

Supporting Information for

Identifying the Causes of Differences in Ozone Production from the CB05 and CBMIV Chemical Mechanisms

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As noted in the main manuscript, the versions of the CB05 and CBMIV mechanisms that are used in the NAQFC systems have been slightly modified from the original published versions. The rate coefficients of both mechanisms have been updated as necessary from their original published values. The CBMIV mechanism used in the NAQFC has been modified in four areas: (i) an unreactive organic nitrate product was added to reactions R55, R64, R68, R78, R81, R92 and R94; (ii) the original isoprene chemistry of CBMIV was replaced by the isoprene chemistry introduced in CB05; (iii) an $\text{SO}_2 + \text{OH} \rightarrow$ sulfate reaction was added (R82); and, (iv) additional peroxy radical – operator reactions were adopted from CB05 (R86-R89).

Table S-1: Definition of species used in the NAQFC implementations of the CBMIV and CB05 gas-phase chemical mechanisms.

CBMIV Species	CB05 Species	Remarks
NO	NO	Nitric oxide
NO2	NO2	Nitrogen dioxide
O3	O3	Ozone
O	O	Oxygen atom – O ³ (P)
O1D	O1D	Oxygen atom – O ¹ (D)
OH	OH	Hydroxyl radical
HO2	HO2	Hydroperoxy radical
H2O2	H2O2	Hydrogen peroxide
NO3	NO3	Nitrate radical
N2O5	N2O5	Dinitrogen pentoxide
HONO	HONO	Nitrous acid
HNO3	HNO3	Nitric acid
PNA	PNA	Peroxynitric acid (HO ₂ NO ₂)
CO	CO	Carbon monoxide
HCHO	HCHO	Formaldehyde
ALD2	ALD2	CB05: acetaldehyde CBMIV: C ₂ and higher aldehydes
C2O3	C2O3	CB05: peroxyacetyl radical CBMIV: ≥C ₂ peroxyacyl radical
PAN	PAN	CB05: peroxyacetyl nitrate CBMIV: ≥C ₂ peroxyacyl nitrate
	ALDX	CB05 only: ≥C ₃ aldehyde
	CXO3	CB05 only: ≥C ₃ peroxyacyl radical
	PANX	CB05 only: ≥C ₃ peroxyacyl nitrate
XO2	XO2	NO to NO ₂ conversion from alkylperoxy radical
XO2N	XO2N	NO to organic nitrate conversion from alkylperoxy radical
NTR	NTR	Organic nitrate (RNO ₃)
ETOH	ETOH	Ethanol
CH4	CH4	Methane
	MEO2	CB05 only: methylperoxy radical
MEOH	MEOH	Methanol
	MEPX	CB05 only: methylhydroperoxide
	FACD	CB05 only: formic acid
	ETHA	CB05 only: ethane
	ROOH	CB05 only: higher organic peroxide
AACD	AACD	≥C ₂ carboxylic acid
PACD	PACD	≥C ₂ peroxy-carboxylic acid
PAR	PAR	Paraffin carbon bond (C-C)
ROR	ROR	Secondary alkoxy radical
ETH	ETH	Ethene
OLE	OLE	Olefinic carbon bond (C=C)
	IOLE	CB05 only: internal olefinic carbon bond (R-C=C-R)
ISOP	ISOP	Isoprene
ISPD	ISPD	Isoprene product (lumped methacrolein, methyl vinyl ketone, etc.)
	TERP	CB05 only: terpene
TOL	TOL	Toluene
XYL	XYL	Xylene
CRES	CRES	Cresol and higher phenols
TO2	TO2	Toluene-hydroxyl radical adduct
OPEN	OPEN	Aromatic ring opening product
CRO	CRO	Methylphenoxy radical
MGLY	MGLY	Methylglyoxal
SO2	SO2	Sulfur dioxide
SULF	SULF	Sulfuric acid (gaseous)

Figure S-1: Mechanism listing of the CB05 gas-phase mechanism as it is implemented in the NAQFC.

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#EQUATIONS {of the CMAQ version of the CB05 mechanism}

