

SUGGESTIONS MADE REGARDING MECHANISM AND DOCUMENTATION NOTES.

Reaction 1

	Notes	
Phot Set= NO2	1,2	NO2 + HV = NO + O3P

Notes

1	See Table (number to be determined by Carter) for listing of absorption cross sections and quantum yields. Set used is given in the "Type" column.
2	Absorption cross sections and quantum yields from IUPAC recommendation (Atkinson et al, 1997a), except that quantum yields for $\lambda > 410$ nm are from NASA (1997), which are consistent with IUPAC (Atkinson et al, 1997a) values except they are more precise. Note that more recent IUPAC recommendations (Atkinson et al, 1997b) gives slightly different absorption cross sections based on data from a more recent study, but the differences are not significant.

Table of absorption cross sections and quantum yields is not yet defined. The recommendations for this reaction are consistent with current knowledge.

Reaction 2

k(300)	A	Ea	B	Notes	
5.91e-34	5.91e-34	0.00	-2.8	3	O3P + O2 + M = O3 + M

Notes

3	Rate constant expression derived from IUPAC (Atkinson et al, 1997b) recommendations for M = 20.9% O2 and 79.1% N2.
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The reactants and products formed by Reaction 2 are consistent with current knowledge but the rate constant should be revised.

IUPAC DATA

k(300)	A	B	
5.6e-34	5.6e-34	-2.8	O3P + O2 + N2 = O3 + N2
6.0e-34	6.0e-34	-2.8	O3P + O2 + O2 = O3 + O2

Averaging the two A factors according to the abundances of oxygen and nitrogen.

$$0.791 * 5.6e-34 + 0.219 * 6.0e-34 = 5.74e-34$$

Recommended Revision to Reaction 2

k(300)	A	B	Notes	
5.74e-34	5.91e-34	-2.8	3	O3P + O2 + M = O3 + M

Reaction 3

k(300)	A	Ea	Notes	
8.34e-15	8.00e-12	4.09	4,5	O3P + O3 = #2 O2

Notes

4	Rate constant is IUPAC, Supplement VI (Atkinson et al, 1997b) and NASA (1997) recommendation.
5	This reaction is probably not important in air, but is included to increase range of applicability.

The reactants and products formed by Reaction 3 are consistent with current knowledge and the rate parameters are those recommended by IUPAC and NASA. The reaction is not important in the lower troposphere under most conditions. However is it a key reaction in the stratosphere and therefore is it not correct to state that it is not important in air.

Recommendation

Note 5 should be revised to read: “This reaction is probably not important in the troposphere, but is included to increase range of applicability.”

Reaction 4

k(300)	A	B	Notes	
1.00e-31	1.00e-31	-1.6	6,7,5	O3P + NO + M = NO2 + M

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
7	Recommended rate constant given for N2 is assumed to be applicable to air.
5	This reaction is probably not important in air, but is included to increase range of applicability.

The reactants and products formed by Reaction 4 are consistent with current knowledge and the rate parameters are those recommended by IUPAC. It should be noted that NASA (1997) treats this reaction as a recombination reaction with a rate parameter described by the Troe expression.

The reaction is not important in the lower troposphere under most conditions. However is it a key reaction in the stratosphere and therefore is it not correct to state that it is not important in air.

Recommendation

Modify Note 5 as suggested under Reaction 3.

Reaction 5

k(300)	A	Ea	Notes
9.70e-12	6.50e-12	-0.24	4,5
$O_3P + NO_2 = NO + O_2$			

Notes

4	Rate constant is IUPAC, Supplement VI (Atkinson et al, 1997b) and NASA (1997) recommendation.
5	This reaction is probably not important in air, but is included to increase range of applicability.

The reactants and products formed by Reaction 5 are consistent with current knowledge and the rate parameters are those recommended by IUPAC and NASA.

The reaction is not important in the lower troposphere under most conditions. However is it a key reaction in the stratosphere and therefore is it not correct to state that it is not important in air. Recommendation: Modify Note 5 as suggested under Reaction 3.

Reaction 6

k(300)	Falloff, F	Notes
1.79e-12	0.80	4,7,5
$O_3P + NO_2 = NO_3 + M$		
	A	B
k₀	9.00e-32	-2.0
k	2.20e-11	0.0

Notes

4	Rate constant is IUPAC, Supplement VI (Atkinson et al, 1997b) and NASA (1997) recommendation.
7	Recommended rate constant given for N2 is assumed to be applicable to air.
5	This reaction is probably not important in air, but is included to increase range of applicability.

The reactants and products formed by Reaction 6 are consistent with current knowledge. The rate parameters for k_0 and k are those recommended by IUPAC and NASA. However NASA recommends 0.6 for all recombination reactions and this leads to a difference in the $K(300)$ that would be calculated from the IUPAC and NASA data. The IUPAC value is $1.79\text{e-}12 \text{ cm}^3 \text{ s}^{-1}$ while the NASA calculated value is $1.56\text{e-}12 \text{ cm}^3 \text{ s}^{-1}$.

Recommendations

The differences between the final calculated rate parameters for this reaction between the NASA and IUPAC rate parameters should be noted in the footnotes. Modify Note 5 as suggested under Reaction 3.

Reaction 7

No reaction with that label.

