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Computational Investigations into the Decomposition Pathways and Mechanisms of Hydrochlorofluorocarbons and Hydrofluorocarbons

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Abstract

Hydrochlorofluorocarbons and hydrofluorocarbons are a harmful class of compounds for the atmosphere due to be phased out of use by 2020 in developed countries and 2030 in undeveloped countries via incineration by combustion chamber. This research is aimed at modeling the high energy decompositions of these molecules computationally using primarily DFT methods for optimization as well as CCSD(T) energy corrections and a combination of CASSCF and various model chemistries for calculations involving binding energy. A novel and interesting reaction pathway has been discovered through this research that involves the formation of a gas phase carbene-HX complex following 1,1-HX elimination. This complex can in some cases persist through subsequent isomerizations by providing a pathway with a lower threshold for activation. This type of reaction could potentially be relevant in systems studied by other groups, so it is important to investigate thoroughly. Currently, it has been found that this pathway is experimentally relevant in the molecule C_2D_5CHFCl following 1,1-HF elimination with the assisted isomerization proceeding at 3.9 kcal/mol lower threshold energy than the dissociation of the carbene complex. Other interesting results follow from studies into substituent effects on these carbene complexes. It has been found that resonance donation can strengthen the binding energy as in the case of 1-phenyl-1-chlorocarbene complexed to HF with a binding energy of 11.6 kcal/mol, stronger than the water-water H-bond. Substituent effects will continue to be studied as well as possible implications for nitrene complexes that may also prove relevant in some cases.

1. Introduction

Hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) are a harmful class of compounds with high ozone depletion potential and/or high Global Warming Potential. They are currently in use, most commonly as refrigerants, foam blowing agents, propellants, etc. For example, Freon 134 (HFC-134), also known as CHF_2CHF_2 (whose modeling was recently published by members of our research group),[1] can be found in most auto shops as car air conditioning refrigerant. These compounds are under the Montreal protocol and are due to be phased out of use by 2020 in developed countries and 2030 in undeveloped countries.[2] Once these gases have been removed, current plans for their safe disposal involve very high temperatures, as the leading plan is combustion. This research will serve to study the rates and mechanisms for the reactions undergone by these common Freons in high-energy systems.

Computational research is an important route for studying these systems because it has been shown to be effective for matching rate constants and for elucidation of reaction mechanisms.[1,3] With the recent discoveries of decomposition pathways involving Post-Transition State Complexes (PTSCs) and Complex-Assisted Migrations in exit channels of 1,1-HX elimination pathways from these HCFCs and HFCs, computational research becomes all the more necessary since these pathways may be important to the kinetics.[4,5] Non-covalent interactions are among the most exciting routes in computational research with hydrogen bonding on sulfur centers,[6] π-stacking interactions,[7,8] and other dipole related interactions[9] all garnering attention from researchers.

A common method used in computational research is Density Functional Theory (DFT), a theory that uses functionals in quantum mechanics to model electron density and calculate structures and energies for molecules. Other methods, such as *ab initio* methods, which are theoretically derived quantum chemical methods that include many different types of calculations, are important as well since many have multi-reference capabilities that can distinguish when fragments in a calculation are not interacting and treat them separately in the same calculation.[10] This research will employ each of these methods in order to better model and understand the decomposition behavior of various HCFCs, HFCs, and other molecules that may exhibit similar decomposition pathways.

Ultimately, the aim of the project has two goals. One is to computationally model the kinetics of important HCFCs and HFCs before they are phased out in 2020, while the other is to further develop the chemical understanding of the novel reaction pathways discovered in these systems. While gas phase H-bonded complexes have been observed experimentally, there have not been descriptions of these involving carbenes, and certainly none involving complexed transition state geometries.[16] Using advanced rate simulation techniques should allow for completion of an accurate picture of how these complexes can affect kinetics in gas phase systems. Additionally, a series of PTSCs testing for substituent effects on dissociation energy and longevity in terms of likelihood to persist through a subsequent isomerization will add to the field of chemistry by describing novel reaction pathways and broadening the knowledge surrounding non-covalent interactions. The results will also be important to industries currently using these compounds and those that could make use of their byproducts such as the fluorocarbon polymer industry that would seek to harvest any potential C-F bonds remaining in these compounds.