{R1.} NO2 + hv = NO + O : 8.89E-3*SUN ;
{R2.} O + O2 + M = O3 : ARR(6.0E-34, 0.0, -2.4);
{R3.} O3 + NO = NO2 : ARR2(3.0E-12, -1500.0) ;
{R4.} O + NO2 = NO : ARR2(5.6E-12, 180.0) ;
{R5.} O + NO2 = NO3 : TERM(2.5E-31, -1.8, 0.0, 2.2E-11, -0.7, 0.0, 0.6) ;
{R6.} O + NO = NO2 : TERM(9.0E-32, -1.5, 0.0, 3.0E-11, 0.0, 0.0, 0.6) ;
{R7.} O3 + NO2 = NO3 : ARR2(1.2E-13, -2450.0) ;
{R8.} O3 + hv = O : 3.556E-04*SUN ; {4.0E-2*RCONST(1) ;}
{R9.} O3 + hv = O1D : 2.489E-05*SUN ; {2.8E-3*RCONST(1) ;}
{R10.} O1D + M = O : ARR2(2.1E-11, 102.0) ;
{R11.} O1D + H2O = 2OH : 2.2E-10 ;
{R12.} O3 + OH = HO2 : ARR2(1.7E-12, -940.0) ;
{R13.} O3 + HO2 = OH : ARR2(1.0E-14, -490.0) ;
{R14.} NO3 + hv = NO2 + O : 0.195*SUN ; {21.9*RCONST(1) ;}
{R15.} NO3 + hv = NO : 0.021*SUN ; {2.4*RCONST(1) ;}
{R16.} NO3 + NO = 2 NO2 : ARR2(1.5E-11, 170.0) ;
{R17.} NO3 + NO2 = NO + NO2 : ARR2(4.5E-14, -1260.0) ;
{R18.} NO3 + NO2 = N2O5 : TERM(2.0E-30, -4.4, 0.0, 1.4E-12, -0.7, 0.0, 0.6) ;
{R19.} N2O5 + H2O = 2 HNO3 : 2.5E-22 ;
{R20.} N2O5 + H2O + H2O = 2 HNO3 : 1.8E-39 ;
{R21.} N2O5 = NO3 + NO2 : TERM(1.0E-03, -3.5, -11000.0, 9.7E+14, 0.1, -11080.0, 0.45) ;
{R22.} 2 NO + O2 = 2 NO2 : ARR2(3.3E-39, 530.0) ;
{R23.} NO + NO2 + H2O = 2 HONO : 5.0E-40 ;
{R24.} OH + NO = HONO : TERM(7.0E-31, -2.6, 0.0, 3.6E-11, -0.1, 0.0, 0.6) ;
{R25.} HONO + hv = OH + NO : 1.511E-03*SUN ; {0.17*RCONST(1);}
{R26.} OH + HONO = NO2 : ARR2(1.8E-11, -390.0) ;
{R27.} 2 HONO = NO + NO2 : 1.0E-20 ;
{R28.} OH + NO2 = HNO3 : TERM(2.0E-30, -3.0, 0.0, 2.5E-11, 0.0, 0.0, 0.6) ;
{R29.} OH + HNO3 = NO3 : KTYP2(2.4E-14, 460.0, 2.7E-17, 2199.0, 6.5E-34, 1335.0) ;
{R30.} HO2 + NO = OH + NO2 : ARR2(3.5E-12, 250.0) ;
{R31.} HO2 + NO2 = PNA : TERM(1.8E-31, -3.2, 0.0, 4.7E-12, 0.0, 0.0, 0.6) ;
{R32.} PNA = HO2 + NO2 : TERM(4.1E-5, 0.0, -10650.0, 4.8E+15, 0.0, -11170.0, 0.6) ;
{R33.} OH + PNA = NO2 : ARR2(1.3E-12, 380.0) ;
{R34.} 2 HO2 = H2O2 : KTYP3(2.3E-13, 600.0, 1.7E-33, 1000.0) ;
{R35.} 2 HO2 + H2O = H2O2 : KTYP3(3.22E-34, 2800.0, 2.38E-54, 3200.0) ;
{R36.} H2O2 + hv = 2 OH : 6.312E-06*SUN ; {7.1E-4*RCONST(1);}
{R37.} OH + H2O2 = HO2 : ARR2(2.9E-12, -160.0) ;
{R38.} O1D + H2 = OH + HO2 : 1.1E-10 ;
{R39.} OH + H2 = HO2 : ARR2(5.5E-12, -2000.0) ;
{R40.} OH + O = HO2 : ARR2(2.2E-11, 120.0) ;
{R41.} OH + OH = O : ARR2(4.2E-12, -240.0) ;
{R42.} OH + OH = H2O2 : TERM(6.9E-31, -1.0, 0.0, 2.6E-11, 0.0, 0.0, 0.6) ;
{R43.} OH + HO2 = PROD : ARR2(4.8E-11, 250.0) ;
{R44.} HO2 + O = OH : ARR2(3.0E-11, 200.0) ;
{R45.} H2O2 + O = OH + HO2 : ARR2(1.4E-12, -2000.0) ;
