Table 1. Data summary for the substitution of DMA for NH_3 in the 3-2 ammonium bisulfate cluster and for the substitution of NH_3 for DMA in the 3-2 dimethylaminium bisulfate cluster.

Substitution with DMA[a]	**Pseudo-first order rate constant (s^{-1})**	**Second order rate constant ($cm^3 \cdot molecule^{-1} \cdot s^{-1}$)**	***K***	***ΔG* (kJ/mol)**	**Collisional Rate Constant ($cm^3 \cdot molecule^{-1} \cdot s^{-1}$)**	**Uptake Coefficient (γ)**
$[(NH_4)_3(HSO_4)_2]^+ \rightarrow [(NH_4)_2(HDMA)(HSO_4)_2]^+$	0.49 ± 0.03	1.1 ± 0.3 x 10^{-9}	> 1500 ± 600	< -18.1 ± 0.9	1.3 ± 0.3 x 10^{-9}	0.85 ± 0.26
$[(NH_4)_2(HDMA)(HSO_4)_2]^+ \rightarrow [(NH_4)(HDMA)_2(HSO_4)_2]^+$	0.41 ± 0.02	9.3 ± 3.0 x 10^{-10}	> 620 ± 250	< -15.9 ± 0.8	1.3 ± 0.3 x 10^{-9}	0.72 ± 0.22
$[(NH_4)(HDMA)_2(HSO_4)_2]^+ \rightarrow [(HDMA)_3(HSO_4)_2]^+$	0.43 ± 0.03	9.7 ± 3.0 x 10^{-10}	> 26000 ± 10000	< -25.2 ± 1.3	1.3 ± 0.3 x 10^{-9}	0.75 ± 0.23
Substitution with NH_3[b]						
$[(HDMA)_3(HSO_4)_2]^+ \rightarrow [(NH_4)(HDMA)_2(HSO_4)_2]^+$	< 5 ± 3 x 10^{-4}	< 3.8 ± 1.1 x 10^{-14}	< 4 ± 2 x 10^{-5}	> 25.2 ± 1.3	2.0 ± 0.4 x 10^{-9}	< 1.9 ± 0.6 x 10^{-5}
$[(NH_4)(HDMA)_2(HSO_4)_2]^+ \rightarrow [(NH_4)_2(HDMA)(HSO_4)_2]^+$	< 1.8 ± 0.8 x 10^{-3}	< 1.5 ± 0.5 x 10^{-12}	< 1.6 ± 6 x 10^{-3}	> 15.9 ± 0.8	2.0 ± 0.4 x 10^{-9}	< 7.6 ± 2.3 x 10^{-4}
$[(NH_4)_2(HDMA)(HSO_4)_2]^+ \rightarrow [(NH_4)_3(HSO_4)_2]^+$	< 9 ± 2 x 10^{-4}	< 7.5 ± 2.3 x 10^{-13}	< 7 ± 3 x 10^{-4}	> 18.1 ± 0.9	2.0 ± 0.4 x 10^{-9}	< 3.8 ± 1.1 x 10^{-4}

[a]Pressure: 1.2 ± 0.2 x 10^{-8} torr

[b]Pressure: For $[(HDMA)_3(HSO_4)_2]^+$: 3.7 ± 0.7 x 10^{-7} torr; For $[(NH_4)(HDMA)_2(HSO_4)_2]^+$ and $[(NH_4)_2(HDMA)(HSO_4)_2]^+$: 3.4 ± 0.7 x 10^{-8} torr

Table 2. ΔG values (kJ/mol) for the substitution reactions of bisulfate clusters at 298 K.

	Sub. 1	**Sub. 2**	**Sub. 3**	**Sub. 4**
$[(NH_4)_2(HSO_4)]^+$ with DMA	< -15.1 ± 0.8	< -22.9 ± 1.2		
$[(NH_4)_3(HSO_4)_2]^+$ with DMA	< -18.1 ± 0.9	< -15.9 ± 0.8	< -25.2 ± 1.3	
$[(NH_4)_4(HSO_4)_3]^+$ with DMA	< -16.5 ± 0.8	< -15.2 ± 0.8	< -12.0 ± 0.6	< -26.5 ± 1.3
$[(NH_4)_2(HSO_4)]^+$ with TMA	< -14.1 ± 0.7	< -20.7 ± 1.0		
$[(NH_4)_3(HSO_4)_2]^+$ with TMA	< -7.0 ± 0.4	< -7.7 ± 0.4	< -15.3 ± 0.8	
$[(NH_4)_4(HSO_4)_3]^+$ with TMA	< -12.8 ± 0.6			
$[(HDMA)_2(HSO_4)]^+$ with TMA	-14.0 ± 0.7	-9.5 ± 0.5		
$[(HDMA)_3(HSO_4)_2]^+$ with TMA	-1.1 ± 0.1	-0.37 ± 0.02	7.9 ± 0.4	

