

TS2 Custom Rate Constants

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1 Introduction

This document builds on the TS1 Custom Rate Constants document, adding treatments for custom rate constant functions used in the TS2 mechanism that are not also present in TS1.

2 usr_ISOPNO3_NOa and usr_ISOPNO3_NOn

/cam/src/chemistry/mozart/mo_usrrxt.F90 (1213,1231)

```
!-----
!      ... ISOPNO3_NOn Temp/Pressure Dependent Nitrate Yield
!-----
      if( usr_ISOPNO3_NOn_ndx > 0 ) then
        nyield = (1._r8-0.135_r8)/0.135_r8
        natom = 9.0_r8
        exp_natom = exp( natom )
        acorr = (2.0e-22_r8*exp_natom*2.45e19_r8)/(1._r8+((2.0e-22_r8* &
          exp_natom*2.45e19_r8)/(0.43_r8*(298._r8*(1._r8/293._r8))**8._r8))) * &
          0.41_r8**((1._r8/(1._r8+(log10((2.0e-22_r8*exp_natom*2.45e19_r8)/ &
            (0.43_r8*(298._r8*(1._r8/293._r8))**8._r8)))**2._r8))
        aterm(:) = (2.0e-22_r8*exp_natom*m(:,k))/(1._r8+((2.0e-22_r8* &
          exp_natom*m(:,k))/(0.43_r8*(298._r8*tinv(:))**8._r8))) * &
          0.41_r8**((1._r8/(1._r8+(log10((2.0e-22_r8*exp_natom*m(:,k))/ &
            (0.43_r8*(298._r8*tinv(:))**8._r8)))**2._r8))
        call comp_exp( exp_fac, 360._r8*tinv, ncol )
        rxt(:,k,usr_ISOPNO3_NOn_ndx) = 2.7e-12_r8 * exp_fac(:)*aterm(:)/(aterm(:)+acorr*nyield)
        rxt(:,k,usr_ISOPNO3_NOa_ndx) = 2.7e-12_r8 * exp_fac(:)*acorr*nyield/(aterm(:)+acorr*nyield)
      end if
```

This appears to be based on eqs (1)–(6) of [1], which define the rate constant for each branch as a function of four parameters (X, Y, Z, n):

$$\begin{aligned}
 k_{\text{nitrate}} &= \left(X e^{-Y/T} \right) \left(\frac{A(T, [M], n)}{A(T, [M], n) + Z} \right) \\
 k_{\text{alkoxy}} &= \left(X e^{-Y/T} \right) \left(\frac{Z}{Z + A(T, [M], n)} \right) \\
 A(T, [M], n) &= \frac{2 \times 10^{-22} e^n [M]}{1 + \frac{2 \times 10^{-22} e^n [M]}{0.43(T/298)^{-8}}} 0.41^{(1 + [\log(\frac{2 \times 10^{-22} e^n [M]}{0.43(T/298)^{-8}})]^2)^{-1}}
 \end{aligned} \tag{1}$$

where T is temperature (K) and $[M]$ is the number density of air (molecules cm^{-3}). To retain the detail of the current implementation of these rate constant functions, Z is defined as a function of two parameters (α_0, n):

$$Z(\alpha_0, n) = A(T = 293\text{K}, [M] = 2.45 \times 10^{19} \frac{\text{molec}}{\text{cm}^3}, n) \frac{(1 - \alpha_0)}{\alpha_0} \tag{2}$$

This reaction has been added to Music Box as WENBERG_NO_R02. The `usr_ISOPNO3_NOn` and `usr_ISOPNO3_NOa` rate constants can then be calculated according to the above equations with $X = 2.7 \times 10^{-12}$, $Y = -360$, $\alpha_0 = 0.135$, and $n = 9$, with `usr_ISOPNO3_NOn` corresponding to k_{nitrate} and `usr_ISOPNO3_NOa` corresponding to k_{alkoxy} .

Similar custom rate constant functions are summarized in Table 1.

3 usr_ISOPZD1O2

Table 1: Wennberg NO + RO₂ rate constant parameters by custom rate constant function name

Function name	X	Y	a_0	n
usr_ISOPB1O2_NO	2.7×10^{-12}	-360	0.14	6
usr_ISOPB4O2_NO	2.7×10^{-12}	-360	0.13	6
usr_ISOPD1O2_NO	2.7×10^{-12}	-360	0.12	6
usr_ISOPD4O2_NO	2.7×10^{-12}	-360	0.12	6
usr_ISOPZD1O2_NO	2.7×10^{-12}	-360	0.12	6
usr_ISOPZD4O2_NO	2.7×10^{-12}	-360	0.12	6
usr_ISOPNO3_NO	2.7×10^{-12}	-360	0.135	9
usr_MVKO2_NO	2.7×10^{-12}	-360	0.04	6
usr_MACRO2_NO	2.7×10^{-12}	-360	0.06	6
usr_IEPOXOO_NO	2.7×10^{-12}	-360	0.025	8
usr_ISOPN1DO2_NO	2.7×10^{-12}	-360	0.084	11
usr_ISOPN2BO2_NO	2.7×10^{-12}	-360	0.065	11
usr_ISOPN3BO2_NO	2.7×10^{-12}	-360	0.053	11
usr_ISOPN4DO2_NO	2.7×10^{-12}	-360	0.165	11
usr_ISOPNBNO3O2_NO	2.7×10^{-12}	-360	0.203	11
usr_ISOPNOOHBO2_NO	2.7×10^{-12}	-360	0.141	12
usr_ISOPNOOHD02_NO	2.7×10^{-12}	-360	0.045	12
usr_NC4CHOO2_NO	2.7×10^{-12}	-360	0.021	11

