Supplementary data

Atmospheric chemistry of thiourea: the nucleation with urea and the roles in NO_2 hydrolysis

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Table S1 The geometrical information of N-H···O and O-H···O in conformers at the MP2/6-311G(d,p) level of theory (angles in degree; lengths in Å).

Conformer	N-H···O		O-H···O	
	r	θ	r	θ
W-W1	–	–	1.939	174.2
U-U1	1.900(1.901)	175.0(175.1)	–	–
U-W1	2.047	144.5	1.916	151.8
TU-TU1	–	–	–	–
TU-W1	1.912	157.6	–	–
U-TU1	1.853	166.4	–	–
U-TU-W1	1.773	170.6	1.802	169.6
U-TU-W2	1.900(2.040,2.029)	162.3(147.6,146.9)	–	–
U-TU-W3	1.851(1.930)	165.4(157.5)	–	–
U-TU-W4	1.871(2.043)	166.9(145.9)	1.912	153.4
U-TU-W5	1.900	174.4	2.086	152.2
U-TU-W6	2.068(1.889)	142.9(158.3)	1.868	153.6
TU-TU-U1	1.846	168.8	–	–
TU-TU-U2	2.077	144.2	–	–
W-W-U1	1.878	178.1	1.774(1.792)	162.2(169.1)
TU-TU-W1	1.919	157.8	–	–
U-U-W1	1.912(2.058,1.887)	175.5(145.1,175.4)	1.893	154.0
W-W-TU1	1.819	176.3	1.797	159.3
U-U-TU1	1.945(2.032,1.995)	158.9(176.7,154.0)	–	–
U-U-TU2	1.877(2.047)	157.2(148.2)	–	–

Table S2 Calculated binding energy (Δ*E*), zero point energy (ΔZPE), enthalpy of formation (Δ*H*) and Gibbs free energy of formation (Δ*G*) at 298.15 K for the lower energy clusters.

Conformer	Δ*E*	ΔZPE	Δ*H*	Δ*G*
W-W2	-1.92	2.96	-2.36	4.29
U-U2	-10.02	1.65	-10.59	-0.96
U-W2	-4.85	2.85	-4.82	2.84
TU-TU2	-8.96	1.02	-9.93	-0.86
TU-W2	-5.26	1.63	-5.69	3.13
U-TU2	-10.76	2.33	-10.35	-0.55
W-W-U2	-12.36	2.06	-12.99	4.29
TU-TU-W2	-16.97	2.93	-17.36	1.26
U-U-W2	-16.66	1.96	-16.65	1.89
W-W-TU2	-13.61	2.03	-14.21	3.19

Table S3 The total rate constants (k, for $2NO_2 + H_2O$ from the level of CCSD(T)/6-311++G(3df,2p)//B3LYP/6-311++G(3df,2p) and for $2NO_2 + H_2O$ +TU from the level of CCSD(T)/6-311++G(d,p)//MP2/6-311G(d,p)) at the temperatures T = 298 K and 300 K.

Reaction	T (K)	calc, k^a	calc, k^b	expt, k^c
$2NO_2 + H_2O$	298	1.78×10^{-39}	—	1.52×10^{-37}
	300	2.21×10^{-39}	1.49×10^{-37}	—
$2NO_2 + H_2O$ +TU	298	3.28×10^{-54}	—	—
	300	4.34×10^{-54}	—	—

[a]In unit of cm^6 $molecules^{-2}$ s^{-1} for $2NO_2 + H_2O$ reaction and cm^9 $molecules^{-3}$ s^{-1} for $2NO_2 + H_2O$+TU reaction.

[b]Reference 1.

[c]Reference 2.

Table S4 The calculated rate constants (k_{tot}, in cm^3 $molecules^{-1}$ s^{-1}) for the reactions of N_2O_4 hydrolysis in the absence and presence of thiourea from the level of CCSD(T)/6-311++G(d,p)//MP2/6-311G(d,p) at the temperatures T = 220 – 320 K.

