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):

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

where T is temperature (K) and $[\mathrm{M}]$ 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):

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

This reaction has been added to Music Box as `WENNBERG_NO_RO2`. 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 + RO$_2$ 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_ISOPNOOHDO2_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)
!-----------------------------------------------------------------
!        ... ISOPZD1O2 --> HPALD etc. Wennberg 2018 for rate
!-----------------------------------------------------------------
       if( usr_ISOPZD1O2_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_ISOPZD1O2_ndx) = ko(:)*exp_fac(:)
       end if
```

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

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

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 --> TERPACO3 + no2 + m
!-----------------------------------------------------------------
       if( usr_TERPAPAN_M_ndx > 0 ) then
          if( tag_TERPACO3_NO2_ndx > 0 ) then
             rxt(:,k,usr_TERPAPAN_M_ndx) = rxt(:,k,tag_TERPACO3_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_TERPACO3_NO2_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": {
    "TERPACO3": { },
    "NO2": { },
    "M": { }
  },
  "products": {
    "TERPAPAN": { },
    "M": { }
  }
},
```

and can be rearranged as a Troe reaction:

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

$$k_0 = A_0 e^{\left(\frac{C_0}{T}\right)} \left(\frac{T}{300}\right)^{B_0} \tag{4}$$

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

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*tinv, ncol )
```

`/cam/src/chemistry/mozart/mo_usrrxt.F90 (1026,1035)`
```
!-----------------------------------------------------------------
!        ... TERPA2PAN + m --> TERPA2CO3 + no2 + m
!-----------------------------------------------------------------
      if( usr_TERPA2PAN_M_ndx > 0 ) then
         if( tag_TERPA2CO3_NO2_ndx > 0 ) then
            rxt(:,k,usr_TERPA2PAN_M_ndx) = rxt(:,k,tag_TERPA2CO3_NO2_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_TERPA2CO3_NO2_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": {
            "TERPA2CO3": { },
            "NO2": { },
            "M": { }
          },
          "products": {
            "TERPA2PAN": { },
            "M": { }
          }
        },
```

and can be rearranged as a Troe reaction:

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

$$k_0 = A_0 e^{\left(\frac{C_0}{T}\right)} \left(\frac{T}{300}\right)^{B_0} \tag{5}$$

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

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 $C_{inf} = -14000$.

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 --> TERPA3CO3 + no2 + m
!-----------------------------------------------------------------
       if( usr_TERPA3PAN_M_ndx > 0 ) then
          if( tag_TERPA3CO3_NO2_ndx > 0 ) then
             rxt(:,k,usr_TERPA3PAN_M_ndx) = rxt(:,k,tag_TERPA3CO3_NO2_ndx) * 1.111e28_r8 * exp_fac(:)
          else
             rxt(:,k,usr_TERPA3PAN_M_ndx) = 0._r8
          end if
       end if
```

Following the same logic as for `usr_PBZNIT_M`, the `tag_TERPA3CO3_NO2_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": {
            "TERPA3CO3": { },
            "NO2": { },
            "M": { }
          },
          "products": {
```

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

and can be rearranged as a Troe reaction:

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

$$k_0 = A_0 e^{\left(\frac{C_0}{T}\right)} \left(\frac{T}{300}\right)^{B_0} \tag{6}$$

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

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 $C_{inf} = -14000$.

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 `WENNBERG_TUNNELING` reaction:

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

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.