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Supplement of

Kinetic and mechanistic study of the reaction between methane sulfonamide ($CH_3S(O)_2NH_2$) and OH

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Table S1. Experimental and calculated vibrational wavenumbers for the dimer of $CH_3SO_2NH_2$.

mode	IR Gas[a]	Frequencies (cm^{-1})[a,b]			Mode description
		6-31++G(d,p)	Aug-CC-pVTZ	ratio	
ν_1, ν_2	3362 (18.1)	3599 (21.3)	3531 (17.8)	0.952	NH_2asym. stretch
ν_3	3266 (100)	3393 (100.0)	3326 (100.0)	0.982	NH_2 sym. stretch
ν_4		3373 (<0.1)	3304 (0.2)		NH_2 sym. stretch
ν_5, ν_6		3192 (<0.1)	3131 (<0.1)		CH_3 deformation
ν_7, ν_8	3030 (1.3)	3185 (0.1)	3124 (<0.1)	0.970	CH_3asym. stretch
ν_9, ν_{10}	2940 (0.7)	3079 (0.1)	3029 (<0.1)	0.971	CH_3 sym. stretch
ν_{11}		1619 (1.0)	1610 (0.5)		NH_2 bend
ν_{12}	1557 (4.2)	1610 (4.1)	1604 (2.8)	0.971	NH_2 bend
ν_{13}, ν_{14}		1461 (0.7)	1461 (0.8)		CH_3 rocking
ν_{15}, ν_{16}	1419 (0.7)	1460 (1.0)	1461 (0.6)	0.971	CH_3asym. bend
ν_{17}, ν_{18}		1364 (1.6)	1358 (1.4)		CH_3 umbrella
ν_{19}		1306 (16.7)	1273 (13.9)		SO_2asym. stretch
ν_{20}	1326 (36.9)	1299 (41.1)	1267 (34.4)	1.047	SO_2asym. stretch
ν_{21}	1216 (2.0)	1135 (3.3)	1128 (3.6)	1.078	NH_2 rocking
ν_{22}		1125 (2.0)	1122 (4.0)		NH_2 rocking
ν_{23}	1157 (22.9)	1114 (26.2)	1084 (22.5)	1.065	SO_2 sym. stretch
ν_{24}	1105 (3.4)	1092 (5.3)	1061 (4.5)	1.041	SO_2 sym. stretch
ν_{25}		1000 (2.0)	997 (2.0)		CH_3 wagging
ν_{26}	989 (4.1)	998 (4.1)	994 (4.0)	0.995	CH_3 wagging
ν_{27}, ν_{28}		985 (0.3)	985 (0.2)		CH_3 twisting
ν_{29}		916 (9.0)	906 (7.1)		C-S stretch
ν_{30}	885 (1.4)	894 (12.3)	888 (10.6)	0.997	C-S stretch
ν_{31}	773 (3.8)	738 (19.5)	736 (20.7)	1.050	NH_2 wagging

736 (<0.1), ν_{32}; 705 (2.0), ν_{33}; 695 (12.1), ν_{34}; 491 (4.3), ν_{35}; 489 (3.4), ν_{36}; 465 (3.7), ν_{37}; 464 (<0.1), ν_{38}; 424 (<0.1), ν_{39}; 420 (1.2), ν_{40}; 358 (0.4), ν_{41}; 355 (2.3), ν_{42}; 302 (0.5), ν_{43}; 302 (2.4), ν_{44}; 291 (0.1), ν_{45}; 289 (0.1), ν_{46}; 225 (0.3), ν_{47}; 224 (<0.1), ν_{48}; 139 (2.0), ν_{49}; 117 (0.1), ν_{50}; 98 (<0.1), ν_{51}; 41 (0.4), ν_{52}; 32 (1.2), ν_{53}; 25 (<0.1), ν_{54}.[b]

a) Relative absorbance at band maximum in parentheses.

b) Calculated using the B3LYP method.

