH_3O_2 + CH_2O + CH_3CO_3$ | $5.0(-12)\exp(500/T)$ | 5,*d* |
| $MCO_3 + MCO_3 \rightarrow 2CO_2 + 2CH_2O + 2CH_3CO_3$ | $2.5(-12)\exp(500/T)$ | 5,*d* |

| Chemical reaction mechanism and kinetic rates (continued) | | |
|---|---|---|
| *Reaction* | *Rate* | *Ref.* |
| $MCO_3 + NO_2 \rightarrow MPAN$ | $1.1(-11)(300/T)^{1.0}$ | 5 |
| $MPAN \rightarrow MCO_3 + NO_2$ | $K_{eq} = 9.0(-29)\exp(14000/T)$ | 5 |
| $CH_3COCHO + OH \rightarrow CH_3CO_3 + CO + H_2O$ | $8.4(-13)\exp(830/T)$ | 5 |
| $CH_3COCHO + NO_3 \rightarrow HNO_3 + CO + CH_3CO_3$ | $1.4(-12)\exp(-1860/T)$ | 5 |
| $APIN + OH \rightarrow 1.7ISOPO_2$ | $1.2(-11)\exp(444/T)$ | $f$,7 |
| $APIN + O_3 \rightarrow 0.68MACR + 0.34MVK$ | $1.01(-15)\exp(-732/T)$ | $f$,12 |
| $+0.17O_3 + 0.459OH + 0.119C_3H_6$ | | |
| $+1.02CH_2O + 0.51CO + 0.102HO_2$ | | |
| $+0.34MCO_3 + 0.34CH_3COOH$ | | |
| $APIN + NO_3 \rightarrow 1.7ISOPO_2 + NO_2$ | $9.3(-13)\exp(565/T)$ | 5,13 |
| $ONITR + OH \rightarrow HNO_3 + 0.5CO + HO_2$ | $1.5(-11)$ | 5,$e$ |
| $+HYDRALD + 0.5CH_2O$ | | |
| $ONITR + NO_3 \rightarrow HO_2 + NO_2 + HYDRALD$ | $1.4(-12)\exp(-1860/T)$ | 5 |
| $OH + HYDRALD \rightarrow XO_2$ | $1.86(-11)\exp(175/T)$ | 5 |
| $XO_2 + NO \rightarrow NO_2 + 1.5HO_2 + CO$ | $2.7(-12)\exp(350/T)$ | 5 |
| $+0.25(HYAC + CH_3COCHO + GLYALD)$ | | |
| $XO_2 + NO_3 \rightarrow NO_2 + 1.5HO_2 + CO$ | $2.5(-12)$ | 5,8 |
| $+0.25(HYAC + CH_3COCHO + GLYALD)$ | | |
| $XO_2 + HO_2 \rightarrow XOOH$ | $1.82(-13)\exp(1300/T)$ | 8 |
| $XO_2 + CH_3O_2 \rightarrow 0.3CH_3OH + HO_2$ | $5.0(-13)\exp(400/T)$ | 5 |
| $+0.7CH_2O + 0.4CO$ | | |
| $+0.1(HYAC + CH_3COCHO + GLYALD)$ | | |
| $XO_2 + CH_3CO_3 \rightarrow CO + CH_3O_2 + 1.5HO_2$ | $1.3(-12)\exp(640/T)$ | 5 |
| $+0.25(HYAC + CH_3COCHO + GLYALD)$ | | |
| $XOOH + OH \rightarrow H_2O + XO_2$ | $1.9(-12)\exp(190/T)$ | 9 |
| $XOOH + OH \rightarrow H_2O + OH$ | $7.69(-17)\exp(253/T)T^2$ | 9 |
| $ISOPOOH + OH \rightarrow 0.5XO_2 + 0.5ISOPO_2$ | $3.8(-12)\exp(200/T)$ | 5 |
| $CH_3OH + OH \rightarrow HO_2 + CH_2O$ | $6.7(-12)\exp(-600/T)$ | 1 |
| $MPAN + OH + M \rightarrow 0.5(HYAC + NO_3$ | $k_0 = 8.(-27)(300/T)^{3.5}$ | 5 |
| $+CH_2O + HO_2) + M$ | $k_\infty = 3.0(-11)$ | |
| | $Fc = 0.5$ | |
| $PAN + OH \rightarrow CH_2O + NO_3$ | $4.0(-14)$ | 1 |
| $OH + HYAC \rightarrow CH_3COCHO + HO_2$ | $3.0(-12)$ | 5 |
| $OH + GLYALD \rightarrow 0.8CH_3CO_3 + 0.4CO + 0.6HO_2$ | $1.0(-11)$ | 5 |
| $OH + H_2S \rightarrow HO_2 + SO_2$ | $6.(-12)\exp(-75/T)$ | 1 |
| $OH + COS \rightarrow HO_2 + SO_2$ | $1.1(-13)\exp(-1200/T)$ | 1,10 |
| $OH + DMS \rightarrow SO_2 + 2CH_2O$ | $1.2(-11)\exp(-260/T)$ | 1,10 |
| $OH + DMS \rightarrow 0.6SO_2 + 1.2CH_2O$ | $3.04(-12)\exp(350/T)(\alpha/(1+\alpha))$ | 1 |
| $+0.4(0.6SO_2 + 0.4SO_4 + 1.5CH_2O)$ | $\alpha = 1.159(-31)\exp(7460/T)[M]$ | |

