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THEORETICAL STUDIES OF SILICON AND RELATED ELEMENTS
REACTION SURFACES AND DYNAMICS OF POTENTIAL HIGH ENERGY SPECIES
AFOSR/NC-90-0052
FINAL TECHNICAL REPORT
MARK S. GORDON

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I. STRAINED RING COMPOUNDS

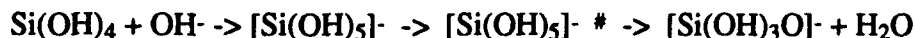
Sita et al. found that while it is not difficult to synthesize 1,1-difluoro-1-stannacyclobutane, they are unable to isolate the analogous 3-membered ring. The question is whether this occurs because (a) the 4-membered ring is kinetically more stable, (b) the 3-membered ring is not a minimum on the potential energy surface (PES) or (c) the 3-membered ring is thermodynamically disfavored. Another question is whether stannacyclopentene is a weakly bound π complex. We have performed *ab initio* calculations¹ on the reactions $EX_2 + HCCH \rightarrow$ metallocyclopropene, with $E=C, Si, Ge, Sn$ and $X=H, F$. Since CH_2 is rather unstable, one expects a very exothermic reaction with little or no barrier for $E=C$ and $X=H$. SnF_2 is expected to be quite stable, so a less exothermic reaction with a larger barrier is expected. As long as $X=H$, all reactions are quite exothermic with no barrier, although the exothermicity decreases as E gets heavier. When F replaces H , there is a large decrease in exothermicity. The reaction for $E=Sn$ and $X=F$ is predicted to be *endothermic* and to have a substantial barrier. This explains the difficulty in preparing the 3-membered ring. No evidence is found that the bonding in these compounds can be described as π complexation.

A systematic analysis has been carried out on two series of compounds whose parents are disiloxane ($H_3Si-O-SiH_3$) and disilane ($H_3Si-SiH_3$). For each series a H atom on each Si is successively replaced by a bridging O^2 . The final compound in each series has three oxo bridges. In the first series this produces a bicyclopentane analog, while in the second series one obtains an analog of [1.1.1]propellane. The molecules in the second series with two and three oxo bridges are diradicals with little bonding between the bridgehead Si atoms. So, these species must be described by multi-configuration (MC) wavefunctions, and the conclusions drawn from previous calculations are unreliable.

II. HYPERVALENT BONDING

The anion $[(CH_3)_2AlO]^-$ was prepared in a flowing afterglow selected ion flow tube (FA-SIFT). In addition, acidity studies coupled with thermodynamic analyses have established that the conjugate acid of $[AlO]^-$ is $AlOH$, rather than $HAIO$. Companion *ab initio* calculations have been performed to (a) determine the gas phase acidities and heats of formation of $HAIO$ and $AlOH$ and (b) study the reaction of trimethylaluminum with OH^- .³ Using G1 theory, it is shown that, in agreement with the experimental observations, the $AlOH$ isomer is more than 40 kcal/mol lower in energy than $HAIO$. The reaction of trimethyl aluminum with hydroxide is completely analogous with the similar reaction of tetramethylsilicon studied earlier. The association reaction to form $[(CH_3)_3AlOH]^-$ is predicted to be downhill by 83 kcal/mol, at the MP2/6-31++G(d,p)//SCF/6-31G(d) level of theory. The preferred elimination channel from the aluminate is overwhelmingly that of methane loss. The transition state for this elimination is found to be 35 kcal/mol below the initial reactants, and it is found to resemble the analogous elimination transition state for the corresponding silicate: one finds a dissociative anionic proton transfer, with the transition state resembling a leaving CH_3^- group which abstracts a proton as it departs. The elimination of water is a much higher-energy process.