{R46.} NO3 + O = NO2 : 1.0E-11 ;
{R47.} NO3 + OH = HO2 + NO2 : 2.2E-11 ;
{R48.} NO3 + HO2 = HNO3 : 3.5E-12 ;
{R49.} NO3 + O3 = NO2 : 1.0E-17 ;
{R50.} NO3 + NO3 = 2 NO2 : ARR2(8.5E-13, -2450.0) ;
{R51.} PNA + hv = 0.61 HO2 + 0.61 NO2 : 6.76E-6*SUN ; {7.6E-4*RCONST(1) ;}
+ 0.390 OH + 0.390 NO3 : 7.91E-7*SUN ; {8.9E-5*RCONST(1) ;}
{R52.} HNO3 + hv = OH + NO2 : 5.16E-5*SUN ; {5.8E-3*RCONST(1) ;}
{R53.} N2O5 + hv = NO2 + NO3 : ARR2(2.6E-12, 365.0) ;
{R54.} XO2 + NO = NO2 : ARR2(2.6E-12, 365.0) ;
{R55.} XO2N + NO = NTR : ARR2(7.5E-13, 700.0) ;
{R56.} XO2 + HO2 = ROOH : ARR2(7.5E-13, 700.0) ;
{R57.} XO2N + HO2 = ROOH : 6.8E-14 ;
{R58.} 2 XO2 = PROD : 6.8E-14 ;
{R59.} XO2N + XO2N = PROD : 6.8E-14 ;
{R60.} XO2N + XO2 = PROD : 6.8E-14 ;
{R61.} NTR + OH = HNO3 + HO2 : ARR2(5.9E-13, -360.0) ;
+ 0.330 HCHO :
+ 0.330 ALD2 :
+ 0.330 ALDX :
- 0.660 PAR :
{R62.} NTR + hv = NO2 + HO2 : 3.11E-6*SUN ; {3.5E-4*RCONST(1) ;}
+ 0.330 HCHO :
+ 0.330 ALD2 :
+ 0.330 ALDX :
- 0.660 PAR :
{R63.} ROOH + OH = XO2 + 0.500 ALD2 : ARR2(3.01E-12, 190.0) ;
+ 0.500 ALDX :
{R64.} ROOH + hv = OH + HO2 :
+ 0.500 ALD2 :
+ 0.500 ALDX :
{R65.} OH + CO = HO2 : 5.60E-6*SUN ; {6.3E-4*RCONST(1) ;}
{R66.} OH + CH4 = MEO2 : KTYP3(1.44E-13, 0.0, 3.43E-33, 0.0) ;
{R67.} MEO2 + NO = HCHO + HO2 + NO2 : ARR2(2.45E-12, -1775.0) ;
{R68.} MEO2 + HO2 = MEPX : ARR2(2.8E-12, 300.0) ;
{R69.} MEO2 + MEO2 = 1.370 HCHO : ARR2(4.1E-13, 750.0) ;
+ 0.740 HO2 :
+ 0.630 MEOH :
{R70.} MEPX + OH = 0.700 MEO2 : ARR2(9.5E-14, 390.0) ;
+ 0.300 XO2 :
+ 0.300 HO2 :
{R71.} MEPX + hv = HCHO + HO2 + OH : ARR2(3.8E-12, 200.0) ;
{R72.} MEOH + OH = HCHO + HO2 : 5.60E-6*SUN ; {6.3E-4*RCONST(1) ;}
ARR2(7.3E-12, -620.0) ;
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{R73.} HCHO + OH = HO2 + CO : 9.0E-12 ;
{R74.} HCHO + hv {+ 2 O2} = 2 HO2 + CO : 2.845E-05*SUN ; {3.2E-3*RCONST(1);}
{R75.} HCHO + hv = CO : 3.734E-05*SUN ; {4.2E-3*RCONST(1);}
{R76.} HCHO + O = OH + HO2 + CO : ARR2(3.4E-11, -1600.0) ;
{R77.} HCHO + NO3 = HNO3 + HO2 + CO : 5.8E-16 ;
{R78.} HCHO + HO2 = HCO3 : ARR2(9.7E-15, 625.0) ;
{R79.} HCO3 = HCHO + HO2 : ARR2(2.4E+12, -7000.0) ;
{R80.} HCO3 + NO = FACD + NO2 + HO2 : 5.6E-12 ;
{R81.} HCO3 + HO2 = MEPX : ARR2(5.6E-15, 2300.0) ;
{R82.} FACD + OH = HO2 : 4.0E-13 ;
{R83.} ALD2 + O = C2O3 + OH : ARR2(1.8E-11, -1100.0) ;
{R84.} ALD2 + OH = C2O3 : ARR2(5.6E-12, 270.0) ;
{R85.} ALD2 + NO3 = C2O3 + HNO3 : ARR2(1.4E-12, -1900.0) ;
{R86.} ALD2 + hv = MEO2 + CO + HO2 : 4.00E-06*SUN ; {4.5E-4*RCONST(1);}

