

Table 1. Data summary for the substitution of DMA for NH<sub>3</sub> in the 3-2 ammonium bisulfate cluster and for the substitution of NH<sub>3</sub> for DMA in the 3-2 dimethylaminium bisulfate cluster.

Substitution with DMA <sup>a</sup>	Pseudo-first order rate constant (s <sup>-1</sup> )	Second order rate constant (cm <sup>3</sup> ·molecule <sup>-1</sup> ·s <sup>-1</sup> )	<i>K</i>	$\Delta G$ (kJ/mol)	Collisional Rate Constant (cm <sup>3</sup> ·molecule <sup>-1</sup> ·s <sup>-1</sup> )	Uptake Coefficient ( $\gamma$ )
[(NH <sub>4</sub> ) <sub>3</sub> (HSO <sub>4</sub> ) <sub>2</sub> ] <sup>+</sup> → [(NH <sub>4</sub> ) <sub>2</sub> (HDMA)(HSO <sub>4</sub> ) <sub>2</sub> ] <sup>+</sup>	0.49 ± 0.03	1.1 ± 0.3 × 10 <sup>-9</sup>	> 1500 ± 600	< -18.1 ± 0.9	1.3 ± 0.3 × 10 <sup>-9</sup>	0.85 ± 0.26
[(NH <sub>4</sub> ) <sub>2</sub> (HDMA)(HSO <sub>4</sub> ) <sub>2</sub> ] <sup>+</sup> → [(NH <sub>4</sub> )(HDMA) <sub>2</sub> (HSO <sub>4</sub> ) <sub>2</sub> ] <sup>+</sup>	0.41 ± 0.02	9.3 ± 3.0 × 10 <sup>-10</sup>	> 620 ± 250	< -15.9 ± 0.8	1.3 ± 0.3 × 10 <sup>-9</sup>	0.72 ± 0.22
[(NH <sub>4</sub> )(HDMA) <sub>2</sub> (HSO <sub>4</sub> ) <sub>2</sub> ] <sup>+</sup> → [(HDMA) <sub>3</sub> (HSO <sub>4</sub> ) <sub>2</sub> ] <sup>+</sup>	0.43 ± 0.03	9.7 ± 3.0 × 10 <sup>-10</sup>	> 26000 ± 10000	< -25.2 ± 1.3	1.3 ± 0.3 × 10 <sup>-9</sup>	0.75 ± 0.23
<b>Substitution with NH<sub>3</sub><sup>b</sup></b>						
[(HDMA) <sub>3</sub> (HSO <sub>4</sub> ) <sub>2</sub> ] <sup>+</sup> → [(NH <sub>4</sub> )(HDMA) <sub>2</sub> (HSO <sub>4</sub> ) <sub>2</sub> ] <sup>+</sup>	< 5 ± 3 × 10 <sup>-4</sup>	< 3.8 ± 1.1 × 10 <sup>-14</sup>	< 4 ± 2 × 10 <sup>-5</sup>	> 25.2 ± 1.3	2.0 ± 0.4 × 10 <sup>-9</sup>	< 1.9 ± 0.6 × 10 <sup>-5</sup>
[(NH <sub>4</sub> )(HDMA) <sub>2</sub> (HSO <sub>4</sub> ) <sub>2</sub> ] <sup>+</sup> → [(NH <sub>4</sub> ) <sub>2</sub> (HDMA)(HSO <sub>4</sub> ) <sub>2</sub> ] <sup>+</sup>	< 1.8 ± 0.8 × 10 <sup>-3</sup>	< 1.5 ± 0.5 × 10 <sup>-12</sup>	< 1.6 ± 6 × 10 <sup>-3</sup>	> 15.9 ± 0.8	2.0 ± 0.4 × 10 <sup>-9</sup>	< 7.6 ± 2.3 × 10 <sup>-4</sup>
[(NH <sub>4</sub> ) <sub>2</sub> (HDMA)(HSO <sub>4</sub> ) <sub>2</sub> ] <sup>+</sup> → [(NH <sub>4</sub> ) <sub>3</sub> (HSO <sub>4</sub> ) <sub>2</sub> ] <sup>+</sup>	< 9 ± 2 × 10 <sup>-4</sup>	< 7.5 ± 2.3 × 10 <sup>-13</sup>	< 7 ± 3 × 10 <sup>-4</sup>	> 18.1 ± 0.9	2.0 ± 0.4 × 10 <sup>-9</sup>	< 3.8 ± 1.1 × 10 <sup>-4</sup>

