Atmospheric Chemistry

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Heteroatom Tuning of Bimolecular Criegee Reactions and Its Implications

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Abstract: *High-level quantum-chemical calculations have been performed to understand the key reactivity determinants of bimolecular reactions of Criegee intermediates and H_2X ($X = O$, S, Se, and Te). Criegee intermediates are implicated as key intermediates in atmospheric, synthetic organic, and enzymatic chemistry. Generally, it is believed that the nature and location of substituents at the carbon of the Criegee intermediate play a key role in determing the reactivity. However, the present work suggests that it is not only the substitution of the Criegee intermediate, but the nature of the heteroatom in H_2X that also plays a crucial role in determining the reactivity of the interaction between the Criegee intermediate and H_2X. The barriers for the reactions of Criegee intermediates and H_2X satisfy an inverse correlation with the bond strength of X−H in H_2X, and a direct correlation with the first pK_a of H_2X. This heteroatom tuning causes a substantial barrier lowering of 8–11 $kcal\,mol^{-1}$ in the Criegee reaction barrier in going from H_2O to H_2Te. An important implication of these results is that the reaction of the Criegee intermediate and H_2S could be a source of thioaldehydes, which are important in plantery atmospheres and synthetic organic chemistry. By performing the reaction of Criegee intermediates and H_2S under water or acid catalysis, thioladehydes could be detected in a hydrogen-bonded complexed state, which is significantly more stable than their uncomplexed form. As a result, simpler aliphatic thioaldehydes could be selectively synthesized in the laboratory, which, otherwise, has been a significant synthetic challenge because of their ability to oligomerize.*

Understanding reaction chemistry of Criegee intermediates has become a hot topic of research in the recent past. Criegee intermediates are carbonyl oxides that are principally produced in the ozone–olefin cycloaddtions.[1] The unimolecular and bimolecular Criegee reactions play a crucial role in the tropospheric budgets of hydroxy radicals, organic acids, hydroperoxides, nitrates, sulfates and secondary organic aerosols.[2–9] At the same time, Criegee chemistry is a key component of ozonolysis-based syntheses that offer safe and scalable routes for synthesizing pharmaceutical intermediates and other useful commodities.[10–12] Criegee intermediates are also implicated in the reaction cycles of flavin-dependent Baeyer–Villiger monooxygenases[13] that provide an environmentally benign route for forming enantiopure drugs.[14]

Because of its broad profile, factors influencing the reactivity of Criegee intermediates have been extensively investigated by experimental and theoretical means. The nature and location of the substituents on the Criegee intermediate significantly tune its reactivity.[15] Criegee intermediates having a methyl substituent in the *anti* position react faster than Criegee intermediates having a methyl substituent in *syn* position. Criegee intermediates with electron-withdrawing substituents and zwitterionic character react faster than those having electron-releasing substituents. Substitution in the Criegee intermediate can cause up to ten orders of magnitude differences in its reactivity. The unimolecular and bimolecular reactions of the Criegee intermediate CH_3CHOO represent one of the well-studied conformer-dependent Criegee reactivity profile.

Criegee intermediates participate in various bimolecular reactions. Though the effect of Criegee substitution in bimolecular reactions has been well explored, the effect of substituent in the non-Criegee reacting partner is less so. For example, the most probable bimolecular Criegee reaction in troposphere is the reaction with water. However, it is not clear whether the nature of heteroatom X in H_2X ($X = O$, S, Se, and Te) would alter the energetics of the reaction of Criegee intermediates and H_2X. Does there exist any correlation between the Criegee reaction barrier and the heteroatom nature? If yes, what are its implications? If not, what other factors influence the reaction of Criegee intermediates and H_2X? A detailed knowledge of these determinants may provide general guidelines for synthesizing useful organic compounds, which are otherwise difficult to synthesize, and in addition, may also reveal new source of atmospherically important thioaldehydes, thus improving molecular details of existing atmospheric models.