Reaction		T(K)						
		220	240	260	280	298	300	320
N_2O_4+W	K_{eq}	2.51×10^{-22}	7.64×10^{-23}	2.82×10^{-23}	1.20×10^{-23}	6.20×10^{-24}	5.78×10^{-24}	3.06×10^{-24}
	K_{ui}	4.60×10^{9}	8.96×10^{9}	1.59×10^{10}	2.60×10^{10}	3.85×10^{10}	4.01×10^{10}	5.88×10^{10}
	K_{tot}	1.15×10^{-12}	6.85×10^{-13}	4.48×10^{-13}	3.13×10^{-13}	2.38×10^{-13}	2.32×10^{-13}	1.80×10^{-13}
N_2O_4-W+TU	K_{eq}	1.48×10^{-20}	1.96×10^{-21}	3.55×10^{-22}	8.19×10^{-23}	2.57×10^{-23}	2.29×10^{-23}	7.49×10^{-24}
	K_{ui}	7.75×10^{12}	8.13×10^{12}	8.52×10^{12}	8.91×10^{12}	9.27×10^{12}	9.31×10^{12}	9.72×10^{12}
	K_{tot}	1.14×10^{-7}	1.59×10^{-8}	3.03×10^{-9}	7.30×10^{-10}	2.39×10^{-10}	2.13×10^{-10}	7.28×10^{-11}
TU-W+N_2O_4	K_{eq}	4.87×10^{-24}	1.22×10^{-24}	3.79×10^{-25}	1.39×10^{-25}	6.30×10^{-26}	5.80×10^{-26}	2.71×10^{-26}
	K_{ui}	7.75×10^{12}	8.13×10^{12}	8.52×10^{12}	8.91×10^{12}	9.27×10^{12}	9.31×10^{12}	9.72×10^{12}
	K_{tot}	3.77×10^{-11}	9.91×10^{-12}	3.23×10^{-12}	1.24×10^{-12}	$5.84\times10E^{-13}$	5.40×10^{-13}	2.63×10^{-13}

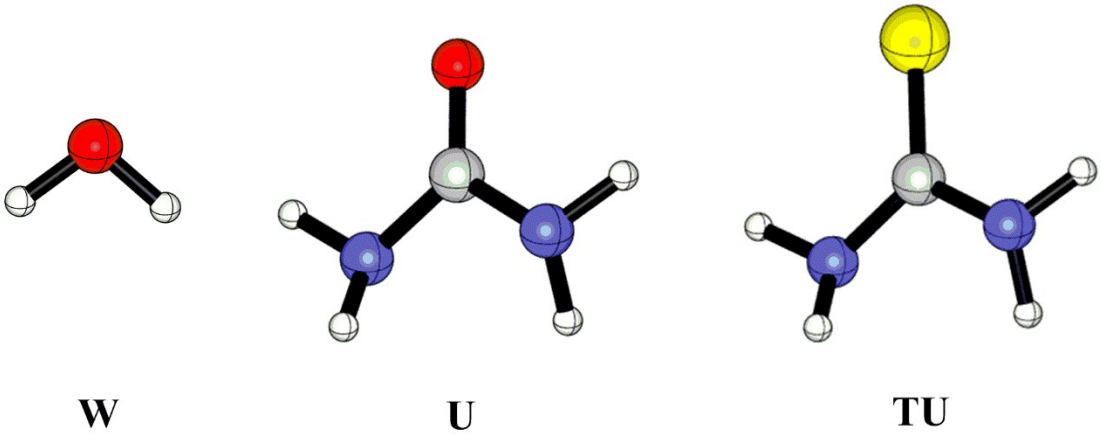

Figure S1. The geometrical configurations of monomers water, urea and thiourea optimized at the MP2/6-311G(d,p) level.