{R87.} C2O3 + NO = MEO2 + NO2 : ARR2(8.1E-12, 270.0) ;
{R88.} C2O3 + NO2 = PAN : TERM(2.7E-28, -7.1, 0.0, 1.2E-11, -0.9, 0.0, 0.3) ;
{R89.} PAN = C2O3 + NO2 : TERM(4.9E-3, 0.0, -12100.0, 5.4E+16, 0.0, -13830.0, 0.3) ;
{R90.} PAN + hv = C2O3 + NO2 : 8.8E-7*SUN ; {9.9E-5*RCONST(1) ;}
{R91.} C2O3 + HO2 = 0.800 PACD + 0.200 AACD + 0.200 O3 : ARR2(4.3E-13, 1040.0) ;
{R92.} C2O3 + MEO2 = 0.900 MEO2 + 0.900 HO2 + HCHO : ARR2(2.0E-12, 500.0) ;
{R93.} C2O3 + XO2 = 0.900 MEO2 + 0.100 AACD : ARR2(4.4E-13, 1070.0) ;
{R94.} C2O3 + C2O3 = 2 MEO2 : ARR2(2.9E-12, 500.0) ;
{R95.} PACD + OH = C2O3 : ARR2(4.0E-13, 200.0) ;
{R96.} PACD + hv = MEO2 + OH : 0.000*SUN ;
{R97.} AACD + OH = MEO2 : ARR2(4.0E-13, 200.0) ;
{R98.} ALDX + O = CXO3 + OH : ARR2(1.3E-11, -870.0) ;
{R99.} ALDX + OH = CXO3 : ARR2(5.1E-12, 405.0) ;
{R100.} ALDX + NO3 = CXO3 + HNO3 : 6.5E-15 ;
{R101.} ALDX + hv = MEO2 + CO + HO2 : 2.04E-5*SUN ; {2.3E-3*RCONST(1) ;}
{R102.} CXO3 + NO = ALD2 + NO2 + HO2 + XO2 : ARR2(6.7E-12, 340.0) ;
{R103.} CXO3 + NO2 = PANX : TERM(2.7E-28, -7.1, 0.0, 1.2E-11, -0.9, 0.0, 0.3) ;
{R104.} PANX = CXO3 + NO2 : TERM(4.9E-3, 0.0, -12100.0, 5.4E+16, 0.0, -13830.0, 0.3) ;
{R105.} PANX + hv = CXO3 + NO2 : 8.8E-7*SUN ; {9.9E-5*RCONST(1) ;}
{R106.} PANX + OH = ALD2 + NO2 : 3.0E-13 ;
{R107.} CXO3 + HO2 = 0.800 PACD + 0.200 AACD + 0.200 O3 : ARR2(4.3E-13, 1040.0) ;
{R108.} CXO3 + MEO2 = 0.900 ALD2 + 0.900 XO2 + HO2 + 0.100 AACD : ARR2(2.0E-12, 500.0) ;
{R109.} CXO3 + XO2 = 0.900 ALD2 + 0.100 AACD : ARR2(4.4E-13, 1070.0) ;
{R110.} CXO3 + CXO3 = 2 ALD2 + 2 XO2 + 2 HO2 : ARR2(2.9E-12, 500.0) ;
{R111.} CXO3 + C2O3 = MEO2 + XO2 + HO2 + ALD2 : ARR2(2.9E-12, 500.0) ;
{R112.} PAR + OH = 0.87 XO2 + 0.13 XO2N + 0.11 HO2 + 0.06 ALD2 + 0.05 ALDX + 0.76 ROR - 0.11 PAR : 8.1E-13 ;
{R113.} ROR = 0.60 ALD2 + 0.96 XO2 + 0.94 HO2 + 0.04 XO2N + 0.50 ALDX + 0.02 ROR - 2.10 PAR : ARR2(1.0E+15, -8000.0) ;
{R114.} ROR = HO2 : 1.6E+03 ;
{R115.} ROR + NO2 = NTR : 1.5E-11 ;
{R116.} O + OLE = 0.20 ALD2 + 0.30 HO2 + 0.20 XO2 + 0.2 CO + 0.2 HCHO + 0.01 XO2N + 0.20 PAR + 0.1 OH : ARR2(1.0E-11, -280.0) ;
{R117.} OH + OLE = 0.80 HCHO + 0.33 ALD2 + 0.62 ALDX + 0.80 XO2 + 0.95 HO2 - 0.70 PAR : 3.2E-11 ;
{R118.} O3 + OLE = 0.18 ALD2 + 0.74 HCHO + 0.32 ALDX + 0.22 XO2 + 0.10 OH + 0.33 CO + 0.44 HO2 - 1.00 PAR : ARR2(6.5E-15, -1900.0) ;
{R119.} NO3 + OLE = NO2 + HCHO + 0.91 XO2 + 0.09 XO2N + 0.56 ALDX + 0.35 ALD2 - 1.00 PAR : ARR2(7.0E-13, -2160.0) ;
{R120.} O + ETH = HCHO + 0.7 XO2 + CO + 1.7 HO2 + 0.3 OH : ARR2(1.04E-11, -792.0) ;
{R121.} OH + ETH = XO2 + 1.56 HCHO + HO2 + 0.22 ALDX : TERM(1.0E-28, -0.8, 0.0, 8.8E-12, 0.0, 0.0, 0.6) ;
{R122.} O3 + ETH = HCHO + 0.63 CO + 0.13 HO2

