

Supporting Information

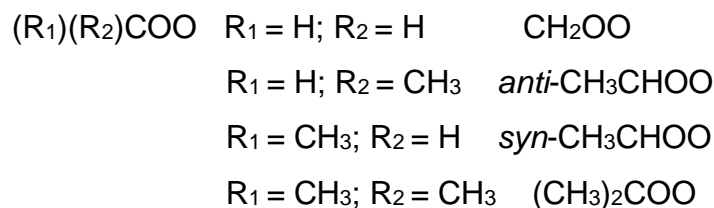
Heteroatom Tuning of Bimolecular Criegee Reactions and Its Implications

*Manoj Kumar and Joseph S. Francisco**

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Supporting Information

Computational Details. All calculations reported in this work were performed using Gaussian09¹ software. The gas-phase reactions of four different Criegee intermediates with chalcogen hydrides (H₂X; X = O, S, Se, and Te) were investigated. The following Criegee intermediates were considered in the present work:



The R₁ group in the (R₁)(R₂)COO is located in *syn* position with regard to terminal Criegee oxygen. The reactions of (R₁)(R₂)COO with H₂S were also examined in the catalytic presence of an additional water molecule. The equilibrium and transition state structures were fully optimized using the M06-2X² level of density functional theory and the augmented correlation-consistent triplet zeta basis set, aug-cc-pVTZ.³ Note that there is no all electron "aug-cc-pVTZ" basis set defined for Te. However, there is a variant of this basis set reported in the literature for Te that use an ECP to replace the core electrons and then an "aug-cc-pVTZ" quality basis set for the valence. This variant is called "aug-cc-pVTZ-PP" in the literature⁴ and has been used in all the H₂Te involving reactions in the present work. The energetics of these reactions was further refined using the coupled cluster single and double substitution method with a perturbative treatment of triple excitations (CCSD(T))⁵ and the aug-cc-pVTZ basis set. In specific, the zero-point-corrected CCSD(T)/aug-cc-pVTZ electronic energies at the M06-2X/aug-cc-pVTZ-optimized geometries have been used. We have used notation, CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ to represent CCSD(T) energies. This level of theory has been previously shown to perform really well for the hydrogen atom transfer-based unimolecular and bimolecular Criegee reactions.^{6,7} For all the reactions, the M06-2X/aug-cc-pVTZ calculated vibrational frequencies were used to estimate the zero-point correction for the reactants, products, transition states, and intermediates. The presence of zero or single imaginary frequency was used to identify all the stationary points as minima or transition states.

References:

