CHY3011 Research Literature Project

TUTORIAL REVIEW

Spectroscopic Studies of Criegee Intermediates

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Criegee intermediates are carbonyl oxides involved in ozonolysis reactions. They are important species to consider when studying tropospheric chemistry and researching global climate control, as they play a key role in shaping Earth's lower atmosphere. In particular, they provide a source of HO_x and partake in the oxidation of nitrous and sulfur oxides, as well as acting as intermediates in some hydrocarbon reactions. Criegee intermediates are elusive chemicals that have been historically difficult to view, as a result of kinetics with involved mechanisms. There have been numerous analytical techniques imposed upon CH_2OO after the successful production of the molecule from a reaction with CH_2I and O_2. It has been shown by many researchers there is a certain sense of duality to this molecule, and its behavior is indeed unique.

Key Learning Points

1. The discovery of Criegee intermediates, including the initial proposal
2. Historical difficulty of viewing Criegee intermediates and the kinetics surrounding this
3. Importance of Criegee intermediates in Earth's atmosphere
4. Successful spectroscopic studies and their revelations
5. How Criegee intermediates are involved in pollutant removal

Introduction

Critical in gas-phase ozonolysis, among other processes, carbonyl oxides, known as Criegee intermediates (CIs), are species studied in tropospheric chemistry. Proposed by Rudolf Criegee in 1949 [3], these short-lived intermediates experience thermalized reactions with trace atmospheric species that are often fast. Described as having biradical/zwitterion character, they would not be seen through spectroscopic means until 2008. Despite the inability to view these materials, there was extended research into the kinetics and thus many mechanisms involving Criegee intermediates were confirmed decades prior to the spectroscopic study.

A principle motivation for studying these intermediates is the nature of the reactions in which they are involved in. Namely, CIs interact with sulfur and nitrogen dioxides in Earth's troposphere, alongside providing a source of HO_x in numerous other reactions. Understanding the structure and having the ability to view these molecules via spectroscopic means provides valuable information about our troposphere. This is especially vital as a result of the involvement of these species with known pollutants. This knowledge could be the basis of future research into global climate control: a very pressing matter that will affect all aspects of life. The present work will showcase the difficulty faced by researchers in this area and the reactions involving CIs. It will then delve into successful analytical techniques that highlighted key information about CIs, including: bond distance, their reactions with species in our lower atmosphere and how they are involved in pollutant removal.

An especially prevailing method by which scientists can study species in depth is spectroscopy. As a result of recent advances, we are able to scan molecules with lasers that work on nanosecond timescales, this could prove particularly useful when studying intermediates that are known to have rapid reactions, as was previously stated. Spectroscopic techniques applied to this area include: photoionization, electronic and infra-red. As sources of information about the electronic and geometrical structures, the aforementioned techniques are noteworthy.

Its most simple form is a product of the reaction between an alkene and ozone (O_3), [figure 1]. Criegee proposed a mechanism including 1,3-cycloadddition of O3 across a double bond, which would dissociate into a carbonyl oxide (CI) and a carbonyl compound [3]. Before reaching this point there is a primary ozonide (molozonide) formed as a brief intermediate. The simple CIs present in this work are the product of small, unbranched alkenes. Short chain alkenes are most common in urban areas as a product of combustion emissions. This is another reason it is paramount to study these particular CIs that have 4 carbons or less, their production is largely due to human activity.
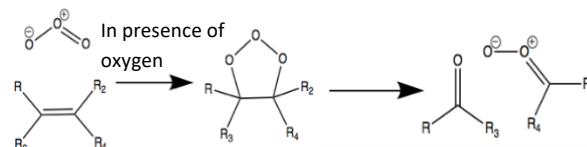

Figure 1. This is the general mechanism for a simple alkene with Ozone (O3) to produce a Criegee intermediate (CI) and a carbonyl. This is the scheme first postulated by Rudolf Criegee. The First step produces a primary ozonide, which then dissociates to the product we are going to discuss in this review.