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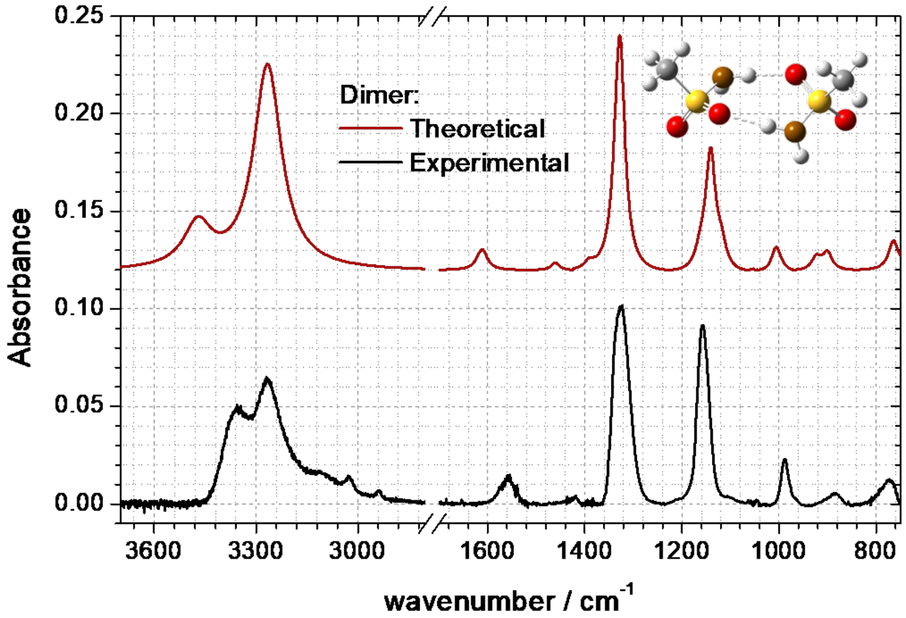

Figure S1. Comparison of the experimental spectrum of the MSAM-dimer (black line, after the subtraction of the monomer) and the simulated spectrum at the same level of theory as used for the monomer (red line).

Table S2. Reaction mechanism used for the kinetic simulation.