<sup>a</sup>Pressure: 1.2 ± 0.2 × 10<sup>-8</sup> torr

<sup>b</sup>Pressure: For [(HDMA)<sub>3</sub>(HSO<sub>4</sub>)<sub>2</sub>]<sup>+</sup>: 3.7 ± 0.7 × 10<sup>-7</sup> torr; For [(NH<sub>4</sub>)(HDMA)<sub>2</sub>(HSO<sub>4</sub>)<sub>2</sub>]<sup>+</sup> and [(NH<sub>4</sub>)<sub>2</sub>(HDMA)(HSO<sub>4</sub>)<sub>2</sub>]<sup>+</sup>: 3.4 ± 0.7 × 10<sup>-8</sup> torr

Table 2.  $\Delta G$  values (kJ/mol) for the substitution reactions of bisulfate clusters at 298 K.

	Sub. 1	Sub. 2	Sub. 3	Sub. 4
$[(\text{NH}_4)_2(\text{HSO}_4)]^+$ with DMA	$< -15.1 \pm 0.8$	$< -22.9 \pm 1.2$		
$[(\text{NH}_4)_3(\text{HSO}_4)_2]^+$ with DMA	$< -18.1 \pm 0.9$	$< -15.9 \pm 0.8$	$< -25.2 \pm 1.3$	
$[(\text{NH}_4)_4(\text{HSO}_4)_3]^+$ with DMA	$< -16.5 \pm 0.8$	$< -15.2 \pm 0.8$	$< -12.0 \pm 0.6$	$< -26.5 \pm 1.3$
$[(\text{NH}_4)_2(\text{HSO}_4)]^+$ with TMA	$< -14.1 \pm 0.7$	$< -20.7 \pm 1.0$		
$[(\text{NH}_4)_3(\text{HSO}_4)_2]^+$ with TMA	$< -7.0 \pm 0.4$	$< -7.7 \pm 0.4$	$< -15.3 \pm 0.8$	
$[(\text{NH}_4)_4(\text{HSO}_4)_3]^+$ with TMA	$< -12.8 \pm 0.6$			
$[(\text{HDMA})_2(\text{HSO}_4)]^+$ with TMA	$-14.0 \pm 0.7$	$-9.5 \pm 0.5$		
$[(\text{HDMA})_3(\text{HSO}_4)_2]^+$ with TMA	$-1.1 \pm 0.1$	$-0.37 \pm 0.02$	$7.9 \pm 0.4$	

Table 3. Uptake coefficients for the substitution reactions of bisulfate clusters.

