

# **Kinetic and mechanistic study of the reaction between methane sulphonamide ( $\text{CH}_3\text{S}(\text{O})_2\text{NH}_2$ ) and OH**

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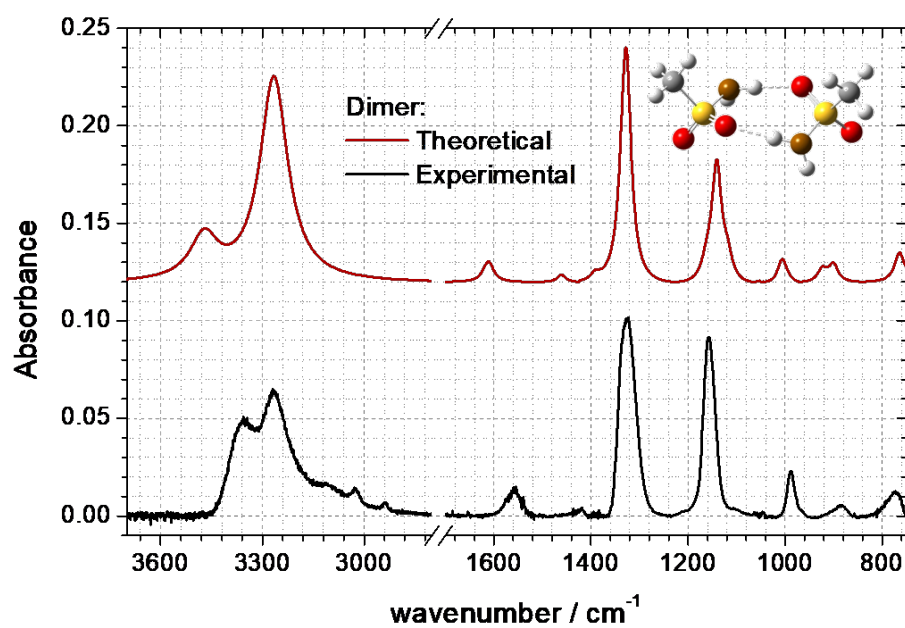
**Supplementary Information**

**Table S1.** Experimental and calculated vibrational wavenumbers for the dimer of CH<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub>.

mode	IR Gas <sup>a</sup>	Frequencies (cm <sup>-1</sup> ) <sup>a,b</sup>			Mode description
		6-31++G(d,p)	Aug-CC-pVTZ	ratio	
v <sub>1</sub> , v <sub>2</sub>	3362 (18.1)	3599 (21.3)	3531 (17.8)	0.952	NH <sub>2</sub> asym. stretch
v <sub>3</sub>	3266 (100)	3393 (100.0)	3326 (100.0)	0.982	NH <sub>2</sub> sym. stretch
v <sub>4</sub>		3373 (<0.1)	3304 (0.2)		NH <sub>2</sub> sym. stretch
v <sub>5</sub> , v <sub>6</sub>		3192 (<0.1)	3131 (<0.1)		CH <sub>3</sub> deformation
v <sub>7</sub> , v <sub>8</sub>	3030 (1.3)	3185 (0.1)	3124 (<0.1)	0.970	CH <sub>3</sub> asym. stretch
v <sub>9</sub> , v <sub>10</sub>	2940 (0.7)	3079 (0.1)	3029 (<0.1)	0.971	CH <sub>3</sub> sym. stretch
v <sub>11</sub>		1619 (1.0)	1610 (0.5)		NH <sub>2</sub> bend
v <sub>12</sub>	1557 (4.2)	1610 (4.1)	1604 (2.8)	0.971	NH <sub>2</sub> bend
v <sub>13</sub> , v <sub>14</sub>		1461 (0.7)	1461 (0.8)		CH <sub>3</sub> rocking
v <sub>15</sub> , v <sub>16</sub>	1419 (0.7)	1460 (1.0)	1461 (0.6)	0.971	CH <sub>3</sub> asym. bend
v <sub>17</sub> , v <sub>18</sub>		1364 (1.6)	1358 (1.4)		CH <sub>3</sub> umbrella
v <sub>19</sub>		1306 (16.7)	1273 (13.9)		SO <sub>2</sub> asym. stretch
v <sub>20</sub>	1326 (36.9)	1299 (41.1)	1267 (34.4)	1.047	SO <sub>2</sub> asym. stretch
v <sub>21</sub>	1216 (2.0)	1135 (3.3)	1128 (3.6)	1.078	NH <sub>2</sub> rocking
v <sub>22</sub>		1125 (2.0)	1122 (4.0)		NH <sub>2</sub> rocking
v <sub>23</sub>	1157 (22.9)	1114 (26.2)	1084 (22.5)	1.065	SO <sub>2</sub> sym. stretch
v <sub>24</sub>	1105 (3.4)	1092 (5.3)	1061 (4.5)	1.041	SO <sub>2</sub> sym. stretch
v <sub>25</sub>		1000 (2.0)	997 (2.0)		CH <sub>3</sub> wagging
v <sub>26</sub>	989 (4.1)	998 (4.1)	994 (4.0)	0.995	CH <sub>3</sub> wagging
v <sub>27</sub> , v <sub>28</sub>		985 (0.3)	985 (0.2)		CH <sub>3</sub> twisting
v <sub>29</sub>		916 (9.0)	906 (7.1)		C-S stretch
v <sub>30</sub>	885 (1.4)	894 (12.3)	888 (10.6)	0.997	C-S stretch
v <sub>31</sub>	773 (3.8)	738 (19.5)	736 (20.7)	1.050	NH <sub>2</sub> wagging

