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E-98-M1

Appendix: Extensions to Chemical Mechanism

In this appendix, extensions to the published chemical mechanism of Carter [25] are listed to document the chemical mechanism used in this study.

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! File = AIRTOXIC.RXN
! Temperature for parameters =  300.00
!
.ACT
!         ---- Defaults for ----
!       Conc(0)  Mwt    #C's  #N's
!
CH4       0.0     16.04   1.0   0     methane
C2H6      0.0     30.07   2.0   0     ethane
ETHE      0.0     28.05   2.0   0     ethene
C6H6      0.0     78.11   6.0   0     benzene
TOLU      0.0     92.14   7.0   0     toluene
ETBZ      0.0    106.17   8.0   0     ethylbenzene
IPBZ      0.0    120.19   9.0   0     isopropylbenzene
XYLO      0.0    106.17   8.0   0     o-xylene
XYLM      0.0    106.17   8.0   0     m-xylene
XYLP      0.0    106.17   8.0   0     p-xylene
STYR      0.0    104.15   8.0   0     styrene
BD13      0.0     56.10   4.0   0     1,3-butadiene
ISOP      0.0     70.13   5.0   0     isoprene
APIN      0.0    136.24  10.0   0     alpha-pinene
BPIN      0.0    136.24  10.0   0     beta-pinene
TCA       0.0    133.40   2.0   0     1,1,1-trichloroethane
PERC      0.0    165.83   2.0   0     perchloroethylene
EGLY      0.0     62.07   2.0   0     ethylene glycol
PHEO      0.0     94.11   6.0   0     phenol
CREO      0.0    108.14   7.0   0     o-cresol
CREP      0.0    108.14   7.0   0     p-cresol
MIBK      0.0    100.16   6.0   0     methyl isobutyl ketone
ACRO      0.0     56.07   3.0   0     acrolein
H2CO      0.0     30.05   1.0   0     formaldehyde (directly emitted)
H3CO      0.0     30.05   1.0   0     formaldehyde (boundary/initial)
C2HO      0.0     44.05   2.0   0     acetaldehyde (directly emitted)
C3HO      0.0     44.05   2.0   0     acetaldehyde (boundary/initial)
A2RO      0.0     56.07   3.0   0     acrolein (direclty emitted)
ACE2      0.0     58.08   3.0   0     acetone (directly emitted)
ACE3      0.0     58.08   3.0   0     acetone (boundary/initial)
PHE2      0.0     94.11   6.0   0     phenol (directly emitted)
GALD      0.0     60.05   2.0   0     glycolaldehyde
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E-98-M2

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!
!    The individual reactions added to the chemical mechanism
!    are listed below.  Each reaction includes a reaction
!    label, followed by kinetic parameters (A, E, and B),
!    and then the list of reactant and product species.
!
!    Default rate parameter input is:  A, E, B
!    where:  k = A * (T/TREF)**B * exp (-E/RT),
!    TREF=300K, k and A are in cm - molecule - sec units, and
!    E is in kcal/mole.  If only a single value is stated, then
!    E and B are assumed to be zero.
!
.RXN
!
! benzene + OH:  see Table 7 of Carter [25]
! phenol yield from Atkinson et al. [16]
!
!       (A)       (E)    (B)
BBOH) 2.500E-12  0.397  0.000 ;C6H6 + HO. = #.236 PHEO + #.207 GLY &
                               + #.49 AFG1 + #.764 RO2-R. + #.236 HO2. &
                               + #3.19 -C + #.764 RO2.
!
!
! toluene + OH:  see Table 7 of Carter [25]
! cresol yields from Atkinson et al. [16]:  o-cresol (CREO) is the
! predominant cresol formed, the remainder (m+p-cresol) is mostly p-cresol
! or "CREP" (Gery et al., [27])
!
TTOH) 1.810E-12 -0.705  0.000 ;TOLU + HO. = #.085 BALD + #.204 CREO &
                               + #.118 GLY + #.131 MGLY + #.41 AFG2 &
                               + #.74 RO2-R. + #.26 HO2. + #2.726 -C &
                               + #.74 RO2. + #.048 CREP
!
!
! ethylbenzene + OH:  see Table 7 of Carter [25]
! same oxidation products as toluene, except the cresol species (CRES)
! formed in this reaction is a surrogate
!
ETBZ) 7.100E-12               ;ETBZ + HO. = #.085 BALD + #.26 CRES &
                                 + #.118 GLY + #.131 MGLY + #.41 AFG2 &
                                 + #.74 RO2-R. + #.26 HO2. + #3.726 -C &
                                 + #.74 RO2.
!
!
! isopropylbenzene + OH:  see Table 7 of Carter [25]
! and comment above for ethylbenzene
!
IPBZ) 6.500E-12               ;IPBZ + HO. = #.085 BALD + #.26 CRES &
                                 + #.118 GLY + #.131 MGLY + #.41 AFG2 &
                                 + #.74 RO2-R. + #.26 HO2. + #4.726 -C &
                                 + #.74 RO2.
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E-98 - M3