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

	γ_1	γ_2	γ_3	γ_4
$[(NH_4)_2(HSO_4)]^+$ with DMA	1.05 ± 0.26	0.97 ± 0.24		
$[(NH_4)_3(HSO_4)_2]^+$ with DMA	0.85 ± 0.22	0.72 ± 0.18	0.75 ± 0.19	
$[(NH_4)_4(HSO_4)_3]^+$ with DMA	0.61 ± 0.15	0.56 ± 0.14	0.58 ± 0.15	0.83 ± 0.21
$[(HMMA)_2(HSO_4)]^+$ with DMA	1.05 ± 0.26	0.70 ± 0.18		
$[(HMMA)_3(HSO_4)_2]^+$ with DMA	0.82 ± 0.20	0.71 ± 0.18	0.64 ± 0.16	
$[(HMMA)_4(HSO_4)_3]^+$ with DMA	0.85 ± 0.21	0.80 ± 0.20	0.69 ± 0.17	0.66 ± 0.16
$[(HTMA)_2(HSO_4)]^+$ with DMA	$8.6 \pm 2.2 \times 10^{-3}$	$1.8 \pm 0.5 \times 10^{-3}$		
$[(HTMA)_3(HSO_4)_2]^+$ with DMA	0.51 ± 0.13	0.22 ± 0.05	0.18 ± 0.05	
$[(NH_4)_2(HSO_4)]^+$ with TMA	0.90 ± 0.26	0.65 ± 0.26		
$[(NH_4)_3(HSO_4)_2]^+$ with TMA	0.66 ± 0.26	0.45 ± 0.26	0.57 ± 0.26	
$[(NH_4)_4(HSO_4)_3]^+$ with TMA	0.64 ± 0.26	0.48 ± 0.26	0.39 ± 0.26	1.07 ± 0.26
$[(HMMA)_2(HSO_4)]^+$ with TMA	1.07 ± 0.27	0.54 ± 0.13		
$[(HMMA)_3(HSO_4)_2]^+$ with TMA	0.75 ± 0.19	0.60 ± 0.15	0.39 ± 0.10	
$[(HMMA)_4(HSO_4)_3]^+$ with TMA	0.76 ± 0.19	0.69 ± 0.17	0.55 ± 0.14	0.13 ± 0.03
$[(HDMA)_2(HSO_4)]^+$ with TMA	0.62 ± 0.15	0.47 ± 0.12		
$[(HDMA)_3(HSO_4)_2]^+$ with TMA	0.33 ± 0.08	0.30 ± 0.07	0.025 ± 0.006	
$[(HDMA)_4(HSO_4)_3]^+$ with TMA	0.36 ± 0.09	0.050 ± 0.013	0.014 ± 0.004	$3.9 \pm 1.0 \times 10^{-3}$
$[(HMMA)_2(HSO_4)]^+$ with NH_3	$< 1.1 \pm 0.3 \times 10^{-3}$	$< 1.7 \pm 0.5 \times 10^{-3}$		
$[(HMMA)_3(HSO_4)_2]^+$ with NH_3	$3 \pm 1 \times 10^{-4}$	$< 3.1 \pm 0.9 \times 10^{-4}$	$< 3 \pm 1 \times 10^{-4}$	
$[(HMMA)_4(HSO_4)_3]^+$ with NH_3	$< 1.0 \pm 0.3 \times 10^{-4}$	$< 8 \pm 3 \times 10^{-5}$	$< 4 \pm 1 \times 10^{-4}$	$< 4 \pm 1 \times 10^{-4}$
$[(HDMA)_2(HSO_4)]^+$ with NH_3	$< 6 \pm 2 \times 10^{-5}$	$< 1.6 \pm 0.5 \times 10^{-3}$		
$[(HDMA)_3(HSO_4)_2]^+$ with NH_3	$< 1.9 \pm 0.6 \times 10^{-5}$	$< 8 \pm 2 \times 10^{-4}$	$< 4 \pm 1 \times 10^{-4}$	
$[(HDMA)_4(HSO_4)_3]^+$ with NH_3	$< 1.2 \pm 0.4 \times 10^{-5}$	$< 3.0 \pm 0.9 \times 10^{-3}$	$< 8 \pm 2 \times 10^{-4}$	$< 5 \pm 2 \times 10^{-4}$
$[(HTMA)_2(HSO_4)]^+$ with NH_3	$< 9 \pm 3 \times 10^{-5}$	$< 1.7 \pm 0.5 \times 10^{-3}$		
$[(HTMA)_3(HSO_4)_2]^+$ with NH_3	$< 6 \pm 2 \times 10^{-4}$	$< 1.1 \pm 0.3 \times 10^{-2}$	$< 2.1 \pm 0.6 \times 10^{-2}$	
$[(HTMA)_4(HSO_4)_3]^+$ with NH_3				$< 1.9 \pm 0.6 \times 10^{-3}$