Here it is shown using high-level quantum-chemical calculations that such a tuning of the barrier for the reaction of the Criegee intermediate and H_2X is indeed possible and more importantly, this heteroatom tuning is also found to be a general trend among other atmospherically important reactions. Firstly, examining the gas-phase reaction between the simplest Criegee intermediate, CH_2OO, and H_2X; the reaction energetics are computed by performing single-point calculations using the coupled-cluster single and double substitution method with a perturbative treatment of triple excitations (CCSD(T)) and the augmented correlation-consistent triplet zeta basis set, aug-cc-pVTZ at the M06-2X/aug-cc-pVTZ optimized geometries. (See the Supporting Information for details.) The CH_2OO-H_2X reaction is a multi-step reaction that converts the Criegee moiety, -COO into -C=X

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functional group. The reaction consists of two main steps namely chalcogen hydride (H_2X) addition and hydrogen peroxide (H_2O_2) elimination with the latter step being its rate-limiting step (see Figure 1 and Table S1 in the Supporting Information). Overall, the reaction is at least 24.1 kcal mol^{-1} exoergic. For the CH_2OO–H_2O reaction, the addition step has a barrier of 9.2 kcal mol^{-1} relative to **Int$_1$** whereas the elimination step has a barrier of 49.1 kcal mol^{-1} relative to **Int$_3$**, $H_2C(OH)(OOH)$. These barriers are signficantly reduced upon changing the heteroatom X in H_2X. For the CH_2OO–H_2S reaction, the addition barrier is just 2.5 kcal mol^{-1} and the H_2O_2 elimination barrier is 44.1 kcal mol^{-1}. For the H_2Se and H_2Te reactions, the addition steps involve barriers smaller than 1.0 kcal mol^{-1} whereas the barriers for the elimination step are lowered to 41.1 and 38.4 kcal mol^{-1}, respectively. It is important to mention here that the hydroperoxide in the addition step (**Int$_2$** or **Int$_3$**) is formed with an excess energy of at least 42.2 kcal mol^{-1} that significantly compensates the high barrier for the elimination step. These results clearly suggest that there is a correlation between the Criegee reaction barrier and the nature of X in H_2X. This correlation can be explained in terms of the H–X bond length or atomic radius of X (Figure 2). Moving down the chalcogen group, the atomic radius increases and the H–X bond becomes weaker. Since the H_2X addition to the Criegee intermediate involves breakage of one of the H–X bonds, a weaker H–X bond in H_2X would promote the H_2X addtion across the Criegee moiety. The oxygen atom has the shortest atomic radius of 66 pm, and the O–H bond (96 pm) with an enthalpy of 463 kJ mol^{-1} is the strongest X–H bond whereas Te atom has the largest radius (138 pm), and the Te–H bond (169 pm) with an enthalpy of 267 kJ mol^{-1} is the weakest X–H bond.[16] This explains why the H_2O reaction has the largest barriers whereas the H_2Te reaction has the lowest ones. The barriers for the H_2X reactions also directly correlate with first pK_a value of H_2X (Figure S1). H_2O has the largest pK_a value of 15.7 where H_2Te has the lowest pK_a value of 3.0, which is consistent with the barrier trends.[17] This implies that chalcogen hydrides with heteroatoms lying in the lower end of the periodic table would react faster with Criegee intermediate.

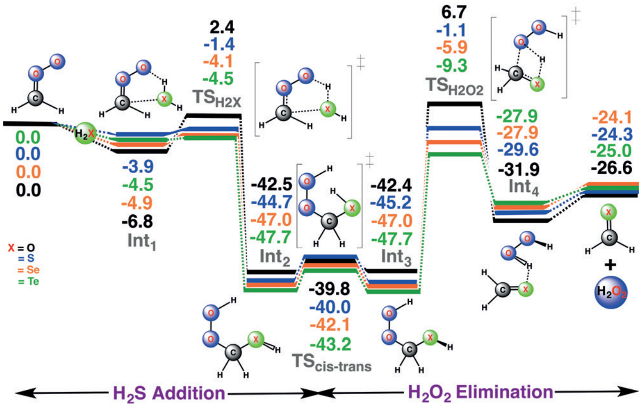

Figure 1. CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated zero-point-corrected reaction profiles for the reaction between the simplest Criegee intermediate, CH_2OO and various chalcogen hydrides, H_2X (X = O, S, Se, and Te). The energies are given in kcal mol^{-1} units.

