



Supplement of

Pyruvic acid, an efficient catalyst in SO₃ hydrolysis and effective clustering agent in sulfuric-acid-based new particle formation

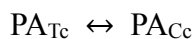
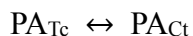
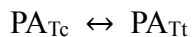
Narcisse Tsona Tchinda et al.

Correspondence to: Lin Du (lindu@sdu.edu.cn)

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S1 Equilibrium distribution of PA conformers

From our calculations, three PA conformers (PA_{Tc} , PA_{Tt} and PA_{Ct} shown in **Fig. S1**) were found to participate in the SO_3 hydrolysis. In real atmosphere, PA conformers are believed to be in equilibrium:



Using their Gibbs free energies (given in **Table S1**), calculated relative to the most stable conformer (PA_{Tc}), and applying the law of mass action, we determined the relative abundances of all PA conformers at 298 K and their values are given in **Table S1**.

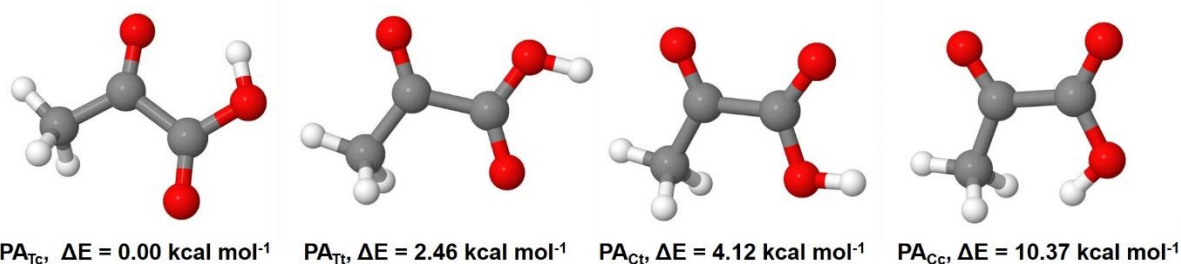


Figure S1: Conformers of PA optimized with the M06-2X/6-311++G(3df,3pd) method. Energies values, calculated at the M06-2X/6-311++G(3df,3pd) level of theory, are given relative to the energy of PA_{Tc} .

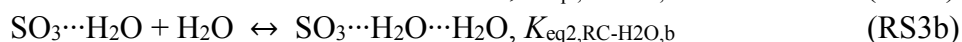
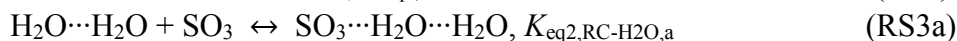
Table S1 Gibbs free energies (ΔG) values of PA conformers, calculated at the M06-2X/6-311++G(3df,3pd) level of theory relative to PA_{Tc} energy, and their corresponding relative abundance. Energies are calculated at 298 K and 1 atm, and units are kcal mol^{-1} .

Conformer	PA_{Tc}	PA_{Tt}	PA_{Ct}	PA_{Cc}
ΔG	0	1.81	3.13	9.18
Relative abundance	0.95	0.04	0.01	0.00

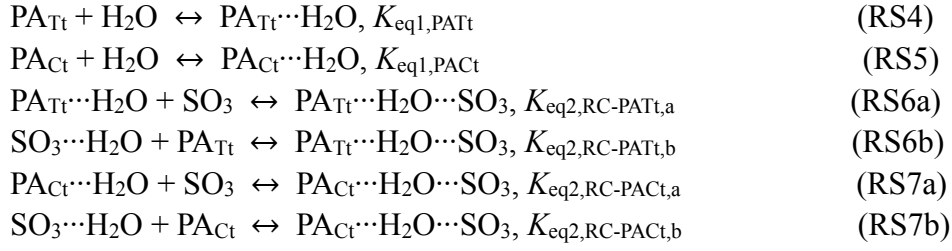
S2 Different equilibria involved in the X-catalyzed SO_3 hydrolysis, X = H_2O , PA

