

Perhemiacetal Formation and Cl/NO₃-initiated chemistry of Hydroperoxymethylthioformate (HPMTF) in atmospheric DMS oxidation

— Supporting Information —

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A. Energy diagram for formation of thio-perhemiacetal from HPMTF

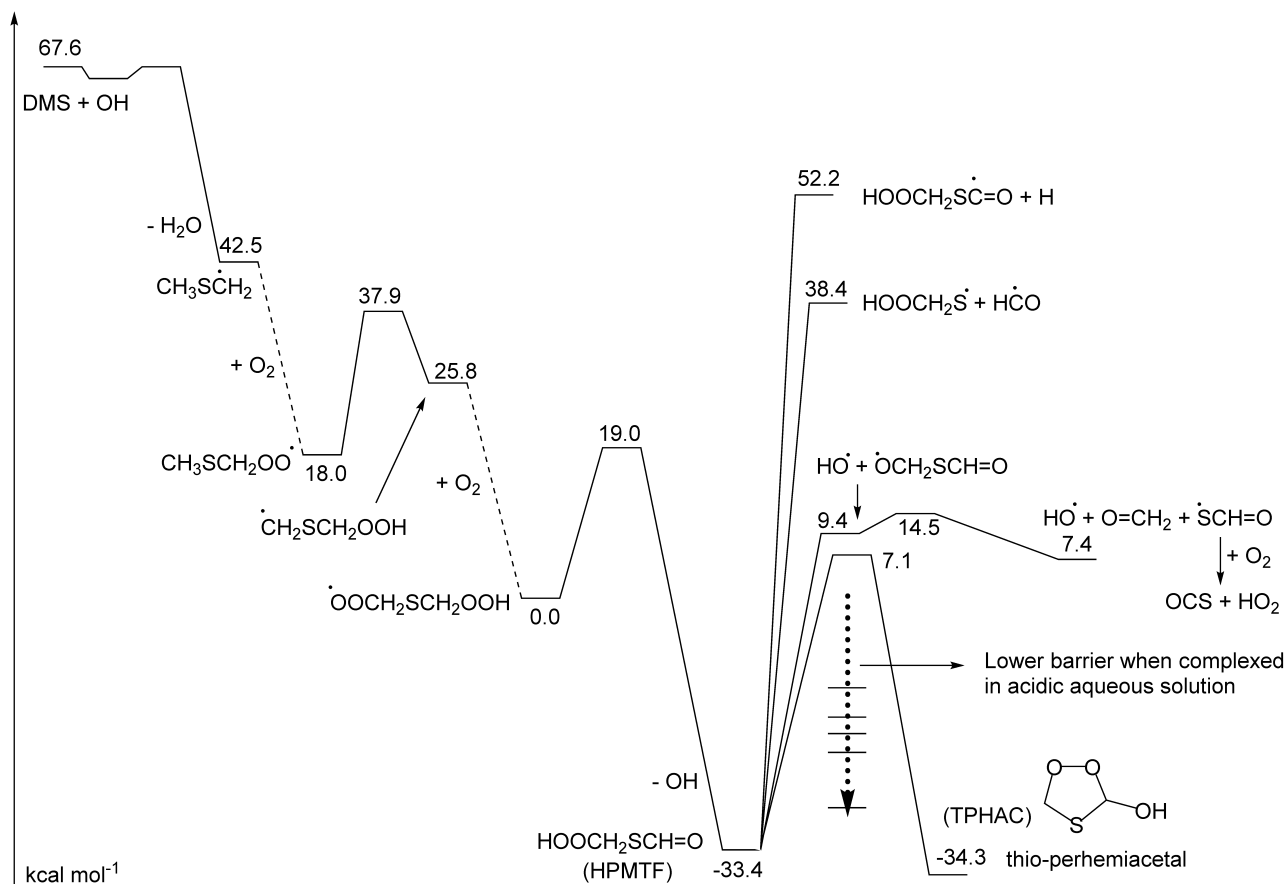


Figure 1S: PES for formation of hydroperoxymethylthioformate (HPMTF) from DMS, and HPMTF isomerisation and dissociation pathways, calculated at the CCSD(T)/aug-cc-pV(Q+d)Z//M06-2X-D3/aug-cc-pV(T+d)Z level of theory in Jernigan et al. (2022) and this work.

