TS1 Custom Rate Constants

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1 Introduction

To output chemical mechanisms from the Chemistry Café in Music Box format, the custom rate constants in CAM need to be addressed individually and either rearranged into one or more standard Music Box reaction types, or used to create new reaction types in Music Box. For now aerosol surface reactions will be ignored. For the gas-phase reactions of the TS1 mechanism, it appears that all but one reaction that uses a custom rate constant can be rearranged into sets of standard Music Box reactions. The one remaining reaction has been added to Music Box as the 'ternary chemical activation' reaction type.

The following sections present the original rate constant functions for all non-standard gas-phase TS1 reactions from `cam/src/chemistry/mozart/mo_usrrxt.F90`, include notes I made as I navigated this code for the first time, and present a proposed refactoring into standard Music Box reaction types.

2 usr_DMS_OH

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (1062,1070)
!----------------------------------------------------------------
!       ... DMS + OH  --> .5 * SO2
!----------------------------------------------------------------
      if( usr_DMS_OH_ndx > 0 ) then
         call comp_exp( exp_fac, 7460._r8*tinv, ncol )
         ko(:) = 1._r8 + 5.5e-31_r8 * exp_fac * m(:,k) * 0.21_r8
         call comp_exp( exp_fac, 7810._r8*tinv, ncol )
         rxt(:,k,usr_DMS_OH_ndx) = 1.7e-42_r8 * exp_fac * m(:,k) * 0.21_r8 / ko(:)
      end if
```

This is equivalent to:

$$k = \frac{1.7 \times 10^{-42} e^{\frac{7810}{T}} [\mathrm{M}] 0.21}{1 + 5.5 \times 10^{-31} e^{\frac{7460}{T}} [\mathrm{M}] 0.21} \tag{1}$$

This can be rearranged as a Troe reaction,

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

where $F_C = 1$, $A_0 = 0.21 \times 1.7 \times 10^{-42}$, $B_0 = 0$, $C_0 = 7810$, $A_{inf} = \frac{1.7 \times 10^{-42}}{5.5 \times 10^{-31}}$, $B_{inf} = 0$, and $C_{inf} = 7810 - 7460$.

3 usr_GLYOXAL_aer

Aerosol surface reaction

4 usr_PBZNIT_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 (1006,1015)
!-----------------------------------------------------------------
!       ... pbznit + m --> acbzo2 + no2 + m
!-----------------------------------------------------------------
       if( usr_PBZNIT_M_ndx > 0 ) then
          if( tag_ACBZO2_NO2_ndx > 0 ) then
             rxt(:,k,usr_PBZNIT_M_ndx) = rxt(:,k,tag_ACBZO2_NO2_ndx) * 1.111e28_r8 * exp_fac(:)
          else
             rxt(:,k,usr_PBZNIT_M_ndx) = 0._r8
          end if
       end if
```