k[a]	Reaction	References / notes
$8.5 \times 10^{-5}\ \mathrm{s^{-1}}$	$O_3 \rightarrow O_2 + O(^1D)$	b
1.2×10^{-10}	$O(^1D) + H_2 \rightarrow OH + H$	IUPAC
6.7×10^{-15}	$OH + H_2 \rightarrow H_2O + H$	IUPAC
1×10^{-12}	$H + O_2 \rightarrow HO_2$	IUPAC
2.8×10^{-11}	$H + O_3 \rightarrow OH + O_2$	IUPAC
1.6×10^{-12}	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	IUPAC
2.0×10^{-15}	$HO_2 + O_3 \rightarrow OH + 2\ O_2$	IUPAC
1.4×10^{-13}	$CH_3SO_2NH_2 + OH \rightarrow CH_2SO_2NH_2 + H_2O$	This work
8.3×10^{-12}	$CH_2SO_2NH_2 + O_2 \rightarrow O_2CH_2SO_2NH_2$	c
6×10^{-12}	$2\ O_2CH_2SO_2NH_2 \rightarrow O_2 + 2\ OCH_2SO_2NH_2$	d
8×10^{-12}	$O_2CH_2SO_2NH_2 + NO \rightarrow NO_2 + OCH_2SO_2NH_2$	e
$> 1 \times 10^{9}\ \mathrm{s^{-1}}$	$OCH_2SO_2NH_2 \rightarrow CH_2O + SO_2NH_2$	f
8.5×10^{-12}	$CH_2O + OH \rightarrow HCO + H_2O$	IUPAC
6.5×10^{-12}	$O_2CH_2SO_2NH_2 + HO_2 \rightarrow HOOCH_2SO_2NH_2 + O_2$	g
6×10^{-12}	$HOOCH_2SO_2NH_2 + OH \rightarrow HOOCHSO_2NH_2 + H_2O$	h
$\alpha \times 1 \times 10^{15}$	$HOOCHSO_2NH_2 \rightarrow HC(O)OH + SO_2NH_2$	i
$(1-\alpha) \times 1 \times 10^{15}$	$HOOCHSO_2NH_2 \rightarrow OH + HC(O)SO_2NH_2$	i
1.5×10^{-11}	$HC(O)SO_2NH_2 + OH \rightarrow C(O)SO_2NH_2 + H_2O$	j
1×10^{-11}	$C(O)SO_2NH_2 + O_2 + M \rightarrow O_2C(O)SO_2NH_2 + M$	k
0 or 1×10^{10}	$C(O)SO_2NH_2 \rightarrow CO + SO_2NH_2$	l
1.4×10^{-11}	$O_2C(O)SO_2NH_2 + HO_2 \rightarrow OH + CO_2 + O_2 + SO_2NH_2$	m
2.01×10^{-13}	$CH_2O + OH \rightarrow HCOOH + H$	IUPAC
5.6×10^{-12}	$HCO + O_2 \rightarrow HO_2 + CO$	IUPAC
1.5×10^{-13}	$CO + OH\ (+O_2) \rightarrow CO_2 + HO_2$	IUPAC
$500\ \mathrm{s^{-1}}$	$SO_2NH_2 \rightarrow SO_2 + NH_2$	n
1.9×10^{-13}	$NH_2 + O_3 \rightarrow NH_2O + H_2O$	KP 1999
3.2×10^{-11}	$NH_2 + HO_2 \rightarrow NH_2O + OH$	KP 1999
4.8×10^{-12}	$NH_2 + HO_2 \rightarrow HNO + H_2O$	KP 1999
1.9×10^{-12}	$NH_2 + NO \rightarrow HO_2 + OH + N_2$	KP 1999
1.41×10^{-11}	$NH_2 + NO \rightarrow H_2O + N_2$	KP 1999
1.2×10^{-11}	$NH_2 + NO_2 \rightarrow N_2O + H_2O$	KP 1999
8×10^{-12}	$NH_2 + NO_2 \rightarrow NH_2O + NO$	KP 1999
1.2×10^{-14}	$NH_2O + O_3 \rightarrow NH_2 + O_2$	KP 1999
$1300\ \mathrm{s^{-1}}$	$NH_2O \rightarrow NHOH$	KP 1999
9.3×10^{-15}	$NH + O_2 \rightarrow NO + OH$	KP 1999
4.9×10^{-11}	$NH + NO \rightarrow OH + N_2$	KP 1999

1.49×10^{-11}	$HNO + OH \rightarrow NO + H_2O$	KP 1999
1.04×10^{-14}	$HNO + NHOH \rightarrow NH_2OH + NO$	KP 1999
9.6×10^{-12}	$NHOH + O_2 \rightarrow HNO + HO_2$	KP 1999
4.86×10^{-12}	$HONO + OH \rightarrow NO_2 + H_2O$	KP 1999
3.16×10^{-14}	$NH_2OH + OH \rightarrow NHOH + H_2O$	KP 1999
7.2×10^{-21}	$HNO + O_2 \rightarrow HO_2 + NO$	KP 1999
8.5×10^{-12}	$NO + HO_2 \rightarrow NO_2 + OH$	KP 1999
1.20×10^{-11}	$NO_2 + OH \rightarrow HNO_3$	KP 1999
5×10^{-5} s^{-1}	$HNO_3 \rightarrow$ wall	p

[a] Units of cm^3 molecule^{-1} s^{-1} unless otherwise stated. Calculated for 1 bar and 298 K.

[b] Adjusted to match the observed loss rate of a hydrocarbon e.g. acetone during photolysis.

[c] Set equal to the rate constant for the reaction $CH_3CH_2 + O_2 \rightarrow CH_3CH_2O_2$ at 1 bar.

[d] Set equal to the rate constant for the reaction $2\ CH_3C(O)CH_2OO \rightarrow O_2 + 2\ CH_3C(O)CH_2O$.

[e] Set equal to the rate constant for the reaction $CH_3C(O)CH_2O_2 + NO \rightarrow NO_2 + CH_3C(O)CH_2O$.

[f] Calculated with G4MP2 level of theory. As this is the only reaction of $OCH_2SO_2NH_2$ that we consider, any lifetime shorter than a few seconds would give the same simulation result.

