Custom Rate Constants - Beyond TS1 and TS2

Matt Dawson

May 13, 2021

1 Introduction

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

2 usr_MCO3_XNO2

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (796,796)
       tp(:)             = 300._r8 * tinv(:)


/cam/src/chemistry/mozart/mo_usrrxt.F90 (958,966)
!-----------------------------------------------------------------
!     ... mco3 + no2 -> mpan
!-----------------------------------------------------------------
       if( usr_MCO3_NO2_ndx > 0 ) then
          rxt(:,k,usr_MCO3_NO2_ndx) = 1.1e-11_r8 * tp(:) / m(:,k)
       end if
       if( usr_MCO3_XNO2_ndx > 0 ) then
          rxt(:,k,usr_MCO3_XNO2_ndx) = 1.1e-11_r8 * tp(:) / m(:,k)
       end if
```

As discussed in the TS1 document sections 11 and 19, this appears to have been replaced by a Troe reaction. The proposed reworking of this function (TS1 section 19) included removing M from the reactants and products and using a standard Arrhenius reaction:

$$k = Ae^{(\frac{C}{T})}(\frac{T}{D})^B(1.0 + E \times P), \tag{1}$$

with $A = 1.1 \times 10^{-11}$, $B = -1$, $C = 0$, $D = 300$, and $E = 0$.

However, it appears that the CAM preprocessor may ignore M as a reactant, meaning that this reaction would require a new reaction type in Music Box.

Should a new reaction type be added to Music Box for this reaction? Or is this no longer used?

3 usr_XOOH_OH

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (1046,1052)
!-----------------------------------------------------------------
!       ... xooh + oh -> h2o + oh
!-----------------------------------------------------------------
       if( usr_XOOH_OH_ndx > 0 ) then
          call comp_exp( exp_fac, 253._r8*tinv, ncol )
          rxt(:,k,usr_XOOH_OH_ndx) = temp(:ncol,k)**2._r8 * 7.69e-17_r8 * exp_fac(:)
       end if
```

This can be rearranged as an Arrhenius reaction:

$$k = Ae^{(\frac{C}{T})}(\frac{T}{D})^B(1.0 + E \times P), \tag{2}$$

with $A = 7.69 \times 10^{-17}$, $B = 2$, $C = 253$, $D = 1$, and $E = 0$.

4 usr_OA_O2

/cam/src/chemistry/mozart/mo_usrrxt.F90 (800,808)

```
!-----------------------------------------------------------------
! ... o + o2 + m --> o3 + m (JPL15-10)
!-----------------------------------------------------------------
       if( usr_O_O2_ndx > 0 ) then
          rxt(:,k,usr_O_O2_ndx) = 6.e-34_r8 * tp(:)**2.4_r8
       end if
       if( usr_OA_O2_ndx > 0 ) then
          rxt(:,k,usr_OA_O2_ndx) = 6.e-34_r8 * tp(:)**2.4_r8
       end if
```

Same as `usr_O_O2` (TS1 section 5).

5 usr_XNO2NO3_M and usr_NO2XNO3_M

/cam/src/chemistry/mozart/mo_usrrxt.F90 (849,875)

```
!-----------------------------------------------------------------
! ... n2o5 + m --> no2 + no3 + m (JPL15-10)
!-----------------------------------------------------------------
       if( usr_N2O5_M_ndx > 0 ) then
          if( tag_NO2_NO3_ndx > 0 ) then
             call comp_exp( exp_fac, -10840.0_r8*tinv, ncol )
             rxt(:,k,usr_N2O5_M_ndx) = rxt(:,k,tag_NO2_NO3_ndx) * 1.724138e26_r8 * exp_fac(:)
          else
             rxt(:,k,usr_N2O5_M_ndx) = 0._r8
          end if
       end if
       if( usr_XNO2NO3_M_ndx > 0 ) then
          if( tag_NO2_NO3_ndx > 0 ) then
             call comp_exp( exp_fac, -10840.0_r8*tinv, ncol )
             rxt(:,k,usr_XNO2NO3_M_ndx) = rxt(:,k,tag_NO2_NO3_ndx) *1.724138e26_r8 * exp_fac(:)
          else
             rxt(:,k,usr_XNO2NO3_M_ndx) = 0._r8
          end if
       end if
       if( usr_NO2XNO3_M_ndx > 0 ) then
          if( tag_NO2_NO3_ndx > 0 ) then
             call comp_exp( exp_fac, -10840.0_r8*tinv, ncol )
             rxt(:,k,usr_NO2XNO3_M_ndx) = rxt(:,k,tag_NO2_NO3_ndx) * 1.734138e26_r8 * exp_fac(:)
          else
             rxt(:,k,usr_NO2XNO3_M_ndx) = 0._r8
          end if
       end if
```