Within the past decade, there has been a large amount of interest in noncovalent interactions for computational chemists. The Wheeler and Houk groups have focused specifically on π-based interactions such as stacking, anion interactions, and aryl interactions. In one specifically about π-anion interactions, the Houk group asserted that differences in binding energy based on substitution of a benzene ring were due more to direct interactions between anion and substituent than to a change in the nature of the π-orbital.[8] Another group computationally led by Wategaonkar focuses more on the classic hydrogen bond. Specifically interested in sulfur centers as the acceptors, the group has looked at dissociation energies of the complexes in comparison to experimental values with a variety of computational methods.[6]

What these groups have in common is their use of DFT functionals in their methodology. Both use long-range corrected, hybrid DFT functionals and similar triple-zeta quality basis sets, but Wheeler claims accuracy with M06-2X, while Wategaonkar claims ωB97x-D is more effective, both matching experimental energy values closely. Gao and Wang developed their own functional and did a comparison to a wide array of available functionals for calculations involving non-covalently interacting dimers. For hydrogen bonding, M06-2X-D3 was closely followed by M06-2X and their functional for performance with little error from any of the three.[7] Truhlar, in his article unveiling the M06-2X functional, his group showed its performance was more consistent and accurate than several commonly used functionals in a variety of performance categories such as accurate Bond Dissociation Energy (BDE) calculation for complexes and in geometry optimizations for main group elements.[3] Most authors active in the field agree that these kinds of functionals are more effective in calculations involving non-covalent complexes.

This is not to say, though, that calculations involving ab initio methods have been ignored in recent computational chemistry. Specifically important in the area of BDE calculation are multireference theories such as certain methods derived from couple cluster (CC) theory and the complete active space self-consistent field (CASSCF) theory, although CC theory is not truly multireference being an approximation from single reference. Because of their multireference capabilities, which allow them to treat groups of non-interacting atoms as separate bodies, they are effective in generating dissociation curves that involve a transformation from a single bonded entity into two. In a paper by Shen and Li, several CASSCF-like methods were surveyed and compared. In the calculation of barrier heights, however, each method largely overestimated the barrier with complete active space second order perturbation theory (CASPT2) performing the best at 5.8 kcal/mol higher than experimental.[10] Couple cluster theory such as couple cluster singles, doubles, and analytical triple excitations (CCSD(T)) is one of the most popular ab initio methods, often used for calculations in which highly accurate energies are desired. Szabó and Czakó showed in one paper involving ion-dipole complexes that the CCSD(T) method was of adequate size for accuracy in their system of $Cl^- + CH_3I$.[9] This method is quite computationally expensive however, which has led to many groups looking for an ab intio method to use the Møller-Plesset n^{th} order perturbation theory (MPn), most commonly MP2, which has been used by our research group for rate constant matching of CHF_2CHF_2 decomposition. Barriers here were again reported to be unreasonably high for certain pathways.[1]

Even more recently of interest, though, both to our research group and others, is how pre- and post-reactive complexes can affect the Potential Energy Surface (PES) and kinetics of a reaction. A group investigating NO_x reaction pathways reported finding several van der Waals complexes in M06-2X that affected the PES. They used a program known as Master Equation Solver for Multi-Energy well Reactions (MESMER), which employs Microcanonical Transition State Theory (μTST) models, to calculate rates for the reactions because it is capable of handling the barrierless transitions involved in complex formation and dissociation.[11] Similarly, another group very recently described the effects of pre- and post-reactive complexes on the PES for radical reactions involving cyclopentanone. Complexes reported here led to a submerged transition state similar to ones our group has studied, but since they were unimportant at the high temperatures with which the report was concerned, they were left out of rate calculations. However, since the rate calculations were done using Multiwell, which updated to allow for barrierless transitions in February 2017, their rate methods could be applied to our situations as well.[5]

Another area of research in the chemical literature that provides a route into deeper exploration involves compounds similar to carbenes such as nitrenes. An article from 1991 describes the insertion of simple nitrenes into water, hydrogen sulfide, and hydrogen halides, the latter being the reverse of a reaction analogous to the 1,1-HX eliminations our group would study.[12] Research into this would provide a wider base for studies related to characterizing these novel, hydrogen-bond like complexes.