The reactions of $\text{Si}(\text{OH})_4$ with several substrates have been studied⁴, with 6-31G(d) geometry optimizations, followed by the evaluation of energetics at the MP2/6-31++G(d,p) level of theory, as well as with AM1. The first reaction of interest is



The *ab initio* calculations predict the first step in the above process to be exothermic by nearly 60 kcal/mol. The transition state for water elimination lies 36 kcal/mol below separated reactants, and only 2 kcal/mol above the final products, so the entire process can occur with no additional energy. The AM1 calculations are in essential agreement with these findings. A Bader atoms in molecules (AIM) electron density analysis has been performed on each species in this process. Substantial intramolecular hydrogen bonding is found in the transition state, undoubtedly stabilizing this structure. The second sequence of reactions was designed to investigate the interactions of several neutral species, NH_3 , H_2O , and HF with silicic acid. Ammonia and HF are potential drying agents in the sol-gel process. In each case, we find one or more minima corresponding to hypervalent silicon structures. For ammonia, a 6-membered ring structure, with a double hydrogen bond, is found to be about 4 kcal/mol more stable than the pentavalent $\text{Si}(\text{OH})_4\text{-NH}_3$ structure. For water, two different hydrogen bonded minima are found. One of these is the 6-membered ring structure analogous to the one found for NH_3 . This is predicted to be very slightly more stable than a structure with a single hydrogen bond. No minimum is found that corresponds to a pentacoordinated structure $\text{Si}(\text{OH})_4\text{-OH}_2$. For HF , the weakest proton acceptor, only the 6-membered ring double hydrogen bond structure is found. No minimum energy structure is found for the hypervalent species $\text{Si}(\text{OH})_4\text{-FH}$.

A series of SiX_6 compounds ($\text{X} = \text{H}, \text{F}, \text{CH}_3, \text{OH}, \text{OCH}_3$) has been investigated with *ab initio* and AM1 calculations⁵. All of these species correspond to minima, with barriers to dissociation to $\text{SiX}_5 + \text{X}^-$. For $\text{X}=\text{F}$, the barrier to dissociation is > 20 kcal/mol with MP2/6-31+G(d). However, some of the molecules are unstable to autoionization; e.g, SiH_6^+ has a negative ionization potential. If enough electronegative ligands are placed around the Si, a positive IP is found; e.g, the IP of SiF_6^+ is > 1 eV. D orbitals play a minor role in the bonding of these compounds, and the Si center remains quite positive.

Silatranes have been prepared in both the gas phase and in crystalline form. Whereas the apparent Si-N dative bond is rather short in the X-ray structure, the gas phase distance is much longer. To determine if there is actually a bond in the latter, a combined *ab initio* and AM1 investigation was undertaken⁶. Although the Si-N distance does increase as each ethylenic bridge is added, the full silatrane maintains a Si-N bond. Squeezing the Si-N bond to the distance observed in the crystal only requires about 6 kcal/mol.

To obtain an understanding of one of the basic differences in bonding between C and Si, *ab initio* calculations were performed on both MH_5 and MH_5^- compounds, with $\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$ ⁷. While C-H bonds exhibit shared interactions, M-H bonds ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$) are closed shell (ionic) in nature. There is substantially more electron density located at the C-H bond critical points than in the others. The H in the C-H bonds withdraws negligible electron density from C, but for the heavier systems, the H withdraws a significant amount of electron density from M. SiH_5^- is more stable energetically than SiH_5 because the axial and equatorial H's are stabilized to a greater extent than the Si is destabilized, and because the Si-H bonds in the anion are more ionic than the Si-H bonds in the radical. Similar results are found for Ge and Sn. On the other hand, the C destabilization upon CH_5^- formation is greater than the stabilization of the H's. So CH_5^- is less stable than CH_5 .

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Hypervalent bridge compounds with the general structure $[XSiR_3-Y-SiR_3X]^m$, with $m=0,-1$, have been implicated in various mechanisms for organosilicon reactions. We have undertaken a series of calculations on the anionic compounds with $R = H$, $X = H$ or F , and $Y = H, CH_3, NH_2, OH, F^8$. The nature of the substituent X has a profound impact on the stability of these bridge compounds relative to $SiH_3X + SiH_3XY^-$. When $X = H$, the bridge compounds are only marginally stable, whereas, the stability is as large as 40 kcal/mol for $X = F$. When $X = F$, the order of stability for Y is $NH_2 > OH > F, H \gg CH_3$.