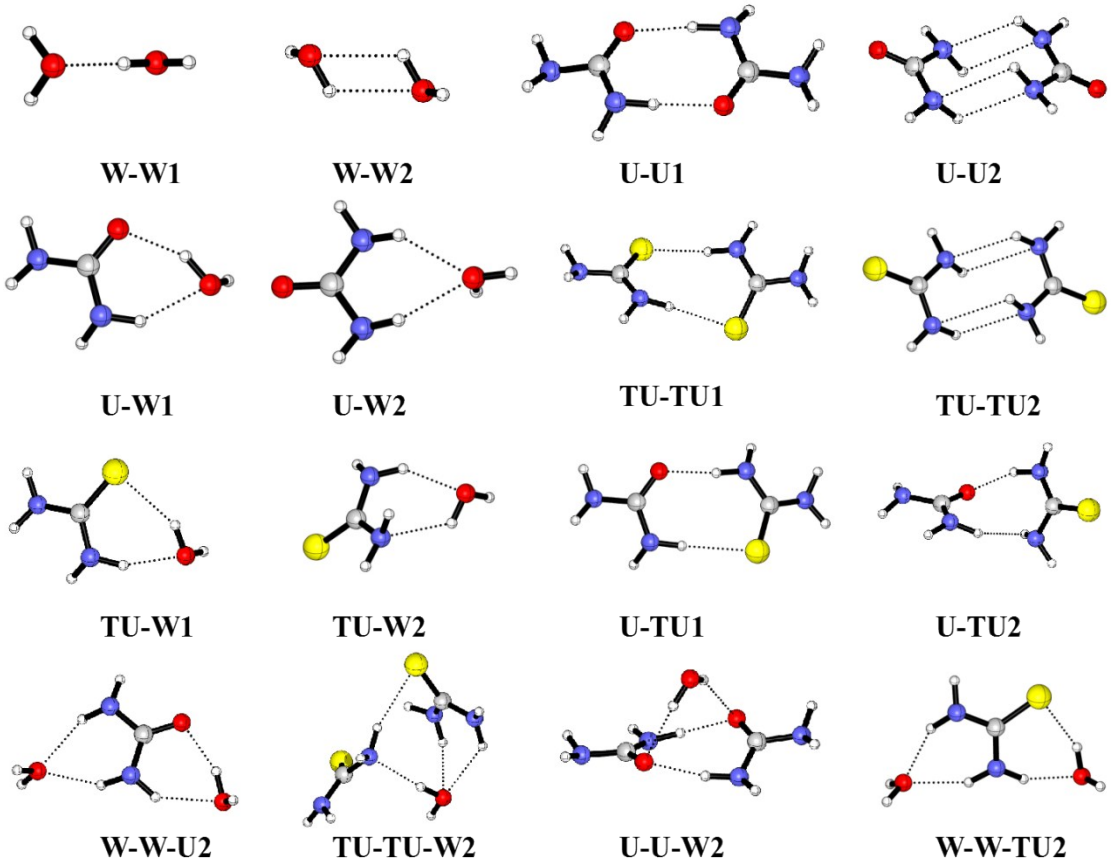

Figure S2. The geometrical configurations of dimers and part of trimers optimized at the MP2/6-311G(d,p) level.