In the past, our group has been much more concerned with computational chemistry for matching of rate constants, with some elucidation of mechanisms; however most recently, our computational focus has shifted to focus more on the mechanistic approach. Recently our group has found a novel reaction pathway, and we are interested in investigating kinetics of the pathways, likely using one of the above kinetic methods, and substituent affects on the reaction.[4] Additionally, other members of our group in the past have computationally investigated reaction mechanisms using Quantum Theory of Atoms in Molecules (QTAIM) to look at the PES and determine when bonds break and form as the reaction progresses.[13]

Our research group has specifically used the methods described above as well as other types of methodology in computational chemistry. When working on computational projects linked to experimental studies, it is also important to calculate rate constants based on the structures. Continued use of the rate theory our group has used in the past, RRKM rate theory, to match rate constants from theory to our experimental values remains important in assigning threshold energies.[14] It is also important to gather information on vibrational frequencies, which has usually been done with the DFT method used to optimize the structures of the ground and transition state geometries.[15]

Another method that will be important to my research that has been used by our group in the past is the Complete Basis Set (CBS) model chemistry. CBS-QB3 being the one specifically employed by our group is capable of calculating energy differences between fragments. Most methods including DFT and MP2 are not capable of this due to the issue of Basis Set Superposition Error (BSSE). BSSE is caused by basis sets calculating the number of basis functions based on the number of atoms in the structure, but a complete molecule will have more basis functions than the sum of two of its fragments. One way of combating this is using a multireference method like CASSCF, but CBS methods are able to minimize BSSE by using increasingly large basis sets and extrapolating to the maximal point at which energy differences caused by different numbers of basis functions will be negligible. Our group specifically chose CBS-QB3 to calculate binding energies of the carbene complexes because it is computationally less expensive than a CASSCF generated Morse Potential curve and it retains similar geometries to the DFT functional M06-2X also used on these systems.[15] Additionally, a similar model chemistry known as G3B3 is useful for its ability to accomplish the same types of calculations as CBS-QB3 with the addition of being able to handle period 4 elements such as Bromine which is a substituent in some of our experimental systems.

2. Methods

All calculations done in this report used the UNC-Asheville Chemistry Department Shiva supercomputer and the Gaussian09 and Gaussian16 suites of codes. DFT calculations were done using the M06-2X global hybrid functional developed by Truhlar and Zhao of the University of Minnesota in 2006 with double Hartree-Fock exchange compared to the standard M06, intended to improve kinetic and non-covalent interaction calculations.[3] This was combined with the diffuse function augmented-correlation consistent-polarized triple zeta basis set, aug-cc-pVTZ.

Additionally, the Complete Basis Set (CBS) model chemistry method modified with the Becke, 3-parameter, Lee-Yang-Parr (B3-LYP) geometry and frequencies, or CBS-QB3, was used for complex binding energy calculations. Binding energy was calculated by computing the energy of the complex and subtracting the individual energies of the carbene and eliminated HX. This was also done for the Gaussian-3 model chemistry method (G3) modified with the hybrid DFT functional B3-LYP geometry and frequencies, or G3B3.

Finally, the Complete Active Space-Self Consistent Field (CASSCF) method was used with varying basis sets to calculate a Morse Potential curve for the complex dissociation. The highest level basis set used with success with these calculations was the polarized 6-311G(2d,p) basis set. This calculation involved a relaxed potential energy surface scan, which takes the starting geometry optimization and then steps out or in a selected geometrical parameter. In this case, the (FH)C:-H(F) C-H bond was stepped out from a point inside the optimized distance to just below 5

Angstroms away to develop a nearly complete curve. Due to lack of control over active space at intermediate points in this calculation type, errors occurred towards the farthest distance calculations that could have completed the calculation, but this would have resulted in miniscule differences.

Additionally, the CCSD(T) and MP4 methods as described above are used as single-point energy calculation methods in some cases for refinement of the PES picture, especially in the propane systems where smaller energy differences can drastically effect kinetics due to the flatter exit channels of 1,1-HCl eliminations. These methods involve taking a geometry optimized in a computationally less expensive method such as M06-2X or MP2 and running a frozen, electronic energy-only calculation with the higher level method.

3. Results and Discussion

3.1 Substituent Effects on Carbene Complexes

To date, geometries have been calculated for a series of carbenes that will test substituent effects. Bulk was tested for with methyl, ethyl, and t-butyl groups, resonance with vinyl and phenyl groups, and electronegativity with halogens and hydroxyl groups as well as various halocarbon combinations. BDE using CBS-QB3 was used for comparison of complex strength.

Results include the Morse Potential curve generated for the HFC:--HF complex dissociation (Figure 1) which provides the basis for comparison to suggest the validity of the CBS-QB3 method for calculating BDE, as well as a series of complex binding energies summarized in Table 1 and below.