III. THERMOCHEMISTRY

Using homodesmotic reactions, heats of formation have been predicted for all methylated disilanes⁹. This is the first consistent, systematic prediction for these compounds, experimental or theoretical, and provides an important data base for Si thermochemistry. Several new experiments have been prompted by these results, resulting in excellent agreement between experiment and theory. The heats of formation of two prototypical double bonded species, silene and disilene, and their silylene isomers have been predicted using G1 theory¹⁰. This is the first experimental or theoretical systematic prediction for these compounds. These results are extremely important, because once the heats of formation for these prototypes are established, homodesmotic reactions may be used to predict the thermochemistry of substituted compounds. We have now completed a systematic investigation of the heats of formation for all methyl-substituted silenes and disilenes¹¹.

IV. Π Bonding.

Calculations were performed for prototypical high valent transition metal-alkylidene complexes, using ECP's for the metals¹². The complexes include Group IVB (Ti, Zr, Hf) and Group VB (Nb and Ta) alkylidenes with hydride ligands, as well as models for the four coordinate olefin metathesis catalysts (Mo-, W-, and Re-alkylidenes). The predicted geometries are in good agreement with available experimental data. Localized MCSCF/CI orbitals are used to determine quantitatively for the first time, the principle resonance contributors to the $M=C$ bonds. Resonance structures in which the C is at the negative end of the $M-C$ bond contribute 50% to the total wavefunction, whereas those in which the bond is neutral contribute 45%. The wavefunctions are consistently dominated by five primary resonance contributors. One of these, never discussed before, corresponds to a dative C to M bond plus a covalent π bond and contributes roughly 33% of the total wavefunction. The effect of substituents on the C and ligands on the metal has also been examined¹³. Significant changes in the electronic structure are found to be effected in three ways: (1) The introduction of a highly electropositive substituent (e.g., Li) makes the $M-C$ bond closer to a triple bond for the Ta alkylidenes. (2) A change in the metal atom, since the heavier metals result in a much more nucleophilic carbon. (3) The use of π donor substituents increases the electrophilicity of the alpha C.

The nature of the $M=Si$ double bond has been investigated with FORS MCSCF wavefunctions and ECPs¹⁴. The species studied were silylene complexes of the form $MSiH_2^+$ ($M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni$). The LMO/MCSCF/CI method was used to determine the main resonance contributors, and the results were compared with the C, Ge, and Sn analogues. Substantial changes are predicted in the electronic structure of the MSi bond upon moving from left to right across the periodic table. The MSi bonds are considerably weaker than their MC analogues; however, these bonds are stronger than the corresponding MGe and MSn bonds. Since examples of the latter species are known experimentally, the MSi species should be experimentally accessible.

The electronic structures of complexes arising from the formation of a double bond between a

silylene and a high valent transition metal fragment have been investigated, using LMO/MCSCF/CI¹⁵. A prime motivation for this work was that complexes of this type, unlike their C analogs, have so far eluded attempts at experimental characterization. We have concluded that (a) It is necessary to include electron correlation to obtain an adequate description of the MSi π bond, whereas the σ bond is well represented at the Hartree Fock level; (b) The kinetic and thermodynamic stability increase when H ligands and/or substituents are replaced by electronegative species; (c) Group VB MSi bonds are more stable than their Group IVB analogues; (d) MSi double bonds are stronger when the MSi π bond is made more backbonding in nature. Strategies for designing stable M=Si species are suggested. The electronic structures of the transition metal-disilene complexes $MCl_2(Si_2H_4)$, with M = Ti, Zr, Mo, and W, and the complexes of disilene with $PtCl_3^-$ and $Pt(PH_3)_2$ have also been investigated¹⁶.