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Experimental and Methods

Kinetics

One of the contributing factors in making these species difficult to isolate is the kinetics of ozone reactions. The rate constants for ozonolysis are small [6] and the reactions are exothermic. This means the production of Criegee intermediates happens quite slowly. As an example of the exothermicity, the reaction equation 'RE2' (see photoionization) is quoted with a -12.5 kcal mol^{-1} [6] enthalpy. This exothermic nature [1] of ozonolysis leads to further dissociation and isomerization from the CI, which can be in the form of unimolecular decay or collisional stabilization [20]. Dissociation from this point is typically fast as a result of the energy released into the system from the formation of the CI. These facts all contribute to concentrations of CIs being very low at given points in these systems. This, in turn, led to an inability to view Criegee intermediates in gas-phase reactions until recently (2008). Indirect determination of CI's kinetics was previously the best way to provide derived rate coefficients. Combatting these difficult kinetic factors is a primary part of the majority of techniques present.

Reacting with tropospheric species, including pollutants

Sulfur pollutants and Criegee intermediates. Chemistry involving the lower atmosphere is where these molecules are most prevalent. CIs can react with sulfur dioxide and nitrogen oxides in our atmosphere. This theory has long been postulated [12] and as a result of recent ventures, the direct studies have been made possible. The involved kinetics within this area of chemistry are particularly important, the readings are only achievable by considering the various rates and other factors impacting the interactions studied. Firstly, considering the reactions that are initiated by cycloaddition we find mechanisms between our CIs and sulfur dioxide (SO$_2$). Early practical studies suggested the rate coefficients for these reactions were slow. More recently, various methods have been adopted to produce insight on the interactions between these species. Had the earlier studies been correct in their analyses, one would not expect a CI to appear in the recent reports that were considering the rate of removal of SO$_2$. This is as a result of the perceived negligible interactions between the two molecules, due to the incorrect belief that the rates were low.

Analytical techniques performed to determine relationships in this area have largely been the result of kinetic studies. The results and discussion will elaborate on some specific investigations.
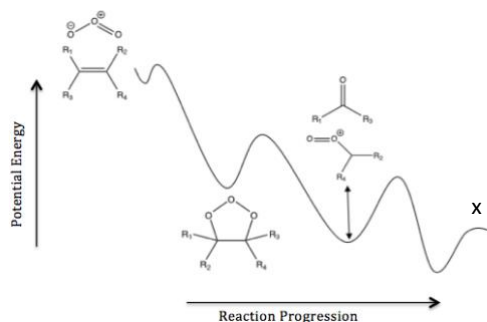
Figure 2. This is a potential energy diagram for Criegee's generic alkene Ozonolysis involving CI. The CI products are lower in energy than the reactants, this leads to excess energy being released (exothermic). The label 'x' refers to species resulting from further reaction, including: dioxiranes and vinoxy radicals.

Carboxylic acid and Criegee intermediates. Alongside the reactions our species have with SO$_2$ and NO$_2$, there are other known pollutants that have notable interactions with CIs. Carboxylic acid is one such example. Carboxylic acids in our atmosphere have an influential effect upon the environment. These acids are produced by combustion (including combustion engines) and vegetation, amongst other reactions [13]. Recent advancements have shown gas-phase removal via CIs is one possibility to deal with these harmful chemicals, as a result of rapid reactions between the two molecules [12]. The reactions with carboxylic acids and CIs can exceed the gas-kinetic collisional limit and produce stable ester adducts that show low volatility.

One technique adopted for the study of CIs and carboxylic acids is structure-activity relationship (SAR). SAR founded by a dipole-capture model, predicts reactivity of combinations of Criegee intermediates with the polluting molecules [12]. The variety of both CIs and carboxylic acids (both anthropogenic and biogenic) in the atmosphere leads to a range of possible reactions. SARs compensate for the large amount of reaction rates, which is why using them is vital in this area of research.

