TS2 Custom Rate Constants

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1 Introduction

Contained are notes on the coversion of custom rate constant equations from the TS2 mechanism to standard MICM reaction types, building on the custom rate constant equation notes for TS1. The original rate constant functions are taken from the CAM source code, at `cam/src/chemistry/mozart/mo_usrrxt.F90`. These notes represent a snapshot in time, and the CAM code will likely have changed since this document was written. The code snippets are included to provide context.

2 Note on [M] in Troe reactions

The species 'M' seems to be included in most (maybe all?) standard Troe reactions as a reactant and a product. However, the CAM preprocessor appears to ignore 'M' as a species, and instead includes it in the calculation of the rate constant:

```
/cam/src/chemistry/pp_trop_strat_mam4_ts2/m_spc_id.F90 (27,27)
      integer, parameter :: id_C2H2 = 25


/cam/src/chemistry/pp_trop_strat_mam4_ts2/m_spc_id.F90 (295,295)
      integer, parameter :: id_OH = 293


/cam/src/chemistry/pp_trop_strat_mam4_ts2/m_rxt_id.F90 (324,324)
      integer, parameter :: rid_C2H2_OH_M = 322


/cam/src/chemistry/pp_trop_strat_mam4_ts2/mo_setrxt.F90 (928,930)
      ko(:) = 5.5e-30_r8
      kinf(:) = 8.3e-13_r8 * itemp(:)**(-2._r8)
      call jpl( rate(:,322), m, 0.6_r8, ko, kinf, n )


/cam/src/chemistry/mozart/mo_jpl.F90 (9,39)
      subroutine jpl( rate, m, factor, ko, kinf, ncol )
!-----------------------------------------------------------------
!        ... Calculate JPL troe rate
!-----------------------------------------------------------------

      use shr_kind_mod, only : r8 => shr_kind_r8

      implicit none

!-----------------------------------------------------------------
!        ... Dummy args
!-----------------------------------------------------------------
      integer, intent(in)   ::   ncol
      real(r8), intent(in)  ::   factor
      real(r8), intent(in)  ::   ko(ncol)
      real(r8), intent(in)  ::   kinf(ncol)
      real(r8), intent(in)  ::   m(ncol)
      real(r8), intent(out) ::   rate(ncol)

!-----------------------------------------------------------------
!        ... Local variables
!-----------------------------------------------------------------
      real(r8)  ::  xpo(ncol)

      xpo(:)  = ko(:) * m(:) / kinf(:)
      rate(:) = ko(:) / (1._r8 + xpo(:))
```

```
      xpo(:)  = log10( xpo(:) )
      xpo(:)  = 1._r8 / (1._r8 + xpo(:)*xpo(:))
      rate(:) = rate(:) * factor**xpo(:)

      end subroutine jpl
```

```
/cam/src/chemistry/pp_trop_strat_mam4_ts2/mo_prod_loss.F90 (197,198)
        loss(k,84) = (rxt(k,321)* y(k,57) +rxt(k,322)* y(k,293) + het_rates(k,25)) &
               * y(k,25)
```

Is it ok to always ignore 'M' as a species in Troe reactions (with it included in the rate constant calculation)?

3 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):

$$
\begin{aligned}
k_{nitrate} &= \left(Xe^{-Y/T}\right)\left(\frac{A(T,[\mathrm{M}],n)}{A(T,[\mathrm{M}],n)+Z}\right) \\
k_{alkoxy} &= \left(Xe^{-Y/T}\right)\left(\frac{Z}{Z+A(T,[\mathrm{M}],n)}\right) \\
A(T,[\mathrm{M}],n) &= \frac{2\times10^{-22}e^{n}[\mathrm{M}]}{1+\frac{2\times10^{-22}e^{n}[\mathrm{M}]}{0.43(T/298)^{-8}}}0.41^{(1+[log(\frac{2\times10^{-22}e^{n}[\mathrm{M}]}{0.43(T/298)^{-8}})]^2)^{-1}}
\end{aligned}
\tag{1}
$$

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):

$$
Z(\alpha_0, n) = A(T = 293\mathrm{K}, [\mathrm{M}] = 2.45\times10^{19}\frac{\mathrm{molec}}{\mathrm{cm}^3}, n)\frac{(1-\alpha_0)}{\alpha_0} \tag{2}
$$

This reaction has been added to Music Box as `BRANCHED`. The usr_ISOPNO3_NOn and usr_ISOPNO3_NOa rate constants can then be calculated according to the above equations with $X = 2.7\times10^{-12}$, $Y = -360$, $\alpha_0 =$

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

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.

4 usr_ISOPZD1O2

```
/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]:

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

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

5 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,
  "kinf_B": -1.5,
  "reactants": {
    "TERPACO3": { },
    "NO2": { },
    "M": { }
  },
  "products": {
    "TERPAPAN": { },
    "M": { }
  }
},
```

and can be rearranged as a Troe reaction:

$$
\begin{aligned}
k &= \frac{k_0[\mathrm{M}]}{1 + k_0[\mathrm{M}]/k_{\mathrm{inf}}} F_C^{(1+1/N[log_{10}(k_0[\mathrm{M}]/k_{\mathrm{inf}})]^2)^{-1}} \\
k_0 &= A_0 e^{\left(\frac{C_0}{T}\right)} \left(\frac{T}{300}\right)^{B_0} \\
k_{inf} &= A_{inf} e^{\left(\frac{C_{inf}}{T}\right)} \left(\frac{T}{300}\right)^{B_{inf}}
\end{aligned}
\tag{4}
$$

where $F_C = 0.6$, $N = 1.0$, $A_0 = 9.7 \times 10^{-29} \times 1.111 \times 10^{28}$, $B_0 = -5.6$, $C_0 = -14000$, $A_{inf} = 9.3 \times 10^{-12} \times 1.111 \times 10^{28}$, $B_{inf} = -1.5$, and $C_{inf} = -14000$.

6 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,
  "kinf_B": -1.5,
  "reactants": {
    "TERPA2CO3": { },
    "NO2": { },
    "M": { }
  },
  "products": {
    "TERPA2PAN": { },
    "M": { }
  }
},
```

and can be rearranged as a Troe reaction:

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

where $F_C = 0.6$, $N = 1.0$, $A_0 = 9.7 \times 10^{-29} \times 1.111 \times 10^{28}$, $B_0 = -5.6$, $C_0 = -14000$, $A_{inf} = 9.3 \times 10^{-12} \times 1.111 \times 10^{28}$, $B_{inf} = -1.5$, and $C_{inf} = -14000$.

7 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,
```

```
      "kinf_B": -1.5,
      "reactants": {
        "TERPA3CO3": { },
        "NO2": { },
        "M": { }
      },
      "products": {
        "TERPA3PAN": { },
        "M": { }
      }
    },
```

and can be rearranged as a Troe reaction:

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

where $F_C = 0.6$, $N = 1.0$, $A_0 = 9.7 \times 10^{-29} \times 1.111 \times 10^{28}$, $B_0 = -5.6$, $C_0 = -14000$, $A_{inf} = 9.3 \times 10^{-12} \times 1.111 \times 10^{28}$, $B_{inf} = -1.5$, and $C_{inf} = -14000$.

8 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 `BRANCHED` reaction:

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

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

9 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.