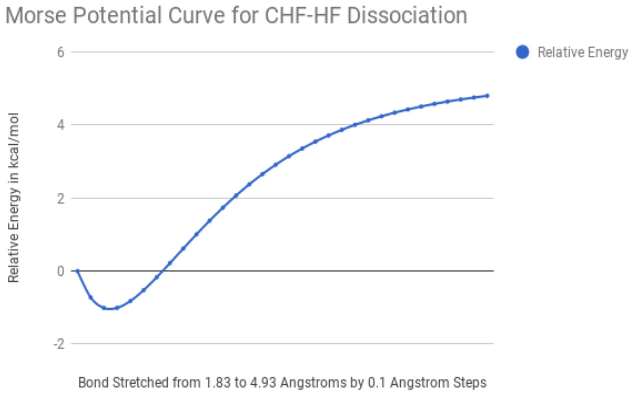

Figure 1. Relaxed potential energy surface scan in CASSCF(6,6)/6-311G(2d,p) in which the bond distance was stepped out from 1.83 Angstroms to 4.93 Angstroms by 0.1 Angstrom steps for HFC:--HF.

The information presented in Table 1 suggests that the strongest binding complexes are those with electron-donating R-groups on the carbene with an HF being eliminated to form the complex. Additionally, since the 1,1-HX elimination must occur on a carbon with at least one H and two halogens, the halogen remaining after elimination being chlorine results in stronger binding. Bromines were not surveyed in this position because the energies required for a 1,1-HF elimination to become experimentally relevant are significantly higher than the BDE of a typical C-Br bond and comparative analysis would require different methodology, the use of G3B3.

Table 1**.** BDEs of various carbene complexes from halomethanes (left) and haloethanes (right) with carbene-HF complexes in white and carbene-HCl complexes in blue.

Molecule	Complex	Binding Energy (kcal/mol)	Molecule	Complex	Binding Energy (kcal/mol)
CHF_3	HF	4.3	CF_3CHF_2	HF	5.4
CHF_2Cl	HF	5.3	CF_3CHFCl	HF	6.3
CHF_2Cl	HCl	2.1	CF_3CHFCl	HCl	2.8
$CHFCl_2$	HF	6.5			
$CHFCl_3$	HCl	3.1	CF_3CHCl_2	HCl	4.0
$CHCl_3$	HCl	4.2			
CH_2F_2	HF	7.1	CH_3CHF_2	HF	9.3
CH_2FCl	HF	7.9	CH_3CHFCl	HF	9.9
CH_2FCl	HCl	3.8	CH_3CHFCl	HCl	5.8
CH_2Cl_2	HCl	4.9	CH_3CHCl_2	HCl	N/A

The table shows trends in inductive effects on complex binding strength as expected. Since the complex forms between the electron lone pair and the electron-poor hydrogen of the eliminated HX, groups that are less electronegative or are electron donating on the carbene will result in higher density in the lone pair and a stronger binding energy. Another interesting trend that presents itself in this data is that replacing an F with a CF_3 results in a ~1 kcal/mol increase in complex binding energy and replacing an H with a CH_3 results in a ~2 kcal/mol increase.

The complex formed from CH_3CHCl_2 does not have a binding energy listed because a geometry for the complex was not found using the CBS-QB3 calculations. An optimized geometry using M06-2X was calculated, but CBS-QB3 uses B3-LYP for geometry optimization, so it presumably was unable to discern between the similar geometries of the complex and the 1,1-HCl elimination transition state. This similarity in structure between the two geometries occurs across all the HCFC systems surveyed for the HCl case, which has led to some difficulty in computational modeling. Further investigation should help to elucidate a more accurate picture of the full 1,1-HCl elimination exit channel.

Further interesting trends were seen especially with the resonance substituent effects. Examining the trend across chlorofluoro- systems with the HF complexed to the carbene showed the strongest binding with the conjugated phenyl group. Interestingly, the atoms in this geometry were entirely coplanar, despite unfavorable sterics, to allow for the conjugation of the pi-system to the empty p-orbital on the carbene. This added electron density on the carbene contributes to the strength of the interaction to result in a calculated BDE of 11.6 kcal/mol, the strongest of all the complexes surveyed through this project thus far. This additional binding strength is not attributed to inductive effects because BDE for the complexes with methyl, ethyl, or t-butyl R groups were 9.9 kcal/mol, 9.4 kcal/mol, and 10.2 kcal/mol, respectively. These data suggest small effects of induction beyond the initial methyl substituent and little effect of sterics on BDE.