Spectroscopic studies

Photoionization mass spectrometry. As with other spectroscopic studies present, photoionization utilizes alternative synthetic routes to achieve isolation of CIs in the gas phase [20]. There have been various schemes adopted to achieve a successful reading. Using a scheme produced by Rubik Asatryan and Joseph Bozzelli that linked chlorine-initiated oxidation of dimethyl sulfoxide and CH$_2$OO [6], Taatjes et al. achieved the first experimental detection of a CI [1]. Multiplexed photoionization mass spectrometry (MPIMS) was used in tandem with a synchrotron. Although the spectrum was described as too noisy and therefore not conclusive, it was instrumental in the successful experiments that followed.

$$Cl + CH_3S(O)CH_3 \rightarrow HCl + CH_2S(O)CH_3 \qquad \text{(RE1)}$$

$$CH_2S(O)CH_3 + O_2 \rightarrow CH_2OO + CH_3SO \qquad \text{(RE2)}$$

Another alternative route for synthesizing a CI in the gas phase included the photolysis of a precursor (CH$_2$I$_2$) that led to the production of CH$_2$OO. This route has also been proven to generate CH$_3$CHOO [20]. It was acknowledged that the kinetics surrounding this reaction were unlike most gas phase CI reactions previously observed. As previously discussed, the reactions to form CIs are usually considerably exothermicIn this case, however, the enthalpy of formation holds a value of -2 kcal mol^{-1} [9], meaning the excess energy does not lead to further isomerization.
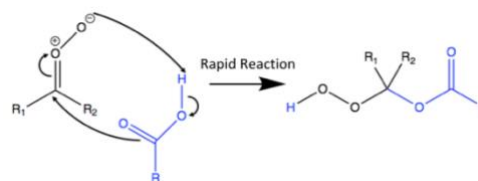
Figure 3. Insertion Reaction of a Criegee Intermediate with a carboxylic acid forming a hydroperoxide ester that shows low volatility. Scheme used by Chhantyal-Pun et al. [13].

In tandem with an uncharacteristically high rate coefficient (k_{RE4} = 1.39 x 10^{-12} cm^3 molecule^{-1} s^{-1}) this certain reaction produces remarkably high [CH$_2$OO] at any given point in the reaction. This is very beneficial when trying to achieve substantial observations.

$$CH_2I_2 + UV\ light\ (248\ nm) \rightarrow CH_2I + I \qquad\qquad (RE3)$$

$$CH_2I + O \rightarrow CH_2OO + I \qquad\qquad (RE4)$$
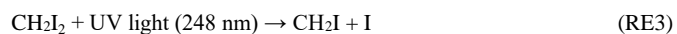
Electronic spectroscopy. Another important spectroscopic technique is electronic spectroscopy (ES). ES measures kinetic energies of emitted electrons using radiation [21]. Previous studies, giving insight to the electronic structure of any CI, were all theoretical. In 2012, simulations of the electronic structure were produced for CH$_2$OO [15]. This study relied upon high-level electronic structure calculations and Franck-Condon factor calculations. In the same year, the first UV spectrum of CH$_2$OO was also discovered using a time-of-flight mass spectrometer that was attached to a quartz capillary (where the molecules: CH$_2$I$_2$, Ar and O$_2$ were expanded) [1]. From the CH$_2$I radical (which was produced via laser dissociation) and O$_2$, the reaction in the capillary produced CH$_2$OO. The dissociation laser that focused upon the capillary was pulsed [1]. Modern advances in technology leading to the production of such accurate equipment have indeed been vastly influential on the studies of our CIs.

Infra-red spectroscopy. Despite the difficulties often faced by researchers in this area, one spectroscopic technique that has proved fruitful is IR. IR spectroscopy is commonly used to identify functional groups and provide information about target molecules [10]. This type of spectroscopy collects data by passing a beam of infra-red light through a sample. Once the infra-red light comes into contact with a bond or collection of bonds, absorption will ensue. One method of IR employed to the research of CIs is step-scan FTIR spectrometry coupled with a multi-reflection white cell. This records temporally resolved IR spectra [22]. Haung et al. used a KrF excimer laser (102F, 248 nm, 9 Hz, 97 mJ pulse^{-1}, beam size 1.3 × 1.2 cm^2) that passed through quartz windows located on the white cell to photodissociate CH$_2$I$_2$ and O$_2$ to eventually produce CH$_2$OO. This reaction has previously been mentioned for its uses in photoionization spectroscopy, and similar reactions have also been employed for most spectroscopic techniques when attempting to isolate CIs.