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

a) Relative absorbance at band maximum in parentheses.  
b) Calculated using the B3LYP method.



**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
$8.5 \times 10^{-5} \text{ s}^{-1}$	$\text{O}_3 \rightarrow \text{O}_2 + \text{O}(^1\text{D})$	b
$1.2 \times 10^{-10}$	$\text{O}(^1\text{D}) + \text{H}_2 \rightarrow \text{OH} + \text{H}$	IUPAC
$6.7 \times 10^{-15}$	$\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$	IUPAC
$1 \times 10^{-12}$	$\text{H} + \text{O}_2 \rightarrow \text{HO}_2$	IUPAC
$2.8 \times 10^{-11}$	$\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$	IUPAC
$2.0 \times 10^{-15}$	$\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2 \text{O}_2$	IUPAC
$1.4 \times 10^{-13}$	$\text{CH}_3\text{SO}_2\text{NH}_2 + \text{OH} \rightarrow \text{CH}_2\text{SO}_2\text{NH}_2 + \text{H}_2\text{O}$	This work
$8.3 \times 10^{-12}$	$\text{CH}_2\text{SO}_2\text{NH}_2 + \text{O}_2 \rightarrow \text{O}_2\text{CH}_2\text{SO}_2\text{NH}_2$	c
$5.99 \times 10^{-12}$	$2 \text{O}_2\text{CH}_2\text{SO}_2\text{NH}_2 \rightarrow \text{O}_2 + 2 \text{OCH}_2\text{SO}_2\text{NH}_2$	d
$8 \times 10^{-12}$	$\text{O}_2\text{CH}_2\text{SO}_2\text{NH}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OCH}_2\text{SO}_2\text{NH}_2$	e
$4.2 \times 10^{25} \text{ s}^{-1}$	$\text{OCH}_2\text{SO}_2\text{NH}_2 \rightarrow \text{CH}_2\text{O} + \text{SO}_2\text{NH}_2$	f
$8.5 \times 10^{-12}$	$\text{CH}_2\text{O} + \text{OH} \rightarrow \text{HCO} + \text{H}_2\text{O}$	IUPAC
$2.01 \times 10^{-13}$	$\text{CH}_2\text{O} + \text{OH} \rightarrow \text{HCOOH} + \text{H}$	IUPAC
$5.6 \times 10^{-12}$	$\text{HCO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO}$	IUPAC
$1.5 \times 10^{-13}$	$\text{CO} + \text{OH} (+\text{O}_2) \rightarrow \text{CO}_2 + \text{HO}_2$	IUPAC
$500 \text{ s}^{-1}$	$\text{SO}_2\text{NH}_2 \rightarrow \text{SO}_2 + \text{NH}_2$	g