The π bond energies in all group IV compounds with the formula $H_2A=BH_2$ (A,B = C, Si, Ge, Sn) have been investigated with SOCI/3-21G(d)/MCSCF/3-21G(d), by calculating the rotation barriers for these species¹⁷. The out-of-plane bend potential becomes flatter as A,B become heavier and the π bond energies appear to reach a lower limit of 20 kcal/mol, once A and/or B is Ge or Sn.

V. POTENTIAL ENERGY SURFACES AND DYNAMICS

The effect of SiH_3 , GeH_3 , and SnH_3 groups on ethyl cation has been investigated using isodesmic reactions at the MP2/3-21G(d) level of theory¹⁸. The stabilization effect increases steadily as the group IV substituent gets larger. The predicted effect is not as dramatic as is observed experimentally, suggesting that there is an additional kinetic effect, so the next step is to determine the transition states and associated energy barriers.

The global PES for the reaction $O(^3P) + HCl \rightarrow OH + Cl$ has been investigated at the MP2/6-311G(d,p) level of theory¹⁹. The transition state is rather bent, in agreement with the experimental observation that the product OH is rotationally hot. The global PES has been scaled using known experimental data and then fit to an analytic form. This surface has been used to investigate the dynamics of the reaction using quantal close coupling methods. Tunneling plays a very important role in determining the rates and branching ratios. The transition state for the $Cl + HCl$ reaction is found to be nonlinear, albeit rather flat. It requires at least an MP2 or MCSCF+CI wavefunction to obtain a proper PES. This effort used MP2 and multi-reference CI wavefunctions to map the PES²⁰. A large number of points on the PES have been obtained, and are now being fit to an analytical form, in preparation for an analysis of the dynamics of the reaction.

Pseudorotation in SiH_5^- has been investigated by following the minimum energy path (MEP) from the tetragonal transition state to the trigonal bipyramidal minimum, using MP2/6-31G(d,p) energies²¹. The reaction path hamiltonian was then determined. Using this RPH, we have predicted the rate of the pseudorotational motion at several temperatures using variational transition state theory (VTST) and the small curvature tunneling approximation. We are now in the process of fitting the PES to an analytic form, in preparation for investigating trajectories on this surface. A series of substituted pentacoordinated Si anions is being investigated in an analogous manner²². For SiH_4F^- , if correlated wavefunctions and/or extended basis sets are used, the equatorial isomer becomes a transition state. So the simple Berry notion of pseudorotation is an over-simplification for complex species. Similar results are found for polysubstituted pentacoordinated anions. PH_4F is isoelectronic with SiH_4F^- and exhibits a pseudorotation surface which is similar to that of the anion²³. For this molecule, the MEP and several associated paths have been followed to demonstrate that as one proceeds from the highest transition state (square pyramid) down to the lower energy transition state (equatorial), the imaginary frequency disappears before the new imaginary frequency (corresponding to the MEP leading from

equatorial to axial) appears. This is expected to have a major impact on pseudorotational dynamics. The PES for PH_4F will be fit to an analytic form to study the dynamics of this process.

A systematic analysis of all thermal decomposition paths for silanol has been carried out²⁴. Transition states and activation barriers for all reactions have been determined, as well as MEPs for all of the reactions which have transition states. Unlike all other such species studied to date, the 1,2-elimination of H_2 is competitive with the 1,1-elimination.

The decomposition PES from bridged disilyne to $\text{Si}_2 + \text{H}_2$ has been explored, using a full valence, state-averaged MCSCF calculation, followed by first order configuration interaction for energetics²⁵. It is predicted that the energy increases monotonically along the dissociation path, with no intervening barrier.

We have studied the PESs for the thermal decompositions of metalloamines, as a function of the metal and the ligand on the metal²⁶. In the transition state for HX elimination ($\text{X} = \text{H}, \text{CH}_3, \text{Cl}, \text{NH}_2, \text{SiH}_3$), electropositive and electroneutral X give rise to metal-transannular hydrogen (H_t) distances only slightly longer than normal metal-terminal H bond lengths, while electronegative X groups yield substantially long MH_t distances. This observation may be connected to the larger elimination barrier that occurs for electronegative X groups.