Results and Discussion

Electronic structure determination calculations

Criegee's proposed structure. Chemists acknowledged the existence of Criegee intermediates (CIs) as a result of studies on ozone. Solution phase kinetics also contributed to the validation, however, as stated, they could not be viewed experimentally until recently. The electronic structure of the carbonyl oxide found in the products of figure 1 has various configurations as a result of resonance stabilization. Considering the stability, it is clear the singlet zwitterion (a) should be the presiding configuration of the ground electronic state [4]. Unfortunately, experiments on the

immediate mechanism have not provided such clear outcomes historically. This is partially down to the complexity of the gas-phase ozonolysis in consideration. As the name suggests, these species act as intermediates and they are indeed reactive, making them even harder to measure and study [5].

Molecular structure of ozone. Firstly, understanding the structure and symmetry of ozone is paramount when looking at these reactions. It can be described as C$_{2v}$ in its ground state [2], having biradical nature. This description essentially means it has two vertical mirror planes, alongside the symmetry elements E and C$_2$. The geometry changes when in its zwitterion state, the effect of the two ions distort the bond lengths so they are not equal, causing symmetry to change from C$_{2v}$ to C$_s$[8]. Similarly, these issues will be important when considering the electronic structure and indeed the excited state structure of CIs. The aforementioned processes will impact the exact structure of each CI, however, as a result of being more complex than ozone, the overall symmetry assignment is likely to be unchanged.

Molecular structure of carbonyl oxides. It was first proposed by Criegee that the carbonyl oxide molecules had a shorter CO bond length and a longer OO bond length [3]. Essentially, he assumed a zwitterion structure, similar to 'figure 4' (a). Typically, one would expect the less electronegative carbon atom to hold less delocalization than the oxygen, one of the key arguments against a biradical structure. However, as discussed with ozone, this biradical also needs to be considered. In fact, the first calculations of electronic structure, using generalized valence bond theory [8] on formaldehyde oxide (CH$_2$OO) found the biradical structure more fitting. Using the valence bond theory in tandem with configuration interaction Wadt *et al.* proposed bond structures for lowest lying states in both the planar CH$_2$OO and perpendicular CH$_2$OO molecules. They stated the planar molecule was more favorable than the perpendicular. This was a result of a repulsive factor between the central oxygen pi pair and the CH bonds [8], arising from the Pauli principle. The repulsion was not present for the planar form, whereby the px orbital of carbon is orthogonal to the pi pair and there is some delocalization of charge onto the carbon.

This research would be continued and improved 3 years later (1978) by Goddard (who worked with Wadt) and Harding. The two obtained bond lengths for CO and OO in the singlet ground state ^{1}A (R_{CO} = 1.343 Å, R_{OO} = 1.362 Å) [19]. The values fell in between the usual values for single and double bonds for both CO and OO cases, supporting the biradical structure being dominant in this ground ^{1}A state for formaldehyde oxide.
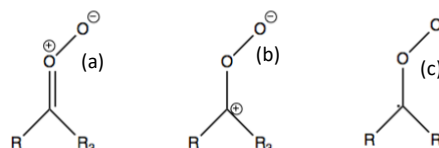

Figure 4. The proposed electronic structures for general Criegee intermediates. Two zwitterions: (a) and (b) and a biradical: (c).
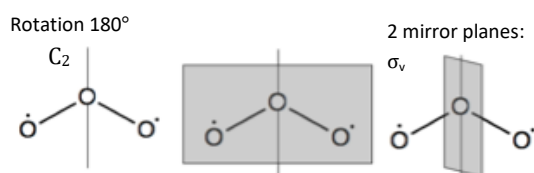
Rotation 180°
C₂

2 mirror planes:
σᵥ

Figure 5. illustrates the symmetry in biradical ozone (C₂ᵥ). Remember bond lengths will be affected in its excited states (zwitterion form)

There have been many other calculations using a variety of models to deduce the structure of our CIs. The team of Cremer *et al.* is another such example; they used coupled cluster theory and attained bond lengths that supported the zwitterion structure. Moreover, their determined charge distribution for the carbon atom and oxygen atom in question were +0.4 and -0.4 respectively [4], these values befitting a zwitterion structure. The difference in opinions over the decades highlights the difficulty and intrigue these molecules have caused the scientific community. The importance of isolating CIs in the gas phase cannot be overstated, without this, the scientific community would lack key data about their structure.