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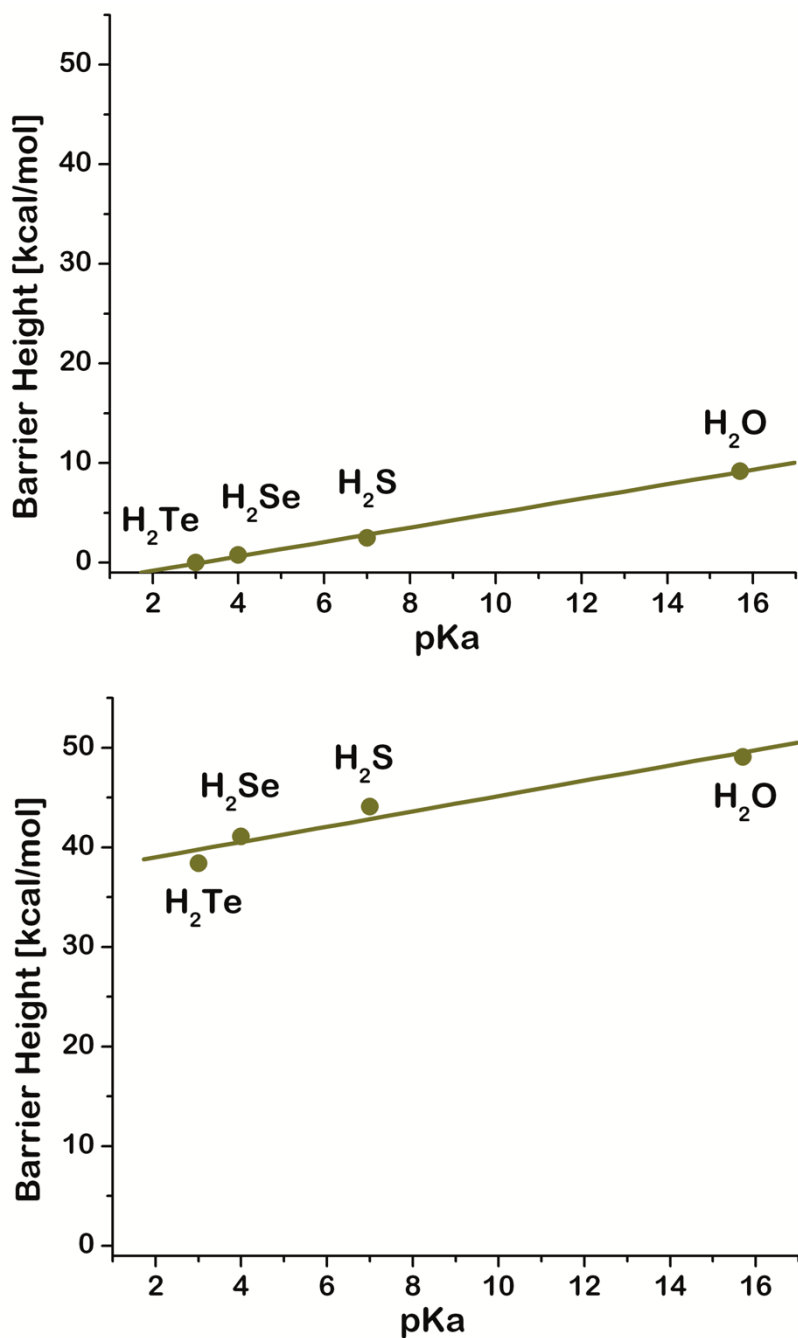


Figure S1. CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated zero-point-corrected barriers for the CH₂OO-H₂X (X = O, S, Se, and Te) addition reactions (*top panel*) and the subsequent H₂O₂ elimination reactions (*bottom panel*) plotted against the first pKa of H₂X.