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!
!
! o-xylene + OH:  see Table 7 of Carter [25]
!
XYLO) 1.37OE-11                ;XYLO + HO. = #.04 BALD + #.18 CRES &
                                 + #.108 GLY + #.37 MGLY + #.666 AFG2 &
                                 + #.82 RO2-R. + #.18 HO2. + #3.136 -C &
                                 + #.82 RO2.
!
!
! m-xylene + OH:  see Table 7 of Carter [25]
!
XYLM) 2.36OE-11                ;XYLM + HO. = #.04 BALD + #.18 CRES &
                                 + #.108 GLY + #.37 MGLY + #.666 AFG2 &
                                 + #.82 RO2-R. + #.18 HO2. + #3.136 -C &
                                 + #.82 RO2.
!
!
! p-xylene + OH:  see Table 7 of Carter [25]
!
XYLP) 1.43OE-11                ;XYLP + HO. = #.04 BALD + #.18 CRES &
                                 + #.108 GLY + #.37 MGLY + #.666 AFG2 &
                                 + #.82 RO2-R. + #.18 HO2. + #3.136 -C &
                                 + #.82 RO2.
!
!
! phenol + OH:  same as reaction G46 of Carter [25]
!
PHOH) 2.63E-11                 ;PHEO + HO. = #.15 RO2-NP. + #.85 RO2-R. + &
                                 #.2 GLY + #4.7 -C + RO2.
!
! identical reaction for directly emitted phenol (PHE2)
!
P2OH) 2.63E-11                 ;PHE2 + HO. = #.15 RO2-NP. + #.85 RO2-R. + &
                                 #.2 GLY + #4.7 -C + RO2.
!
!
! phenol + NO3:  rate constant of Atkinson et al. [30];  otherwise
!           same as reaction G51 of Carter [25]
!
PHN3) 3.92E-12                 ;PHEO + NO3 = HNO3 + BZ-O.
!
! identical reaction for directly emitted phenol (PHE2)
!
P2N3) 3.92E-12                 ;PHE2 + NO3 = HNO3 + BZ-O.
!
!
! o-cresol + OH:  same as reaction G52 of Carter [25]
!
CROH) 4.20E-11                 ;CREO + HO. = #.15 RO2-NP. + #.85 RO2-R. + &
                                 #.2 MGLY + #5.5 -C + RO2.
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E-98-24