Alkyl substitution has a significant effect on the gas phase acidities of hydrocarbons. The effect of analogous substitutions on the corresponding Si compounds is the source of some controversy among experimental groups, with some finding the same effect as in the C compounds and others seeing little or no effect. We have carried out MP4 calculations with very large basis sets on SiH_3OH , MeSiH_2OH , and EtSiH_2OH and the corresponding deprotonated anions²⁷. The calculations predict that these compounds have essentially the same gas phase acidities. Similar predictions apply to the analogous S compounds, where the calculations have predicted a serious error in experimental results. Theory has been determined to be correct.

The insertions of CH_2 and SiH_2 into the X-Y bonds of ethane, methylsilane, and disilane have been investigated and compared with the analogous insertion into the X-H bonds²⁸. Insertions into the X-Y bonds have much larger barriers than the X-H insertions for each bond type (i.e., C-C vs. C-H ; Si-Si vs. Si-H). Otherwise, the barrier heights appear to correlate more with bond length than with bond strength, since there is a steady increase in barrier height upon going from C-C to C-Si to Si-Si . When the X-Y bond is in a strained environment, such as the C-C bond in cyclopropane, the insertion barrier is dramatically reduced.

The insertion of SiH_2 into water was studied in this laboratory several years ago. Recent experiments by Walsh and co-workers suggest that the height of the barrier separating the addition complex $\text{H}_2\text{Si}---\text{OH}_2$ from silanol is much lower than that predicted by the earlier calculations. We have probed this PES with much improved wavefunctions²⁹ and verified the earlier predictions. Since the actual experiments were performed on dimethylsilylene, the calculations were repeated on the substituted species. The effect of the methyls bring theory and experiment into acceptable agreement (within 2 kcal/mol).

Recent experiments indicate a "negative activation energy" in the insertion of SiH_2 into SiH_4 to form disilane. This suggests the existence of a long-range minimum on the PES. Using MP2/6-311G(d,p) calculations, we have found a $\text{SiH}_2\text{-SiH}_4$ complex on the Si_2H_6 PES³⁰. A transition state has been found that corresponds to a very small barrier separating the complex from product disilane. When

zero point vibrational corrections or higher level correlation corrections are added, the barrier disappears. So, at best, there is a very flat region in this area of the PES. We are now examining this PES in greater detail, in order to understand the reaction and the related dynamics. Because of its importance to the chemical vapor deposition process, we have also investigated the insertion of SiH₂ into diatomic SiH³¹. Although the barriers to insertion for SiH₂ into SiH₄ and H₂ and for the insertion of CH₂ into SiH are all zero, a nonzero barrier of about 6 kcal/mol is predicted for this reaction at several levels of theory. This is in agreement with the recent experimental findings of Jasinski and appears to result from a combination of steric and electronic effects.

The stability of the asymmetric dimer of NO (a-N₂O₂) with respect to spin forbidden radiationless decay has been investigated³². The spin-allowed decay channel a-N₂O₂(¹A') -> N₂O(X¹Σ⁺) + O(¹D) is endoergic. However, the spin forbidden decay channel a-N₂O₂(¹A') -> N₂O(X¹Σ⁺) + O(³P) is exoergic. Large-scale multi-reference CI wave functions, approximately 300,000 - 1,400,000 configuration state functions, based on double zeta plus polarization and triple zeta plus polarization bases sets were used to study this process. The minimum energy crossing point of the ground singlet state and the lowest excited triplet state was determined, as was the interstate spin-orbit coupling. This electronic structure data was used in the context of a simple one-dimensional model to show that a-N₂O₂ is rapidly predissociated to N₂O(X¹Σ⁺) + O(³P). This means a-N₂O₂ is not a good HEDM candidate, despite the high energy content of this compound.