Same as `usr_N2O5_M` (TS1 section 7)

6 usr_XHNO3_OH

/cam/src/chemistry/mozart/mo_usrrxt.F90 (877,897)

```
!-----------------------------------------------------------------
! set rates for:
!   ... hno3 + oh --> no3 + h2o
!           ho2no2 + m --> ho2 + no2 + m
!-----------------------------------------------------------------
       if( usr_HNO3_OH_ndx > 0 ) then
```

```
         call comp_exp( exp_fac, 1335._r8*tinv, ncol )
         ko(:) = m(:,k) * 6.5e-34_r8 * exp_fac(:)
         call comp_exp( exp_fac, 2199._r8*tinv, ncol )
         ko(:) = ko(:) / (1._r8 + ko(:)/(2.7e-17_r8*exp_fac(:)))
         call comp_exp( exp_fac, 460._r8*tinv, ncol )
         rxt(:,k,usr_HNO3_OH_ndx) = ko(:) + 2.4e-14_r8*exp_fac(:)
      end if
      if( usr_XHNO3_OH_ndx > 0 ) then
         call comp_exp( exp_fac, 1335._r8*tinv, ncol )
         ko(:) = m(:,k) * 6.5e-34_r8 * exp_fac(:)
         call comp_exp( exp_fac, 2199._r8*tinv, ncol )
         ko(:) = ko(:) / (1._r8 + ko(:)/(2.7e-17_r8*exp_fac(:)))
         call comp_exp( exp_fac, 460._r8*tinv, ncol )
         rxt(:,k,usr_XHNO3_OH_ndx) = ko(:) + 2.4e-14_r8*exp_fac(:)
      end if
```

Same as `usr_HNO3_OH` (TS1 section 18).

7 usr_XHO2NO2_M

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (898,913)
      if( usr_HO2NO2_M_ndx > 0 ) then
         if( tag_NO2_HO2_ndx > 0 ) then
            call comp_exp( exp_fac, -10900._r8*tinv, ncol )
            rxt(:,k,usr_HO2NO2_M_ndx) = rxt(:,k,tag_NO2_HO2_ndx) * exp_fac(:) / 2.1e-27_r8
         else
            rxt(:,k,usr_HO2NO2_M_ndx) = 0._r8
         end if
      end if
      if( usr_XHO2NO2_M_ndx > 0 ) then
         if( tag_NO2_HO2_ndx > 0 ) then
            call comp_exp( exp_fac, -10900._r8*tinv, ncol )
            rxt(:,k,usr_XHO2NO2_M_ndx) = rxt(:,k,tag_NO2_HO2_ndx) * exp_fac(:) / 2.1e-27_r8
         else
            rxt(:,k,usr_XHO2NO2_M_ndx) = 0._r8
         end if
      end if
```

Same as `usr_HO2NO2_M` (TS1 section 8).

8 usr_XPAN_M

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (968,985)
!-----------------------------------------------------------------
! ... pan + m --> ch3co3 + no2 + m (JPL15-10)
!-----------------------------------------------------------------
      call comp_exp( exp_fac, -14000._r8*tinv, ncol )
      if( usr_PAN_M_ndx > 0 ) then
         if( tag_CH3CO3_NO2_ndx > 0 ) then
            rxt(:,k,usr_PAN_M_ndx) = rxt(:,k,tag_CH3CO3_NO2_ndx) * 1.111e28_r8 * exp_fac(:)
         else
            rxt(:,k,usr_PAN_M_ndx) = 0._r8
         end if
      end if
      if( usr_XPAN_M_ndx > 0 ) then
         if( tag_CH3CO3_NO2_ndx > 0 ) then
            rxt(:,k,usr_XPAN_M_ndx) = rxt(:,k,tag_CH3CO3_NO2_ndx) * 1.111e28_r8 * exp_fac(:)
```

```
      else
         rxt(:,k,usr_XPAN_M_ndx) = 0._r8
      end if
   end if
```