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!
! o-cresol + NO3:  rate constant of Atkinson et al. [30];  otherwise
! same as reaction G57 of Carter [25]
!
CRN3) 1.37E-11                ;CREO + NO3 = HNO3 + BZ-O. + -C
!
! p-cresol + OH: rate constant of Atkinson et al. [16];  products
! same as reaction G52 of Carter [25]
!
CPOH) 4.70E-11                ;CREP + HO. = #.15 RO2-NP. + #.85 RO2-R. + &
                                #.2 MGLY + #5.5 -C + RO2.
!
! p-cresol + NO3:  rate constant of Atkinson et al. [30];  otherwise
! same as reaction G57 of Carter [25]
!
CPN3) 1.07E-11                ;CREP + NO3 = HNO3 + BZ-O. + -C
!
!
! 1,3-butadiene + OH reaction: from Carter [25] except acrolein
! product is now explicitly represented instead of being treated as
! propionaldehyde (RCHO)
!
BDOH) 1.480E-11 -0.890  0.000 ;BD13 + HO. = RO2-R. + RO2. + HCHO + ACRO
!
!
! 1,3-butadiene + O3 from Carter [25] with acrolein represented
! explicitly
!
BDO3) 3.300E-14  4.968  0.000 ;BD13 + O3 = #.135 RO2-R. + #.165 HO2. &
                              + #.135 RO2. + #.5 HCHO + #.15 CCHO + #.5 ACRO &
                              + #.21 MEK + #.295 CO + #.565 -C + #.06 HO. &
                              + #.285 O3OL-SB
!
!
! 1,3-butadiene + NO3 as per Carter [25] with slight update to rate
! constant (Ea value) from Atkinson [71] and explicit treatment of
! acrolein
!
BDN3) 1.480E-11  2.959  0.000 ;BD13 + NO3 = R2O2. + RO2. + HCHO + ACRO &
                                + NO2
!
!
! 1,3-butadiene + O as per Carter [25]
!
BDOA) 2.100E-11  0.000  0.000 ;BD13 + O = #.4 HO2. + #.5 RCHO + #.5 MEK &
                                + #.5 -C
!
!
! acrolein + OH:  rate constant of Atkinson [17];  assumes
! predominant reaction pathway is hydrogen abstraction from CHO group
!
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```
ACRO) 1.99E-11          ;ACRO + HO. = C2CO-O2. + RCO3.
!
! same reaction as above for directly emitted acrolein (A2RO)
!
A2RO) SAMEK ACRO        ;A2RO + HO. = C2CO-O2. + RCO3.
!
! acrolein + NO3:  rate constant of Atkinson [17];  assumes
! predominant reaction pathway is hydrogen abstraction from CHO group
!
ACN3) 1.20E-15          ;ACRO + NO3 = HNO3 + C2CO-O2. + RCO3.
!
! same reaction as above for directly emitted acrolein (A2RO)
!
ACN4) SAMEK ACN3        ;A2RO + NO3 = HNO3 + C2CO-O2. + RCO3.
!
! note other reactions of acrolein (photolysis; reaction with O3)
! are negligible relative to reaction with OH (Atkinson [17])
!
!
! styrene + OH reaction from Carter [28].  Assumed to react like
! an olefin (i.e., at the double bond), rather than as an aromatic
! hydrocarbon.
!
SYOH) 1.070E-11 -1.000  0.000 ;STYR + HO. = RO2-R. + RO2. + HCHO + BALD
!
! styrene + O3 reaction (Carter [28])
!
SYO3) 3.460E-15  3.144  0.000 ;STYR + O3 = #.06 HO2. + #.25 R2O2. &
                               + #.25 RO2. + #.5 HCHO + #.47 CO + #.5 BALD &
                               + #2.03 -C + #.25 HO. + #.435 O3OL-SB &
                               + #.25 BZ-O.
!
! styrene + NO3 reaction (Carter [28])
!
SYN3) 6.550E-12  2.233  0.000 ;STYR + NO3 = R2O2. + RO2. + HCHO + BALD &
                               + NO2
!
! styrene + O reaction (Carter [28])
!
SYOA) 1.210E-11 -0.235  0.000 ;STYR + O = #.4 HO2. + #.5 RCHO + #.5 MEK &
                               + #4.5 -C
!
!
! 1,1,1-trichloroethane (TCA) + OH:  rate constant of Atkinson et al. [31]
! with hydrogen abstraction and formation of a chlorinated C2 species
!
TCA)  3.10E-12   3.299  0.00  ;TCA + HO. = RO2-R. + RO2. + GALD
!
! perchloroethylene (PERC) + OH: rate constant of Atkinson et al. [31]
! see comments above for TCA.
!
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E-98-N6