$1.9 \times 10^{-13}$	$\text{NH}_2 + \text{O}_3 \rightarrow \text{NH}_2\text{O} + \text{H}_2\text{O}$	KP 1999
$3.2 \times 10^{-11}$	$\text{NH}_2 + \text{HO}_2 \rightarrow \text{NH}_2\text{O} + \text{OH}$	KP 1999
$4.8 \times 10^{-12}$	$\text{NH}_2 + \text{HO}_2 \rightarrow \text{HNO} + \text{H}_2\text{O}$	KP 1999
$1.9 \times 10^{-12}$	$\text{NH}_2 + \text{NO} \rightarrow \text{HO}_2 + \text{OH} + \text{N}_2$	KP 1999
$1.41 \times 10^{-11}$	$\text{NH}_2 + \text{NO} \rightarrow \text{H}_2\text{O} + \text{N}_2$	KP 1999
$1.2 \times 10^{-11}$	$\text{NH}_2 + \text{NO}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$	KP 1999
$8 \times 10^{-12}$	$\text{NH}_2 + \text{NO}_2 \rightarrow \text{NH}_2\text{O} + \text{NO}$	KP 1999
$1.2 \times 10^{-14}$	$\text{NH}_2\text{O} + \text{O}_3 \rightarrow \text{NH}_2 + \text{O}_2$	KP 1999
$1300 \text{ s}^{-1}$	$\text{NH}_2\text{O} \rightarrow \text{NHOH}$	KP 1999
$9.3 \times 10^{-15}$	$\text{NH} + \text{O}_2 \rightarrow \text{NO} + \text{OH}$	KP 1999
$4.9 \times 10^{-11}$	$\text{NH} + \text{NO} \rightarrow \text{OH} + \text{N}_2$	KP 1999
$1.49 \times 10^{-11}$	$\text{HNO} + \text{OH} \rightarrow \text{NO} + \text{H}_2\text{O}$	KP 1999
$1.04 \times 10^{-14}$	$\text{HNO} + \text{NHOH} \rightarrow \text{NH}_2\text{OH} + \text{NO}$	KP 1999
$1.66 \times 10^{-12}$	$\text{NHOH} + \text{OH} \rightarrow \text{HNO} + \text{H}_2\text{O}$	KP 1999
$4.86 \times 10^{-12}$	$\text{HONO} + \text{OH} \rightarrow \text{NO}_2 + \text{H}_2\text{O}$	KP 1999
$3.16 \times 10^{-14}$	$\text{NH}_2\text{OH} + \text{OH} \rightarrow \text{NHOH} + \text{H}_2\text{O}$	KP 1999
$7.2 \times 10^{-21}$	$\text{HNO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{NO}$	KP 1999
$8.5 \times 10^{-12}$	$\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$	KP 1999
$1.20 \times 10^{-11}$	$\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$	KP 1999
$5 \times 10^{-5} \text{ s}^{-1}$	$\text{HNO}_3 \rightarrow \text{wall}$	h