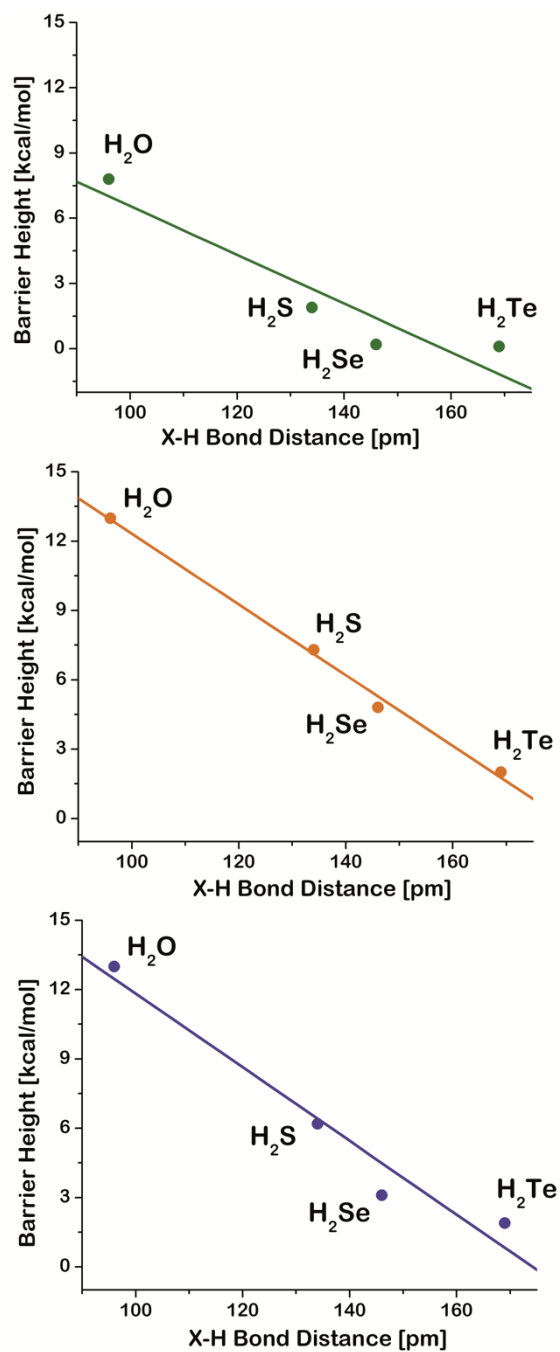


Figure S2. CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated zero-point-corrected barriers for the (R₁)(R₂)COO-H₂X (X = O, S, Se, and Te) addition reactions (*top*: R₁=H;R₂=CH₃, *middle*: R₁=CH₃;R₂=H, and *bottom*: R₁=CH₃;R₂=CH₃) plotted against the X-H bond distance in H₂X. The R₁ group in (R₁)(R₂)COO is located *syn* to terminal Criegee oxygen.