S2.1 Assessing the effect of different pathways in the formation of pre-reactive intermediates

For the H_2O -catalyzed SO_3 hydrolysis, the main equilibria contributing to the formation of the pre-reactive intermediate are:



The pre-reactive intermediates in the PA-catalyzed SO_3 hydrolysis are formed from two main interactions, $\text{PA} \cdots \text{H}_2\text{O} + \text{SO}_3$ and $\text{PA} + \text{SO}_3 \cdots \text{H}_2\text{O}$, according to the following equilibria, and in addition to reaction (RS2):



The equilibrium constants can be expressed by the equations below and their numerical values are given in **Table S2**:

$$K_{\text{eq1,H2O}} = \frac{[\text{H}_2\text{O}\cdots\text{H}_2\text{O}]}{[\text{H}_2\text{O}][\text{H}_2\text{O}]} \quad (\text{S1})$$

$$K_{\text{eq1,SO3}} = \frac{[\text{SO}_3\cdots\text{H}_2\text{O}]}{[\text{SO}_3][\text{H}_2\text{O}]} \quad (\text{S2})$$

$$K_{\text{eq2,RC-H2O,a}} = \frac{[\text{SO}_3\cdots\text{H}_2\text{O}\cdots\text{H}_2\text{O}]}{[\text{H}_2\text{O}\cdots\text{H}_2\text{O}][\text{SO}_3]} \quad (\text{S3a})$$

$$K_{\text{eq2,RC-H2O,b}} = \frac{[\text{SO}_3\cdots\text{H}_2\text{O}\cdots\text{H}_2\text{O}]}{[\text{SO}_3\cdots\text{H}_2\text{O}][\text{H}_2\text{O}]} \quad (\text{S3b})$$

$$K_{\text{eq1,PATt}} = \frac{[\text{PA}_{\text{Tt}}\cdots\text{H}_2\text{O}]}{[\text{PA}_{\text{Tt}}][\text{H}_2\text{O}]} \quad (\text{S4})$$

$$K_{\text{eq1,PACt}} = \frac{[\text{PA}_{\text{Ct}}\cdots\text{H}_2\text{O}]}{[\text{PA}_{\text{Ct}}][\text{H}_2\text{O}]} \quad (\text{S5})$$

$$K_{\text{eq2,RC-PATt,a}} = \frac{[\text{PA}_{\text{Tt}}\cdots\text{H}_2\text{O}\cdots\text{SO}_3]}{[\text{PA}_{\text{Tt}}\cdots\text{H}_2\text{O}][\text{SO}_3]} \quad (\text{S6a})$$

$$K_{\text{eq2,RC-PATt,b}} = \frac{[\text{PA}_{\text{Tt}}\cdots\text{H}_2\text{O}\cdots\text{SO}_3]}{[\text{SO}_3\cdots\text{H}_2\text{O}][\text{PA}_{\text{Tt}}]} \quad (\text{S6b})$$

$$K_{\text{eq2,RC-PACt,a}} = \frac{[\text{PA}_{\text{Ct}}\cdots\text{H}_2\text{O}\cdots\text{SO}_3]}{[\text{PA}_{\text{Ct}}\cdots\text{H}_2\text{O}][\text{SO}_3]} \quad (\text{S7a})$$

$$K_{\text{eq2,RC-PACt,b}} = \frac{[\text{PA}_{\text{Ct}}\cdots\text{H}_2\text{O}\cdots\text{SO}_3]}{[\text{SO}_3\cdots\text{H}_2\text{O}][\text{PA}_{\text{Ct}}]} \quad (\text{S7b})$$

Table S2 Equilibrium constants of different processes involved in the formation of pre-reactive intermediates, as given by reactions (RS1)-(RS7b) and Eqs. (S1)-(S7b). Calculations were performed at 298 K and units are $\text{cm}^3 \text{ molecule}^{-1}$.