The reaction rates set in `mo_usrrxt::usrrxt()` do not appear to include those for `tag_ACBZO2_NO2_ndx`. As the `rxt(:,:)` array is an `intent(inout)` argument, it could already contain this rate when the function is called. The `mo_usrrxt::usrrxt()` function is called by `mo_gas_phase_chemdr::gas_phase_chemdr()`, which declares and initializes an array called `reaction_rates(:,:,:)` which is passed to `mo_usrrxt::usrrxt()` as `rxt(:,:)`. Prior to calling `mo_usrrxt::usrrxt()`, the functions `ratecon_sfstrat()` and `mo_setrxt::setrxt()` are called, passing `reaction_rates(:,:,:)` as an argument:

```
cam/src/chemistry/mozart/mo_gas_phase_chemdr.F90 (242,252)
!-----------------------------------------------------------------------
!-----------------------------------------------------------------------
  subroutine gas_phase_chemdr(lchnk, ncol, imozart, q, &
                              phis, zm, zi, calday, &
                              tfld, pmid, pdel, pint,  &
                              cldw, troplev, troplevchem, &
                              ncldwtr, ufld, vfld,  &
                              delt, ps, xactive_prates, &
                              fsds, ts, asdir, ocnfrac, icefrac, &
                              precc, precl, snowhland, ghg_chem, latmapback, &
                              drydepflx, wetdepflx, cflx, fire_sflx, fire_ztop, nhx_nitrogen_flx, noy_nitrogen_flx,

...

cam/src/chemistry/mozart/mo_gas_phase_chemdr.F90 (387,387)
    real(r8)     ::  reaction_rates(ncol,pver,max(1,rxntot))      ! reaction rates

...

cam/src/chemistry/mozart/mo_gas_phase_chemdr.F90 (487,488)
    ! initialize to NaN to hopefully catch user defined rxts that go unset
    reaction_rates(:,:,:) = nan

...

cam/src/chemistry/mozart/mo_gas_phase_chemdr.F90 (705,712)
       !-----------------------------------------------------------------------
       !        ... call aerosol reaction rates
       !-----------------------------------------------------------------------
       call ratecon_sfstrat( ncol, invariants(:,:,indexm), pmid, tfld, &
            radius_strat(:,:,1), sad_strat(:,:,1), sad_strat(:,:,2), &
            sad_strat(:,:,3), h2ovmr, vmr, reaction_rates, &
            gprob_n2o5, gprob_cnt_hcl, gprob_cnt_h2o, gprob_bnt_h2o, &
            gprob_hocl_hcl, gprob_hobr_hcl, wtper )

...

cam/src/chemistry/mozart/mo_gas_phase_chemdr.F90 (735,738)
    !-----------------------------------------------------------------------
```

```
!       ...  Set rates for "tabular" and user specified reactions
!-----------------------------------------------------------------------
call setrxt( reaction_rates, tfld, invariants(1,1,indexm), ncol )
```

...

```
cam/src/chemistry/mozart/mo_gas_phase_chemdr.F90 (774,776)
    call usrrxt( reaction_rates, tfld, ion_temp_fld, ele_temp_fld, invariants, h2ovmr, &
                 pmid, invariants(:,:,indexm), sulfate, mmr, relhum, strato_sad, &
                 troplevchem, dlats, ncol, sad_trop, reff, cwat, mbar, pbuf )
```

There are a number of different definitions of the `mo_setrxt` module, presumably for different model configurations, which must be chosen in some way during the build process. Each of these modules appears to set different rates, with hard-coded indices and no description of what these rates correspond to. For example, the `mo_setrxt::setrxt()` function sets four rates:

```
components/cam/src/chemistry/pp_trop_mam7/mo_setrxt.F90 (38,41)
      rate(:,:,3) = 2.9e-12_r8 * exp( -160._r8 * itemp(:,:) )
      rate(:,:,5) = 9.6e-12_r8 * exp( -234._r8 * itemp(:,:) )
      rate(:,:,7) = 1.9e-13_r8 * exp( 520._r8 * itemp(:,:) )
      rate(:,:,8) = 1.7e-12_r8 * exp( -710._r8 * itemp(:,:) )
```

Is there a way to know what reaction rates these indices correspond to?

I will assume that these modules are written by some pre-processor and hope that the rate they set for whatever index corresponds to `tag_ACBZO2_NO2_ndx` is based on the following reaction that appears in the TS1 mechanism:

```
{
  "type": "TROE",
  "k0_A": 9.7e-29,
  "k0_B": -5.6,
  "kinf_A": 9.3e-12,
  "N": 1.5,
  "Fc": 0.6,
  "reactants": {
    "ACBZO2": { },
    "NO2": { },
    "M": { }
  },
  "products": {
    "PBZNIT": { },
    "M": { }
  }
},
```

as this is the only reaction with `ACBZO2` and `NO2` as reactants. If this is the case, the `usr_PBZNIT_M` rate is:

$$
\begin{aligned}
k &= \frac{k_0[\mathrm{M}]}{1 + k_0[\mathrm{M}]/k_{\mathrm{inf}}} F_C^{(1+1/N[log_{10}(k_0[\mathrm{M}]/k_{\mathrm{inf}})]^2)^{-1}} 1.111 \times 10^{28} e^{\left(\frac{-14000}{T}\right)} \\
k_0 &= A_0 e^{\left(\frac{C_0}{T}\right)} \left(\frac{T}{300}\right)^{B_0} \\
k_{inf} &= A_{inf} e^{\left(\frac{C_{inf}}{T}\right)} \left(\frac{T}{300}\right)^{B_{inf}}
\end{aligned}
\tag{3}
$$

where $F_C = 0.6$, $N = 1.5$, $A_0 = 9.7 \times 10^{-29}$, $B_0 = -5.6$, $C_0 = 0$, $A_{inf} = 9.3 \times 10^{-12}$, $B_{inf} = 0$, and $C_{inf} = 0$. This can be rearranged into a Troe reaction as:

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

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

5 usr_O_O2

```
cam/src/chemistry/mozart/mo_usrrxt.F90 (799,807)
      tp(:)             = 300._r8 * tinv(:)

...

cam/src/chemistry/mozart/mo_usrrxt.F90 (799,807)
!-----------------------------------------------------------------
! ... 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
```

This is equivalent to:

$$
k = 6.0 \times 10^{-34} \left(\frac{300}{T}\right)^{2.4}, \tag{5}
$$

which can be rearranged into an Arrhenius reaction as:

$$
k = A e^{\left(\frac{-E_a}{k_b T}\right)} \left(\frac{T}{D}\right)^{B} (1.0 + E \times P), \tag{6}
$$

with $A = 6.0 \times 10^{-34}$, $B = -2.4$, $E_a = 0$, $D = 300$, and $E = 0$.

6 usr_HO2_aer

Aerosol surface reaction

7 usr_N2O5_M

```
cam/src/chemistry/mozart/mo_usrrxt.F90 (849,859)
!-----------------------------------------------------------------
! ... 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
```

Following the same logic as for `usr_PBZNIT_M`, the `tag_NO2_NO3_ndx` reaction is identified as:

```
{
  "type": "TROE",
  "k0_A": 2.4e-30,
  "k0_B": -3,
  "kinf_A": 1.6e-12,
  "N": -0.1,
  "Fc": 0.6,
  "reactants": {
    "NO3": { },
    "NO2": { },
    "M": { }
  },
  "products": {
    "N2O5": { },
    "M": { }
  }
},
```

and can be rearranged as a Troe reaction:

$$
\begin{aligned}
k &= \frac{k_0[\mathrm{M}]}{1 + k_0[\mathrm{M}]/k_{\mathrm{inf}}} F_C^{(1+1/N[log_{10}(k_0[\mathrm{M}]/k_{\mathrm{inf}})]^2)^{-1}} \\
k_0 &= A_0 e^{\left(\frac{C_0}{T}\right)} \left(\frac{T}{300}\right)^{B_0} \\
k_{inf} &= A_{inf} e^{\left(\frac{C_{inf}}{T}\right)} \left(\frac{T}{300}\right)^{B_{inf}}
\end{aligned}
\tag{7}
$$

where $F_C = 0.6$, $N = -0.1$, $A_0 = 2.4 \times 10^{-30} \times 1.724138 \times 10^{26}$, $B_0 = -3$, $C_0 = -10840$, $A_{inf} = 1.6 \times 10^{-12} \times 1.724138 \times 10^{26}$, $B_{inf} = 0$, and $C_{inf} = -10840$.