Reaction 8

k(300)	A	Ea	Notes
1.87e-14	1.80e-12	2.72	6

$$\text{O}_3 + \text{NO} = \text{NO}_2 + \text{O}_2$$
Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
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The reactants and products formed by Reaction 8 are consistent with current knowledge and the choice of rate parameters by Dr. Carter is acceptable. There is a small difference between the rate parameters recommended by NASA and IUPAC. The NASA recommended values are given below.

k(300)	A	Ea
1.88e-14	2.00e-12	2.78

$$\text{O}_3 + \text{NO} = \text{NO}_2 + \text{O}_2$$

The differing sets of rate parameters give almost the same values at 300 K although the A factors differ by 10%. No changes are recommended for this reaction.

Reaction 9

k(300)	A	Ea	B	Notes
3.72e-17	1.40e-13	4.91		6

$$\text{O}_3 + \text{NO}_2 = \text{O}_2 + \text{NO}_3$$
Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
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The reactants and products formed by Reaction 9 are consistent with current knowledge and the choice of rate parameters by Dr. Carter is acceptable. Given that there is a change in the two IUPAC recommendations during 1997, and since they differ from NASA, Dr. Carter might want to make a brief note of the reasons for this in his documentation.

Reaction 10

k(300)	A	Ea	B	Notes
2.60e-11	1.80e-11	-0.22		6
NO + NO ₃ = #2 NO ₂				

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
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The reactants and products formed by Reaction 10 are consistent with current knowledge and the choice of rate parameters by Dr. Carter is acceptable. There is a small difference between the IUPAC and NASA recommendations.

Reaction 11

k(300)	A	Ea	B	Notes
1.93e-38	3.30e-39	-1.05		6
NO + NO + O ₂ = #2 NO ₂				

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
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The reactants and products formed by Reaction 11 are consistent with current knowledge and the choice of rate parameters by Dr. Carter is in agreement with NASA and IUPAC. It might be noted that this reaction is only important in plumes with very high NO concentrations. There have been no new data on this reaction since 1985.

Reaction 12

k(300)	Falloff, F	Notes
1.53e-12	0.45	6,7
NO ₂ + NO ₃ = N ₂ O ₅		
	A	B
k_o	2.80e-30	-3.5
k	2.00e-12	0.2

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
7	Recommended rate constant given for N ₂ is assumed to be applicable to air.

N₂O₅ is in equilibrium with NO₃ and NO₂; the reactants and products formed by Reaction 12 are consistent with current knowledge. The rate parameters for k_o and k are those recommended by IUPAC. Given that there is a change in the two IUPAC recommendations during 1997, and since they differ from NASA, Dr. Carter might want to make a brief note of the reasons for this in his documentation.

Reaction 13

k(300)	Falloff, F	Ea	Notes
6.74e-2	0.45		6,7
	A		B
k₀	1.00e-3	21.86	-3.5
k	9.70e+14	22.02	0.1



Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
7	Recommended rate constant given for N ₂ is assumed to be applicable to air.

N₂O₅ is in equilibrium with NO₃ and NO₂; the reactants and products formed by Reaction 13 are consistent with current knowledge. To understand the form of the rate constant it is necessary to refer to the IUPAC review. It is recommended that formulas to calculate all types of rate constants, Arrhenius, recombination, etc. be given before the mechanism table. There is some difference between the two IUPAC recommendations, especially for the falloff, F_c, that might be noted in the documentation.

Reaction 14

k(300)	A	Ea	B	Notes
2.60e-22	2.60e-22			8



Notes

8	The data of Mentel et al (1996) indicate that the reaction occurs through pathways which are first order and second order in H ₂ O, where the latter is presumed to be surface-dependent. We assume that the process which is first order in H ₂ O represents a gas-phase reaction, and use the rate expression of Mentel et al (1996) for this process. Note that the IUPAC (Atkinson et al, 1997b) recommendation that the gas-phase rate constant is less than $2 \times 10^{-21} \text{ cm}^{-3} \text{ molec}^{-1} \text{ s}^{-1}$.
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The products and reactants are reasonable but the extent of the occurrence of Reaction 14 as a gas-phase reaction has been a subject of long term debate. The entropy of the supposed transition state is a significant barrier to the occurrence of this reaction. The choice of the Mentel et al (1996) data is very reasonable, especially considering that it is lower than the upper limit of the NASA evaluation.

Reaction 15

k(300)	Notes
Slow	9



Notes

9	Photolysis of N ₂ O ₅ is assumed to be negligible compared to decomposition under atmospheric conditions.
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Dr. Carter's conclusion regarding Reaction 15 appears to be correct since the NASA evaluation reports that the quantum yield for O^3P is less than 0.1 at 290 nm. In any case there is little N_2O_5 in the polluted troposphere due to the fast photolysis of NO_3 . However, the footnote should read: "negligible compared to".

Reaction 16

k(300)	Notes	
Slow	9	$N_2O_5 + HV = NO_3 + NO_2$

Notes

9	Photolysis of N_2O_5 is assumed to be negligible compare to decomposition under atmospheric conditions.
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It is reasonable to exclude Reaction 16 from mechanisms for the lower troposphere due to the low concentrations of N_2O_5 in the polluted troposphere due to the fast photolysis of NO_3 . The reaction should also be slow because according to the NASA review the quantum yield for the formation of NO_3 is unity at 289 nm but the absorption cross sections are very low at wavelengths above 240 nm. However, the footnote should read: "negligible compared to".