$K_{\text{eq1,H2O}}$	4.86×10^{-22}
$K_{\text{eq1,SO3}}$	7.16×10^{-21}
$K_{\text{eq1,PATt}}$	1.69×10^{-20}
$K_{\text{eq1,PACt}}$	3.87×10^{-20}
$K_{\text{eq2,RC-H2O,a}}$	1.65×10^{-19}
$K_{\text{eq2,RC-H2O,b}}$	1.12×10^{-20}
$K_{\text{eq2,RC-PATt,a}}$	1.93×10^{-19}
$K_{\text{eq2,RC-PATt,b}}$	4.53×10^{-19}
$K_{\text{eq2,RC-PACt,a}}$	5.06×10^{-19}
$K_{\text{eq2,RC-PACt,b}}$	2.71×10^{-18}

Considering **reactions (RS6)** and **(RS7)**, the contribution of each path to the formation of the corresponding pre-reactive intermediate can be evaluated by determining the relative concentrations of $\text{SO}_3 \cdots \text{H}_2\text{O}$ and $\text{PA} \cdots \text{H}_2\text{O}$. Taking the formation of $\text{PA}_{\text{Tt}} \cdots \text{H}_2\text{O} \cdots \text{SO}_3$, rearrangement of **Eqs. (S1)** and **(S2)** leads to:

$$\frac{[\text{PA}_{\text{Tt}} \cdots \text{H}_2\text{O}]}{[\text{SO}_3 \cdots \text{H}_2\text{O}]} = \frac{K_{\text{eq1,PA}_{\text{Tt}}}}{K_{\text{eq1,SO}_3}} \times \frac{[\text{PA}_{\text{Tt}}]}{[\text{SO}_3]}$$

Likewise, rearranging **Eqs. (S1)** and **(S3)** gives

$$\frac{[\text{PA}_{\text{Ct}} \cdots \text{H}_2\text{O}]}{[\text{SO}_3 \cdots \text{H}_2\text{O}]} = \frac{K_{\text{eq1,PA}_{\text{Ct}}}}{K_{\text{eq1,SO}_3}} \times \frac{[\text{PA}_{\text{Ct}}]}{[\text{SO}_3]}$$

Taking into account the relative abundances of PA conformers (0.95 for PA_{Tt} , 0.04 for PA_{Tt} and 0.01 for PA_{Ct}), considering atmospheric PA and SO_3 concentrations of $\sim 10^{10} \text{ cm}^{-3}$ and $\sim 10^6 \text{ cm}^{-3}$, respectively, and taking the values of equilibrium constants in **Table S2**, we find that regardless of the PA conformer, $\text{PA} \cdots \text{H}_2\text{O}$ will contribute by more than 99.99% to the formation of $\text{PA} \cdots \text{H}_2\text{O} \cdots \text{SO}_3$ while $\text{SO}_3 \cdots \text{H}_2\text{O}$ will contribute by less than 0.01%.