[g] Set equal to the rate constant for the reaction $C_2H_5O_2 + HO_2$

[h] Set equal to the rate constant for the reaction $C_2H_5OOH + OH$

[i] As these are the only reactions of $HOOCHSO_2NH_2$ that we consider, any lifetime shorter than a few seconds would give the same simulation result. α was varied to match the observed HC(O)OH concentration.

[j] Set equal to the rate constant for the reaction $OH + CH_3CHO$

[k] Set equal to the rate constant for the reaction $CH_3C(O) + O_2$

[l] set to zero when considering reaction of $C(O)SO_2NH_2$ with O_2. At 1×10^{10} s^{-1}, the reaction with O_2 is insignificant.

[m] Set equal to the rate constant for the reaction $CH_3CO3 + HO_2$

[n] Set to the thermal decomposition rate coefficient for CH_3SO_2 (see manuscript for details). Note that any value greater than 10^{-3} s^{-1} yields in the same simulation result.

[p] Adjusted to obtain best agreement with the observed HNO_3 profile.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation, (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.) http://iupac.pole-ether.fr/index.html., 2019.

KP 1999: Kohlmann, J.-P., and Poppe, D.: The tropospheric gas-phase degradation of NH_3 and its impact on the formation of N_2O and NO_x, J. Atmos. Chem., 32, 397-415, 1999.