<sup>a</sup> Units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  unless otherwise stated.

<sup>b</sup> Adjusted to match the observed loss rate of a hydrocarbon e.g. acetone during photolysis.

<sup>c</sup> Set equal to the rate constant for the reaction  $\text{CH}_3\text{CH}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{O}_2$  at 1 bar.

<sup>d</sup> Set equal to the rate constant for the reaction  $2 \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OO} \rightarrow \text{O}_2 + 2 \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}$ .

<sup>e</sup> Set equal to the rate constant for the reaction  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}$ .

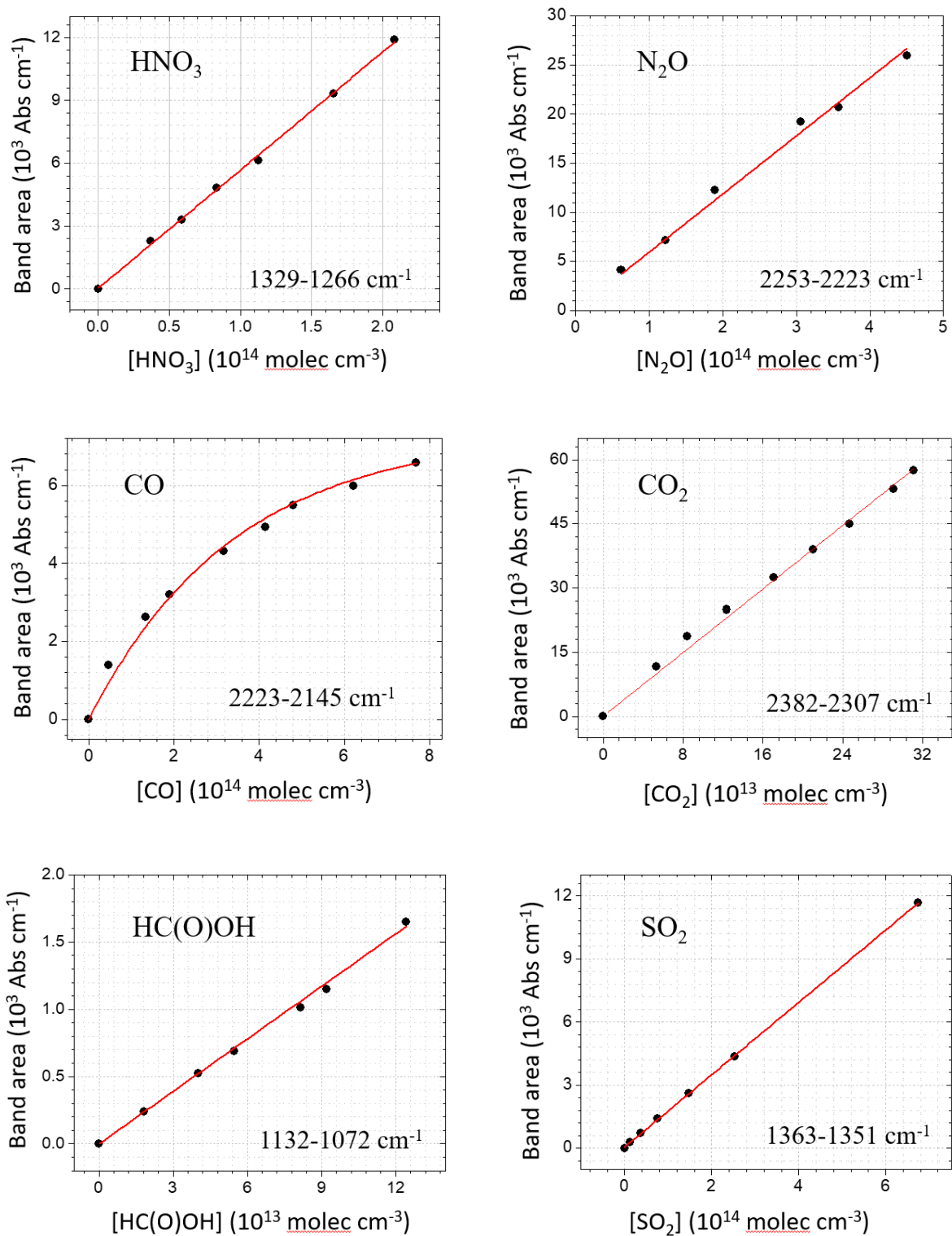
<sup>f</sup> Calculated with G4MP2 level of theory. Note that as this is the only fate of  $\text{OCH}_2\text{SO}_2\text{NH}_2$ , any lifetime shorter than a few seconds would give the same simulation result.

<sup>g</sup> Set to the thermal decomposition rate coefficient for  $\text{CH}_3\text{SO}_2$  (see manuscript for details). Note that any value greater than  $10^{-3} \text{ s}^{-1}$  yields in the same simulation result.