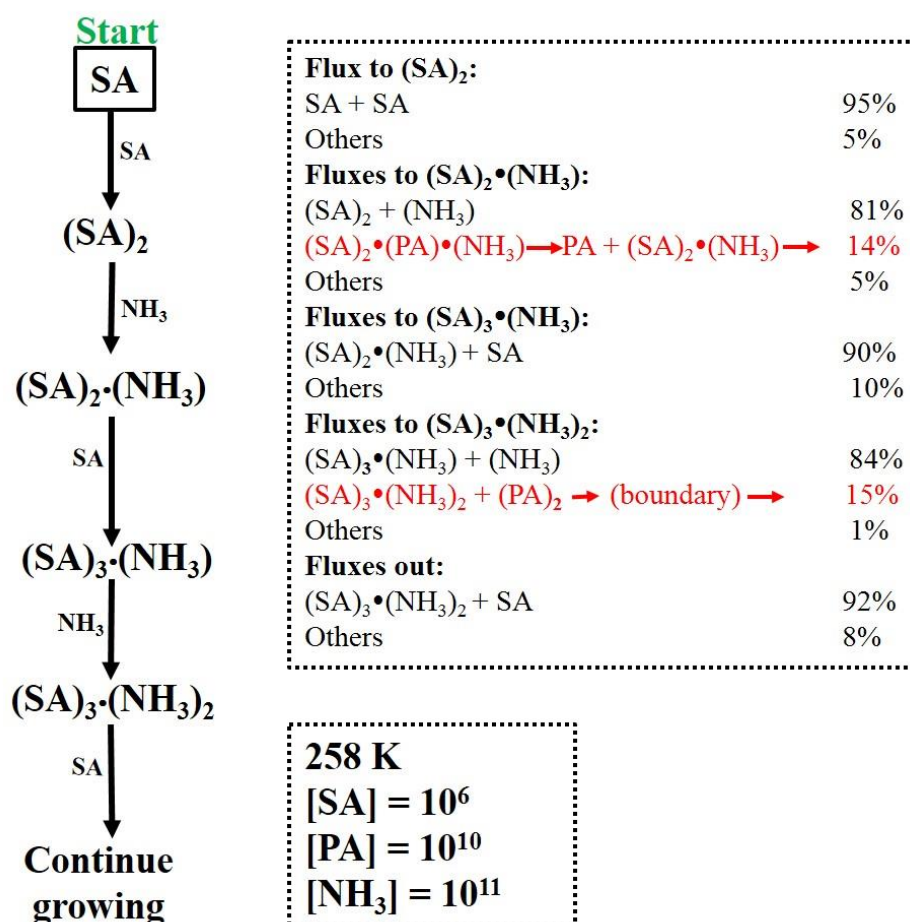


Figure S2: Main cluster pathways at 258 K, $[\text{SA}] = 10^6 \text{ cm}^{-3}$, $[\text{PA}] = 10^{10} \text{ cm}^{-3}$, and $[\text{NH}_3] = 10^{11} \text{ cm}^{-3}$. Red color indicates the path involving PA.

Table S3 Numerical values of unimolecular rate constants ($k_{\text{uni},x}$ in s^{-1}) of decomposition of pre-reactive intermediates and overall rate constant (k_x in $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$) of reaction (R2) described by Eq. (1), in the presence of catalyst X ($X = \text{H}_2\text{O}$, PA_{Tt} , and PA_{Ct}), and calculated at 298 K.

Catalyst	$k_{\text{uni},x}$ (s^{-1})	k_x ($\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$)
H_2O	1.35×10^8	1.09×10^{-32}
PA_{Tt}	9.03×10^{11}	2.95×10^{-27}
PA_{Ct}	1.80×10^{12}	3.52×10^{-26}

Table S4: Electronic (ΔE) and Gibbs free energies at 298 K and 1 atm (ΔG) of formation of all intermediate in H_2O -catalyzed and PA-catalyzed SO_3 hydrolysis. Corresponding structures are shown in **Fig. 1** and **Fig. 2** in the main article. Energies units are kcal mol^{-1} .

Clusters	Without ZPE correction		With ZPE correction	
	ΔE	ΔG	ΔE	ΔG
$\text{H}_2\text{O} \cdot \text{H}_2\text{O}$	-5.00	2.62	-2.90	4.72
$\text{SO}_3 \cdot \text{H}_2\text{O}$	-9.00	1.02	-6.67	3.35
$\text{PA}_{\text{Tt}} \cdot \text{H}_2\text{O}$	-10.26	0.51	-8.03	2.75
$\text{PA}_{\text{Ct}} \cdot \text{H}_2\text{O}$	-10.90	0.02	-8.64	2.29
Water-catalyzed reaction				
RC	-20.91	1.78	-15.40	7.30
TS	-13.72	8.36	-9.93	12.15
PC	-34.98	-11.51	-29.25	-5.78
PA-catalyzed reaction				
RC_{Tt}	-24.59	-0.41	-20.60	3.59
TS_{Tt}	-22.01	0.91	-20.25	2.67
PC_{Tt}	-39.13	-14.87	-34.81	-10.55
RC_{Ct}	-26.11	-1.47	-22.15	2.49
TS_{Ct}	-24.01	-0.60	-24.01	1.34
PC_{Ct}	-41.16	-16.49	-34.73	-12.05

Table S5: Electronic and Gibbs free energies of clusters formation in the sulfuric acid-pyruvic acid-ammonia system. Energies units are kcal mol^{-1} .