3.2 Accurate Modeling of the HFC/HCFC Systems for Kinetic Analysis

Results include calculations of energy profiles and rate constants for the decompositions of the CF_3CHF_2, $CD_2ClCHFCl$, C_2D_5CHFCl, and C_2D_5CHFBr systems. These were the first systems for which our group characterized the energy profiles containing carbene complexes. In the CF_3CHF_2 system, it was found the carbene-HF complex formed after 1,1-HF elimination could persist through the subsequent isomerization to an alkene and result in an overall lower threshold for the isomerization (Figure 2). In this case, the threshold energy for F migration with the complexed HF versus without was lowered by 9.9 kcal/mol while the analogous comparison in CH_3CHF_2 for H migration, an isomerization that does occur, was lowered by 9.2 kcal/mol.

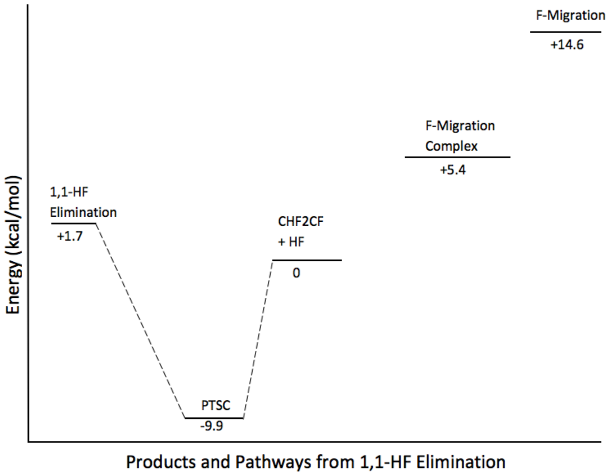

Figure 2. Decomposition pathway following 1,1-HF Elimination from the CF_3CHF_2 molecule. Dotted lines represent path taken in experimental conditions. F-Migration Complex not observed but would be the lowest energy pathway to alkene isomerization.

For this system, our experimental conditions did not provide enough energy for the isomerization to occur, but with $CD_2ClCHFCl$, the isomerization did occur. This system, however, showed evidence that without a sufficient energy difference estimated at approximately 4-5 kcal/mol, between the isomerization transition state geometry and the dissociated carbene and HF, the complex would simply dissociate (Figure 3).

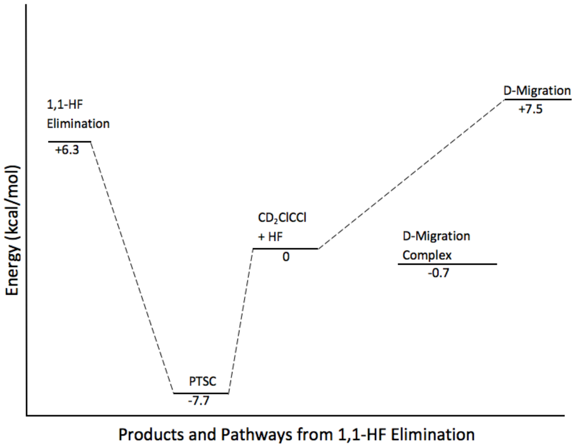

Figure 3. Decomposition pathway following 1,1-HF Elimination from the $CD_2ClCHFCl$ molecule. Dotted lines represent path taken in experimental conditions. D-Migration Complex not observed but would be the lowest energy pathway to alkene isomerization.

For the $CD_2ClCHFCl$ system, the calculated 1,1-HX Elimination threshold energies using M06-2X/aug-cc-pVTZ optimized geometries with a CCSD(T)/aug-cc-pVTZ single point energy were 66.8 kcal/mol for 1,1-HCl and 72.7 kcal/mol for 1,1-HF elimination. The CCSD(T) corrected energies were closer matching to experiment than the standard M06-2X energies.[14]

Studies into the C_2D_5CHFCl molecule have shown promise for experimental relevance with a complexed isomerization barrier 3.9 kcal/mol lower than the dissociation energy (Figure 4).