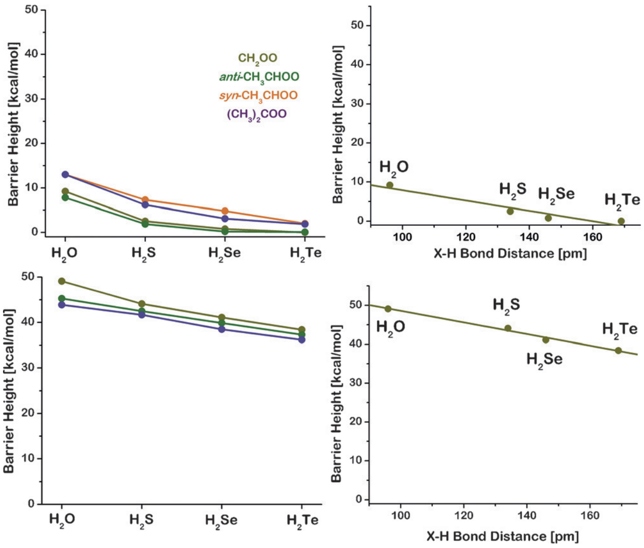

Figure 2. CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated zero-point-corrected barriers (top panels: addition reactions and bottom panels: elimination reactions) for the reactions between various Criegee intermediates and chalcogen hydrides. The barriers are given in kcal mol^{-1} units. The correlations betweeen the calculated barriers for the reactions of the simplest Criegee intermediate, CH_2OO with chalcogen hydrides and X–H (X = O, S, Se, and Te) bond distances are given in right side panels.

We then examined the reactions of the next larger Criegee intermediate, CH_3CHOO with H_2X. There are two conformers possible for CH_3CHOO: i) *anti*-CH_3CHOO and ii) *syn*-CH_3CHOO. We studied reactions involving both of these conformers. The calculations suggest that the barriers for the *anti*-CH_3CHOO reactions are relatively lower than those for the *syn*-CH_3CHOO reactions (Figure 2), which is consistent with previous studies[8,15] suggesting that *anti*-CH_3CHOO is more reactive than *syn*-CH_3CHOO towards bimolecular reactions. For the H_2O or H_2S reactions, the addition barrier for the *anti*-CH_3CHOO case is about 5.0 kcal mol^{-1} lower than that for the *syn*-CH_3CHOO case. More importantly, the calculated barriers for the addition and elimination steps of the *anti*- and *syn*-CH_3CHOO-H_2X reactions correlate well with the bond length of X–H bond of H_2X (Figures S2 and S3) or their first pK_a values. In going from $H_2O \rightarrow H_2Te$, the addition barrier for the *anti*-CH_3CHOO case is lowered by 7.8 kcal mol^{-1} and the H_2X addition occurs in a near-barrierless manner for X = Se or Te. For the *syn*-CH_3CHOO case, the larger barrier lowering of 11.0 kcal mol^{-1} is observed in moving from $H_2O \rightarrow H_2Te$. Since the H_2X addition to *anti* or *syn*-CH_3CHOO should lead to the same hydroperoxide, $(HX)(CH_3)(H)COOH$, we only examined H_2O_2 elimination from the *anti*-$CH_3CHOO + H_2X$ reaction. The barrier for the H_2O_2 elimination from the $(HX)(CH_3)(H)COOH$ is lowered from 45.3 kcal mol^{-1} to 37.3 kal mol^{-1} in going from $H_2O \rightarrow H_2Te$, which again inversely correlates with the X–H bond strength or directly correlates with first pK_a value of H_2X.

The calculated addition and elimination barriers for the reactions of $(CH_3)_2COO$ with H_2X also satisfy a correlation with the X−H bond length (Figures 2, S2 and S3) or first pK_a value of H_2X, which is indicative of the fact that the correlation between the Criegee reaction barrier and the nature of X in H_2X is a common reactivity trend, and is independent of the structure of the Criegee intermediate involved in the reaction. The comparative analysis suggests that the calculated elimination barriers for the $(CH_3)_2COO$ reactions are not only lower than those for the *syn*-CH_3CHOO, but are the lowest ones. For example, the elimination barriers for H_2O and H_2Te reactions are lowered from 49.1 and 38.4 kcal mol^{-1} to 43.9 and 36.2 kcal mol^{-1}, respectively, in going from CH_2OO to $(CH_3)_2COO$. This is due to the fact that the substitution at the hydroperoxy carbon of $(HX)(R_1)(R_2)COOH$ promotes the H_2O_2 elimination, that is, the greater the extent of substitution, the lower would be the elimination barrier.