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+ 0.13 OH
+ 0.37 FACD
{R123.} NO3 + ETH = NO2 + XO2 + 2 HCHO : ARR2(1.2E-14, -2630.0) ;
{R124.} IOLE + O = 1.24 ALD2 : ARR2(3.3E-12, -2880.0) ;
+ 0.66 ALDX
+ 0.10 HO2
+ 0.10 XO2
+ 0.10 CO
+ 0.10 PAR : 2.3E-11 ;
{R125.} IOLE + OH = 1.30 ALD2
+ 0.70 ALDX : ARR2(1.0E-11, 550.0) ;
+ HO2 + XO2
{R126.} IOLE + O3 = 0.65 ALD2
+ 0.35 ALDX
+ 0.25 HCHO
+ 0.25 CO
+ 0.50 O
+ 0.50 OH
+ 0.50 HO2 : ARR2(8.4E-15, -1100.0) ;
{R127.} IOLE + NO3 = 1.18 ALD2
+ 0.64 ALDX
+ HO2 + NO2 : ARR2(9.6E-13, -270.0) ;
{R128.} OH + TOL = 0.08 XO2 + 0.36 CRES
+ 0.44 HO2 + 0.56 TO2 : ARR2(1.8E-12, 355.0) ;
{R129.} TO2 + NO = 0.9 NO2 + 0.9 OPEN + 0.9 HO2 + 0.1 NTR : 8.1E-12 ;
{R130.} TO2 = HO2 + CRES : 4.20 ;
{R131.} OH + CRES = 0.4 CRO + 0.6 XO2 + 0.6 HO2 + 0.3 OPEN : 4.1E-11 ;
{R132.} NO3 + CRES = CRO + HNO3 : 2.2E-11 ;
{R133.} CRO + NO2 = NTR : 1.4E-11 ;
{R134.} CRO + HO2 = CRES : 5.5E-12 ;
{R135.} OPEN + hv = C2O3 + CO + HO2 : 5.334E-05*SUN ; {6.0E-3*RCONST(1);}
{R136.} OH + OPEN = XO2 + C2O3 + 2 HO2 + 2 CO + HCHO : 3.0E-11 ;
{R137.} O3 + OPEN = 0.03 ALDX + 0.62 C2O3
+ 0.7 HCHO + 0.03 XO2 + 0.69 CO
+ 0.08 OH + 0.76 HO2 + 0.2 MGLY : ARR2(5.4E-17, -500.0) ;
{R138.} OH + XYL = 0.7 HO2 + 0.5 XO2 + 0.2 CRES + 0.8 MGLY
+ 1.10 PAR + 0.3 TO2 : ARR2(1.7E-11, 116.0) ;
{R139.} OH + MGLY = XO2 + C2O3 : 1.80E-11 ;
{R140.} MGLY + hv = C2O3 + CO + HO2 : 1.654E-04*SUN ; {1.86E-2*RCONST(1);}
{R141.} O + ISOP = 0.75 ISPD + 0.50 HCHO + 0.25 XO2
+ 0.25 HO2 + 0.25 CXO3 + 0.25 PAR : 3.6E-11 ;
{R142.} OH + ISOP = 0.912 ISPD + 0.629 HCHO + 0.991 XO2
+ 0.912 HO2 + 0.088 XO2N : ARR2(2.54E-11, 407.0) ;
{R143.} O3 + ISOP = 0.65 ISPD + 0.60 HCHO + 0.20 XO2
+ 0.066 HO2 + 0.266 OH + 0.20 CXO3
+ 0.15 ALDX + 0.35 PAR + 0.066 CO : ARR2(7.86E-15, -1912.0) ;
{R144.} NO3 + ISOP = 0.20 ISPD + 0.80 NTR + XO2
+ 0.80 HO2 + 0.20 NO2 + 0.80 ALDX
+ 2.4 PAR : ARR2(3.03E-12, -448.0) ;
{R145.} ISPD + OH = 1.565 PAR + 0.167 HCHO + 0.713 XO2
+ 0.503 HO2 + 0.334 CO + 0.168 MGLY
+ 0.252 ALD2 + 0.210 C2O3
+ 0.120 ALDX + 0.250 CXO3 : 3.36E-11 ;
{R146.} ISPD + O3 = 0.114 C2O3 + 0.150 HCHO + 0.850 MGLY
+ 0.154 HO2 + 0.268 OH + 0.064 XO2
+ 0.020 ALD2 + 0.360 PAR + 0.225 CO : 7.1E-18 ;
{R147.} ISPD + NO3 = 0.357 ALDX + 0.282 HCHO + 1.282 PAR
+ 0.925 HO2 + 0.643 CO + 0.850 NTR
+ 0.075 CXO3 + 0.075 XO2 + 0.150 HNO3 : 1.00E-15 ;
{R148.} ISPD + hv = 0.333 CO + 0.067 ALD2 + 0.900 HCHO
+ 0.832 PAR + 1.033 HO2 + 0.700 XO2
+ 0.967 C2O3 : 1.6E-6*SUN ; {0.0036*0.05*RCONST(1)} ;
{R149.} TERP + O = 0.150 ALDX + 5.12 PAR : 3.6E-11 ;
{R150.} TERP + OH = 0.750 HO2 + 1.250 XO2 + 0.250 XO2N
+ 0.280 HCHO + 1.66 PAR + 0.470 ALDX : ARR2(1.5E-11, 449.0) ;
{R151.} TERP + O3 = 0.570 OH + 0.070 HO2 + 0.760 XO2
+ 0.180 XO2N + 0.240 HCHO + 0.001 CO
+ 7.000 PAR + 0.210 ALDX + 0.390 CXO3 : ARR2(1.2E-15, -821.0) ;
{R152.} TERP + NO3 = 0.470 NO2 + 0.280 HO2 + 1.030 XO2
+ 0.250 XO2N + 0.470 ALDX + 0.530 NTR : ARR2(3.7E-12, 175.0) ;
{R153.} SO2 + OH = SULF + HO2 : TERM(3.0E-31, -3.3, 0.0, 1.5E-12, 0.0, 0.0, 0.6) ;
{R154.} ETOH + OH = HO2 + 0.90 ALD2
+ 0.050 ALDX + 0.100 HCHO + 0.100 XO2 : ARR2(6.9E-12, -230.0) ;
{R155.} ETHA + OH = 0.991 ALD2 + 0.991 XO2 + 0.009 XO2N
+ HO2 : ARR2(8.7E-12, -1070.0) ;
{R156.} ISOP + NO2 = 0.20 ISPD + 0.80 NTR + XO2
+ 0.80 HO2 + 0.20 NO + 0.80 ALDX
+ 2.4 PAR : 1.5E-19 ;