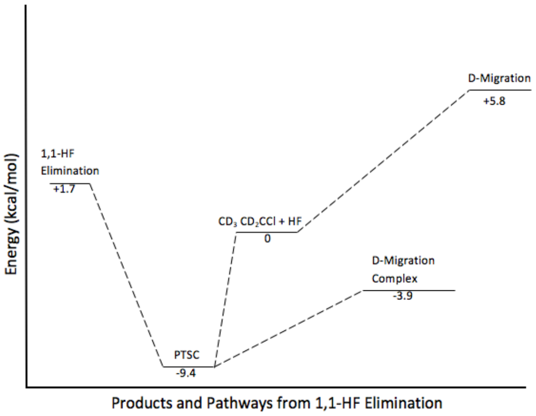

Figure 3. Decomposition pathway following 1,1-HF Elimination from the C_2D_5CHFCl molecule. Dotted lines represent path taken in experimental conditions. D-Migration Complex suspected as dominant exit channel

Further refinement of the energies with CCSD(T) calculations then analysis via VTST provided strong evidence that the 1,1-HF elimination proceeds through this exit channel. Investigation into rates using Multiwell could provide further answers and support.

Specifically for the C_2D_5CHFCl system, the accuracy of the energy surface around the 1,1-HCl elimination channel was of the utmost importance. Due to close nature of both geometry and energy seen in the elimination transition state geometry and the complex geometry, CCSD(T) corrections were used, which widened the gap in energies by 0.7 kcal/mol and raised the threshold for elimination by 12.5 kcal/mol to strengthen the confidence in the existence of the complex and more closely match experimental data.

Finally, the C_2D_5CHFBr system showed many similarities to the C_2D_5CHFCl system, but with a few key differences. Relative ordering of decomposition pathways by activation energy remains the same, but overall thresholds for those decompositions involving Bromine rather than Chlorine were much lower. Some uncertainty remains in these comparisons, however, since different computational methods were used. The 1,1-HBr elimination transition state geometry was found with MP2/6-311G(2d,p) but not with the M06-2X methods used previously for the other systems discussed, so MP2 was used to describe the system.

The results for this gave barrier heights of 53.9, 65.6, 66.3, and 76.3 kcal/mol for 2,1-DBr, 2,1-DF, 1,1-HBr, and 1,1-HF, respectively. These calculated values matched relatively well with experimental values except for the 1,1-HF, which experimentally was determined to be around 71 kcal/mol from product ratios following decomposition from the chemically activated molecule.

4. Conclusion

The most important findings of this project so far most certainly involve the novel reaction pathway discovered in which the carbene complex assists in the subsequent isomerization to an alkene. Although similar reactions have never been reported to the knowledge of this research group these findings utilize well characterized methods that have proven effective in both non-covalent interactions and in potential calculations involving complex transition state geometries, so there exists strong evidence that the methodology is properly oriented for today's chemical literature.

Specifically, certain characteristics have been identified that make this pathway more likely to become experimentally relevant. First off, a strong binding energy is necessary to prevent the complex from dissociating immediately. In addition, it seems that there must be a large stabilization from the elimination transition state geometry to the complex to prevent the reaction from moving backwards. Future investigations could determine what other effects may stabilize the complexed transition state.

Because this new pathway can affect the kinetics of decomposition in these gases, its discovery is important for the accurate modeling of these gas systems imminently in need of research. Beyond that, it may also prove an important discovery for research on unrelated systems from other groups. The survey of substituent effects would be most relevant to other groups needing a broad picture of how these complexes behave.

In this regard, results showing the effects of electron donation and withdrawal or the effects of sterics will be useful. The results presented here suggest that electron donation can significantly and predictably alter the strength of these carbene complexes while sterics do not seem to have a particularly large or predictable affect. Beyond that resonance donation is also a factor for increasing the electron density on the carbene when the pi system is conjugated to the empty p-orbital of the carbene, also increasing its potential for strong binding.

Beyond these novel findings, this project still has significance for the kinetic data for each of the systems on which this project focused. The energy calculations as well as rate data generated from them and the geometric data were useful in determining rate constants for each relevant decomposition pathway. These rate constants will be useful for industrial disposal procedures when these gases start begin to be phased out. The computational support strengthens the conclusions made by our experimental group.

The future of this research is focused on completing the work done into these categories already. Additionally, expansion into the realm of nitrenes may prove useful as well. It is still a goal to incorporate Multiwell software calculations for rate constants because of its capability to handle barrierless transitions. Such a calculation is directly suited for the systems currently under investigation by our group, but lack of availability of the software on our computer system may limit this goal.

5. Acknowledgments

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