The gas-phase reactions of trimethylaluminates and a variety of acids were considered from both an experimental and theoretical perspective³³. The experimental work involved product and kinetic studies of ten aluminates, [(CH₃)₃AlX]⁻. Both X and methyl cleavage are observed in these reactions. Since X cleavage occurs for several aluminates, in contrast to the thermochemical predictions of MP2/6-31++G(d,p) calculations, it is concluded that the reactions are kinetically controlled. Therefore, studies of the reaction paths for the reactions of [(CH₃)₃AlX]⁻, X = F, OH, with HCl have been carried out. These calculations properly predict the observed cleavage results for X and methyl cleavage and give a qualitative interpretation of the reaction dynamics.

An analysis of the electronic structure of high-valent transition metal alkylidenes as models for olefin metathesis catalysts was performed with *ab initio*/ECP wavefunctions³⁴. Of particular interest was the elucidation of the fundamental differences between those complexes known as the "Fischer" type [MCl₂(Y)(CH₂)] and those complexes known as the "Schrock" type [M(OH)₂(XH)(CH₂)]. The effect on the bonding caused by modification of either the metal, ligands, or substituents was considered.

Damrauer and co-workers have studied the reactions of HCSi⁻ with several neutral triatomic molecules. While reaction products are observed for the reaction with CO₂, COS, and SO₂, no reaction is observed with CS₂. A detailed analysis of the corresponding PESs was undertaken³⁵. The first step established that linear HCSi⁻ is the only minimum on that PES. All four reactions are overall exothermic. The most exothermic reaction is the one which is not observed experimentally suggesting a kinetic explanation. For each reaction, we find two cyclic intermediates. Yet another, zigzag minimum is found in this valley. For all four reactions, no barrier is found in the exit channel; however, for the reaction with CS₂, a very large barrier is found in the entrance channel between the reactants and first cyclic intermediate. Since no such barrier is found for the other reactions, this nicely explains the experimental observations.

VI. MODEL DEVELOPMENT

To study large compounds, novel ways must be developed to perform reliable calculations. One can, in principle, splice together two different levels of *ab initio* wavefunctions, *ab initio* with effective core potentials, *ab initio* with semi-empirical, etc. We have explored splicing together STO-3G with 6-31G(d) for a series of small molecules³⁶. The procedure works amazingly well, as long as the minimal basis set is placed sufficiently far away from the functional group.

The study of PESs for chemical reactions often involves more than one electronic state. When this occurs, it is necessary to determine the spin-orbit coupling among these states. We have devised a general scheme for directly calculating the one-electron matrix elements and then using these results to parametrize the two-electron contributions, all using the GAMESS MCSCF programs. The predictive ability of this method for diatomics and small polyatomic molecules is quite good³⁷. The next step is to develop general algorithms to permit the calculation of the full spin-orbit matrix elements.

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THEORETICAL STUDIES OF SILICON AND RELATED ELEMENTS
REACTION SURFACES AND DYNAMICS OF POTENTIAL HIGH ENERGY SPECIES
AFOSR/NC-90-0052
11/1/89-10/31/92
COMPLETED PROJECT SUMMARY
MARK S. GORDON

SUMMARY

The objectives of this project were to study a variety of main group compounds and their reactions, with special emphasis on the chemistry of silicon and how the behavior of this element relates to problems of Air Force interest. The processes investigated included the detailed mechanism of the chemical vapor deposition (CVD) process, the polymerization mechanism of silanols, the role of hypervalent silicon in polymerization mechanisms, and the relationship of hypervalent silicon to hypervalent aluminum. Toward the end of the project, the effort broadened into investigations of the interactions of silicon with transition metals, in view of the role of the transition metals as catalysts in a variety of reactions.

The second main area of investigation has been the design and study of high energy content molecules, with the intent of designing new potentially high energy fuels. One compound that had been previously proposed by others, the asymmetric dimer of NO, was shown by us to predissociate. So, this compound will not be a realistic H₂DM compound. We think, however, that other isomers of the NO dimer have greater potential for new fuels, and these possibilities will be explored.

The methods used in these studies include state-of-the-art quantum chemical techniques, some of which were developed as part of this project.

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