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Figure S-2: Mechanism listing of the CBMIV gas-phase mechanism as it is implemented in the NAQFC.

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#EQUATIONS {of the CMAQ version of the CBM-IV mechanism}

{ 1.} NO2 + hv = NO + O : 8.89E-3*SUN ;
{ 2.} O + O2 {+ M} = O3 : TERM(6.0E-34, -2.3, 0.0, 2.8E-12, 0.0, 0.0, 0.6) ;
{ 3.} O3 + NO = NO2 : ARR2(1.8E-12, -1370.0) ;
{ 4.} O + NO2 = NO : 9.3E-12 ;
{ 5.} O + NO2 = NO3 : TERM(9.0E-32, -2.0, 0.0, 2.2E-11, 0.0, 0.0, 0.6) ;
{ 6.} O + NO = NO2 : TERM(9.0E-32, -1.5, 0.0, 3.0E-11, 0.0, 0.0, 0.6) ;
{ 7.} O3 + NO2 = NO3 : ARR2(1.2E-13, -2450.0) ;
{ 8.} O3 + hv = O : 3.556E-04*SUN ; {4.0E-2*RCONST(1)} ;
{ 9.} O3 + hv = O1D : 2.489E-05*SUN ; {2.8E-3*RCONST(1)} ;
{10a.} O1D + N2 = O : ARR2(1.8E-11, 107.0) ;
{10b.} O1D + O2 = O : ARR2(3.2E-11, 67.0) ;
{11.} O1D + H2O = 2OH : 2.2E-10 ;
{12.} O3 + OH = HO2 : ARR2(1.6E-12, -940.0) ;
{13.} O3 + HO2 = OH : ARR2(1.4E-14, -580.0) ;
{14.} NO3 + hv = 0.89 NO2 + 0.89 O : 1.378E-01*SUN ; {15.5*RCONST(1)} ;
      + 0.11 NO : ARR2(1.3E-11, 250.0) ;
{15.} NO3 + NO = 2 NO2 : ARR2(2.5E-14, -1230.0) ;
{16.} NO3 + NO2 = NO + NO2 : TERM(2.2E-30, -4.3, 0.0, 1.5E-12, -0.5, 0.0, 0.6) ;
{17.} NO3 + NO2 = N2O5 : 1.3E-21 ;
{18.} N2O5 + H2O = 2 HNO3 : TERM(2.2E-30, -4.3, 0.0, 1.5E-12, -0.5, 0.0,
{19.} N2O5 = NO3 + NO2 : 0.6)/ARR2(2.7E-27, -11000.0) ;
{20.} 2 NO + O2 = 2 NO2 : ARR2(3.3E-39, 530.0) ;
{21.} NO + NO2 + H2O = 2 HONO : 4.4E-40 ;
{22.} OH + NO = HONO : TERM(6.7E-31, -3.3, 0.0, 3.0E-11, -1.0, 0.0, 0.6) ;
{23.} HONO + hv = OH + NO : 1.511E-03*SUN ; {0.17*RCONST(1)} ;
{24.} OH + HONO = NO2 : 6.6E-12 ;
{25.} 2 HONO = NO + NO2 : 1.0E-20 ;
{26.} OH + NO2 = HNO3 : TERM(2.6E-30, -3.2, 0.0, 2.4E-11, -1.3, 0.0, 0.6) ;
{27.} OH + HNO3 = NO3 : KTYP2(7.2E-15, 785.0, 4.1E-16, 1440.0, 1.9E-33, 725.0) ;
{28.} HO2 + NO = OH + NO2 : ARR2(3.7E-12, 240.0) ;
{29.} HO2 + NO2 = PNA : TERM(2.3E-31, -4.6, 0.0, 4.2E-12, 0.2, 0.0, 0.6) ;
{30.} PNA = HO2 + NO2 : TERM(2.3E-31, -4.6, 0.0, 4.2E-12, 0.2, 0.0,
0.6)/ARR2(2.1E-27, -10900.0) ;
{31.} OH + PNA = NO2 : ARR2(1.3E-12, 380.0) ;
{32.} 2 HO2 = H2O2 : ARR2(5.9E-14, 1150.0) ;
{33.} 2 HO2 + H2O = H2O2 : ARR2(2.2E-38, 5800.0) ;
{34.} H2O2 + hv = 2 OH : 6.312E-06*SUN ; {7.1E-4*RCONST(1)} ;
{35.} OH + H2O2 = HO2 : ARR2(3.1E-12, -187.0) ;
{36.} OH + CO = HO2 : KTYPCO(1.5E-13, 0.6) ;
{37.} HCHO + OH = HO2 + CO : 1.0E-11 ;
{38.} HCHO + hv {+ 2 O2} = 2 HO2 + CO : 2.845E-05*SUN ; {3.2E-3*RCONST(1)} ;
{39.} HCHO + hv = CO : 3.734E-05*SUN ; {4.2E-3*RCONST(1)} ;
{40.} HCHO + O = OH + HO2 + CO : ARR2(3.0E-11, -1550.0) ;
{41.} HCHO + NO3 = HNO3 + HO2 + CO : 6.3E-16 ;
{42.} ALD2 + O = C2O3 + OH : ARR2(1.2E-11, -986.0) ;
{43.} ALD2 + OH = C2O3 : ARR2(7.0E-12, 250.0) ;
{44.} ALD2 + NO3 = C2O3 + HNO3 : 2.5E-15 ;
{45.} ALD2 + hv {+ 2 O2} = HCHO + XO2 + CO + 2 HO2 : 4.00E-06*SUN ; {4.5E-4*RCONST(1)} ;
{46.} C2O3 + NO = HCHO + XO2 + HO2 + NO2 : ARR2(3.49E-11, -180.0) ;
{47.} C2O3 + NO2 = PAN : ARR2(2.63E-12, 380.0) ;
{48.} PAN = C2O3 + NO2 : ARR2(2.00E+16, -13500.0) ;
{49.} 2 C2O3 = 2 HCHO + 2 XO2 + 2 HO2 : 2.5E-12 ;
{50.} C2O3 + HO2 = 0.79 HCHO + 0.79 XO2 + 0.79 HO2 : 6.5E-12 ;
      + 0.79 OH + 0.21 PACD : ARR2(2.4E-12, -1710.0) ;
{51.} CH4 + OH = HCHO + XO2 + HO2 : 8.1E-13 ;
{52.} PAR + OH = 0.87 XO2 + 0.13 XO2N : 8.1E-13 ;
      + 0.11 HO2 + 0.11 ALD2 :
      + 0.76 ROR - 0.11 PAR :
{53.} ROR = 1.1 ALD2 + 0.96 XO2 : 8.1E-13 ;
      + 0.94 HO2 + 0.04 XO2N :