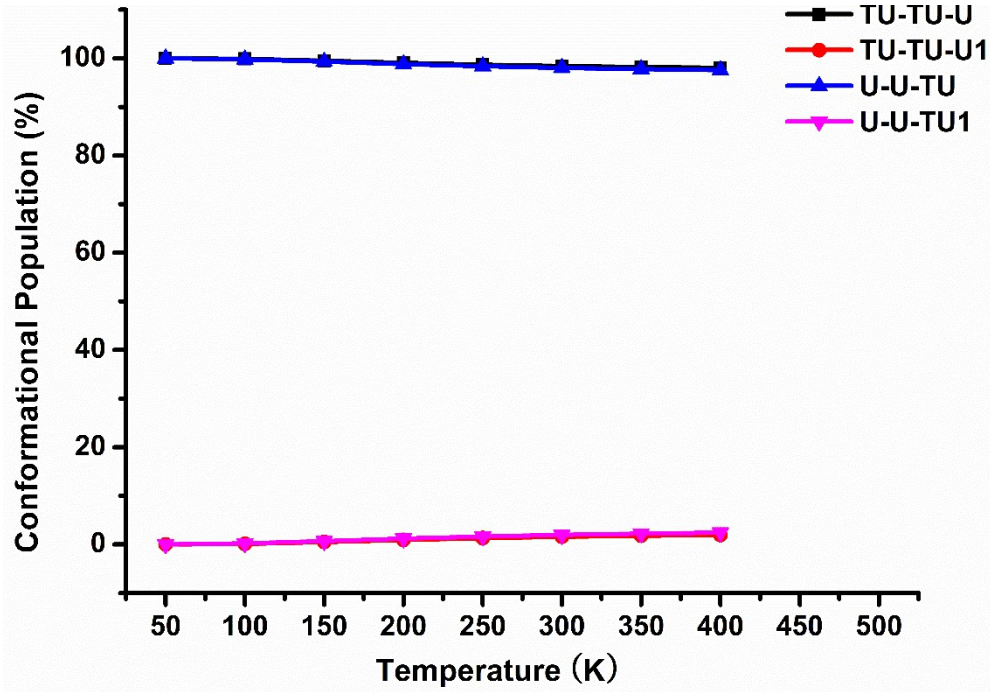

Figure S3. The conformational population change for isomers of U-U-TU1 and U-U-TU2, TU-TU-U1 and TU-TU-U2 clusters as a function of the temperature from 50 K to 400 K.

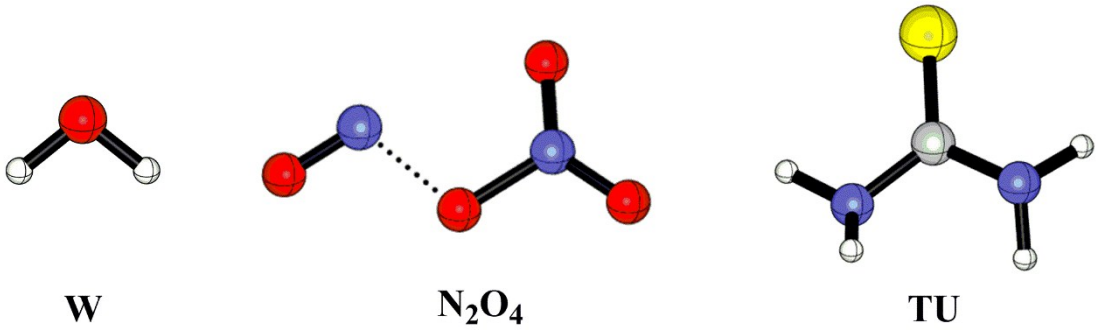

Figure S4. The geometrical configurations of monomers involved in NO_2 hydrolysis reaction in the presence of TU obtained at the MP2/6-311G(d,p) level.

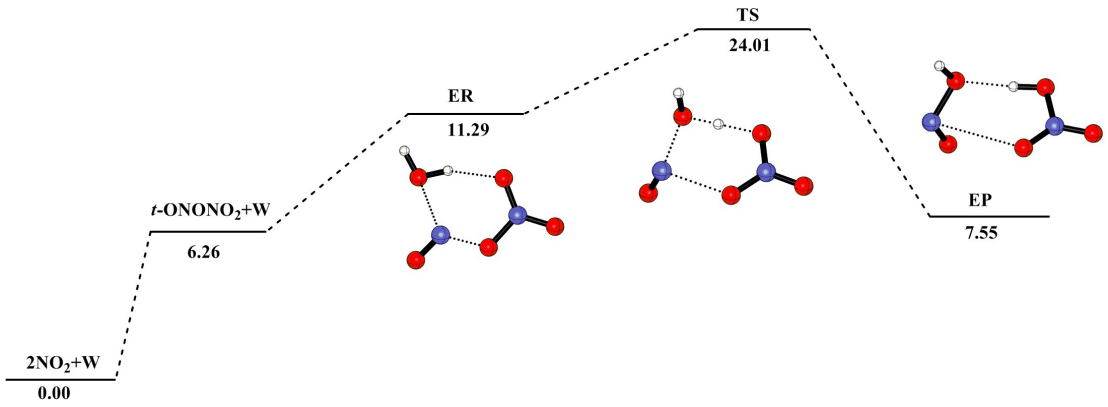

Figure S5. The free energy profiles of paths for the reaction of $2NO_2+H_2O$ obtained from CCSD(T)/6-311++G(d, p)//MP2/6-311G(d, p) level of theory.