Table 4. Proton affinity and enthalpy of solvation values for NH_3 and the aliphatic amines (Lide, 2010).

	Proton Affinity (kJ/mol)	**Enthalpy of Solvation (kJ/mol)**
NH_3	853.6	-35.4
MMA	899.0	-45.3
DMA	929.5	-53.1
TMA	948.9	-52.7

Table 5. *ΔG* values (kJ/mol) for the substitution reactions of nitrate clusters at 298 K.

	Sub. 1	Sub. 2	Sub. 3
$[(NH_4)_3(NO_3)_2]^+$ with DMA			< -24.2 ± 1.2
$[(HDMA)_2(NO_3)]^+$ with TMA	-13.7 ± 0.7	-9.9 ± 0.5	

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

	γ_1	γ_2	γ_3	γ_4
$[(NH_4)_3(NO_3)_2]^+$ with DMA	0.53 ± 0.21	0.50 ± 0.17	0.68 ± 0.12	
$[(HMMA)_2(NO_3)]^+$ with DMA	0.86 ± 0.25	0.55 ± 0.18		
$[(HMMA)_3(NO_3)_2]^+$ with DMA	0.77 ± 0.21	0.66 ± 0.17	0.47 ± 0.12	
$[(HTMA)_2(NO_3)]^+$ with DMA	$6.4 \pm 1.9 \times 10^{-3}$	$2.0 \pm 0.6 \times 10^{-3}$		
$[(NH_4)_3(NO_3)_2]^+$ with TMA[a]	0.40 ± 0.12			
$[(HMMA)_2(NO_3)]^+$ with TMA	0.84 ± 0.25	0.59 ± 0.18		
$[(HMMA)_3(NO_3)_2]^+$ with TMA	0.71 ± 0.21	0.55 ± 0.17	0.39 ± 0.12	
$[(HMMA)_4(NO_3)_3]^+$ with TMA[b]	0.76 ± 0.23	0.57 ± 0.17	0.43 ± 0.13	xx
$[(HDMA)_2(NO_3)]^+$ with TMA	0.60 ± 0.18	0.40 ± 0.12		
$[(HDMA)_3(NO_3)_2]^+$ with TMA	0.22 ± 0.07	0.16 ± 0.05	0.016 ± 0.006	
$[(HDMA)_4(NO_3)_3]^+$ with TMA[b]	0.13 ± 0.04	0.025 ± 0.008	$5.6 \pm 1.7 \times 10^{-3}$	xx
$[(HMMA)_3(NO_3)_2]^+$ with NH_3	$< 2.2 \pm 0.7 \times 10^{-4}$		< 0.029 ± 0.009	
$[(HDMA)_2(NO_3)]^+$ with NH_3	$< 1.0 \pm 0.3 \times 10^{-4}$			
$[(HDMA)_3(NO_3)_2]^+$ with NH_3	$< 2.5 \pm 0.8 \times 10^{-5}$			
$[(HTMA)_2(NO_3)]^+$ with NH_3	$< 9 \pm 3 \times 10^{-5}$			

[a]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.

[b]For these 4-3 clusters, the final substitution of TMA appeared to induce cluster breakup.