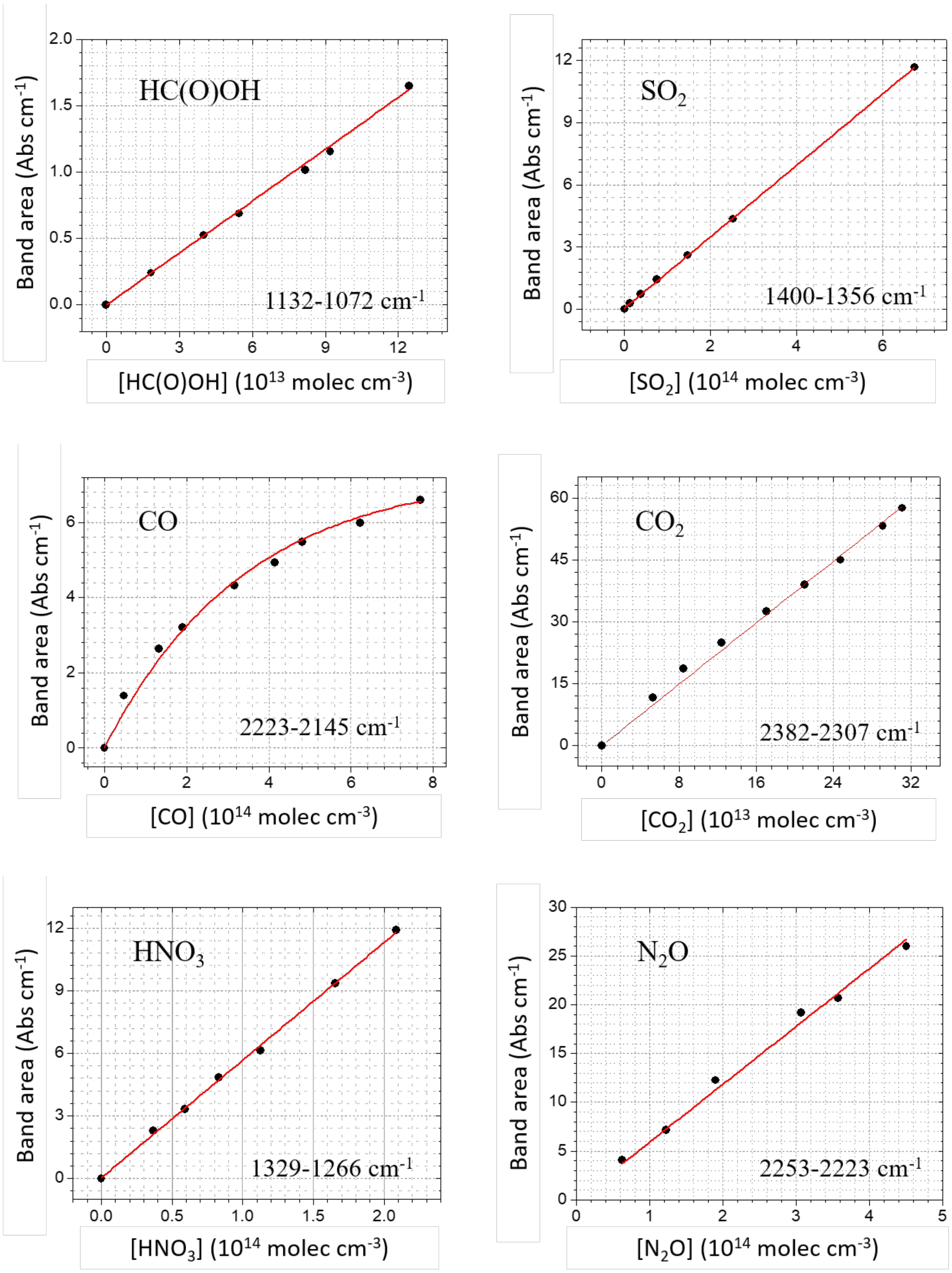

Figure S2. Calibration curves for the main products of the reaction $CH_3SO_2NH_2$ + OH. Experimental conditions were 298 K and 700 Torr synthetic air. Abs = Absorbance [$\log_{10}(I_0/I)$].

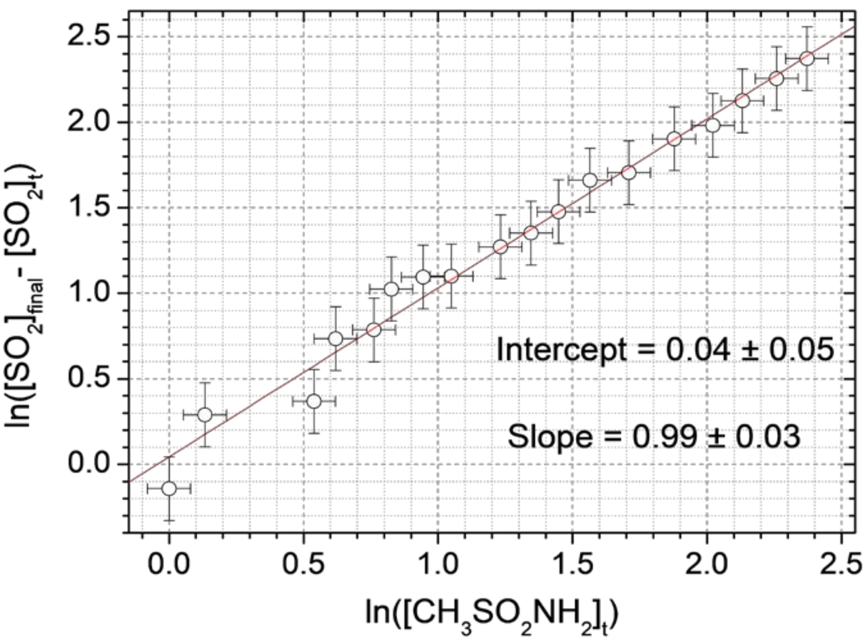

Figure S3. Comparison of the absorbance of SO_2 product with respect to the depletion in absorbance of MSAM during oxidation.