Tropospheric species and CIs

Sulfur Pollutants and CIs. More recently, it has been found that a reaction between CH_2OO and SO_2 is fast [13]. The previous literature values were corrected following this discovery. To support these claims, in Finland Mauldin *et al.* [14] produced a study that implied a fast rate of reaction between CIs and SO_2. Prior to this study, Ozone, hydroxyl radicals and nitrate radicals were generally renowned as the dominant oxidants in the removal of trace gases. Therefore, in previous reports the rate of conversion of SO_2 into sulfuric acid was dependent upon the concentration of these well-researched molecules, and not concentration of CI.

Mauldin and his team reported another species involved in the oxidation of SO_2 alongside other tropospheric gases [14]. They postulated this species could be a Criegee intermediate, or a derivative of one. Sulfur dioxide can be oxidized into sulfuric acid (H_2SO_4). Over a one-week period the team studied $[H_2SO_4]$ alongside concentrations of radical OH and a suggested species [X]. (This suggested 'X' refers to an unknown oxidant or group of oxidants). The dominance of [X] over [OH] was noted especially high during evenings and nights[14], evidence to suggest the compound X was related to surface emissions and ozone chemistry occurring in the boundary layer. They also found a relationship between [X] and $[H_2SO_4]$, essentially providing experimental evidence that there was a species other than radical OH linked to the oxidation of sulfur pollutants in our atmosphere: CIs.

Carboxylic acid and CIs. Studies have shown that reactions between CIs and carboxylic acids are barrier-less, the limiting factor being dipole-dipole attractions. The Dipole capture limit can be described as K_{d-d}. It is measured in cgs units and was adopted by Chhantyal-Pun et al. They tested this proposed behaviour and calculated dipole moment values for Criegee intermediates and various carboxylic acids at the B3LYP/ AVTZ level of theory [13].

$$K_{d-d} = \frac{C\sqrt{\pi}}{\mu}(\mu_{D1}\mu_{D2})^{\left(\frac{2}{3}\right)}(K_B T)^{\left(-\frac{1}{6}\right)} \quad \text{(E1)}$$

In E1, the symbols relate to the following factors: μ_{D1} and μ_{D2} are the dipole moments of the reactants, μ is their reduced mass, k_B is the Boltzmann constant, T is the temperature, and C is a constant. There was a discrepancy noted, between this model and another the group employed. It is postulated to be a consequence of the failure of the dipole capture model to account for rate coefficients in the limit of weak dipole attraction. However, the simulations did provide evidence of the significance of CI's reactions with carboxylic acids in our atmosphere. Ultimately, the studies showed these reactions could lead to a lowering of the predicted lifetimes of the polluting acids and their steady state concentrations in the troposphere.

Spectroscopic Studies

Photoionization and Electronic spectroscopy. Many notable studies have been produced using photoionization spectrometry. Clear data collected by Oliver Welz et al. using a reaction of CH_2I with O_2 can be described as some of the most important. They used an MPIMS to attain spectra, ultimately leading to the identification of CH_2OO, undoubtedly one of the products in reaction equation 'RE4'. From the spectrometry, an m/z value of 46.010 was determined [9], aligning with CH_2OO (m/z = 46.005). The photoionization spectrum for CH_2OO displays vertical transitions, supporting the fact that this molecule is indeed a zwitterion, as opposed to the biradical. Thus, supporting the aforementioned earlier findings of Cremer et al. Deduction of the structure also led to a conformation of a planar structure, which Wadt and Goddard had previously calculated to be more favorable [8]. Furthermore, the ionization energy of 9.98eV quoted by Nguyen et al. is comparable to the observed ionization energy in this experiment (10.0eV) [9].

$$CH_2I + O_2 \rightarrow CH_2OO + I \quad \text{(RE4)}$$

Lee *et al.,* used a reaction involving CH_2I_2 to prepare an isolated sample of CH_2OO. After the reactants expanded into vacuum, the CH_2OO target molecule was detected, a mass to charge ratio of 46 was quoted. This m/z of 46 is consistent with CH_2OO [15]. A vital study, achieving isolation of a CI that also demonstrated a proportional link between the absorption spectra of CH_2OO and the temperature at which reactions took place.