8 usr_HO2NO2_M

```
cam/src/chemistry/mozart/mo_usrrxt.F90 (898,905)
      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
```

Following the same logic as for `usr_PBZNIT_M`, the `tag_NO2_HO2_ndx` reaction is identified as:

```
{
  "type": "TROE",
  "k0_A": 1.9e-31,
  "k0_B": -3.4,
  "kinf_A": 4e-12,
```

```
      "N": 0.3,
      "Fc": 0.6,
      "reactants": {
        "NO2": { },
        "HO2": { },
        "M": { }
      },
      "products": {
        "HO2NO2": { },
        "M": { }
      }
    },
```

and can be rearranged as a Troe reaction:

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

where $F_C = 0.6$, $N = 0.3$, $A_0 = 1.9 \times 10^{-31} / \left(2.1 \times 10^{-27}\right)$, $B_0 = -3.4$, $C_0 = -10900$, $A_{inf} = 4 \times 10^{-12} / \left(2.1 \times 10^{-27}\right)$, $B_{inf} = 0$, and $C_{inf} = -10900$.

9 usr_NO3_aer

Aerosol surface reaction

10 usr_HO2_HO2

```
cam/src/chemistry/mozart/mo_usrrxt.F90 (2212,2219)
!-----------------------------------------------------------------
! ... ho2 + ho2 --> h2o2
! Note: this rate involves the water vapor number density
!-----------------------------------------------------------------
         ko(:)   = 3.0e-13_r8  * exp( 460._r8*tinv(:) )
         kinf(:) = 2.1e-33_r8 * m(:,k) * exp( 920._r8*tinv(:) )
         fc(:)   = 1._r8 + 1.4e-21_r8 * m(:,k) * h2ovmr(:,k) * exp( 2200._r8*tinv(:) )
         rxt(:,k,usr_HO2_HO2_ndx) = (ko(:) + kinf(:)) * fc(:)
```

The term `m(:,k) * h2ovmr(:,k)` should be the water vapor number density (assuming `h2ovmr(:,k)` is in units of mol/mol). This reaction can then be rearranged as four reactions:

$$
\begin{aligned}
&\mathrm{HO_2} + \mathrm{HO_2} \longrightarrow \mathrm{H_2O_2} \\
&\mathrm{HO_2} + \mathrm{HO_2} \xrightarrow{\mathrm{M}} \mathrm{H_2O_2} \\
&\mathrm{HO_2} + \mathrm{HO_2} \xrightarrow{\mathrm{H_2O}} \mathrm{H_2O_2} \\
&\mathrm{HO_2} + \mathrm{HO_2} \xrightarrow{\mathrm{M,H_2O}} \mathrm{H_2O_2}
\end{aligned}
$$

with Arrhenius rate constants:

$$k = Ae^{(\frac{C}{T})}(\frac{T}{D})^B(1.0 + E \times P), \tag{9}$$

with rate constant parameters, respectively:

- $A = 3.0 \times 10^{-13}$, $B = 0$, $C = 460$, and $E = 0$.
- $A = 2.1 \times 10^{-33}$, $B = 0$, $C = 920$, and $E = 0$.
- $A = 3.0 \times 10^{-13} \times 1.4 \times 10^{-21}$, $B = 0$, $C = 2660$, and $E = 0$.
- $A = 2.1 \times 10^{-33} \times 1.4 \times 10^{-21}$, $B = 0$, $C = 3120$, and $E = 0$.

11 usr_MPAN_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 (987,996)
!-----------------------------------------------------------------
! ... 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
```

This rate constant calculation appears to be based on the reaction:

$$MCO_3 + NO_2 \xrightarrow{M} MPAN$$

and this reaction in the mechanism has a custom rate constant:

```
{
  "type": "UNSUPPORTED",
  "label": "usr_MCO3_NO2",
  "reactants": {
    "MCO3": { },
    "NO2": { },
    "M": { }
  },
  "products": {
    "MPAN": { },
    "M": { }
  }
},
```

however, the `usr_MPAN_M` reaction uses `tag_MCO3_NO2_ndx` instead of `usr_MCO3_NO2_ndx`, which I believe indicates that this is a standard (Arrhenius or Troe) reaction rather than a custom reaction. Looking through the code, I see that this reaction does appear to sometimes be treated as a Troe reaction:

```
components/cam/src/chemistry/pp_trop_strat_mam4_ts2/chem_mech.doc (1147,1149)
  tag_MCO3_NO2     (240)    MCO3 + NO2 + M ->  MPAN + M                                  troe : ko=9.70E-29*
                                                                                               ki=9.30E-12*
                                                                                                f=0.60
```

After discussion with Louisa and Becky, the Troe reaction for $MCO_3 + NO_2 \xrightarrow{M}$ MPAN is the correct one to use, with $F_c = 0.6$, $N = 1.5$, $A_0 = 9.7 \times 10^{-29}$, $B_0 = -5.6$, $C_0 = 0$, $A_{inf} = 9.3 \times 10^{-12}$, $B_{inf} = 0$, and $C_{inf} = 0$.

This means the `usr_MPAN_M` reaction can be rearranged as a Troe reaction with $F_c = 0.6$, $N = 1.5$, $A_0 = 9.7 \times 10^{-29} \times 1.111 \times 10^{28}$, $B_0 = -5.6$, $C_0 = -14000$, $A_{inf} = 9.3 \times 10^{-12} \times 1.111 \times 10^{28}$, $B_{inf} = 0$, and $C_{inf} = -14000$.

12 usr_SO2_OH

```
cam/src/chemistry/mozart/mo_usrrxt.F90 (1072,1079)
!-----------------------------------------------------------------
!       ... SO2 + OH  --> SO4  (REFERENCE?? - not Liao)
!-----------------------------------------------------------------
       if( usr_SO2_OH_ndx > 0 ) then
          fc(:) = 3.0e-31_r8 *(300._r8*tinv(:))**3.3_r8
          ko(:) = fc(:)*m(:,k)/(1._r8 + fc(:)*m(:,k)/1.5e-12_r8)
          rxt(:,k,usr_SO2_OH_ndx) = ko(:)*.6_r8**(1._r8 + (log10(fc(:)*m(:,k)/1.5e-12_r8))**2._r8)**(-1._r8)
       end if
```

This is a Troe reaction:

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

where $F_C = 0.6$, $N = 1.0$, $A_0 = 3 \times 10^{-31}$, $B_0 = -3.3$, $C_0 = 0$, $A_{inf} = 1.5 \times 10^{-12}$, $B_{inf} = 0$, and $C_{inf} = 0$.

The parameters for this reaction appear to come from DeMore et al. 1997 (`https://jpldataeval.jpl.nasa.gov/pdf/Atmos97_Anotated.pdf` page 129).

13 usr_CO_OH_a

```
cime/src/share/util/shr_const_mod.F90 (24,24)
   real(R8),parameter :: SHR_CONST_BOLTZ   = 1.38065e-23_R8  ! Boltzmann's constant ~ J/K/molecule


cam/src/utils/physconst.F90 (60,60)
real(r8), public, parameter :: boltz       = shr_const_boltz      ! Boltzman's constant (J/K/molecule)


cam/src/chemistry/utils/mo_constants.F90 (25,25)
  real(r8), parameter ::  boltz_cgs   = boltz*1.e7_r8       ! erg/K


cam/src/chemistry/mozart/mo_usrrxt.F90 (914,920)
!-----------------------------------------------------------------
!           co + oh --> co2 + ho2     (combined branches - do not use with CO_OH_b)
!-----------------------------------------------------------------
```