B. Replication data for the quantum chemical calculations

The raw quantum chemical data is deposited as a text file under repository link

<https://doi.org/10.26165/JUELICH-DATA/8MYZUY>

This data set provides the quantum chemical data characterizing reactions in the NO₃- and Cl-initiated oxidation of dimethylsulfide (DMS), as well as reactions of hydroperoxymethylthioformate (HPMTF), thio-perhemiacetal (TPHAC), and the OH-initiated oxidation of TPHAC. Geometries and vibrational wavenumbers are obtained at the M06-2X-D3/aug-cc-pV(T+d)Z level of theory, with energies refined at the CCSD(T)/aug-cc-pV(Q+d)Z level of theory. The data also includes partition functions and a Boltzmann population analysis for all conformers at 298 K.

C. Kinetic model for atmospheric DMS oxidation, including HPMTF and TPHAC chemistry

The *a priori* mechanism is provided below, in EASY format.

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#####
; Initiation reactions
#####

; The DMS reaction channels not leading to HPMTF are not shown
k[DMS+OH-->CH3SCH2O2+H2O]=CONST(1.2D-11*EXP(-280./T))

k[HOOCH2SCHO + OH --> HOOCH2S + CO + H2O]=CONST((4.58D-27*T@(4.98)*EXP(1802./T))*0.95)
k[HOOCH2SCHO + OH --> OCS + HCHO + OH + H2O]=CONST((4.58D-27*T@(4.98)*EXP(1802./T))*0.05)
k[HOOCH2SCHO + OH --> CHOSCHO + OH + H2O ]=CONST(6.18D-41*T@(9.16)*EXP(3633./T))
k[HOOCH2SCHO + OH --> HCOSCH2OO + H2O]=CONST(1.18D-36*T@(7.54)*EXP(3866./T))

k[HOOCH2SCHO+NO3-->HOOCH2SCO + HNO3]=CONST(1.01D-21*T@(2.89)*EXP(-767./T))
k[HOOCH2SCHO+NO3-->CHOSCHO + OH + HNO3]=CONST(4.72D-34*T@(6.93)*EXP(-920./T))
k[HOOCH2SCHO+NO3-->O2CH2SCHO + HNO3]=CONST(4.36D-27*T@(4.0)*EXP(-534./T))

k[HOOCH2SCHO + CL --> HOOCH2SCO + HCL]=CONST(1.22D-14*T@(1.09)*EXP(88./T))
k[HOOCH2SCHO + CL --> CHOSCHO + OH + HCL]=CONST(1.88D-18*T@(2.38)*EXP(-672./T))
k[HOOCH2SCHO + CL --> O2CH2SCHO + HCL+ Trac2]=CONST(2.37D-21*T@(3.19)*EXP(-277./T))

k[CHOSCHO+OH --> COSCHO +H2O]=CONST(2.43D-22*T@(3.56)*EXP(1524./T))
k[CHOSCHO+NO3-->COSCHO+HNO3]=CONST(3.65D-24*T@(3.87)*EXP(-904./T))
k[CHOSCHO + CL --> COSCHO+HCL]=CONST(7.16D-16*T@(1.49)*exp(-7./T))

#####
; HPMTF mechanism unimolecular reactions
#####

k[CH3SCH2O2 --> HOOCH2SCH2O2]=CONST(2.92D-36*T@(15.10)*EXP(-1941./T))
k[CH3SCH2O --> CH3S + HCHO]=CONST(1.63D11* T @ (0.77)*EXP(-878./T))

k[HOOCH2SCH2O2 --> HOOCH2SCHO+OH]=CONST(1.03D-74*T@(27.50)*EXP(4421./T))

k[HCOSCH2OO --> COSCH2OOH]=CONST(4.16D-50*T@(19.62)*EXP(2304./T))

k[COSCH2OOH --> CO + HOOCH2S]=CONST(4.99D10*T@(1.06)*EXP(-1858./T))
k[COSCH2OOH --> OCS + OH + HCHO]=CONST(2.84D10*T@(0.94)*EXP(-5642./T))
k[COSCH2OOH --> HCOSCH2OO]=CONST(1.21D-46*T@(18.34)*EXP(1323./T))
; additional path to OH + cyc-C(=O)SCH2O- not included as it is not competitive

k[COSCHO --> CO + OCS + HO2]=CONST((2.36D12*T@(0.62)*EXP(1024./T)) +
(1.47D10*T@(0.99)*EXP(-7829./T)))

k[CH3SCH2O --> CH3S + HCHO]=CONST(1.63D11*T@(0.77)*EXP(-878./T))

k[HOOCH2S -->OOCH2SH]=CONST (2.47D-56*T@(21.78)*EXP(2116./T))

k[OOCH2SH --> HOOCH2S]= CONST(2.47D-56*T@(21.78)*EXP(2116./T))
k[OOCH2SH --> CH2S + HO2]= CONST(1.51D12*T@(-0.12)*EXP(-10853./T))