Reaction 17

k(300)	A	Ea	B	Notes
6.75e-16	4.50e-14	2.50		10

$$\text{NO}_2 + \text{NO}_3 = \text{NO} + \text{NO}_2 + \text{O}_2$$
Notes

10	The NASA (1997) evaluation states that the existence of this channel has not been firmly established, but results of a number of studies indicate it may occur. Rate constant expression used is that NASA (1997) states gives best fits to the data. Uncertainty is at least a factor of 2. This reaction was not discussed in the recent IUPAC evaluations (Atkinson et al, 1997a,b).
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Dr. Carter is correct to write that the occurrence of Reaction 17 and its rate parameters are highly uncertain. The reaction is necessary to explain the results of five laboratory investigations and the values used are consistent with the five experiments according to the NASA evaluations.

Reaction 18

	Notes
Phot Set= NO ₃ NO	1,11,12

$$\text{NO}_3 + \text{H}\nu = \text{NO} + \text{O}_2$$
Notes

1	See Table (number to be determined by Carter) for listing of absorption cross sections and quantum yields. Set used is given in the "Type" column.
11	Absorption cross sections from IUPAC (Atkinson et al, 1997a). Values recommended by more recent IUPAC evaluation (Atkinson et al, 1997b) appear to be the same for 298K, though different at lower temperature. Temperature dependence ignored.
12	IUPAC (1997b) and NASA (1997) give no useable recommendations for quantum yields except to recommend that $q_y(\text{NO}_2+\text{O})=1$ for $wl \leq 583$. Quantum yields of Magnotta and Johnson (1980), scaled down by a factor of 1.5 to give unit maximum quantum yields, as incorporated in mechanism of Carter (1990) were retained in this mechanism. The calculated rate constant for solar overhead sun is consistent with the recommendations of Magnotta and Johnson (1980), and reasonably consistent with the IUPAC (1997a) recommendation.

The reactants and products of Reaction 18 are in accord with the recommendations. It is well known that the NO₃ absorption cross sections are temperature dependent, therefore it would be desirable if the error made in ignoring the temperature dependence was quantified in the footnote. There may be more data in Wayne et al. (1991) that should be considered.

Reaction 19

	Notes

Phot Set= NO3NO2	1,11,12	NO3 + HV = NO2 + O3P
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Notes

1	See Table (number to be determined by Carter) for listing of absorption cross sections and quantum yields. Set used is given in the "Type" column.
11	Absorption cross sections from IUPAC (Atkinson et al, 1997a). Values recommended by more recent IUPAC evaluation (Atkinson et al, 1997b) appear to be the same for 298K, though different at lower temperature. Temperature dependence ignored.
12	IUPAC (1997b) and NASA (1997) give no useable recommendations for quantum yields except to recommend that $qy(NO_2+O)=1$ for $wl \leq 583$. Quantum yields of Magnotta and Johnson (1980), scaled down by a factor of 1.5 to give unit maximum quantum yields, as incorporated in mechanism of Carter (1990) were retained in this mechanism. The calculated rate constant for solar overhead sun is consistent with the recommendations of Magnotta and Johnson (1980), and reasonably consistent with the IUPAC (1997a) recommendation.

The reactants and products of Reaction 19 are in accord with the recommendations. It is well known that the NO3 absorption cross sections are temperature dependent, therefore it would be desirable if the error made in ignoring the temperature dependence was quantified in the footnote. There may be more data in Wayne et al. (1991) that should be considered.

Reaction 20

	Notes	
Phot Set= O3O3P	1,14,15	O3 + HV = O3P + O2

Notes

1	See Table (number to be determined by Carter) for listing of absorption cross sections and quantum yields. Set used is given in the "Type" column.
13	Absorption cross sections from IUPAC (Atkinson et al, 1997b). Data are for T=273 K. Temperature dependences for cross section (NASA, 1997) are ignored.
14	Quantum yields for O1D are those tabulated by IUPAC (Atkinson et al, 1997b), which are significantly higher than previous recommendations at $wl > 310$ nm. Quantum yields for O3P based on assuming total quantum yield of unity, though this was not adequately discussed in the evaluations.

The reactants and products of Reaction 20 are consistent with current knowledge. The increase in the quantum yields is also consistent with the most recent recommendations (see Reaction 21 below).

Reaction 21

	Notes	
Phot Set= O3O1D	1,14,15	O ₃ + HV = O*1D ₂ + O ₂

Notes

1	See Table (number to be determined by Carter) for listing of absorption cross sections and quantum yields. Set used is given in the "Type" column.
14	Absorption cross sections from IUPAC (Atkinson et al, 1997b). Data are for T=273 K. Temperature dependences for cross section (NASA, 1997) are ignored.
15	Quantum yields for O1D are those tabulated by IUPAC (Atkinson et al, 1997b), which are significantly higher than previous recommendations at wl > 310 nm. Quantum yields for O3P based on assuming total quantum yield of unity, though this was not adequately discussed in the evaluations.