Clusters	$\Delta E_{0\text{K}}$	$\Delta G_{298\text{K}}$	$\Delta G_{278\text{K}}$	$\Delta G_{258\text{K}}$	$\Delta G_{238\text{K}}$
$(\text{PA})_2$	-15.40	-3.57	-4.30	-5.03	-5.76
$(\text{PA})_3$	-25.38	-1.32	-2.79	-4.26	-5.73
$(\text{PA})_1 \cdot (\text{NH}_3)_1$	-11.60	-2.47	-3.00	-3.53	-4.06
$(\text{PA})_2 \cdot (\text{NH}_3)_1$	-24.17	-3.79	-5.00	-6.21	-7.42
$(\text{PA})_2 \cdot (\text{NH}_3)_2$	-37.04	-3.02	-5.08	-7.13	-9.18
$(\text{PA})_3 \cdot (\text{NH}_3)_1$	-42.41	-3.36	-5.75	-8.14	-10.53
$(\text{PA})_3 \cdot (\text{NH}_3)_2$	-58.56	-6.08	-9.19	-12.31	-15.42
$(\text{PA})_3 \cdot (\text{NH}_3)_3$	-68.39	-7.27	-10.89	-14.50	-18.11

(PA)₁•(SA)₁	-18.46	-6.18	-6.94	-7.70	-8.47
(PA)₁•(SA)₂	-39.05	-12.75	-14.37	-15.99	-17.61
(PA)₁•(SA)₃	-57.28	-15.87	-18.42	-20.98	-23.53
(PA)₂•(SA)₁	-35.49	-11.93	-13.39	-14.85	-16.31
(PA)₂•(SA)₂	-51.12	-13.84	-16.13	-18.42	-20.72
(PA)₂•(SA)₃	-70.31	-17.16	-20.41	-23.66	-26.91
(PA)₁•(SA)₁•(NH₃)₁	-32.16	-9.80	-11.16	-12.52	-13.89
(PA)₁•(SA)₁•(NH₃)₂	-53.85	-15.54	-17.77	-20.00	-22.23
(PA)₂•(SA)₁•(NH₃)₁	-53.25	-15.42	-17.68	-19.95	-22.21
(PA)₂•(SA)₁•(NH₃)₂	-71.95	-22.47	-25.45	-28.42	-31.40
(PA)₂•(SA)₁•(NH₃)₃	-83.24	-22.10	-25.75	-29.40	-33.05
(PA)₁•(SA)₂•(NH₃)₁	-62.19	-24.58	-26.84	-29.10	-31.36
(PA)₁•(SA)₂•(NH₃)₂	-87.35	-32.66	-35.86	-39.05	-42.25
(PA)₁•(SA)₂•(NH₃)₃	-99.35	-35.03	-38.84	-42.64	-46.44
(SA)₂	-21.63	-7.34	-8.20	-9.07	-9.93
(SA)₃	-41.03	-12.94	-14.67	-16.41	-18.14
(SA)₁•(NH₃)₁	-17.40	-6.67	-7.31	-7.95	-8.59
(SA)₂•(NH₃)₁	-47.44	-21.61	-23.13	-24.65	-26.17
(SA)₂•(NH₃)₂	-66.86	-27.60	-29.84	-32.07	-34.31
(SA)₃•(NH₃)₁	-69.61	-30.15	-32.53	-34.91	-37.28
(SA)₃•(NH₃)₂	-96.16	-43.42	-46.46	-49.50	-52.54
(SA)₃•(NH₃)₃	-112.42	-47.83	-51.57	-55.32	-59.06