Infra-red. Huang *et al.* presented work in which they had, by means of an improved IR system, provided IR data at a superior resolution than previously reported for the analysis of the CI CH_2OO [22]. They reported spectra with resolution 0.25 cm^{-1} as opposed to resolution of 1 cm^{-1} that had previously been documented. Vibrational wavenumbers and intensities as well as rotational parameters were produced to a higher degree of accuracy than previously achieved, which allowed for new assignments of bands that align with theoretically predicted values. The experimental vibrational wavenumbers for those assigned are shown in figure 6. There were only small deviations in the values they recorded experimentally and the predicted values from VCI-5 and B3LYP/aug-cc-pVTZ methods.

As stated, detection of smaller CIs has been widely possible via the understanding of the kinetics of involved reactions and vast technological advances. However, in 2014, it was shown that much larger CIs could be isolated and analytical techniques could be adopted to evaluate them [17]. Ahrens *et al.* used stabilized CIs, isolated them in the gas phase during an Ozonolysis reaction with β-pinene, and, in conjunction with FTIR, were able to achieve a successful recognition. They produced a computational simulation of an absorption spectrum for the expected CI's (CI-1 and CI-2) using density functional theory with a 3LYP/6-311+G(2d, 2p) basis set. They then compared this simulation to their experimental FTIR spectra of the Ozonolysis reaction. From this comparison they were able to deduce that the absorption pattern below 950 cm^{-1} corresponded to CI-1 and CI-2, confirming the presence of such intermediates in the reactions they reviewed.

Baeyer-Villiger CI?

Completely separate from the CIs presented, there is a reaction featuring an interesting molecule that should be noted. Baeyer-Villiger oxidation involves the cleavage of a carbon-carbon bond adjacent to a carbonyl, converting ketones to esters and cyclic ketones to lactones. Often referred to as the Criegee rearrangement[23], this oxidation doesn't involve carbonyl oxides. However, there is a hydroxyperacid intermediate involved in this reaction that holds the title 'Criegee intermediate'.

Figure 6. Experimental vibrational wavenumber assignments for the FTIR of CH_2OO. $^{b}n_i^f$ notation where n indicates vibrational mode number and i and f indicate vibrational quantum numbers for initial and final states respectively.

Transition[b]	Mode	Experimental vibrational wavenumber (cm^{-1})
3_0^1	CH_2 scissor/CO stretch	1434.1
4_0^1	CO stretch/ CH_2 scissor	1285.9
5_0^1	CH_2 rock	1213.3
6_0^1	OO stretch	909.26
8_0^1	CH_2 wag	847.44
9_0^2	Overtone of v_9	1234.2
$6_0^1 7_1^1$	Hot band (B_1)	899.8
$4_0^1 7_1^1$	Hot band (B_2)	1282.0
$6_0^1 7_0^1$ or $8_0^1 9_0^1$	Combination band (C_1)	1485.5
unassigned	Band C_2	1289.5
unassigned	Band C_3	1292.1

Summary

The effort of researchers in this field has led to direct observation of Criegee intermediates, resulting in a better understanding of how these species impact society and indeed humankind. Using time-resolved spectra and spectroscopic studies has enabled the exposure of crucial structural and electronic information, alongside data about the chemical reactions of the intermediates. Continuing studies of Criegee intermediates is a necessity when considering tropospheric chemistry. To better understand our ozone and to shorten lifespans of some pollutants (namely the material's reactions with carboxylic acids that have been presented) are amongst the reasons this area is so important.