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (1081,1089)
```

```
!-----
!      ... ISOPZD102 --> HPALD etc. Wennberg 2018 for rate
!-----
      if( usr_ISOPZD102_ndx > 0 ) then
        call comp_exp( exp_fac, -12200._r8*tinv, ncol )
        ko(:) = 5.05e15_r8 * exp_fac(:)
        call comp_exp( exp_fac, 1.e8_r8*tinv**3._r8, ncol )
        rxt(:,k,usr_ISOPZD102_ndx) = ko(:)*exp_fac(:)
      end if
```

This appears to be based on eq. (12) of [1]:

$$k_{\text{tunneling}} = Ae^{-B/T}e^{C/T^3} \quad (3)$$

with $A = 5.05 \times 10^{15}$, $B = 12200$, and $C = 1 \times 10^8$. This reaction has been added to Music Box as WENNBERG_TUNNELING.

4 usr_TERPAPAN_M

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (971,971)
```

```
      call comp_exp( exp_fac, -14000._r8*tinv, ncol )
```

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (1016,1025)
```

```
!-----
!      ... TERPAPAN + m --> TERPAC03 + no2 + m
!-----
      if( usr_TERPAPAN_M_ndx > 0 ) then
        if( tag_TERPAC03_NO2_ndx > 0 ) then
          rxt(:,k,usr_TERPAPAN_M_ndx) = rxt(:,k,tag_TERPAC03_NO2_ndx) * 1.111e28_r8 * exp_fac(:)
        else
          rxt(:,k,usr_TERPAPAN_M_ndx) = 0._r8
        end if
      end if
```

Following the same logic as for `usr_PBZNIT_M`, the `tag_TERPA03_N02_ndx` reaction is identified as:

```
{
  "type": "TROE",
  "k0_A": 9.7e-29,
  "k0_B": -5.6,
  "kinf_A": 9.3e-12,
  "N": 1.5,
  "reactants": {
    "TERPA03": { },
    "N02": { },
    "M": { }
  },
  "products": {
    "TERPAPAN": { },
    "M": { }
  }
},
```

and can be rearranged as a Troe reaction:

$$k = \frac{k_0[M]}{1 + k_0[M]/k_{inf}} F_C^{(1+1/N[\log_{10}(k_0[M]/k_{inf})]^2)^{-1}}$$

$$k_0 = A_0 e^{(\frac{C_0}{T})} \left(\frac{T}{300} \right)^{B_0}$$

$$k_{inf} = A_{inf} e^{(\frac{C_{inf}}{T})} \left(\frac{T}{300} \right)^{B_{inf}} \quad (4)$$

where $F_C = 0.6$, $N = 1.5$, $A_0 = 9.7 \times 10^{-29} \times 1.111 \times 10^{28}$, $B_0 = -5.6$, $C_0 = -14000$, $A_{inf} = 9.3 \times 10^{-12} \times 1.111 \times 10^{28}$, $B_{inf} = 0$, and $C_{inf} = -14000$.

5 usr_TERPA2PAN_M

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (971,971)
  call comp_exp( exp_fac, -14000._r8*tnv, ncol )
```

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (1026,1035)
```

```
!-----
!      ... TERPA2PAN + m --> TERPA2C03 + no2 + m
!-----

if( usr_TERPA2PAN_M_ndx > 0 ) then
  if( tag_TERPA2C03_N02_ndx > 0 ) then
    rxt(:,k,usr_TERPA2PAN_M_ndx) = rxt(:,k,tag_TERPA2C03_N02_ndx) * 1.111e28_r8 * exp_fac(:)
  else
    rxt(:,k,usr_TERPA2PAN_M_ndx) = 0._r8
  end if
end if
```

Following the same logic as for `usr_PBZNIT_M`, the `tag_TERPA2C03_N02_ndx` reaction is identified as:

```
{
  "type": "TROE",
  "k0_A": 9.7e-29,
  "k0_B": -5.6,
  "kinf_A": 9.3e-12,
```