Same as `usr_PAN_M` (TS1 section 17).

9 usr_XMPAN_M

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (987,1003)
!-----------------------------------------------------------------
! ... mpan + m --> mco3 + no2 + m (JPL15-10)
!-----------------------------------------------------------------
   if( usr_MPAN_M_ndx > 0 ) then
      if( tag_MCO3_NO2_ndx > 0 ) then
         rxt(:,k,usr_MPAN_M_ndx) = rxt(:,k,tag_MCO3_NO2_ndx) * 1.111e28_r8 * exp_fac(:)
      else
         rxt(:,k,usr_MPAN_M_ndx) = 0._r8
      end if
   end if
   if( usr_XMPAN_M_ndx > 0 ) then
      if( tag_MCO3_NO2_ndx > 0 ) then
         rxt(:,k,usr_XMPAN_M_ndx) = rxt(:,k,tag_MCO3_NO2_ndx) * 1.111e28_r8 * exp_fac(:)
      else
         rxt(:,k,usr_XMPAN_M_ndx) = 0._r8
      end if
   end if
```

Same as `usr_MPAN_M` (TS1 section 11).

10 usr_C2O3_NO2

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (1444,1449)
   if ( usr_C2O3_NO2_ndx > 0 ) then
      ko(:)   = 2.6e-28_r8 * m(:,k)
      kinf(:) = 1.2e-11_r8
      rxt(:,k,usr_C2O3_NO2_ndx) = (ko/(1._r8+ko/kinf)) * 0.6_r8**(1._r8/(1._r8+(log10(ko/kinf))**2))
   end if
```

This is a Troe reaction:

$$
\begin{aligned}
k &= \frac{k_0[\mathrm{M}]}{1 + k_0[\mathrm{M}]/k_{\mathrm{inf}}} F_C^{(1+1/N[log_{10}(k_0[\mathrm{M}]/k_{\mathrm{inf}})]^2)^{-1}} \\
k_0 &= A_0 e^{\left(\frac{C_0}{T}\right)} \left(\frac{T}{300}\right)^{B_0} \\
k_{inf} &= A_{inf} e^{\left(\frac{C_{inf}}{T}\right)} \left(\frac{T}{300}\right)^{B_{inf}}
\end{aligned}
\tag{3}
$$

where $F_C = 0.6$, $N = 1$, $A_0 = 2.6 \times 10^{-28}$, $B_0 = 0$, $C_0 = 0$, $A_{inf} = 1.2 \times 10^{-11}$, $B_{inf} = 0$, and $C_{inf} = 0$.

11 usr_C2H4_OH

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (1454,1458)
   if ( usr_C2H4_OH_ndx > 0 ) then
```

```
      ko(:)   = 1.0e-28_r8 * m(:,k)
      kinf(:) = 8.8e-12_r8
      rxt(:,k,usr_C2H4_OH_ndx) = (ko/(1._r8+ko/kinf)) * 0.6_r8**(1._r8/(1._r8+(log(ko/kinf))**2))
   end if
```

This is 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 $F_C = 0.6$, $N = 1$, $A_0 = 1.0 \times 10^{-28}$, $B_0 = 0$, $C_0 = 0$, $A_{inf} = 8.8 \times 10^{-12}$, $B_{inf} = 0$, and $C_{inf} = 0$.

12 usr_XO2N_HO2

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (1459,1461)
      if ( usr_XO2N_HO2_ndx > 0 ) then
         rxt(:,k,usr_XO2N_HO2_ndx) = rxt(:,k,tag_XO2N_NO_ndx)* (continued)
           rxt(:,k,tag_XO2_HO2_ndx)/(rxt(:,k,tag_XO2_NO_ndx)+1.e-36_r8)
      end if
```