```
if( usr_CO_OH_a_ndx > 0 ) then
   rxt(:,k,usr_CO_OH_a_ndx) = 1.5e-13_r8 * &
        (1._r8 + 6.e-7_r8*boltz_cgs*m(:,k)*temp(:ncol,k))
end if
```

This can be split into two reactions:

$$\mathrm{CO} + \mathrm{OH} \longrightarrow \mathrm{CO_2} + \mathrm{HO_2}$$
$$\mathrm{CO} + \mathrm{OH} \xrightarrow{\mathrm{M}} \mathrm{CO_2} + \mathrm{HO_2}$$

with Arrhenius rate constants:

$$k = Ae^{(\frac{C}{T})}(\frac{T}{D})^B(1.0 + E \times P), \tag{11}$$

with rate constant parameters, respectively:

- $A = 1.5 \times 10^{-13}$, $B = 0$, $C = 0$, and $E = 0$.
- $A = 1.5 \times 10^{-13} \times 6 \times 10^{-7} \times k_B$, $B = 1$, $C = 0$, $D = 1$, and $E = 0$.

where k_B is the Boltzmann constant [erg K^{-1}]. **Watch out for the non-SI unit erg.**

14 usr_O_O

```
cam/src/chemistry/mozart/mo_usrrxt.F90 (810,815)
!-----------------------------------------------------------------
! ... o + o + m -> o2 + m
!-----------------------------------------------------------------
      if ( usr_O_O_ndx > 0 ) then
         rxt(:,k,usr_O_O_ndx) = 2.76e-34_r8 * exp( 720.0_r8*tinv(:) )
      end if
```

This is an Arrhenius reaction:

$$k = Ae^{(\frac{C}{T})}(\frac{T}{D})^B(1.0 + E \times P), \tag{12}$$

with $A = 2.76 \times 10^{-34}$, $B = 0$, $C = 720$, and $E = 0$.

15 usr_N2O5_aer

Aerosol surface reaction

16 usr_NO2_aer

Aerosol surface reaction

17 usr_PAN_M

```
cam/src/chemistry/mozart/mo_usrrxt.F90 (968,978)
!-----------------------------------------------------------------
! ... 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
```

Following the same logic as for `usr_PBZNIT_M`, the `tag_CH3CO3_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,
   "Fc": 0.6,
   "reactants": {
     "CH3CO3": { },
     "NO2": { },
     "M": { }
   },
   "products": {
     "PAN": { },
     "M": { }
   }
 },
```

and can be rearranged as a Troe reaction:

$$
\begin{aligned}
k &= \frac{k_0[\mathrm{M}]}{1 + k_0[\mathrm{M}]/k_{\mathrm{inf}}} F_C^{(1+1/N[log_{10}(k_0[\mathrm{M}]/k_{\mathrm{inf}})]^2)^{-1}} \\
k_0 &= A_0 e^{\left(\frac{C_0}{T}\right)} \left(\frac{T}{300}\right)^{B_0} \\
k_{inf} &= A_{inf} e^{\left(\frac{C_{inf}}{T}\right)} \left(\frac{T}{300}\right)^{B_{inf}}
\end{aligned}
\tag{13}
$$

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 $C_{inf} = -14000$.

18 usr_HNO3_OH

```
cam/src/chemistry/mozart/mo_usrrxt.F90 (877,889)
!-----------------------------------------------------------------
! 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
```

This can be split into two reactions with the same reactants and products:

$$HNO_3 + OH \longrightarrow NO_3 + H_2O$$

the first with an Arrhenius rate constant:

$$k = Ae^{(\frac{C}{T})}(\frac{T}{D})^B(1.0 + E \times P), \tag{14}$$

with $A = 2.4 \times 10^{-14}$, $B = 0$, $C = 460$, and $E = 0$, and the second with a Troe rate constant:

$$\begin{aligned} k &= \frac{k_0[\mathrm{M}]}{1 + k_0[\mathrm{M}]/k_{\mathrm{inf}}} F_C^{(1+1/N[log_{10}(k_0[\mathrm{M}]/k_{\mathrm{inf}})]^2)^{-1}} \\ k_0 &= A_0 e^{(\frac{C_0}{T})} \left(\frac{T}{300}\right)^{B_0} \\ k_{inf} &= A_{inf} e^{\left(\frac{C_{inf}}{T}\right)} \left(\frac{T}{300}\right)^{B_{inf}} \end{aligned} \tag{15}$$

where $F_C = 1$, $A_0 = 6.5 \times 10^{-34}$, $B_0 = 0$, $C_0 = 1335$, $A_{inf} = 2.7 \times 10^{-17}$, $B_{inf} = 0$, and $C_{inf} = 2199$.