The reactants and products of Reaction 21 are consistent with current knowledge. It seems that a higher base temperature could be chosen for the cross sections this may be important because recent data on the temperature dependence of ozone photolysis (Talukdar et al., 1998) leads to greater O(¹D) formation rates. This could be a problem during the fall and spring because this may lead to more rapid photochemical loss of ozone and greater rates of HO formation.

Reaction 22

k(300)	A	Ea	Notes	
2.20e-10	2.20e-10	---	4	O*1D ₂ + H ₂ O = #2 HO.

Notes

4	Rate constant is IUPAC, Supplement VI (Atkinson et al, 1997b) and NASA (1997) recommendation.
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The reactants, products and rate parameters of Reaction 22 are consistent with current knowledge.

Reaction 23

k(300)	A	Ea	Notes	
2.87e-11	2.09e-11	-0.19	15	O*1D ₂ + M = O ₃ P + M

Notes

14	Calculated using IUPAC (Atkinson et al, 1997b) recommended rate constants for reaction with O ₂ and N ₂ , assuming 20.9% O ₂ and 79.1% N ₂ . Temperature dependence optimized to fit rate constants calculated for T= 270, 300, and 330K.
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The reactants, products and rate parameters of Reaction 23 are consistent with current knowledge. It is not clear why it is necessary to fit the rate constant. It would be somewhat more accurate to calculate the rate parameter as:

$$k = 1.80\text{e-}11 * \exp(107/T) * 0.791 * [\text{M}] + 3.20\text{e-}11 * \exp(67/T) * 0.209 * [\text{M}]$$

Reaction 24

k(300)	Falloff, F	Notes
7.31e-12	0.60	16
	A	B
k_o	7.00e-31	-2.6
k	3.60e-11	-0.1

**Notes**

16	Falloff expression recommended by NASA (1997) used because it gives rate constant for 1 atm N ₂ which is consistent with measurement near those conditions. IUPAC (Atkinson et al, 1997a,b) recommendations are not used because k (1 atm N ₂) are not consistent with these data, being based on high pressure data in He. This is consistent with current recommendation of Atkinson (private communication, 1997).
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The reactants, products and rate parameters of Reaction 24 are consistent with current knowledge. Probably the increase in the rate parameter for the reaction of HO with NO will have little effect on the mechanism's predictions because photolysis will convert all HONO formed through this reaction back to NO and HO.

The signs of the B parameters may be confusing to some readers of the NASA evaluation because the NASA values are given as opposite in sign. It is very important that Dr. Carter provide a table with the equations for all types of rate parameters.

Reaction 25

	Notes
Phot Set= HONO-NO	1,17,18

**Notes**

1	See Table (number to be determined by Carter) for listing of absorption cross sections and quantum yields. Set used is given in the "Type" column.
17	The cross sections from Stockwell and Calvert (1978), used in the previous version of the mechanism, are retained because they are higher resolution than the averaged data recommended by IUPAC (1997b), and the areas under the spectra appear to be consistent.
18	Quantum yields are those recommended by IUPAC (Atkinson et al, 1997b).

The IUPAC and the NASA evaluations favor the HONO cross sections given by Bongartz et al. (1991) over the values given by Stockwell and Calvert (1978). Although the IUPAC evaluations report the Bongartz et al. (1991) cross sections with a 5 nm resolution, the NASA evaluation reports them with the same resolution reported by Stockwell and Calvert (1978), 1 nm resolution. The cross sections of Bongartz et al. (1991) should be used because there are significant differences between the values of Stockwell and Calvert and Bongartz et al. (1991); the cross section reported by Stockwell and Calvert are 20% lower than the values of Bongartz et al. at 354 nm.

Reaction 26

	Notes	
Phot Set= HONO-NO2	1,17,18	HONO + HV = HO2. + NO2

Notes

1	See Table (number to be determined by Carter) for listing of absorption cross sections and quantum yields. Set used is given in the "Type" column.
17	The cross sections from Stockwell and Calvert (1978), used in the previous version of the mechanism, are retained because they are higher resolution than the averaged data recommended by IUPAC (1997b), and the areas under the spectra appear to be consistent.
18	Quantum yields are those recommended by IUPAC (Atkinson et al, 1997b).

The NASA evaluations with the cross sections of Bongartz et al. (1991) should be used rather than the values of Stockwell and Calvert as discussed for Reaction 26. The inclusion of the formation of H atom (as HO₂ in the troposphere) and NO₂ from HONO photolysis is reasonable. This might be expected to improve the model's predictions under high NO_x conditions

Reaction 27

k(300)	A	Ea	Notes
6.42e-12	2.70e-12	-0.52	6

HO. + HONO = H2O + NO2

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
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The reactants, products and rate parameters of Reaction 27 are consistent with current knowledge.