k[HOOCH2SOO --> OCH2SOOH]=CONST(7.57D-7*T@(4.09)*EXP(788./T))
k[HOOCH2SOO --> HOOCH2S + O2]= CONST(1.02D9*T@(1.41)*EXP(-3825./T))
k[HOOCH2SOO --> HOOCHS + HO2]=CONST(7.13D-31*T@(14.02)*EXP(-2556./T))
k[HOOCH2SOO --> HOOCH2SO2]=CONST(1.76D14*T@(-0.59)*EXP(-10798./T))
; additional paths to HOOCH2SO* + O(3P), HO2 + CH2S + O2, and HO2 + CH2SOO* not included as
not competitive

k[OOCH2SOOH-->HOOCH2SOO]=CONST(1.79D2*T@(1.31)*EXP(-1437./T))

k[HOOCH2SO2--> OH + HCHO + SO2 ]=CONST(2.2D3) ; analogous to Chen et al. 2021
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;#####

;####
; HPMTF mechanism bimolecular radical reactions
;####

k[HOOCH2S + O2 --> HOOCH2SOO]= CONST(8.61D-24*T@(3.67)*EXP(-256./T))
k[HOOCH2S + O2 --> HOOCHS + HO2]=CONST CONST(1.65D-99*T@(27.08)*EXP(4511./T))

k[HOOCHS + OH --> OH + OCS + H2O]= CONST(1.64D-22*T@(3.29)*EXP(-108./T))
k[HOOCHS + OH --> OCHS + H2O]= CONST(3.78D-34*T@(7.14)*EXP(388./T))
k[HOOCHS + OH --> HOOCHOHS]= CONST(1.06D-19*T@(2.43)*EXP(566./T))
k[HOOCHS + OH --> OCHSOH + OH]=CONST(5D-11*0.84) ; at 298 K
k[HOOCHS + OH --> OCHS + H2O]=CONST(5D-11*0.16) ; at 298 K

k[OCHSOH + OH --> OH + OCS + H2O]=CONST(1.40D-20*T@(2.92)*EXP(458./T))
k[OCHSOH + OH --> HOSOHCHO]=CONST(6.41D-22*T@(3.02)*EXP(563./T))
k[HOSOHCHO --> OSCHO + H2O]=CONST(5.99D-10*T@(7.53)*EXP(-2916./T))
k[OCHSOH + OH --> OSCHO + H2O]=CONST(1.16D-23*T@(3.60)*EXP(881./T))
k[OSCHO --> OCS]=CONST(kdec) ; assumed conversion to OCS by bimolecular reactions

k[OOCHS --> OCS]=CONST(kdec) ; assumed conversion to OCS by bimolecular reactions
k[HOOCH2S+O3-->HOOCH2SO+O2]=CONST(1.5D-12*EXP(360.0/T))
k[HOOCH2SO+O3-->HOOCH2SO2 + O2]=CONST(4.0D-13)

; RO2 + NO/HO2/RO2/NO3 reactions
k[CH3SCH2O2 + RO2 --> CH3SCH2O+HCHO+HO2]=CONST(2.*(1.03D-13*EXP(365./T)*1.0D-11)@0.5)
k[CH3SCH2O2 + HO2 --> CH3SCH2OOH]=CONST(2.91D-13*EXP(1300./T)*(1.-EXP(-0.245*3.)))
k[CH3SCH2O2 + NO --> CH3SCH2O+NO2]=CONST(4.9D-12*EXP(260./T))
k[CH3SCH2O2 + NO3 --> CH3SCH2O+NO2]=CONST(2.3D-12)

k[OOCH2SH + RO2 --> OCH2SH+HCHO+H2O]=CONST(2.*(1.03D-13*EXP(365./T)*1.0D-11)@0.5)
k[OOCH2SH + HO2 --> HOOCH2SH]=CONST(2.91D-13*EXP(1300./T)*(1.-EXP(-0.245*3.)))
k[OOCH2SH + NO --> OCH2SH+NO2]=CONST(4.9D-12*EXP(260./T))
k[OOCH2SH + NO3 --> OCH2SH+NO2]=CONST(2.3D-12)

k[OOCH2SOOH +RO2 --> OCH2SOOH + HCHO + H2O]=CONST(2.*(1.03D-13*EXP(365./T)*1.0D-11)@0.5)
k[OOCH2SOOH + HO2 --> HOOCH2SOOH]=CONST(2.91D-13*EXP(1300./T)*(1.-EXP(-0.245*3.)))
k[OOCH2SOOH + NO --> OCH2SOOH+NO2]=CONST(4.9D-12*EXP(260./T))
k[OOCH2SOOH + NO3 --> OCH2SOOH+NO2]=CONST(2.3D-12)
;####