| Chemical reaction mechanism and kinetic rates (continued) | | |
|---|---|---|
| *Reaction* | *Rate* | *Ref.* |
| $NO_3 + DMS \rightarrow HNO_3 + SO_2 + 2CH_2O$ | $1.9(-13)\exp(500/T)$ | 1,10 |
| $OH + CS_2 \rightarrow COS + SO_2 + HO_2$ | $8.8(-16)\exp(2300/T)$ | 10 |
| $OH + SO_2 + M \rightarrow SO_4 + HO_2 + M$ | $k_0 = 3(-31)(300/T)^{3.3}$ | 1 |
| | $k_\infty = 1.5(-12)$ | |
| | $Fc = 0.6$ | |
| $SO_2 \rightarrow SO_4$ | in-cloud $SO_2$ | 10 |
| $N_2O_5 + SO_4^{2-} \rightarrow 2HNO_3 + SO_4^{2-}$ | $\gamma = 0.1$ | 14,*h* |
| $NO_3 + SO_4^{2-} \rightarrow HNO_3 + SO_4^{2-}$ | $\gamma = 0.001$ | 14,*h* |
| $HO_2 + SO_4^{2-} \rightarrow 0.5H_2O_2 + SO_4^{2-}$ | $\gamma = 0.2$ | 14,*h* |

Read $2.14(-11)$ as $2.14 \cdot 10^{-11}$; $T$=temperature (K); $[M]$ is the air density (molecule $\mathrm{cm}^{-3}$); $P_{atm}$ is the atmospheric pressure $(\mathrm{atm})$; $\gamma$ is the reaction probability on aerosols. Units for first-, second-, and third-order reactions are $\mathrm{sec}^{-1}$, $\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{sec}^{-1}$ and $\mathrm{cm}^6\mathrm{molecule}^{-2}\mathrm{sec}^{-1}$ 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 $C_2H_5O_2$.

*b*. Rate assumed equal to the rate of the corresponding reaction of $CH_3OOH$.

*c*. Based on Horowitz et al. (2003) assuming that the peroxy radical produced in this reaction reacts with NO. The conversion of NO to $NO_2$ is neglected.

*d*. Rate assumed equal to the rate of the corresponding reaction of $CH_3CO_3$.

*e*. Products as in Horowitz et al. (2003), except that $NO_2$ is replaced by $HNO_3$, 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.** Photodissocations included in the model.

| **Photodissociations** | | | |
|---|---|---|---|
| *Reaction* | *Cross section* | *Quantum yield* | *Products* |
| $O_2 + h\nu \rightarrow O_3 + O_3$ | 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 |
| $MACROOH + h\nu \rightarrow 1.16HO2 + CO$ $+0.84OH + 0.84CH_3COCHO$ $+0.16ACETOOH$ | *l* | *l* | 17 |
| $MPAN + h\nu \rightarrow MCO_3 + NO_2$ | *n* | *n* | 16 |

| Photodissociations (continued) | | | |
|---|---|---|---|
| *Reaction* | *Cross section* | *Quantum yield* | *Products* |