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PERC) 9.40E-12   2.385  0.00  ;PERC + HO. = RO2-R. + RO2. + GALD
!
!
! ethylene glycol + OH:  from Table 8 of Carter [25] except
! glycolaldehyde (GALD) is no longer lumped with acetaldehyde
!
EGLY) 7.70E-12                ;EGLY + HO. = HO2. + GALD
!
!
! methyl isobutyl ketone (MIBK) + OH reaction:  rate constant from
! Atkinson [17];  same reaction mechanism as for MEK (Carter, [25])
!
MIBK) 1.41E-11          ;MIBK + HO. = H2O + #.5 "CCHO + HCHO + CCO-O2. + &
                            C2CO-O2." + RCO3. + #1.5 "R2O2. + RO2." + &
    #2 -C
!
! reactions of directly emitted formaldehyde (H2CO), same as
! reactions of formaldehyde (HCHO) in Carter [25]:
! C1, C2, C3, C4, and C9.
!
S1) SAMEK C1            ;H2CO + HV = #2 HO2. + CO
!
S2) SAMEK C2            ;H2CO + HV = H2 + CO
!
S3) SAMEK C3            ;H2CO + HO. = HO2. + CO + H2O
!
S4) SAMEK C4            ;H2CO + HO2. = HOCOO.
!
S9) SAMEK C9            ;H2CO + NO3 = HNO3 + HO2. + CO
!
! reactions of directly emitted acetaldehyde (C2HO), same as
! reactions of acetaldehyde (CCHO) in Carter [25]: C10, C11A, C12
!
S10) SAMEK C10          ;C2HO + HO. = CCO-O2. + H2O + RCO3.
!
S11A) SAMEK C11A        ;C2HO + HV = CO + HO2. + HCHO + RO2-R. + RO2.
!
S12) SAMEK C12          ;C2HO + NO3 = HNO3 + CCO-O2. + RCO3.
!
!
! reactions of boundary/initial formaldehyde (H3CO), same as
! reactions of formaldehyde (HCHO) in Carter [25]:
! C1, C2, C3, C4, and C9.
!
BC1) SAMEK C1            ;H3CO + HV = #2 HO2. + CO
!
BC2) SAMEK C2            ;H3CO + HV = H2 + CO
!
BC3) SAMEK C3            ;H3CO + HO. = HO2. + CO + H2O
!
BC4) SAMEK C4            ;H3CO + HO2. = HOCOO.
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E-98-07