      + 0.02 ROR - 2.10 PAR : ARR2(1.0E+15, -8000.0) ;
{54.} ROR = HO2 : 1.6E+03 ;
{55.} ROR + NO2 = NTR : 1.5E-11 ;
{56.} O + OLE = 0.63 ALD2 + 0.38 HO2 :
      + 0.28 XO2 + 0.3 CO :
      + 0.2 HCHO + 0.02 XO2N :
      + 0.22 PAR + 0.2 OH : ARR2(1.2E-11, -324.0) ;
{57.} OH + OLE = HCHO + ALD2 + XO2 :
      + HO2 - PAR : ARR2(5.2E-12, 504.0) ;
{58.} O3 + OLE = 0.5 ALD2 + 0.74 HCHO :
      + 0.33 CO + 0.44 HO2 :
      + 0.22 XO2 + 0.20 FACD + 0.20 AACD :
      + 0.1 OH - PAR : ARR2(1.4E-14, -2105.0) ;
{59.} NO3 + OLE = 0.91 XO2 + HCHO :
      + ALD2 + 0.09 XO2N :
      + NO2 - PAR : 7.7E-15 ;
{60.} O + ETH = HCHO + 0.7 XO2 + CO :
      + 1.7 HO2 + 0.3 OH : ARR2(1.0E-11, -792.0) ;
{61.} OH + ETH = XO2 + 1.56 HCHO + HO2 + 0.22 ALD2 : ARR2(2.0E-12, 411.0) ;
{62.} O3 + ETH = HCHO + 0.42 CO + 0.12 HO2 + 0.40 FACD : ARR2(1.3E-14, -2633.0) ;
{63.} OH + TOL = 0.08 XO2 + 0.36 CRES :
      + 0.44 HO2 + 0.56 TO2 : ARR2(2.1E-12, 322.0) ;
{64.} TO2 + NO = 0.9 NO2 + 0.9 OPEN + 0.9 HO2 + 0.1 NTR : 8.1E-12 ;
{65.} TO2 = HO2 + CRES : 4.20 ;
{66.} OH + CRES = 0.4 CRO + 0.6 XO2 + 0.6 HO2 + 0.3 OPEN : 4.1E-11 ;
{67.} NO3 + CRES = CRO + HNO3 : 2.2E-11 ;
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{68.} CRO + NO2 = NTR : 1.4E-11 ;
{69.} OH + XYL = 0.7 HO2 + 0.5 XO2 + 0.2 CRES + 0.8 MGLY : 1.4E-11 ;
      + 1.10 PAR + 0.3 TO2 : ARR2(1.7E-11, 116.0) ;
{70.} OH + OPEN = XO2 + C2O3 + 2 HO2 + 2 CO + HCHO : 3.0E-11 ;
{71.} OPEN + hv = C2O3 + CO + HO2 : 5.334E-05*SUN ; {6.0E-3*RCONST(1) ;}
{72.} O3 + OPEN = 0.03 ALD2 + 0.62 C2O3
      + 0.7 HCHO + 0.03 XO2 + 0.69 CO : 1.70E-11 ;
      + 0.08 OH + 0.76 HO2 + 0.2 MGLY : ARR2(5.4E-17, -500.0) ;
{73.} OH + MGLY = XO2 + C2O3 : 1.70E-11 ;
{74.} MGLY + hv = C2O3 + CO + HO2 : 1.654E-04*SUN ; {1.86E-2*RCONST(1) ;}
{75.} O + ISOP = 0.75 ISPD + 0.50 HCHO + 0.25 XO2
      + 0.25 HO2 + 0.25 C2O3 + 0.25 PAR : 3.6E-11 ;
{76.} OH + ISOP = 0.912 ISPD + 0.629 HCHO + 0.991 XO2
      + 0.912 HO2 + 0.088 XO2N : ARR2(2.54E-11, 407.6) ;
{77.} O3 + ISOP = 0.65 ISPD + 0.60 HCHO + 0.20 XO2
      + 0.066 HO2 + 0.266 OH + 0.20 C2O3
      + 0.15 ALD2 + 0.35 PAR + 0.066 CO : ARR2(7.86E-15, -1912.0) ;
{78.} NO3 + ISOP = 0.20 ISPD + 0.80 NTR + XO2
      + 0.80 HO2 + 0.20 NO2 + 0.80 ALD2
      + 2.4 PAR : ARR2(3.03E-12, -448.0) ;
{79.} XO2 + NO = NO2 : 8.1E-12 ;
{80.} 2 XO2 = PROD : ARR2(1.7E-14, 1300.0) ;
{81.} XO2N + NO = NTR : 8.1E-12 ;
{82.} SO2 + OH = SULF + HO2 : TERM(3.0E-31, -3.3, 0.0, 1.5E-12, 0.0, 0.0, 0.6) ;
{83.} SO2 = SULF : 0.0 ;
{84.} MEOH + OH = PROD : 1.08E-12 ;
{85.} ETOH + OH = PROD : ARR2(1.61E-12, 176.0) ;
{86.} XO2 + HO2 = PROD : ARR2(7.67E-14, 1300.0) ;
{87.} XO2N + HO2 = PROD : ARR2(7.67E-14, 1300.0) ;
{88.} XO2N + XO2N = PROD : ARR2(1.73E-14, 1300.0) ;
{89.} XO2N + XO2 = PROD : ARR2(3.45E-14, 1300.0) ;
{90.} ISPD + OH = 1.565 PAR + 0.167 HCHO + 0.713 XO2
      + 0.503 HO2 + 0.334 CO + 0.168 MGLY
      + 0.273 ALD2 + 0.498 C2O3 : 3.36E-11 ;
{91.} ISPD + O3 = 0.114 C2O3 + 0.150 HCHO + 0.850 MGLY
      + 0.154 HO2 + 0.268 OH + 0.064 XO2
      + 0.020 ALD2 + 0.360 PAR + 0.225 CO : 7.11E-18 ;
{92.} ISPD + NO3 = 0.357 ALD2 + 0.282 HCHO + 1.282 PAR
      + 0.925 HO2 + 0.643 CO + 0.850 NTR
      + 0.075 C2O3 + 0.075 XO2 + 0.075 HNO3 : 1.00E-15 ;
{93.} ISPD + hv = 0.333 CO + 0.067 ALD2 + 0.900 HCHO
      + 0.832 PAR + 1.033 HO2 + 0.700 XO2
      + 0.967 C2O3 : 1.6E-6*SUN ; {0.0036*0.05*RCONST(1);}
{94.} ISOP + NO2 = 0.20 ISPD + 0.80 NTR + XO2
      + 0.80 HO2 + 0.20 NO + 0.80 ALD2
      + 2.4 PAR : 1.49E-19 ;