**References:** 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).

**Notes:** *a*) Hertzberg continuum (205-240 nm) *b*) Schumann-Runge bands (175-205 nm) *c*) Quantum yield is taken equal to 1. *d*) Oxygen and hydrogen atoms as well as HCO and $CH_3O$ radicals produced in the mechanism are assumed to react instantly with $O_2$, an excellent approximation in the troposphere. *e*) 190-280 nm temperature-independent cross sections *f*) 280-350 nm temperature-dependent cross sections *g*) The contribution of near-IR radiation to the photolysis of $HNO_4$ is about $10^{-5}$ $s^{-1}$ during daytime throughout the atmosphere (Roehl et al., 2002; Salawitch et al., 2002). *h*) Use the corresponding $CH_3CHO$ photolysis quantum yield increased by a factor of 1.6 (Bacher et al., 2001). *i*) ONITR is assumed to photolyse as $n$-$C_4H_9ONO_2$. *j*) Constant value of 0.05 (upper limit) *k*) J=J($CH_3OOH$) *l*) J=J($CH_3CHO$) *m*) J=0.28 * J($H_2O_2$) *n*) J=J(PAN)

## References


Atkinson, R.: Gas-Phase tropospheric chemistry of organic compounds, J. Phys. Chem. Ref. Data, Monograph No. 2, 1994.

Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, R. F., Kerr, Jr., J. A., Rossi, M. J., and Troe, J.: Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry, IUPAC Subcommittee on gas kinetic data evaluation for atmospheric chemistry, J. Phys. Chem. Ref. Data, 28, 191–393, 1999.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F.(Jr), Kerr, J. A., Rossi, M. J., and Troe, J.: Summary of Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry, IUPAC Subcommittee on gas kinetic data evaluation for atmospheric chemistry, www.iupac-kinetic.ch.cam.ac.uk, 2002.

Bacher, C., Tyndall, G. S. and Orlando, J. J.: The atmospheric chemistry of glycolaldehyde, J. Atmos. Chem., 39, 171–189, 2001.

Brasseur, G. P., Hauglustaine, D. A., Walters, S., Rasch, P. J., Müller, J.-F., Granier, C. and Tie X.: MOZART, a global chemical transport model for ozone and related tracers, 1. Model Description, J. Geophys. Res., 103, 28265–28289, 1998.

Brocheton, F.: "Représentation des émissions anthropiques dans les modèles de chimie-transport: Sensibilité à la représentation spatiale des émissions et au degré de raffinement du schéma chimique", Ph.D., Université Paris 12 - Val de Marne, 1999.

DeMore, W. B., Sander, S. P., Golden, D. M., Hampson, R. F., Kurylo, M. J., Howard, C. J., Ravishankara, A. R., Kolb, C. E. and Molina, M. J.: Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation number 12, NASA panel for data evaluation, JPL Publication 97-4, Jet Propulsion Laboratory, Pasadena, 1997.

Dentener, F. J. and Crutzen, P. J.: Reaction of $N_2O_5$ on tropospheric aerosols: impact on the global distributions of $NO_x$, $O_3$, and $OH$, J. Geophys. Res., 98, 7149–7163, 1993.

Gierczak, T., Burkholder, J. B., Bauerle, S. and Ravishankara, A. R., Photochemistry of acetone under tropospheric conditions, Chem. Phys., 231, 229–244, 1998.

Jacob, D. J.: Heterogeneous Chemistry and Tropospheric Ozone, Atmos. Environ., 34, 2131–2159, 2000.

Johnston, H. S. Davis and Lee, Y. T.: $NO_3$ photolysis product channels: quantum yields from observed energy thresholds, J. Phys. Chem., 100, 4713–4723, 1996.

Horowitz, L. W., Walters, S., Mauzerall, D. L., Emmons, L. K., Rasch, P. J., Granier, C., Tie X., Lamarque, J.-F., Schultz, M. G., Tyndall, G. S., Orlando, J. J. and Brasseur, G. P.: A global simulation of tropospheric ozone and related tracers: description and evaluation of Mozart, version 2, 108, No. D24, 4784, doi:10.1029/2002JD002853, 2003.