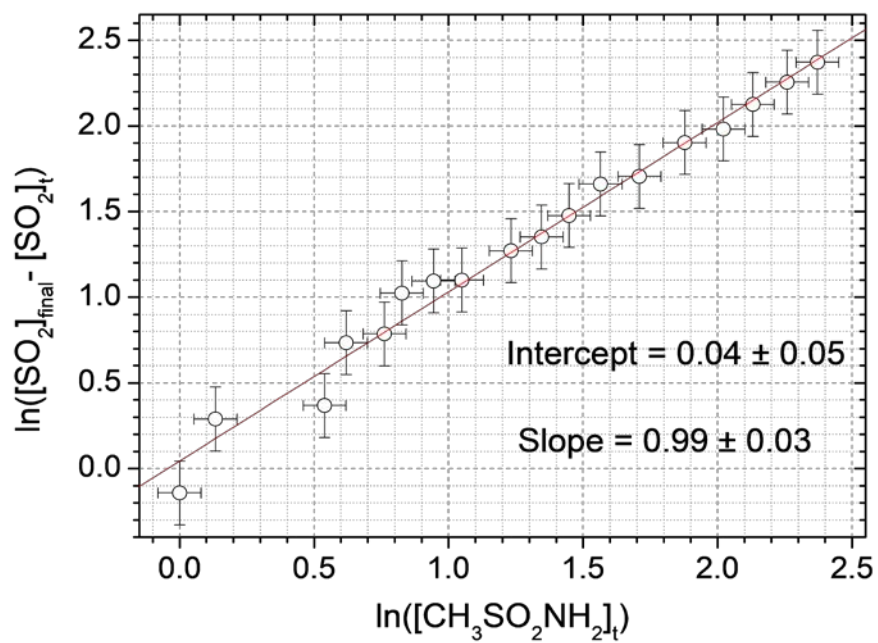
<sup>h</sup> Adjusted to obtain best agreement with the observed  $\text{HNO}_3$  profile.

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.

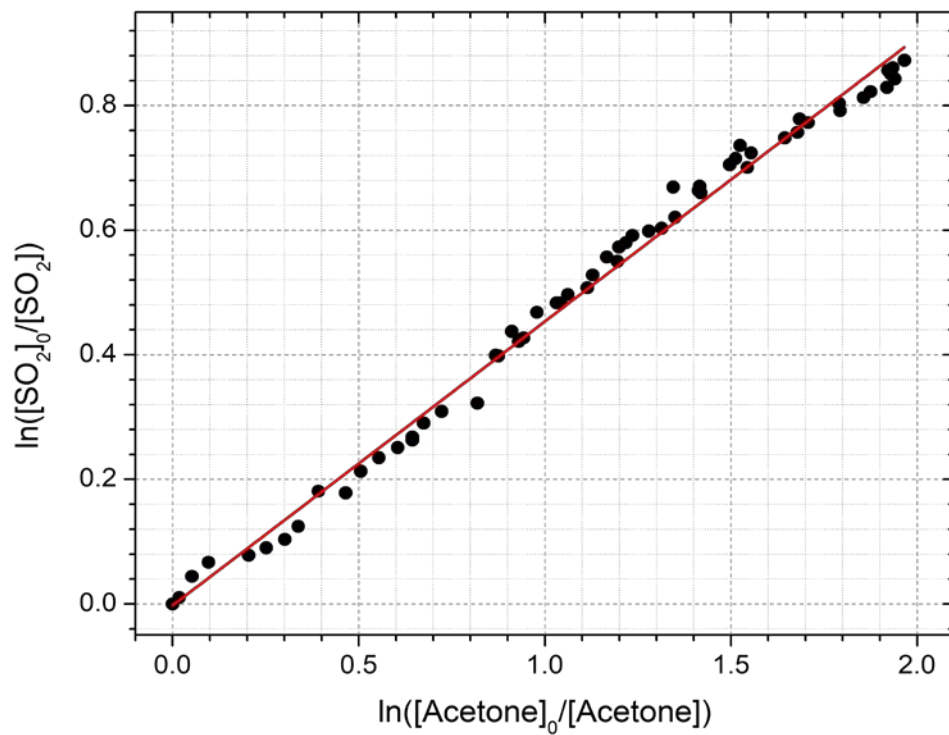
KP 1999: Kohlmann, J.-P., and Poppe, D.: The tropospheric gas-phase degradation of  $\text{NH}_3$  and its impact on the formation of  $\text{N}_2\text{O}$  and  $\text{NO}_x$ , J. Atmos. Chem., 32, 397-415, 1999.



**Figure S2.** Calibration curves for the main products of the reaction  $\text{CH}_3\text{SO}_2\text{NH}_2 + \text{OH}$ . Experimental conditions were 298 K and 700 Torr synthetic air. Abs = Absorbance [ $\log_{10}(I_0/I)$ ].



**Figure S3.** Comparison of the absorbance of  $\text{SO}_2$  product with respect to the depletion in absorbance of MSAM during oxidation.



**Figure S4.** Relative rate study of OH + SO<sub>2</sub> relative to OH + CH<sub>3</sub>C(O)CH<sub>3</sub>. The experiment was conducted at a total pressure of 700 Torr air and at room temperature.