Looking through the Chemistry Café, the `tag_XO2_HO2_ndx` appears to be an Arrhenius reaction with $A = 8 \times 10^{-13}$ and $C = 700$, and the `tag_XO2_NO_ndx` appears to also be an Arrhenius reaction with $A = 2.7 \times 10^{-12}$ and $C = 360$, but I can't find anything corresponding to `tag_XO2N_NO_ndx` in the database or the mechanisms that are stored with the CAM source code.

How should this rate constant be calculated?

13 usr_C2O3_XNO2

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (1449,1453)
      if ( usr_C2O3_XNO2_ndx > 0 ) then
         ko(:)   = 2.6e-28_r8 * m(:,k)
         kinf(:) = 1.2e-11_r8
         rxt(:,k,usr_C2O3_XNO2_ndx) = (ko/(1._r8+ko/kinf)) * 0.6_r8**(1._r8/(1._r8+(log10(ko/kinf))**2))
      end if
```

This is 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 $F_C = 0.6$, $N = 1$, $A_0 = 2.6 \times 10^{-28}$, $B_0 = 0$, $C_0 = 0$, $A_{inf} = 1.2 \times 10^{-11}$, $B_{inf} = 0$, and $C_{inf} = 0$.

14 usr_CLm_H2O_M

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (1909,1910)
        call comp_exp( exp_fac, -6600._r8 * tinv, ncol )
        rxt(:,k,usr_clm_h2o_m_ndx) = 2.e-8_r8 * exp_fac(:)
```

This is an Arrhenius reaction:

$$k = Ae^{(\frac{C}{T})}(\frac{T}{D})^B(1.0 + E \times P), \tag{6}$$

with $A = 2 \times 10^{-8}$, $B = 0$, $C = -6600$, and $E = 0$.

15 usr_CLm_HCL_M

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (1912,1913)
        call comp_exp( exp_fac, -11926._r8 * tinv, ncol )
        rxt(:,k,usr_clm_hcl_m_ndx) =  tinv(:) * exp_fac(:)
```

This is an Arrhenius reaction:

$$k = Ae^{(\frac{C}{T})}(\frac{T}{D})^B(1.0 + E \times P), \tag{7}$$

with $A = 1$, $B = -1$, $C = -11926$, $D = 1$, and $E = 0$.

16 usr_oh_co

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (796,796)
       tp(:)              = 300._r8 * tinv(:)
```