Kockarts, G.: The penetration of solar radiation in the Schumann-Runge bands of molecular oxygen: a robust approximation, Ann. Geophysicae, 12, 1207–1217, 1994.

Knight, G., Ravishankara, A. R. and Burkholder, J.: UV absorption cross section of $HO_2NO_2$ between 343 and 273 K, Phys. Chem. Chem. Phys., 4, 1432–1437, 2002.

Martinez, E., Cabanas, B., Aranda, A., Martin, P. and Salgado, S.: Absolute rate coefficients for the gas-phase reactions of $NO_3$ radical with a series of monoterpenes at T=298 to 433 K, J. Atmos. Chem., 33, 265–282, 1999.

Martinez, R. D., Buitrago, A. A., Howell, N. W., Hearn, C. H. and Joens J. A.: The near U.V. absorption spectra

of several aliphatic aldehydes and ketones at 300 K, Atmos. Environ., 26, 785–792, 1992.

Meller, R. and Moortgat, G. K.: Temperature dependence of the absorption cross sections of formaldehyde between 223 and 323 K in the wavelength range 225-375 nm, J. Geophys. Res., 105, 7089–7101, 2000.

Middleton, P., Stockwell, W. R. and Carter, W. P.: Aggregation and analysis of volatile organic compound emissions for regional modeling, Atmos. Environ., 24, 1107–1133, 1990.

Molina, L. T. and Molina M. J.: Absolute absorption cross sections of ozone in the 185- to 350-nm wavelength range, J. Geophys. Res., 91, 14501–14508, 1986.

Müller, J.-F. and Brasseur, G. P.: IMAGES: A three-dimensional chemical transport model of the global troposphere, J. Geophys. Res., 100, 16445–16490, 1995.

Pham, M., Müller, J.-F., Brasseur, G. P., Granier, C., and Mégie, G.: A three-dimensional study of the tropospheric sulfur cycle, J. Geophys. Res., 100, 26061–26092, 1995.

Raber, W. H. and Moortgat, G. K.: Photodissociation of selected carbonyl compounds in air: methy ethyl ketone, methyl vinyl ketone, methacrolein and methylglyoxal, in Progress and problems in atmospheric chemistry, Barker, J. R., ed., pp. 318–373, World Scientifi c Publ. Co., Singapore, 1996.

Ravishankara, A. R., Dunlea, E. J., Blitz, M. A., Dillon, T. J., Heard, D. E., Pilling, M. J., Strekowski, R. S., Nicovich, J. M. and Wine, P. H.: Redetermination of the rate coeffi cient for the reaction $O(^1D)$ with $N_2$, Geophys. Res. Lett., 29, 10.1029/2002GL014850, 2002.

Roehl, C. A., Nizkorodov, S. A., Zhang, H., Blake, G. and Wennberg, P. O.: Photodissociation of $HNO_4$ in the near IR, J. Phys. Chem. A., 106, 3766–3772, 2002.

Salawitch, R. J., Wennberg, P. O., Toon, G. C., Sen, B. and Blavier, J.-F.: Near IR photolysis of $HO_2NO_2$: Implications for $HO_x$, Geophys. Res. Lett., 29, 10.1029/2002GL015006, 2002.

Sander, S. P., Friedl, R. R., DeMore, W. B., Golden, D. M., Kurylo, M. J., Hampson, R. F., Huie, R. E., Moortgat, G. K., Ravishankara, A. R., Kolb, C. E. and Molina, M. J.: Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation number 13, NASA panel for data evaluation, JPL Publication 00-3, Jet Propulsion Laboratory, Pasadena, 2000.

Saunders, S. M., Jenkin, M. E., Derwent, R. G. and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds, Atmos. Chem. Phys., 3, 161–180, 2003.

Tyndall, G. S., Cox, R. A., Granier, C., Lesclaux, R., Moortgat, G. K., Pilling, M. J., Ravishankara, A. R. and Wallington, T. J.: Atmospheric chemistry of small organic peroxy radicals, J. Geophys. Res., 106, D11, 12157–12182, 2001.

Warneck, P.: Photodissociation of acetone in the troposphere: an algorithm for the quantum yield, Atmos. Environ., 35, 5773–5777, 2001.