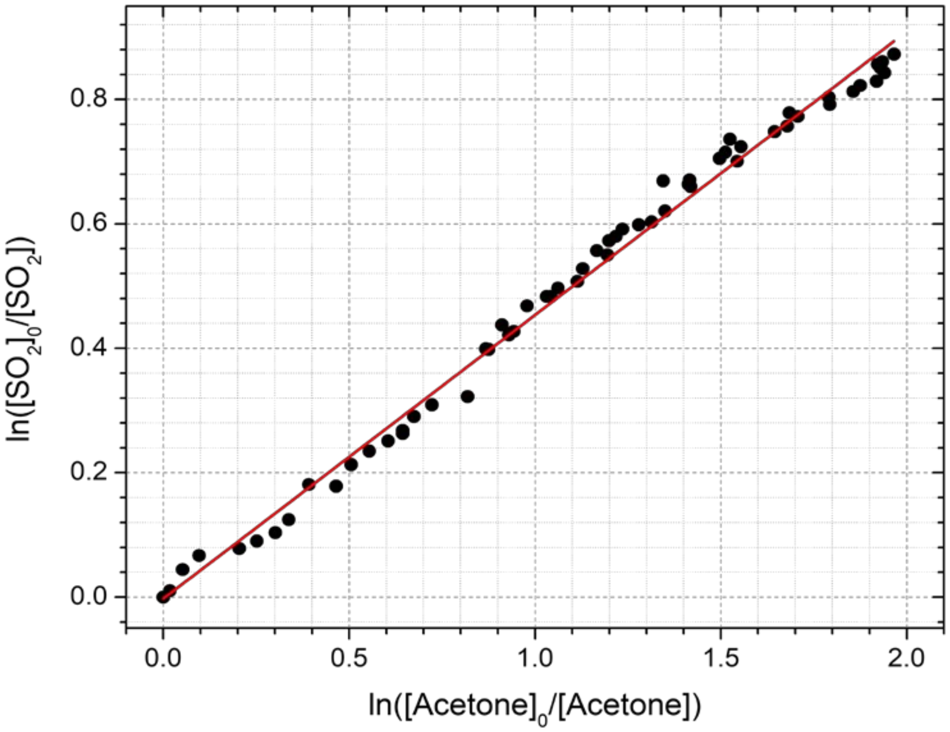

Figure S4. Relative rate study of OH + SO_2 relative to OH + $CH_3C(O)CH_3$. The experiment was conducted at a total pressure of 700 Torr air and at room temperature.

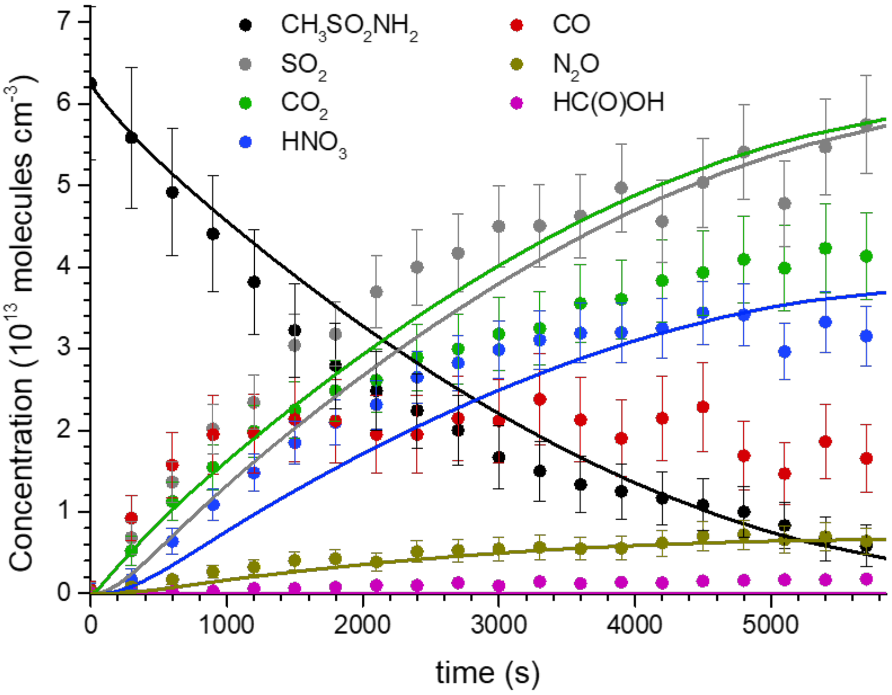

Figure S5. As Fig. 8 of the manuscript but with the fate of the $C(O)SO_2NH_2$ radical modified in the simulation so that CO_2 rather than CO is formed (i.e. R18-R19 are used instead of R17). Note that CO is no longer formed in measurable amounts.