	$\gamma_1$	$\gamma_2$	$\gamma_3$	$\gamma_4$
$[(\text{NH}_4)_2(\text{HSO}_4)]^+$ with DMA	$1.05 \pm 0.26$	$0.97 \pm 0.24$		
$[(\text{NH}_4)_3(\text{HSO}_4)_2]^+$ with DMA	$0.85 \pm 0.22$	$0.72 \pm 0.18$	$0.75 \pm 0.19$	
$[(\text{NH}_4)_4(\text{HSO}_4)_3]^+$ with DMA	$0.61 \pm 0.15$	$0.56 \pm 0.14$	$0.58 \pm 0.15$	$0.83 \pm 0.21$
$[(\text{HMMA})_2(\text{HSO}_4)]^+$ with DMA	$1.05 \pm 0.26$	$0.70 \pm 0.18$		
$[(\text{HMMA})_3(\text{HSO}_4)_2]^+$ with DMA	$0.82 \pm 0.20$	$0.71 \pm 0.18$	$0.64 \pm 0.16$	
$[(\text{HMMA})_4(\text{HSO}_4)_3]^+$ with DMA	$0.85 \pm 0.21$	$0.80 \pm 0.20$	$0.69 \pm 0.17$	$0.66 \pm 0.16$
$[(\text{HTMA})_2(\text{HSO}_4)]^+$ with DMA	$8.6 \pm 2.2 \times 10^{-3}$	$1.8 \pm 0.5 \times 10^{-3}$		
$[(\text{HTMA})_3(\text{HSO}_4)_2]^+$ with DMA	$0.51 \pm 0.13$	$0.22 \pm 0.05$	$0.18 \pm 0.05$	
$[(\text{NH}_4)_2(\text{HSO}_4)]^+$ with TMA	$0.90 \pm 0.26$	$0.65 \pm 0.26$		
$[(\text{NH}_4)_3(\text{HSO}_4)_2]^+$ with TMA	$0.66 \pm 0.26$	$0.45 \pm 0.26$	$0.57 \pm 0.26$	
$[(\text{NH}_4)_4(\text{HSO}_4)_3]^+$ with TMA	$0.64 \pm 0.26$	$0.48 \pm 0.26$	$0.39 \pm 0.26$	$1.07 \pm 0.26$
$[(\text{HMMA})_2(\text{HSO}_4)]^+$ with TMA	$1.07 \pm 0.27$	$0.54 \pm 0.13$		
$[(\text{HMMA})_3(\text{HSO}_4)_2]^+$ with TMA	$0.75 \pm 0.19$	$0.60 \pm 0.15$	$0.39 \pm 0.10$	
$[(\text{HMMA})_4(\text{HSO}_4)_3]^+$ with TMA	$0.76 \pm 0.19$	$0.69 \pm 0.17$	$0.55 \pm 0.14$	$0.13 \pm 0.03$
$[(\text{HDMA})_2(\text{HSO}_4)]^+$ with TMA	$0.62 \pm 0.15$	$0.47 \pm 0.12$		
$[(\text{HDMA})_3(\text{HSO}_4)_2]^+$ with TMA	$0.33 \pm 0.08$	$0.30 \pm 0.07$	$0.025 \pm 0.006$	
$[(\text{HDMA})_4(\text{HSO}_4)_3]^+$ with TMA	$0.36 \pm 0.09$	$0.050 \pm 0.013$	$0.014 \pm 0.004$	$3.9 \pm 1.0 \times 10^{-3}$
$[(\text{HMMA})_2(\text{HSO}_4)]^+$ with $\text{NH}_3$	$< 1.1 \pm 0.3 \times 10^{-3}$	$< 1.7 \pm 0.5 \times 10^{-3}$		
$[(\text{HMMA})_3(\text{HSO}_4)_2]^+$ with $\text{NH}_3$	$3 \pm 1 \times 10^{-4}$	$< 3.1 \pm 0.9 \times 10^{-4}$	$< 3 \pm 1 \times 10^{-4}$	
$[(\text{HMMA})_4(\text{HSO}_4)_3]^+$ with $\text{NH}_3$	$< 1.0 \pm 0.3 \times 10^{-4}$	$< 8 \pm 3 \times 10^{-5}$	$< 4 \pm 1 \times 10^{-4}$	$< 4 \pm 1 \times 10^{-4}$
$[(\text{HDMA})_2(\text{HSO}_4)]^+$ with $\text{NH}_3$	$< 6 \pm 2 \times 10^{-5}$	$< 1.6 \pm 0.5 \times 10^{-3}$		
$[(\text{HDMA})_3(\text{HSO}_4)_2]^+$ with $\text{NH}_3$	$< 1.9 \pm 0.6 \times 10^{-5}$	$< 8 \pm 2 \times 10^{-4}$	$< 4 \pm 1 \times 10^{-4}$	
$[(\text{HDMA})_4(\text{HSO}_4)_3]^+$ with $\text{NH}_3$	$< 1.2 \pm 0.4 \times 10^{-5}$	$< 3.0 \pm 0.9 \times 10^{-3}$	$< 8 \pm 2 \times 10^{-4}$	$< 5 \pm 2 \times 10^{-4}$
$[(\text{HTMA})_2(\text{HSO}_4)]^+$ with $\text{NH}_3$	$< 9 \pm 3 \times 10^{-5}$	$< 1.7 \pm 0.5 \times 10^{-3}$		
$[(\text{HTMA})_3(\text{HSO}_4)_2]^+$ with $\text{NH}_3$	$< 6 \pm 2 \times 10^{-4}$	$< 1.1 \pm 0.3 \times 10^{-2}$	$< 2.1 \pm 0.6 \times 10^{-2}$	
$[(\text{HTMA})_4(\text{HSO}_4)_3]^+$ with $\text{NH}_3$				$< 1.9 \pm 0.6 \times 10^{-3}$

Table 4. Proton affinity and enthalpy of solvation values for NH<sub>3</sub> and the aliphatic amines (Lide, 2010).