19 usr_MCO3_NO2

```
cam/src/chemistry/mozart/mo_usrrxt.F90 (804,804)
      tp(:)             = 300._r8 * tinv(:)
cam/src/chemistry/mozart/mo_usrrxt.F90 (958,996)
!-----------------------------------------------------------------
!     ... 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
```

This can be rearranged as an Arrhenius reaction, **by removing M from the reactants and products**:

$$k = Ae^{(\frac{C}{T})}(\frac{T}{D})^B(1.0 + E \times P), \tag{16}$$

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

20 usr_CH3COCH3_OH

```
cam/src/chemistry/mozart/mo_usrrxt.F90 (1054,1060)
!-----------------------------------------------------------------
!       ... ch3coch3 + oh -> ro2 + h2o
!-----------------------------------------------------------------
      if( usr_CH3COCH3_OH_ndx > 0 ) then
         call comp_exp( exp_fac, -2000._r8*tinv, ncol )
         rxt(:,k,usr_CH3COCH3_OH_ndx) = 3.82e-11_r8 * exp_fac(:) + 1.33e-13_r8
      end if
```

This can be split into two reactions with the same products and reactants:

$$CH_3COCH_3 + OH \longrightarrow RO_2 + H_2O$$

both with Arrhenius rate constants:

$$k = Ae^{(\frac{C}{T})}(\frac{T}{D})^B(1.0 + E \times P), \tag{17}$$

with rate constant parameters:

- $A = 3.82 \times 10^{-11}$, $B = 0$, $C = -2000$, and $E = 0$.
- $A = 1.33 \times 10^{-13}$, $B = 0$, $C = 0$, and $E = 0$.

21 usr_CL2O2_M

```
cam/src/chemistry/mozart/mo_usrrxt.F90 (817,827)
!-----------------------------------------------------------------
!   ... cl2o2 + m -> 2*clo + m  (JPL15-10)
!-----------------------------------------------------------------
      if ( usr_CL2O2_M_ndx > 0 ) then
         if ( tag_CLO_CLO_M_ndx > 0 ) then
            ko(:)            = 2.16e-27_r8 * exp( 8537.0_r8* tinv(:) )
            rxt(:,k,usr_CL2O2_M_ndx) = rxt(:,k,tag_CLO_CLO_M_ndx)/ko(:)
         else
            rxt(:,k,usr_CL2O2_M_ndx) = 0._r8
         end if
      end if
```

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

```
{
  "type": "ARRHENIUS",
  "A": 3e-11,
  "Ea": -3.38259005E-20,
  "reactants": {
    "CLO": { "qty": 2 }
  },
  "products": {
    "CL": { "yield": 2 },
    "O2": { }
  }
},
```

and can be rearranged as an Arrhenius reaction:

$$k = Ae^{(\frac{C}{T})}(\frac{T}{D})^B(1.0 + E \times P), \tag{18}$$

where $A = 3 \times 10^{-11} / \left(2.16 \times 10^{-27}\right)$, $B = 0$, $C = 2450 - 8537$, and $E = 0$.

22 usr_SO3_H2O

```
cam/src/chemistry/mozart/mo_usrrxt.F90 (829,847)
!-----------------------------------------------------------------
```

```
!       ... so3 + 2*h2o --> h2so4 + h2o
!       Note: this reaction proceeds by the 2 intermediate steps below
!           so3 + h2o --> adduct
!           adduct + h2o --> h2so4 + h2o
!               (Lovejoy et al., JCP, pp. 19911-19916, 1996)
! The first order rate constant used here is recommended by JPL 2011.
! This rate involves the water vapor number density.
!-----------------------------------------------------------------

       if ( usr_SO3_H2O_ndx > 0 ) then
          call comp_exp( exp_fac, 6540.0_r8*tinv(:), ncol )
          if( h2o_ndx > 0 ) then
             fc(:) = 8.5e-21_r8 * m(:,k) * h2ovmr(:,k) * exp_fac(:)
          else
             fc(:) = 8.5e-21_r8 * invariants(:,k,inv_h2o_ndx) * exp_fac(:)
          end if
          rxt(:,k,usr_SO3_H2O_ndx) = 1.0e-20_r8 * fc(:)
       end if
```