These species are a fairly new phenomenon when it comes to the physical data and computational studies, especially physical spectrums. This is a result of newly developed technology enabling us to generate stable (CIs) in adequate quantities, allowing measurements to be extracted from these somewhat elusive chemicals.

References

1   D.L. Osborn and C.A. Taatjes, *international reviews Phys. Chem.,* 2015, **34,** 309-360.
2   S.Y. Grebenshchikove, Z.W. Qu, H.Zhu, and R, Schinke, *Phys. Chem. Chem. Phys.,* 2007, **9**, 2044-2064.
3   R. Criegee, *Rec. Chem. Prog.,* 1957, **18**, 111–120.
4   D. Cremer, J. Gauss, E. Kraka, J.F. Stanton, and R.J. Bartlett, *Chem. Phys. Lett.,* 1993, **209**, 547–556.
5   J. Prousek, *Chem. Listy*, 2009, **103**, 271–276.
6   [J.M. Anglada, J. González, and M. Torrent-Sucarrat, *Phys. Chem. Chem. Phys.*, 2011, **13**, 13034–13045.
7   F. Liu, J.M. Beames, A.S. Petit, A.B. McCoy, M.I. Lester, *science.,* 2014, **345**, 1596-1598.
8   W.R. Wadt, and W.A. Goddard, J. Am. *Chem. Soc.*, 1975, **97,** 3004–3021.
9   O. Welz, J.D. Savee, D.L. Osborn, S.S. Vasu, C.J. Percival, D.E. Shallcross, and C.A. Taatjes, *Science,* 2012, **335,** 204–207.
10 P.L. Luo, Y. Endo, and Y.P Lee *J. Phys. Chem. Lett.,* 2018, **9**, 4391–4395.
11 J.M. Anglada, J. González, and M. Torrent-Sucarrat, *Phys. Chem. Chem. Phys.*, 2011, **13**, 13034–13045.
12 R. Chhantyal-Pun, B. Roterva, M.R. McGillen, M. Anwar, H. Khan, A. Eskola, R.L. Caravan, L. Blacker, D.P Tew, D.L. Osborn, C.J Percival, C.A. Taatjes, D.E. Shallcross, and A.J. Orr-Ewing, *Acs Earth Space Chem.,* 2018, **2**, 833-842.
13 D. Heard, *Nature.,* 2012, **488**, 164–165.
14 R.L. Mauldin III, T. Berndt, M. Sipilä, P. Paasonen, T. Petäjä, S. Kim, T. Kurtén, F. Stratmann, V.M. Kerminen, and M. Kulmala, *Nature.*, 2012, **488**, 193–196.
15 E.P.F. Lee, D.K.W. Mok, D.E. Shallcross, C.J. Percival, D.L. Osborn, C.A. Taatjes, and J.M. Dyke, *Chem. Eur. J.,* 2012, **18**, 12411–12423.
16 T.J. Gravestock, M.A. Blitz, W.J. Bloss, and D.E. Heard, *ChemPhysChem.*, 2010, **11**, 3928– 3941.
17 J. Ahrens, P. T. M. Carlsson, N. Hertl, M. Olzmann, M. Pfeifle, J. L. Wolf and T. Zeuch, *Angew. Chem. Int. Ed.*, 2014, **53**, 715-719
18 Y.T. Su, Y.H. Huang, H. A. Witek and Y.P. Lee, *Science* 2013, **340**, 174 – 176.
19 L.B. Harding, and W.A. Goddard, J. Am. *Chem. Soc.,* 1978, **100**, 7180–7188.
20 J.M. Beames, F. Liu, L. Lu, and M.I. Lester, J. *Chem. Phys.*, 2013, **138**, 244307.
21 M.F. Vansco, B. Marchetti, N. Trongsiriwat, T. Bhagde, G. Wang, P.J. Walsh, S.J. Klippenstein, and M.I. Lester *J. Am. Chem. Soc.,* 2019, **141**, 15058–15069.
22 Y.H. Huang, J. Li, H. Guo, and Y.P Lee *J. Chem. Phys.,* 2015, **142**, 214301.
23 R.M. Goodman, and Y. Kishi *J. Am. Chem. Soc.* 1998, **120**, 9392–9393.