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (1757,1770)
       !-----------------------------------------------------------------------
       !     ... CO + OH --> CO2 + HO2
       !-----------------------------------------------------------------------
       if ( usr_oh_co_ndx > 0 ) then
          ko(:)     = 5.9e-33_r8 * tp(:)**1.4_r8
          kinf(:)   = 1.1e-12_r8 * (temp(:ncol,k) / 300._r8)**1.3_r8
          ko_m(:)   = ko(:) * m(:,k)
          k0(:)     = 1.5e-13_r8 * (temp(:ncol,k) / 300._r8)**0.6_r8
          kinf_m(:) = (2.1e+09_r8 * (temp(:ncol,k) / 300._r8)**6.1_r8) / m(:,k)
          rxt(:,k,usr_oh_co_ndx) = (ko_m(:)/(1._r8+(ko_m(:)/kinf(:)))) * &
               0.6_r8**(1._r8/(1._r8+(log10(ko_m(:)/kinf(:)))**2._r8)) + &
               (k0(:)/(1._r8+(k0(:)/kinf_m(:)))) * &
               0.6_r8**(1._r8/(1._r8+(log10(k0(:)/kinf_m(:)))**2._r8))
       endif
```

This rate constant is the sum of a Troe rate constant:

$$\begin{aligned} k &= \frac{k_0[\mathrm{M}]}{1 + k_0[\mathrm{M}]/k_{\mathrm{inf}}} F_C^{(1+1/N[log_{10}(k_0[\mathrm{M}]/k_{\mathrm{inf}})]^2)^{-1}} \\ k_0 &= A_0 e^{(\frac{C_0}{T})} \left(\frac{T}{300}\right)^{B_0} \\ k_{inf} &= A_{inf} e^{\left(\frac{C_{inf}}{T}\right)} \left(\frac{T}{300}\right)^{B_{inf}} \end{aligned} \tag{8}$$

where $F_C = 0.6$, $N = 1$, $A_0 = 5.9 \times 10^{-33}$, $B_0 = -1.4$, $C_0 = 0$, $A_{inf} = 1.1 \times 10^{-12}$, $B_{inf} = 1.3$, and $C_{inf} = 0$, and a ternary chemical activation rate constant:

$$
\begin{aligned}
k &= \frac{k_0}{1 + k_0[\mathrm{M}]/k_{\mathrm{inf}}} F_C^{(1+1/N[log_{10}(k_0[\mathrm{M}]/k_{\mathrm{inf}})]^2)^{-1}} \\
k_0 &= A_0 e^{\left(\frac{C_0}{T}\right)} \left(\frac{T}{300}\right)^{B_0} \\
k_{inf} &= A_{inf} e^{\left(\frac{C_{inf}}{T}\right)} \left(\frac{T}{300}\right)^{B_{inf}}
\end{aligned}
\tag{9}
$$

where $F_C = 0.6$, $N = 1$, $A_0 = 1.5 \times 10^{-13}$, $B_0 = 0.6$, $C_0 = 0$, $A_{inf} = 2.1 \times 10^{9}$, $B_{inf} = 6.1$, and $C_{inf} = 0$.

17 usr_oh_dms

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (1777,1784)
      !-----------------------------------------------------------------------
      !     ... DMS + OH --> 0.75 SO2 + 0.25 MSA
      !-----------------------------------------------------------------------
      if ( usr_oh_dms_ndx > 0 ) then
         o2(:ncol) = invariants(:ncol,k,inv_o2_ndx)
         rxt(:,k,usr_oh_dms_ndx) = 2.000e-10_r8 * exp(5820.0_r8 * tinv(:)) / &
              ((2.000e29_r8 / o2(:)) + exp(6280.0_r8 * tinv(:)))
      endif
```

This does not appear to fit any existing reaction types.

Should this be added as a reaction type to Music Box? If so, is there a reference to use for the documentation?

18 usr_COhc_OH, usr_COme_OH and usr_CO01_OH–usr_CO42_OH

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (1777,1784)
!-----------------------------------------------------------------
!      ... CO tags
!-----------------------------------------------------------------
      if( usr_CO_OH_b_ndx > 0 ) then
         if( usr_COhc_OH_ndx > 0 ) then
            rxt(:ncol,:,usr_COhc_OH_ndx) = rxt(:ncol,:,usr_CO_OH_b_ndx)
         end if
         if( usr_COme_OH_ndx > 0 ) then
            rxt(:ncol,:,usr_COme_OH_ndx) = rxt(:ncol,:,usr_CO_OH_b_ndx)
         end if
         if( usr_CO01_OH_ndx > 0 ) then
            rxt(:ncol,:,usr_CO01_OH_ndx) = rxt(:ncol,:,usr_CO_OH_b_ndx)
         end if
         if( usr_CO02_OH_ndx > 0 ) then
            rxt(:ncol,:,usr_CO02_OH_ndx) = rxt(:ncol,:,usr_CO_OH_b_ndx)
         end if

         ...

         if( usr_CO41_OH_ndx > 0 ) then
            rxt(:ncol,:,usr_CO41_OH_ndx) = rxt(:ncol,:,usr_CO_OH_b_ndx)
         end if
```

```
if( usr_CO42_OH_ndx > 0 ) then
   rxt(:ncol,:,usr_CO42_OH_ndx) = rxt(:ncol,:,usr_CO_OH_b_ndx)
end if
```

Same as `usr_CO_OH_b` (TS1 section 23).