```

    "N": 1.5,
    "reactants": {
      "TERPA2C03": { },
      "N02": { },
      "M": { }
    },
    "products": {
      "TERPA2PAN": { },
      "M": { }
    }
  },

```

and can be rearranged as a Troe reaction:

$$\begin{aligned}
 k &= \frac{k_0[M]}{1 + k_0[M]/k_{\text{inf}}} F_C^{(1+1/N[\log_{10}(k_0[M]/k_{\text{inf}})]^2)^{-1}} \\
 k_0 &= A_0 e^{(\frac{C_0}{T})} \left(\frac{T}{300} \right)^{B_0} \\
 k_{\text{inf}} &= A_{\text{inf}} e^{(\frac{C_{\text{inf}}}{T})} \left(\frac{T}{300} \right)^{B_{\text{inf}}}
 \end{aligned} \tag{5}$$

where $F_C = 0.6$, $N = 1.5$, $A_0 = 9.7 \times 10^{-29} \times 1.111 \times 10^{28}$, $B_0 = -5.6$, $C_0 = -14000$, $A_{\text{inf}} = 9.3 \times 10^{-12} \times 1.111 \times 10^{28}$, $B_{\text{inf}} = 0$, and $C_{\text{inf}} = -14000$.

6 usr_TERPA3PAN_M

```

/cam/src/chemistry/mozart/mo_usrrxt.F90 (971,971)
  call comp_exp( exp_fac, -14000._r8*tinv, ncol )

/cam/src/chemistry/mozart/mo_usrrxt.F90 (1036,1045)
!-----
!      ... TERPA3PAN + m --> TERPA3C03 + no2 + m
!-----
  if( usr_TERPA3PAN_M_ndx > 0 ) then
    if( tag_TERPA3C03_N02_ndx > 0 ) then
      rxt(:,k,usr_TERPA3PAN_M_ndx) = rxt(:,k,tag_TERPA3C03_N02_ndx) * 1.111e28_r8 * exp_fac(:)
    else
      rxt(:,k,usr_TERPA3PAN_M_ndx) = 0._r8
    end if
  end if
end if

```

Following the same logic as for `usr_PBZNIT_M`, the `tag_TERPA3C03_N02_ndx` reaction is identified as:

```

{
  "type": "TROE",
  "k0_A": 9.7e-29,
  "k0_B": -5.6,
  "kinf_A": 9.3e-12,
  "N": 1.5,
  "reactants": {
    "TERPA3C03": { },
    "N02": { },
    "M": { }
  },
  "products": {

```

```

    "TERPA3PAN": { },
    "M": { }
  }
},

```

and can be rearranged as a Troe reaction:

$$\begin{aligned}
 k &= \frac{k_0[M]}{1 + k_0[M]/k_{\text{inf}}} F_C^{(1+1/N[\log_{10}(k_0[M]/k_{\text{inf}})]^2)^{-1}} \\
 k_0 &= A_0 e^{(\frac{C_0}{T})} \left(\frac{T}{300} \right)^{B_0} \\
 k_{\text{inf}} &= A_{\text{inf}} e^{(\frac{C_{\text{inf}}}{T})} \left(\frac{T}{300} \right)^{B_{\text{inf}}}
 \end{aligned} \tag{6}$$

where $F_C = 0.6$, $N = 1.5$, $A_0 = 9.7 \times 10^{-29} \times 1.111 \times 10^{28}$, $B_0 = -5.6$, $C_0 = -14000$, $A_{\text{inf}} = 9.3 \times 10^{-12} \times 1.111 \times 10^{28}$, $B_{\text{inf}} = 0$, and $C_{\text{inf}} = -14000$.

7 usr_ISOPZD4O2

```

/cam/src/chemistry/mozart/mo_usrrxt.F90 (1090,1098)

```

```

!-----
!      ... ISOPZD4O2 --> HPALD etc. Wennberg 2018 for rate
!-----

      if( usr_ISOPZD4O2_ndx > 0 ) then
        call comp_exp( exp_fac, -7160._r8*tinv, ncol )
        ko(:) = 2.22e9_r8 * exp_fac(:)
        call comp_exp( exp_fac, 1.e8_r8*tinv**3._r8, ncol )
        rxt(:,k,usr_ISOPZD4O2_ndx) = ko(:)*exp_fac(:)
      end if

```

This appears to be a WENNBURG_TUNNELING reaction:

$$k_{\text{tunneling}} = A e^{-B/T} e^{C/T^3} \tag{7}$$

with $A = 2.22 \times 10^9$, $B = 7160$, and $C = 1 \times 10^8$.

8 References

References

- [1] Paul O. Wennberg et al. "Gas-Phase Reactions of Isoprene and Its Major Oxidation Products". In: *Chemical Reviews* 118.7 (2018). PMID: 29522327, pp. 3337–3390. DOI: 10.1021/acs.chemrev.7b00439. eprint: <https://doi.org/10.1021/acs.chemrev.7b00439>. URL: <https://doi.org/10.1021/acs.chemrev.7b00439>.