Reaction 28

k(300)	Falloff, F	Notes
8.81e-12	0.60	19
	A	B
k₀	2.43e-30	-3.1
k	1.67e-11	-2.1

HO. + NO2 = HNO3

Notes

19	NASA (1997) and IUPAC (Atkinson et al, 1997a,b) give significantly different recommendations for rate parameters for this important reaction. The falloff expression used here is based on a NASA (1997) and IUPAC (Atkinson et al, 1997a,b) give significantly different recommendations for rate parameters for this important reaction. The falloff expression used here is based on a re-evaluation of the data by Golden (Personal communication, 1998), and is expected to be the recommendation in the next NASA evaluation. This is essentially the same as the NASA (1997) recommendation except for the temperature dependence, which Golden says was due to improper uncertainty weighting. The data with "weak colliders" (i.e., bath gases other than SF6 or CF4) appear to be well fit by this parameterization, including the data of Donahue et al (1997). The data of Forster et al (1995), which are the basis for the high 1997 IUPAC recommendation, are not used because they may be due to a HOONO-forming channel becoming important at high pressure.
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The new rate parameters are about 20% lower than used in many current mechanisms. Dr. Carter's choice of rate parameters appears to be correct based on the current re-evaluations of Dr. Golden that this reviewer has also seen. The 20% decrease in the rate parameter for the reaction of HO with NO₂ is important. It is disturbing that such a "well known reaction" has such these uncertainties in its rate parameter and in the pressure dependence of the rate parameter.

Reaction 29

k(300)	A	Ea	Notes
2.00e-11	2.00e-11	---	6,20

HO. + NO3 = HO2. + NO2

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
20	No recommendation is given concerning the temperature dependence of this rate constant, which is assumed to be small.

The reactants, products and rate parameters of Reaction 291 are consistent with current knowledge.

Reaction 30

k(300)	A	Ea	B	Notes
1.44e-13	5.45e-15	-1.95		21,22
HO. + HNO3 = H2O + NO3				

Notes

21	The rate parameters were derived to fit the rate constants calculated using the NASA (1997) recommended expression for T 270 - 330 K range and 1 atm. total pressure.
22	This rate constant is strictly valid for 1 atm air only, but the error introduced by neglecting the pressure dependence of this reaction is expected to be small.

Is it necessary to fit the real rate expression for Reaction 30? The error in an Arrhenius expression for the rate parameter derived by assuming 1 atmosphere pressure and then fitting the much more complicated rate constant expression for Reaction 30 may be small but there is little advantage in doing this. It is not difficult to program the full rate expression into air quality models. It is also probable that the mechanism will be used in regional models with upper layers up to 10 km or higher and in that case there may be significant differences.

Reaction 31

	Notes
Phot Set= HNO3	1,23
HNO3 + HV = HO. + NO2	

Notes

1	See Table (number to be determined by Carter) for listing of absorption cross sections and quantum yields. Set used is given in the "Type" column.
23	Absorption cross-sections from IUPAC (Atkinson et al, 1997b). Recommend quantum yield for the OH + NO2 pathway is "close to unity" for $\lambda > 260$ nm, though other pathways become important at lower wavelengths.

The sum of the quantum yield for the HO + NO2 producing channel and the quantum yield for the HO + NO + O producing channel is greater than 0.97 for wavelengths greater than 260 nm. But the quantum yield for the HO + NO + O producing channel is only 0.13 at 222 nm and that would be expected to decrease at greater wavelengths.

Therefore the choice of quantum yields and products for Reaction 31 appears to be correct.

Reaction 32A

k(300)	A	Ea	B	Notes	
1.30e-13	1.30e-13	---		24	HO. + CO = HO2. + CO2

Notes

24	The rate constants for the OH + CO reactions are based on expression given by IUPAC (Atkinson et al, 1997a). NASA (1997) gives a similar expression, but without temperature dependence.
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The reactants and products are consistent with current knowledge. This value is consistent with the NASA recommendation but since the IUPAC evaluation provides a rate parameter with a temperature and pressure dependence it is suggested that the full expression be used.

Reaction 32B

k(300)	A	Ea	B	Notes	
3.19e-33	3.19e-33	---		24	HO. + CO + M = HO2. + CO2 + M

Notes

24	The rate constants for the OH + CO reactions are based on expression given by IUPAC (Atkinson et al, 1997a). NASA (1997) gives a similar expression, but without temperature dependence.
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The reactants and products are consistent with current knowledge. Reaction 33 could be combined with Reaction 32A by making the rate constant for Reaction 32A pressure dependent. This value is consistent with the NASA recommendation but since the IUPAC evaluation provides a rate parameter with a temperature and pressure dependence it is suggested that the full expression be used.

Reaction 33

k(300)	A	Ea	Notes	
6.78e-14	1.90e-12	1.99	6	HO. + O3 = HO2. + O2

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
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The reactants, products and rate parameters for Reaction 33 are consistent with current knowledge.

Reaction 34

k(300)	A	Ea	B	Notes
8.36e-12	3.40e-12	-0.54		6

HO₂. + NO = HO. + NO₂

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
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The reactants, products and rate parameters are consistent with current knowledge. It might be noted that the A-factor has been decreased by about 10% from the IUPAC Supplement V evaluation.

Reaction 35

k(300)	Falloff, F	Notes
1.36e-12	0.60	6
k₀	1.80e-31	-3.2
k	4.70e-12	0.0

**Notes**

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
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HO₂NO₂ is in equilibrium with HO₂ and NO₂; the reactants and products formed by Reaction 35 are consistent with current knowledge. To understand the form of the rate constant it is necessary to refer to the IUPAC review. It is recommended that formulas to calculate all types of rate constants, Arrhenius, recombination, etc. be given before the mechanism table.