The correlation between the Criegee reaction barrier and the nature of heteroatom in H_2X may have important implications for atmospheric and synthetic organic chemistry. For example, thioformaldehyde (HCHS) has been detected in dark clouds, the interstellar clouds[18–20] and circumsteller envelope around an asymptotic giant branch star.[21] Few lines of HCHS have also been identified in the Orion KL nebula[22] and in the atmosphere of the comet Hale-Bopp.[23] The present calculations suggest that HCHS in the atmosphere could be formed in a near-barrierless manner from the reaction between CH_2OO and H_2S. This reaction could be feasible in the atmosphere because the estimated H_2S concentration in the lower troposphere lies in the 1–1000 ppt range. Another important implication of our results is for the laboratory synthesis of thioaldehydes. In synthetic organic chemistry, thioaldehydes are used as key building blocks. The Diels–Alder additions of thioaldehydes and thioketones offer useful routes for the incorporation of sulfur heteroatoms into the synthesis of heterocycles such as substituted pyridines, furans, and dihydrothiopyrans or natural products.[24–26] However, experimental detection of simpler aliphatic thioaldehydes such as HCHS has been a significant challenge because it is unstable at room temperature and readily trimerizes to s-trithiane.[27] The findings from this work suggest that if the reaction of the Criegee intermediate and H_2S could be performed in the presence of water or a carboxylic acid (Figure 3 and Table S2), thioladehydes would be formed in an extensively hydrogen-bonded complexed state, which is signficantly more stable than their uncomplexed one. Thus, the water or acid-mediated reaction of the Criegee intermediate and H_2S could selectively produce thioaldehyde, avoiding any oligomerization. This could prove useful synthetic guidelines for the laboratory synthesis of simpler thioaldehydes that does not require harsh experimental conditions.

In short, high-level quantum-chemical calculations reveal an inverse correlation between the reaction barrier of Criegee intermediates and H_2X and the bond length of the X−H bond in H_2X or a direct correlation with the first pK_a value of H_2X. This heteroatom-induced tuning causes an 8–12 kcal mol^{-1} lowering in the reaction barrier, thus significantly impacting the overall energetics of the reaction of Criegee intermediates and H_2X. Considering that bimolecular reactions are abundant in atmosphere, the heteratom tuning of the reaction barrier could be a common reactvity determinant of atmospheric addition reactions.

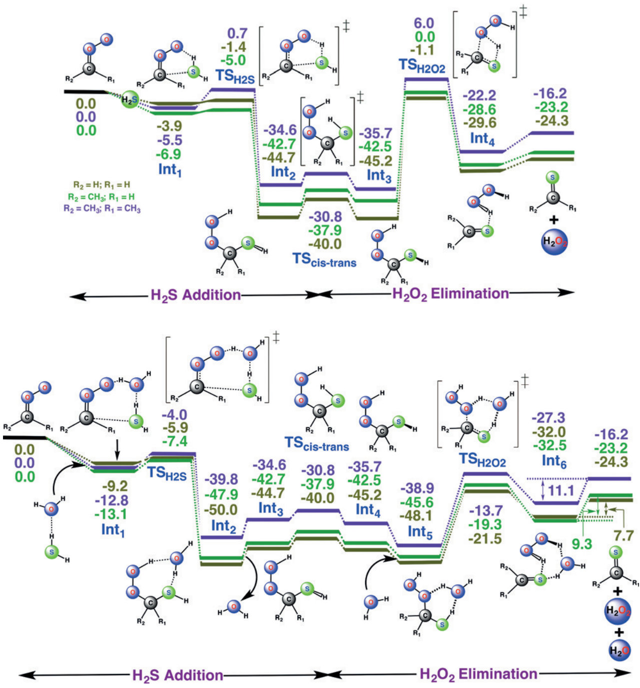

Figure 3. CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated zero-point-corrected reaction profiles for the reactions between various Criegee intermediates and hydrogen sulfide with (bottom panel) and without water catalyst (top panel). The energetics are given in kcal mol^{-1} units.

Keywords: atmospheric chemistry · chalcogen hydrides · Criegee intermediates · organocatalysis · water catalysis

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