;####
; HPTMF/TPHAC partitioning
;####

; The rate constants below lead to fast equilibration as appropriate for 298 K
k[HOOCH2SCHO --> TPHAC]=CONST(0.00421)
k[TPHAC --> HOOCH2SCHO]=CONST(0.0240)
; For other scenarios, the gas phase rates predicted by theory may be more appropriate
; k[HOOCH2SCHO --> TPHAC]=CONST(3.13D-182*T@(62.97)*EXP(6788./T))
; k[TPHAC --> HOOCH2SCHO]=CONST(2.79D-185*T@(64.82)*EXP(6269./T))
; The equilibrium constant is expected to be different for aqueous phase. The
; rates for aqueous phase are not shown here, as the concentrations of the catalysts
; are not available.

;####
; TPHAC mechanism unimolecular reactions
;####

; The .OCH2S. biradical is assumed to convert directly to HCOSH
k[TPHAC --> HCOOH + HCOSH]=CONST(2.10E9*T@(1.66)*EXP(-15982./T))
k[OCHOOCH2S --> OCOOCH2SH]=CONST(1.83D-12*T@(7.60)*EXP(-7025./T))
k[OCHOOCH2SOO --> OCHOOCH2S + O2]=CONST(3.4D10*T@(0.89)*EXP(-3812./T))
k[OCHOOCH2SOO --> OCHOOCH2SOOH]=CONST(6.98D-35*T@(14.05)*EXP(-1785./T))
k[OCHOOCH2SOOH --> OCHOOCH2SOO]=CONST(4.04D-32*T@(13.08)*EXP(2230./T))
k[OCHOOCH2SOOH --> CO2 + OCH2SOOH]=CONST(1D9)

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k[OCHOOCH2SOO --> OCHOOCHS + HO2]=CONST(6.8)
k[OCHOOCH2SOO --> OCHOOCH2SO2]=CONST(1.1D-3)
k[OCHOOCH2SO2 --> OCHOOCH2 + SO2]=CONST(2.2D3) ; analogous to Chen et al (2021)
k[OCHOOCH2 --> HCHO + OCHO]=CONST(kdec) ; From Vereecken 2006 Chem Phys Lett
k[OCOOCH2SH --> CO2 + OCH2SH]=CONST(3.59D-1*T@(4.41)*EXP(-243./T))
k[OCOOCH2SH --> OCHOOCH2S]=CONST(1.03D10*T@(0.98)*EXP(-4908./T))
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#####
; TPHAC mechanism bimolecular reactions
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k[TPHAC + OH --> HCOOH + SCHO + H2O]=CONST(8.9D-25*T@(4.03)*EXP(1475./T))
k[TPHAC + OH --> OCHOOCH2S + H2O]=CONST(1.0D-10)
k[TPHAC + OH --> cycSCH2OOCHO + H2O]=CONST(1.56D-52*T@(13.06)*EXP(3520./T))
k[TPHAC + OH --> OCOHSCH2O + H2O]=CONST(1.52D-33*T@(7.22)*EXP(1215./T))
k[OCHOOCH2S + O2 --> OCHOOCH2SOO]=CONST(1.14D-22*T@(3.20)*EXP(-393./T))
k[OCHO + O2 --> CO2 + HO2]=CONST(2.5D-14*EXP(-300./T) ; KROPRIM from MCMv3.3.1
k[OCH2SH + O2 --> HCOSH + HO2]=CONST(2.5D-14*EXP(-300./T) ; KROSEC from MCMv3.3.1
k[OCHOOCH2S+O3 --> OCHOOCH2SO+O2]=CONST(1.5D-12*EXP(360.0/T))
k[OCHOOCH2SO+O3 --> OCHOOCH2 + SO2]=CONST(4.0D-13)
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#####
; CH3S chemistry following the study by Chen et al.
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k[CH3S + O2 --> CH3SOO]=CONST(1.2D-16*EXP(1580./T))
k[CH3SOO --> CH3S + O2]=CONST(3.5D10*EXP(-3560./T))
k[CH3SOO --> CH3O2 + SO2]=CONST(4.16D14*EXP(-9411./T))
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D. References

Jernigan, C. M., Fite, C. H., Vereecken, L., Berkelhammer, M. B., Rollins, A. W., Rickly, P. S., Novelli, A., Taraborrelli, D., Holmes, C. D., and Bertram, T. H.: Efficient Production of Carbonyl Sulfide in the Low-NO_x Oxidation of Dimethyl Sulfide, *Geophys. Res. Lett.*, 49, e2021GL096838, <https://doi.org/10.1029/2021GL096838>, 2022a.