Reaction 36

k(300)	Falloff, F	Ea	Notes
9.61e-2	0.50		6
	A		B
k₀	4.10e-5	21.16	0.0
k	5.70e+15	22.20	0.0

**Notes**

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
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HO₂NO₂ is in equilibrium with HO₂ and NO₂; the reactants and products formed by Reaction 36 are consistent with current knowledge. To understand the form of the rate constant it is necessary to refer to the IUPAC review. It is recommended that formulas to calculate all types of rate constants, Arrhenius, recombination, etc. be given before the mechanism table. There is some difference between the IUPAC Supplement V evaluation that might be noted in the documentation.

Reaction 37

	Notes
Phot Set= HO2NO2	1,25 HNO4 + HV = #.61 {HO2. + NO2} + #.39 {HO. + NO3}

Notes

1	See Table (number to be determined by Carter) for listing of absorption cross sections and quantum yields. Set used is given in the "Type" column.
25	Absorption cross sections and quantum yields from IUPAC (Atkinson et al, 1997b). Quantum yields are uncertain and based on data for a single wavelength only.

The reactants, products, quantum yields and cross sections for Reaction 37 are consistent with current knowledge.

Reaction 38

k(300)	A	Ea	Notes
4.98e-12	1.50e-12	-0.72	6 HNO4 + HO. = H2O + NO2 + O2

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
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The reactants, products and rate parameters for Reaction 38 are consistent with current knowledge.

Reaction 39

k(300)	A	Ea	Notes
1.89e-15	1.40e-14	1.19	6 HO2. + O3 = HO. + #2 O2

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
---	---

The reactants, products and rate parameters for Reaction 39 are consistent with current knowledge.

Reaction 40A

k(300)	A	Ea	Notes
1.63e-12	2.20e-13	-1.19	26 HO2. + HO2. = HO2H + O2

Notes

26	Reactions and rate constants used for the HO2 + HO2 and HO2 + HO2 + H2O system based on the data of Kircher and Sander (1984) as discussed in the IUPAC (Atkinson et al,
----	--

1997b) evaluation.

The reactants, products and rate parameters for Reaction 40A are consistent with current knowledge.

Reaction 40B

k(300)	A	Ea	Notes	
3.48e-30	3.08e-34	-5.56	26	HO ₂ . + HO ₂ . + H ₂ O = HO ₂ H + O ₂ + H ₂ O

Notes

26	Reactions and rate constants used for the HO ₂ + HO ₂ and HO ₂ + HO ₂ + H ₂ O system based on the data of Kircher and Sander (1984) as discussed in the IUPAC (Atkinson et al, 1997b) evaluation.
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The reactants, products and rate parameters for Reaction 40B are consistent with current knowledge.

Reaction 40C

k(300)	A	Ea	Notes	
4.85e-32	1.85e-33	-1.95	26	HO ₂ . + HO ₂ . + M = HO ₂ H + O ₂ + M

Notes

26	Reactions and rate constants used for the HO ₂ + HO ₂ and HO ₂ + HO ₂ + H ₂ O system based on the data of Kircher and Sander (1984) as discussed in the IUPAC (Atkinson et al, 1997b) evaluation.
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The reactants, products and rate parameters for Reaction 40C are consistent with current knowledge.

Reaction 40D

k(300)	A	Ea	Notes
1.04e-49	2.59e-54	-6.32	26

$$\text{HO}_2 + \text{HO}_2 + \text{M} + \text{H}_2\text{O} = \text{HO}_2\text{H} + \text{O}_2 + \text{M} + \text{H}_2\text{O}$$
Notes

26	Reactions and rate constants used for the HO ₂ + HO ₂ and HO ₂ + HO ₂ + H ₂ O system based on the data of Kircher and Sander (1984) as discussed in the IUPAC (Atkinson et al, 1997b) evaluation.
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The reactants, products and rate parameters for Reaction 40D are consistent with current knowledge.

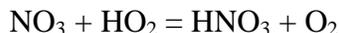
Reaction 41

k(300)	A	Ea	Notes
4.00e-12	4.00e-12	---	27

$$\text{NO}_3 + \text{HO}_2 = \text{HO} + \text{NO}_2 + \text{O}_2$$
Notes

27	Rate constant recommended by IUPAC (Atkinson et al, 1997b). Mechanism based on data of Mellouki et al (1993) as discussed by IUPAC (Atkinson et al, 1997b).
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Although the mechanism is uncertain there probably is a significant radical termination and nitric acid production through the reaction:



this channel should not be ignored. The studies reported in the review by Le Bras (1997) find that the rate of the nitric acid channel is between 20 and 43% of the total reaction rate of NO₃ with HO₂. In fact there is one study by Hjorth that found the reaction channel represented by reaction 41 to be insignificant (Le Bras, 1997). Although that study is probably not correct, it still points to the possible importance of the HNO₃ producing channel.

Reaction 42

k(300)	A	Ea	Notes
2.41e-16	8.50e-13	4.87	28

$$\text{NO}_3 + \text{NO}_3 = 2 \text{NO}_2 + \text{O}_2$$
Notes

29	Rate expression from NASA (1994) evaluation. More recent evaluations neglect this reaction, though it may be non-negligible under some nighttime conditions (Stockwell et al, 1997).
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The reactants, products and rate parameters for Reaction 42 are consistent with current knowledge.

Reaction 43

	Notes	
Phot Set= H2O2	1,29	HO2H + HV = #2 HO.