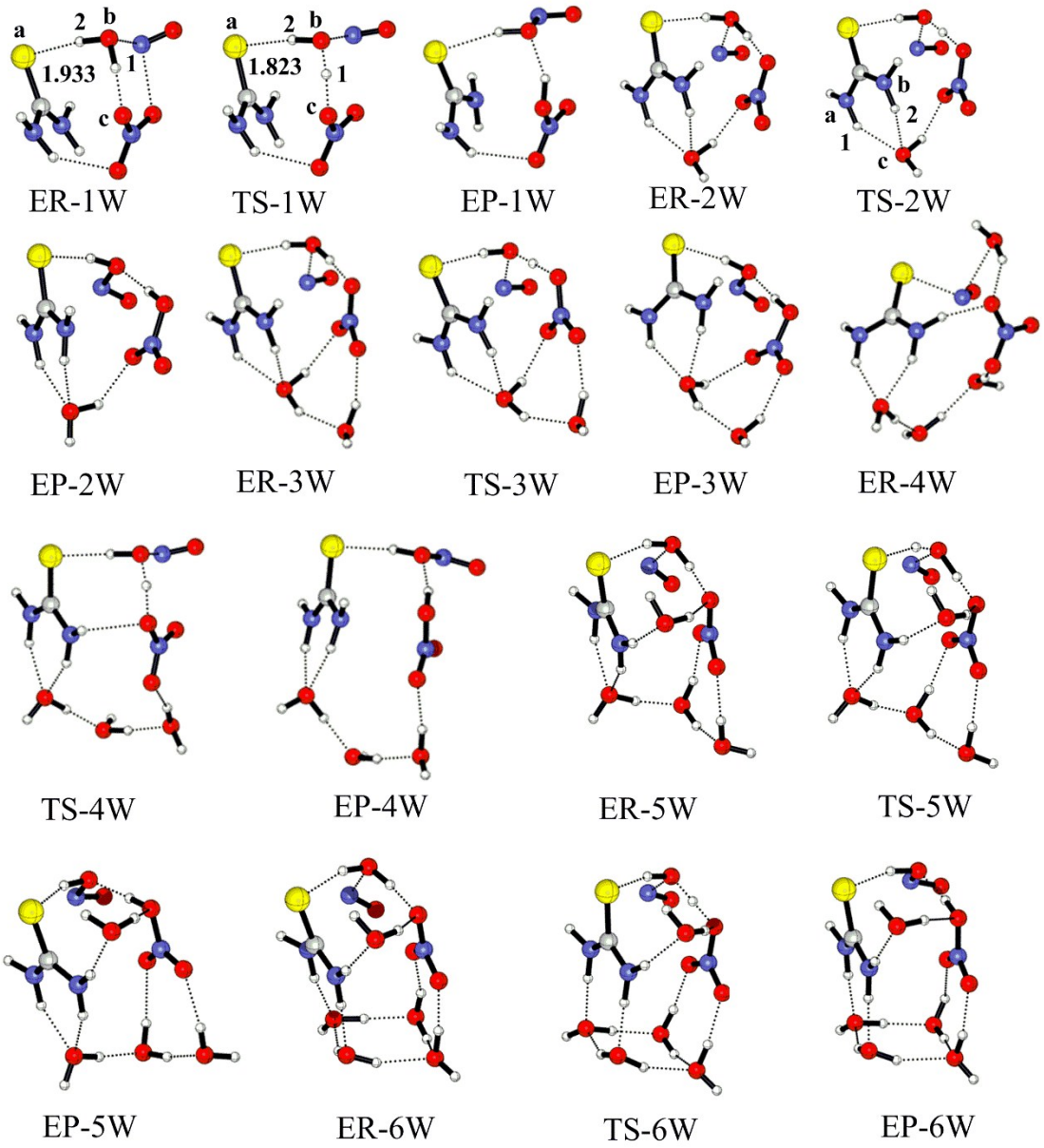

Figure S6. The geometrical configurations of complexes involved in NO_2 hydrolysis reaction containing 1 to 6 water molecules in the presence of TU obtained at the MP2/6-311G(d,p) level.

References

1.R. S. Zhu, K. Y. Lai and M. C. Lin, *J. Phys. Chem. A*, 2012, **116**, 4466-4472.

2.C. E. a. W. H. Corcoran, *Ind. Eng. Chem. Fundam*, 1974, **13**, 373.