As for `usr_HO2_HO2`, the term `m(:,k) * h2ovmr(:,k)` is taken to be the water vapor number density. Interestingly, the use of the `invariants` array here when h2o_ndx $<= 0$ is not used in the calculation of `usr_HO2_HO2`.

Should the invariants array be used for the water number density whenever h2o_ndx $<= 0$?

This can be rearranged as:

$$SO_3 + H_2O \xrightarrow{H2O} H_2SO_4$$

with an Arrhenius rate constant:

$$k = Ae^{(\frac{C}{T})}(\frac{T}{D})^B(1.0 + E \times P), \tag{19}$$

where $A = 8.5 \times 10^{-41}$, $B = 0$, $C = 6540$, and $E = 0$.

23 usr_CO_OH_b

```
cam/src/chemistry/mozart/mo_usrrxt.F90 (227,227)
  real(r8), parameter :: t0     = 300._r8               ! K
```

```
cam/src/chemistry/mozart/mo_usrrxt.F90 (829,847)
!-----------------------------------------------------------------
!   ... co + oh --> co2 + h (second branch JPL15-10, with CO+OH+M)
!-----------------------------------------------------------------
       if( usr_CO_OH_b_ndx > 0 ) then
         kinf(:)  = 2.1e+09_r8 * (temp(:ncol,k)/ t0)**(6.1_r8)
         ko  (:)  = 1.5e-13_r8

         term1(:) = ko(:) / ( (kinf(:) / m(:,k)) )
         term2(:) = ko(:) / (1._r8 + term1(:))
```

```
    term1(:) = log10( term1(:) )
    term1(:) = 1.0_r8 / (1.0_r8 + term1(:)*term1(:))

    rxt(:ncol,k,usr_CO_OH_b_ndx) = term2(:) * (0.6_r8)**term1(:)
  end if
```

From JPL15-10, the second branch is:

$$\mathrm{OH + CO \xrightarrow{M} H + CO_2}$$

which "proceed[s] via bound intermediates. For example, the reaction between HO and CO to yield $\mathrm{H + CO_2}$ takes place on a potential energy surface that contains the radical HOCO. The yield of H and $\mathrm{CO_2}$ is diminished as the pressure rises. The loss of reactants is thus the sum of two processes, an association to yield HOCO and the chemical activation process yielding H and CO2. The total rate constant for loss of reactants is fit by the equation above for the association added to the chemical activation rate constant."

The resulting rate constant equation is a Troe rate constant without [M] in the numerator of the first term:

$$\begin{aligned} k &= \frac{k_0}{1 + k_0[\mathrm{M}]/k_{\mathrm{inf}}} F_C^{(1+1/N[log_{10}(k_0[\mathrm{M}]/k_{\mathrm{inf}})]^2)^{-1}} \\ k_0 &= A_0 e^{\left(\frac{C_0}{T}\right)} \left(\frac{T}{300}\right)^{B_0} \\ k_{inf} &= A_{inf} e^{\left(\frac{C_{inf}}{T}\right)} \left(\frac{T}{300}\right)^{B_{inf}} \end{aligned} \tag{20}$$

This reaction type has been added to Music Box as "`TERNARY_CHEMICAL_ACTIVATION`." For this reaction, the rate constant parameters are: $A_0 = 1.5 \times 10^{13}$, $B_0 = 0$, $C_0 = 0$, $A_{inf} = 2.1 \times 10^9$, $B_{inf} = 6.1$, $C_{inf} = 0$, $F_c = 0.6$, and $N = 1$.