Notes

1	See Table (number to be determined by Carter) for listing of absorption cross sections and quantum yields. Set used is given in the "Type" column.
29	Absorption cross sections recommended by IUPAC (Atkinson et al, 1997a,b) used. Quantum yield assumed to be unity.

The reactants, products, quantum yields and cross sections for Reaction 43 are consistent with current knowledge.

Reaction 44

k(300)	A	Ea	Notes	
1.70e-12	2.90e-12	0.32	6	HO2H + HO. = HO2. + H2O

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
---	---

The reactants, products and rate parameters for Reaction 44 are consistent with current knowledge.

Reaction 45

k(300)	A	Ea	Notes	
1.10e-10	4.80e-11	-0.50	6	HO. + HO2. = H2O + O2

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
---	---

The reactants, products and rate parameters for Reaction 45 are consistent with current knowledge.

Reaction S2OH

K(300)	Falloff, F	Notes	
4.00e-31	0.45	6,30	HO. + SO2 = HO2. + SULF
	A	B	
k _o	2.00e-12	0.0	
k	4.00e-31	-3.3	

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
30	The initially formed HOSO ₂ is assumed to react primarily with O ₂ , forming HO ₂ and SO ₃ . The SO ₃ is assumed to be converted into sulfates, which are represented by the SULF model species.

The reactants, products and rate parameters for Reaction S2OH are consistent with current knowledge. It was first shown by Stockwell and Calvert (1983) that HOSO₂ reacts primarily with O₂, forming HO₂ and SO₃. That reference should be cited in the text.

Methyl Peroxy and Methoxy Reactions

Reaction MER1

k(300)	A	Ea	Notes
7.24e-12	2.80e-12	-0.57	31,32

C-O₂. + NO = NO₂ + HCHO + HO₂.

Notes

31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).
32	The reaction of NO ₂ is ignored because it is rapidly reversed by the decomposition of the peroxyxynitrate, resulting in no net reaction. Calculations not neglecting peroxyxynitrate formation give essentially the same results. However, this may not be valid in low temperature simulations.

The reactants, products and rate parameters for Reaction MER1 are consistent with current knowledge.

Reaction MER3

k(300)	A	Ea	Notes
1.30e-12	1.30e-12		31 C-O ₂ . + NO ₃ = HCHO + HO ₂ . + NO ₂

Notes

31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).
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The reactants, products and rate parameters for Reaction MER4 are consistent with current knowledge.

Reaction MER4

k(300)	A	Ea	Notes
5.12e-12	3.80e-13	-1.55	31 C-O ₂ . + HO ₂ . = COOH + O ₂

Notes

31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).
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The reactants, products and rate parameters for Reaction MER4 are consistent with current knowledge.

Reaction MER5

k(300)	A	Ea	Notes
2.61e-13	2.45e-14	-1.41	33 C-O ₂ . + C-O ₂ . = MEOH + HCHO + O ₂

Notes

33	Total rate constant and rate constant for methoxy radical formation from IUPAC (Atkinson et al, 1997a, 1999) recommendation. Temperature dependence for rate constant for methanol + HCHO formation derived to be consistent with these.
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The total of the overall rate parameter for Reactions MER5 and MER6 is correct. There is some uncertainty in the temperature dependence of the ratio of the rate parameters for

Reactions MER5 and MER6 and this affects the derivation of the individual rate parameters for the two reactions. But the fitted rate constant for Reaction MER5 yields a rate constant that is about 6% greater than the value calculated from the simple difference between the IUPAC recommended values for the total rate parameter (MER5 + MER6) and the recommended value for the HCHO + HO₂ forming reaction.

Reaction MER6

k(300)	A	Ea	Notes
1.08e-13	5.90e-13	1.01	33
C-O ₂ . + C-O ₂ . = #2 {HCHO + HO ₂ .}			

Notes

33	Total rate constant and rate constant for methoxy radical formation from IUPAC (Atkinson et al, 1997a, 1999) recommendation. Temperature dependence for rate constant for methanol + HCHO formation derived to be consistent with these.		
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The rate constant for this channel of the C-O₂. + C-O₂. is consistent with current knowledge.

Reactions of Peroxy Radical Operators with NO

Reaction RRNO

k(300)	A	Ea	Notes
8.96E-12	2.70E-12	-0.72	34,35, 32
RO ₂ -R. + NO = NO ₂ + HO ₂ .			

Notes

34	The RO ₂ -R. operator represents the effects of peroxy radicals which react with NO to form NO ₂ and HO ₂ , and also the effects of peroxy radical reactions on other species. Except as indicated, the organic products from this peroxy radical are not represented.		
35	Rate constant recommended by Atkinson (1997a) for general peroxy radicals.		
32	The reaction of NO ₂ is ignored because it is rapidly reversed by the decomposition of the peroxyxynitrate, resulting in no net reaction. Calculations not neglecting peroxyxynitrate formation give essentially the same results. However, this may not be valid in low temperature simulations.		

This treatment of the generalized peroxy radical, RO₂-R, to react with NO to produce NO₂ and an HO₂ is reasonable. The rate constant is consistent with the cited evaluation. The neglect of the formation of RO₂NO₂ is reasonable because these compounds are believed to be unimportant at most tropospheric temperatures.