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Table S-2: Reaction Rate Coefficient Functions Used in CB05 & CBMIV

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!-----
! SUN is the normalized sunlight intensity, scaled with simulation time to be
! 1.0 at local noon and 0.0 at night. This simplification was used in the box
! model study reported here. In the NAQFC system, the usual CMAQ routines for
! generating photolytic rate constants are employed.
!-----
! function ARR
! REAL(kind=dp) FUNCTION ARR( A0,E0,B0 )
! REAL A0,E0,B0
! ARR = DBLE(A0) * EXP(DBLE(E0)/TEMP) * (TEMP/300.0_dp)**DBLE(B0)
! END FUNCTION ARR
!-----
! function ARR2
! REAL(kind=dp) FUNCTION ARR2( A0,E0 )
! REAL A0,E0
! ARR2 = DBLE(A0) * EXP(DBLE(E0)/TEMP)
! END FUNCTION ARR2
!-----
! function TERM
! REAL(kind=dp) FUNCTION TERM(A0,B0,E0,Ai,Bi,Ei,F)
!
! INTRINSIC LOG10
! REAL, INTENT(IN) :: A0, B0, E0 ! Arrhenius parameters for the low
! ! pressure limit
! REAL, INTENT(IN) :: Ai, Bi, Ei ! Arrhenius parameters for the high
! ! pressure limit
! REAL, INTENT(IN) :: F ! base and exponent parameters
! REAL(kind=dp) :: k0, ki, rk, logrk, g
!
! k0 = ARR(A0,E0,B0)
! ki = ARR(Ai,Ei,Bi)
!
! rk = k0*CAIR/ki
! logrk = LOG10(rk)
!
! g = 1.0_dp/(1.0_dp + (logrk*logrk))
!
! TERM = (k0*CAIR/(1.0_dp + rk))*F**g
!-----

```

```

END FUNCTION TERM
!-----
!
! function KTYP2
REAL(kind=dp) FUNCTION KTYP2(A0,E0,A2,E2,A3,E3)

REAL, INTENT(IN) :: A0, E0          !
REAL, INTENT(IN) :: A2, E2          !
REAL, INTENT(IN) :: A3, E3          !
REAL(kind=dp)    :: k0, k2, k3, k1

k0 = ARR(A0,E0,0.0)
k2 = ARR(A2,E2,0.0)
k3 = ARR(A3,E3,0.0)

k1 = k3*CAIR/(1.0_dp+(k3*CAIR/k2))

KTYP2 = k0 + k1

END FUNCTION KTYP2
!-----
!
! function KTYP3
REAL(kind=dp) FUNCTION KTYP3(A1,E1,A2,E2)

REAL, INTENT(IN) :: A1, E1          !
REAL, INTENT(IN) :: A2, E2          !

REAL(kind=dp)    :: k1, k2

k1 = ARR(A1,E1,0.0)
k2 = ARR(A2,E2,0.0)

KTYP3 = k1 + k2*CAIR

END FUNCTION KTYP3
!-----
!
! function KTYPCO
REAL(kind=dp) FUNCTION KTYPCO(A0, C0)

REAL, INTENT(IN) :: A0, C0

KTYPCO = A0*(1.0_dp + C0*PATM)

END FUNCTION KTYPCO
!-----

```