	<b>Proton Affinity (kJ/mol)</b>	<b>Enthalpy of Solvation (kJ/mol)</b>
<b>NH<sub>3</sub></b>	853.6	-35.4
<b>MMA</b>	899.0	-45.3
<b>DMA</b>	929.5	-53.1
<b>TMA</b>	948.9	-52.7

Table 5.  $\Delta G$  values (kJ/mol) for the substitution reactions of nitrate clusters at 298 K.

	Sub. 1	Sub. 2	Sub. 3
$[(\text{NH}_4)_3(\text{NO}_3)_2]^+$ with DMA			$< -24.2 \pm 1.2$
$[(\text{HDMA})_2(\text{NO}_3)]^+$ with TMA	$-13.7 \pm 0.7$	$-9.9 \pm 0.5$	

Table 6. Uptake coefficients for the substitution reactions of nitrate clusters.

	$\gamma_1$	$\gamma_2$	$\gamma_3$	$\gamma_4$
$[(\text{NH}_4)_3(\text{NO}_3)_2]^+$ with DMA	$0.53 \pm 0.21$	$0.50 \pm 0.17$	$0.68 \pm 0.12$	
$[(\text{HMMA})_2(\text{NO}_3)]^+$ with DMA	$0.86 \pm 0.25$	$0.55 \pm 0.18$		
$[(\text{HMMA})_3(\text{NO}_3)_2]^+$ with DMA	$0.77 \pm 0.21$	$0.66 \pm 0.17$	$0.47 \pm 0.12$	
$[(\text{HTMA})_2(\text{NO}_3)]^+$ with DMA	$6.4 \pm 1.9 \times 10^{-3}$	$2.0 \pm 0.6 \times 10^{-3}$		
$[(\text{NH}_4)_3(\text{NO}_3)_2]^+$ with TMA <sup>a</sup>	$0.40 \pm 0.12$			
$[(\text{HMMA})_2(\text{NO}_3)]^+$ with TMA	$0.84 \pm 0.25$	$0.59 \pm 0.18$		
$[(\text{HMMA})_3(\text{NO}_3)_2]^+$ with TMA	$0.71 \pm 0.21$	$0.55 \pm 0.17$	$0.39 \pm 0.12$	
$[(\text{HMMA})_4(\text{NO}_3)_3]^+$ with TMA <sup>b</sup>	$0.76 \pm 0.23$	$0.57 \pm 0.17$	$0.43 \pm 0.13$	xx
$[(\text{HDMA})_2(\text{NO}_3)]^+$ with TMA	$0.60 \pm 0.18$	$0.40 \pm 0.12$		
$[(\text{HDMA})_3(\text{NO}_3)_2]^+$ with TMA	$0.22 \pm 0.07$	$0.16 \pm 0.05$	$0.016 \pm 0.006$	
$[(\text{HDMA})_4(\text{NO}_3)_3]^+$ with TMA <sup>b</sup>	$0.13 \pm 0.04$	$0.025 \pm 0.008$	$5.6 \pm 1.7 \times 10^{-3}$	xx
$[(\text{HMMA})_3(\text{NO}_3)_2]^+$ with $\text{NH}_3$	$< 2.2 \pm 0.7 \times 10^{-4}$		$< 0.029 \pm 0.009$	
$[(\text{HDMA})_2(\text{NO}_3)]^+$ with $\text{NH}_3$	$< 1.0 \pm 0.3 \times 10^{-4}$			
$[(\text{HDMA})_3(\text{NO}_3)_2]^+$ with $\text{NH}_3$	$< 2.5 \pm 0.8 \times 10^{-5}$			
$[(\text{HTMA})_2(\text{NO}_3)]^+$ with $\text{NH}_3$	$< 9 \pm 3 \times 10^{-5}$			

<sup>a</sup>Breakup of the 3-2 cluster to the 2-1 cluster was quite significant. The uptake coefficient represents the rate of cluster breakup to the 2-1 cluster compared to the collisional rate constant.

<sup>b</sup>For these 4-3 clusters, the final substitution of TMA appeared to induce cluster breakup.