Reaction R2NO

k(300)	A	Ea	Notes
Same as Reaction RRNO			42,43
R ₂ O ₂ . + NO = NO ₂			

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO ₂ -R.).
43	The R ₂ O ₂ . operator represents the effects of peroxy radical reactions causing extra NO to NO ₂ conversions. Its reactions with species other than NO are represented as having no effect other than to consume this operator.

The rate constant is discussed under Reaction RRNO. This treatment of the generalized peroxy radical, R₂NO, to produce only NO₂ is a reasonable compliment to Reaction RRNO.

Reaction R₂NO

k(300)	A	Ea	Notes
Same as Reaction RRNO		42,44	RO ₂ -N. + NO = RNO ₃

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
44	The RO2-N. operator represents the effects of peroxy radicals which react with NO to form higher organic nitrates (represented by RNO3), and also the effects of peroxy radical reactions on other species. It has five carbons.

The rate constant is discussed under Reaction RRNO. This treatment of the generalized peroxy radical, RNNO, to produce higher organic nitrates is a reasonable compliment to Reaction RRNO because a fraction of RO2 radicals react to produce organic nitrates.

Reactions of Peroxy Radical Operators with HO2

Reaction RRH2

k(300)	A	Ea	Notes
1.45E-11	1.90E-13	-2.58	35,36
$\text{RO2-R.} + \text{HO2.} = \text{ROOH} + \text{O2} + \#-3 \text{ XC}$			

Notes

35	Rate constant recommended by Atkinson (1997a) for general peroxy radicals.
36	The organic products from the HO2 reaction are represented by the lumped higher hydroperoxide species. Negative "lost carbons" are added because this is a zero-carbon operator.

This treatment of the generalized peroxy radical, RO2-R, to react with HO2 to produce a generalized organic peroxide is reasonable. The rate constant is consistent with the cited evaluation. The use of negative carbon atoms for carbon balance is reasonable but may give some numerical chemistry solvers problems.

Reaction R2H2

k(300)	A	Ea	Notes
Same as Reaction R2H2			42,43
$\text{R2O2.} + \text{HO2.} = \text{HO2.}$			

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
43	The R2O2. operator represents the effects of peroxy radical reactions causing extra NO to NO2 conversions. Its reactions with species other than NO are represented as having no effect other than to consume this operator.

This treatment of the generalized peroxy radical, R2O2. to react with HO2 to consume R2O2 is reasonable. The rate constant is discussed under Reaction RRH2.

Reaction RNH2

k(300)	A	Ea	Notes
Same as Reaction R2H2		42,44, 45	RO2-N. + HO2. = ROOH + #3 XC

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
44	The RO2-N. operator represents the effects of peroxy radicals which react with NO to form higher organic nitrates (represented by RNO3), and also the effects of peroxy radical reactions on other species. It has five carbons.
45	The organic products from the HO2 reaction are represented by the lumped higher hydroperoxide species. "Lost carbons" are added because this is a five-carbon operator.

This treatment of the generalized peroxy radical, RO2-R, to react with HO2 to produce a generalized organic peroxide is reasonable. The rate constant is discussed under Reaction RRH2. The addition of extra carbon atoms for carbon balance is probably OK.

Reactions of Peroxy Radical Operators with NO3

Reaction RRN3

k(300)	A	Ea	Notes	
2.30E-12	2.30E-12	---	37,38	RO2-R. + NO3 = NO2 + O2 + HO2.

Notes

37	Rate constant based on that recommended by IUPAC (Atkinson et al, 1999) for ethyl peroxy + NO ₃ . Formation of alkoxy + NO ₂ + O ₂ stated to occur >85% of the time.
38	The reaction is assumed to form the corresponding alkoxy radical. The HO ₂ represents the radicals regenerated by the alkoxy radical.

This treatment of the generalized peroxy radical, RO₂-R, to react with NO₃ to produce NO₂ and a 'massless' RO that reacts with O₂ to produce HO₂ is reasonable. The rate constant is consistent with current knowledge.

Reaction R2N3

k(300)	A	Ea	Notes
Same Reaction as RRN3		42,43	R2O ₂ . + NO ₃ = NO ₂

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO ₂ -R.).
43	The R2O ₂ . operator represents the effects of peroxy radical reactions causing extra NO to NO ₂ conversions. Its reactions with species other than NO are represented as having no effect other than to consume this operator.

This treatment of the generalized peroxy radical, R2O₂., to react with NO₃ to produce NO₂ and a 'massless' RO that reacts with O₂ to produce HO₂ is reasonable. The rate constant is discussed under Reaction RRN3.

Reaction RNN3

k(300)	A	Ea	Notes
Same Reaction as RRN3		42,44, 47	RO ₂ -N. + NO ₃ = NO ₂ + O ₂ + HO ₂ . + MEK + #2 XC

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO ₂ -R.).
44	The RO ₂ -N. operator represents the effects of peroxy radicals which react with NO to form higher organic nitrates (represented by RNO ₃), and also the effects of peroxy radical reactions on other species. It has five carbons.
47	This reaction is assumed to form the corresponding alkoxy radical, which is assumed to react products represented by MEK + HO ₂ .

This treatment of the generalized peroxy radical, RRN3. appears to be reasonable. The rate constant is discussed under Reaction RRN3.