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!
BC9) SAMEK C9             ;H3CO + NO3 = HNO3 + HO2. + CO
!
! reactions of boundary/initial acetaldehyde (C3HO), same as
! reactions of acetaldehyde (CCHO) in Carter [25]: C10, C11A, C12
!
BC10) SAMEK C10           ;C3HO + HO. = CCO-O2. + H2O + RCO3.
!
BC11A) SAMEK C11A         ;C3HO + HV = CO + HO2. + HCHO + RO2-R. + RO2.
!
BC12) SAMEK C12           ;C3HO + NO3 = HNO3 + CCO-O2. + RCO3.
!
! glycolaldehyde (GALD) is still represented using the reactions of
! acetaldehyde, but now it is tracked separately so that it is not
! counted with the photochemically-derived acetaldehyde
!
SC10) SAMEK C10           ;GALD + HO. = CCO-O2. + H2O + RCO3.
!
SC11) SAMEK C11A          ;GALD + HV = CO + HO2. + HCHO + RO2-R. + RO2.
!
SC12) SAMEK C12           ;GALD + NO3 = HNO3 + CCO-O2. + RCO3.
!
!
! reactions of directly emitted acetone (ACE2), same as reactions
! C38 and C39 of Carter [25]
!
S38) SAMEK C38            ;ACE2 + HO. = #.8 "MGLY + RO2-R." + #.2 "R2O2. + &
                                HCHO + CCO-O2. + RCO3." + RO2.
!
S39) SAMEK C39            ;ACE2 + HV = CCO-O2. + HCHO + RO2-R. + RCO3. + RO2.
!
!
! reactions of boundary/initial acetone (ACE3), same as reactions
! C38 and C39 of Carter [25]
!
S38) SAMEK C38            ;ACE3 + HO. = #.8 "MGLY + RO2-R." + #.2 "R2O2. + &
                                HCHO + CCO-O2. + RCO3." + RO2.
!
S39) SAMEK C39            ;ACE3 + HV = CCO-O2. + HCHO + RO2-R. + RCO3. + RO2.
!
!
!
! The following species are represented explicitly even though they
! are not considered to be toxic pollutants in this study:
!
! methane (CH4) + OH:  rate constant from Atkinson [17]
!
CH4) 6.255E-13  2.548  2.000 ;CH4 + HO. = RO2-R. + HCHO + RO2.
!
! ethane (C2H6) + OH:  rate constant from Atkinson [17]
!
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```
C2H6) 1.278E-12  0.918  2.000 ;C2H6 + HO. = RO2-R. + CCHO + RO2.
!
! ethene (ETHE) + OH:  same as reaction D1 of Carter [25]
! except glycolaldehyde treated explicitly
!
D1) 1.960E-12 -0.870  0.000 ;ETHE + HO. = RO2-R. + RO2. + #1.56 HCHO &
                              + #.22 GALD
!
! ethene + O3:  same as reaction D6 of Carter [25]
!
D6) 1.200E-14  5.226  0.000 ;ETHE + O3 = #.12 HO2. + HCHO + #.44 CO &
                             + #.56 -C + #.37 O3OL-SB
!
! ethene + O:  same as reaction D8 of Carter [25]
!
D8) 1.040E-11  1.574  0.000 ;ETHE + O = RO2-R. + HO2. + RO2. + HCHO + CO
!
! ethene + NO3:  same as reaction D9 of Carter [25] except rate
! constant updated (Atkinson, [71])
!
D9) 5.430E-12  6.043  0.000 ;ETHE + NO3 = R2O2. + RO2. + #2 HCHO + NO2
!
!
! isoprene  (ISOP) reactions:  see Tables 5 and 9 of Carter [25]
! NO3 reaction rate constants updated (Atkinson, [71])
!
IPOH) 2.540E-11 -0.815  0.000 ;ISOP + HO. = RO2-R. + RO2. + HCHO + RCHO &
                               + -C
!
IPO3) 1.230E-14  4.000  0.000 ;ISOP + O3 = #.135 RO2-R. + #.165 HO2. &
                               + #.135 RO2. + #.5 HCHO + #.15 CCHO + #.5 RCHO &
                               + #.21 MEK + #.295 CO + #1.565 -C + #.06 HO. &
                               + #.285 O3OL-SB
!
IPN3) 3.030E-12  0.886  0.000 ;ISOP + NO3 = R2O2. + RO2. + HCHO + RCHO &
                               + -C + NO2
!
IPOA) 6.000E-11  0.000  0.000 ;ISOP + O = #.4 HO2. + #.5 RCHO + #.5 MEK &
                               + #1.5 -C
!
!
! alpha-pinene  (APIN) reactions:  see Tables 5 and 9 of Carter [25]
! NO3 reaction rate constants updated from (Atkinson, [71])
!
APOH) 1.210E-11 -0.882  0.000 ;APIN + HO. = RO2-R. + RO2. + RCHO + #7 -C
!
APO3) 9.900E-16  1.366  0.000 ;APIN + O3 = #.135 RO2-R. + #.105 HO2. &
                               + #.15 R2O2. + #.285 RO2. + #.05 CCO-O2. &
                               + #.05 C2CO-O2. + #.1 RCO3. + #.05 HCHO &
                               + #.2 CCHO + #.5 RCHO + #.61 MEK + #.075 CO &
                               + #5.285 -C + #.16 HO. + #.1 O3OL-SB
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E-98-n 9

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!
APN3) 1.190E-12 -0.974  0.000 ;APIN + NO3 = R2O2. + RO2. + RCHO + #7 -C &
                                + NO2
!
APOA) 3.000E-11  0.000  0.000 ;APIN + O = #.4 HO2. + #.5 RCHO + #.5 MEK &
                                + #6.5 -C
!
!
! beta-pinene  (BPIN) reactions:  see Tables 5 and 9 of Carter [25]
! NO3 reaction rate constants updated from (Atkinson, [71])
!
BPOH) 2.380E-11 -0.709  0.000 ;BPIN + HO. = RO2-R. + RO2. + HCHO + RCHO &
                                + #6 -C
!
BPO3) 3.550E-15  3.187  0.000 ;BPIN + O3 = #.135 RO2-R. + #.165 HO2. &
                                + #.135 RO2. + #.5 HCHO + #.15 CCHO + #.5 RCHO &
                                + #.21 MEK + #.295 CO + #6.565 -C + #.06 HO. &
                                + #.285 O3OL-SB
!
BPN3) 2.510E-12  0.000  0.000 ;BPIN + NO3 = R2O2. + RO2. + HCHO + RCHO &
                                + #6 -C + NO2
!
BPOA) 2.800E-11  0.000  0.000 ;BPIN + O = #.4 HO2. + #.5 RCHO + #.5 MEK &
                                + #6.5 -C
!
```