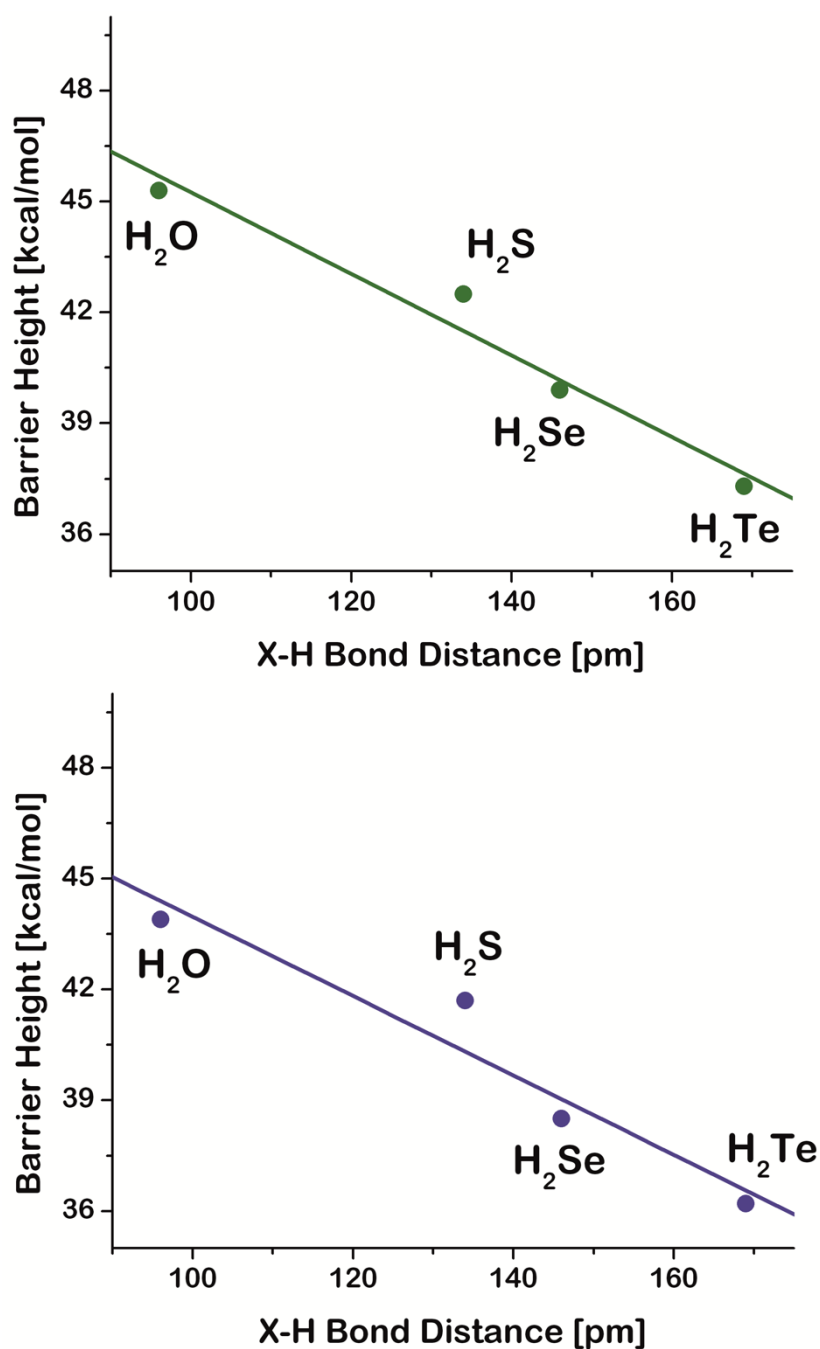


Figure S3. CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated zero-point-corrected barriers for the H_2O_2 releasing step from the $(R_1)(R_2)COO-H_2X$ ($X = O, S, Se,$ and Te) reactions (*top*: $R_1=H; R_2=CH_3$, and *bottom*: $R_1=CH_3; R_2=CH_3$) plotted against the X-H bond distance in H_2X . The R_1 group in $(R_1)(R_2)COO$ is located *syn* to terminal Criegee oxygen.

Table S1. CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated zero-point-corrected electronic energies for the reactions between various Criegee intermediates ((R₁)(R₂)COO) and chalcogen hydrides (H₂X). The R₁ in (R₁)(R₂)COO is located *syn* to terminal Criegee oxygen. Energies are given in kcal/mol units.

Criegee Intermediate, (R ₁)(R ₂)COO	H ₂ X	Int ₁	TS _{H₂X}	Int ₂	TS _{cis-trans}	Int ₃	TS _{H₂O₂}	Int ₄	(R ₁)(R ₂)C=X + H ₂ O ₂
R₁ = H; R₂ = H	X = O	-6.8	2.4	-42.5	-39.8	-42.4	6.7	-31.9	-26.6
	X = S	-3.9	-1.4	-44.7	-40.0	-45.2	-1.1	-29.6	-24.3
	X = Se	-4.9	-4.1	-47.0	-42.1	-47.0	-5.9	-27.9	-24.1
	X = Te	-4.5	-4.5	-47.7	-43.2	-47.7	-9.3	-27.9	-25.0
R₁ = H; R₂ = CH₃	X = O	-9.6	-1.8	-38.7	-38.2	-40.6	4.7	-34.3	-27.5
	X = S	-6.9	-5.0	-42.7	-37.9	-42.5	0.0	-28.6	-23.2
	X = Se	-7.6	-7.4	-45.2	-40.6	-44.8	-4.9	-28.4	-23.2
	X = Te	-6.7	-6.6	-45.5	-42.6	-45.0	-7.7	-28.0	-23.2
R₁ = CH₃; R₂ = H	X = O	-7.6	5.4	-34.4					
	X = S	-4.8	2.5	-37.9					
	X = Se	-5.0	-0.2	-40.0					
	X = Te	-3.9	-0.9	-40.9					
R₁ = CH₃; R₂ = CH₃	X = O	-8.8	4.2	-34.0	-32.3	-34.8	9.1	-30.1	-22.6
	X = S	-5.5	0.7	-34.6	-30.8	-35.7	6.0	-22.2	-16.2
	X = Se	-6.3	-3.2	-38.0	-34.3	-38.2	0.3	-22.3	-16.6
	X = Te	-5.3	-3.4	-38.1	-35.0	-38.0	-1.8	-21.6	-16.3

Table S2. CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated zero-point-corrected electronic energies for the reactions between various Criegee intermediates ((R₁)(R₂)COO) and hydrogen sulfide in the presence of an additional water molecule. The R₁ in (R₁)(R₂)COO is located *syn* to terminal Criegee oxygen. Energies are given in kcal/mol units.

Key species	(R ₁)(R ₂)COO + H ₂ S--H ₂ O → (R ₁)(R ₂)CS + H ₂ O ₂ + H ₂ O		
	R ₁ = H; R ₂ = H	R ₁ = H; R ₂ = CH ₃	R ₁ = CH ₃ ; R ₂ = CH ₃
Int₁	-9.2	-13.1	-12.8
TS_{H₂S}	-5.9	-7.4	-4.0
Int₂	-50.0	-47.9	-39.8
Int₃	-43.2	-41.2	-33.1
TS_{cis-trans}	-38.5	-36.4	-29.3
Int₄	-43.7	-41.0	-34.2
Int₅	-48.1	-45.6	-38.9
TS_{H₂O₂}	-21.5	-19.3	-13.7
Int₆	-32.0	-32.5	-27.3
(R₁)(R₂)CS + H₂O₂ + H₂O	-22.8	-21.7	-14.7