

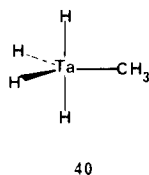
Table II. Extended Hückel Parameters

orbital	H_{ii} , eV	ζ_1	ζ_2	C_1^a	C_2^a
H _{1s}	-13.60	1.30			
C _{2s}	-21.4	1.625			
C _{2p}	-11.4	1.625			
Cl _{3s}	-30.0	2.033			
Cl _{3p}	-15.0	2.033			
Ti _{4s}	-8.97	1.075			
Ti _{4p}	-5.44	0.675			
Ti _{3d}	-10.81	4.55	1.40	0.4206	0.7839

^a Contraction coefficients in the double- ζ expansion.

distortion, one finds the octahedron, an hypothetical d⁰ square-planar complex, and the axial site of a trigonal bipyramid. In a borderline case one finds the basal position of a square-basis pyramid, the equatorial site of a trigonal bipyramid with a distortion in the plane containing the axial ligand, the trigonal complex with a distortion in the plane perpendicular to the molecular plane, and the tetrahedron. In the most unfavorable case one finds the trigonal bipyramid (CH₃ equatorial) and the trigonal complexes for a distortion in the equatorial and molecular plane, respectively.

This order should be the same for all metals, but one should be aware that the *boundary between a possible and an unfavorable distortion may be very much dependant on the nature of the metal*. For instance, methyl distortion in H₄Ta(CH₃)₂⁻ complex (40) leads



to a flat energy curve in the equatorial plane and to a small stabilization on the axial plane.¹⁷ We saw here that a similar system with Ti as metal leads to large and small destabilizations, respectively. Clearly, the same trend is found, but Ta seems to be more efficient in favor of agostic structures. In the same way, calculations on d⁰ octahedral and tetrahedral complexes of tantalum lead to a stabilization in both systems, but the one in the octahedron is twice the one in the tetrahedron. The reason lies in the lower energy level of d orbitals used on the calculations (-12.10 and -10.8 eV for Ta and Ti, respectively): the lower the d orbital level, the smaller the energy gap between the σ_{M-C} and the low-lying empty orbitals. The diffuseness of d orbitals might

also play a role by increasing the overlap between the orbitals. However, since increasing diffuseness usually corresponds to increasing energy of d orbitals, a more quantitative analysis would be required to make predictions.

Conclusions

In this paper, we have proposed a rationale for the unexpected structure of some electron-deficient methyl complexes. A reorganization of the metal-carbon bond seems to be at the heart of the problem. Such a reorganization is possible if the metal-carbon σ bond lies at a high energy level and if an empty low-lying orbital of adequate symmetry on the metal can stabilize this high-lying metal-carbon bond. In these electron-deficient complexes, electron donation from a C-H bond to the metal center always provides a stabilization in the distorted structure. However, when the distortion is too costly in energy for the metal-carbon bond, this factor is not large enough to lead to an overall stabilization. We have discussed how the agosticism is affected by the electronic nature of the ligands and the coordination mode. The results presented may help to control the agosticism of yet unknown systems. The study of ethyl complexes is in progress. We are also investigating the distortion of the ligand field away from the ideal octahedral field in the methyl and ethyl complexes.

Acknowledgment. The authors are grateful to Professors K. Morokuma, M. L. H. Green, M. Brookhart, and G. Girolami for communicating their results prior to publication. They have benefited from the comments of Dr. H. Felkin. The calculations were done at the computer center of Orsay (CIRCE), administered by the CNRS.

Appendix

The calculations were of the extended Hückel type and weighted H_{ij} 's were used.²² Idealized geometries were assumed with Ti-C = 2.15 Å, Ti-H = 1.60 Å, C-H = 1.09 Å, and Ti-Cl = 2.30 Å. All angles at the metal were taken to be 90° in the octahedron and 110° in the tetrahedron. Coulomb integrals and orbital exponents are listed on Table II, and these were taken from earlier work.²³

Registry No. 4, 85944-68-9; 7, 2747-38-8; H₅TiCH₃²⁻, 94138-09-7; H₃TiCH₃, 78499-82-8.

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Ab Initio Study of the Reaction of Silene with Formaldehyde

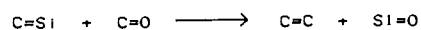
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Abstract: The reaction of silene with formaldehyde to give silanone and ethylene was examined at the SCF level by using the 3-21G, 3-21G(*), and 3-21G* basis sets. All compounds were fully optimized, including the proposed intermediate, 1,2-silaoxetane (5), for which the structure and vibrational frequencies are reported. While the reaction is exothermic by approximately 30 kcal mol⁻¹, the proposed intermediate is more stable than both the products and reactants by at least 50 kcal mol⁻¹. However, if the product is taken to be the dimer of silanone (cyclodisiloxane), 6, the reaction is more exothermic, with the products lying 25 kcal mol⁻¹ below 1,2-silaoxetane. A mechanism is proposed for this reaction based on the energetics and the integrated spatial electron populations. In addition, the unusual geometry of cyclodisiloxane is explained by MO arguments to be caused primarily by large oxygen-oxygen lone-pair repulsions.

Interest in the formation of multiple bonds to silicon has been increasing over the past few years, and many experimental¹⁻⁹ and

Scheme I



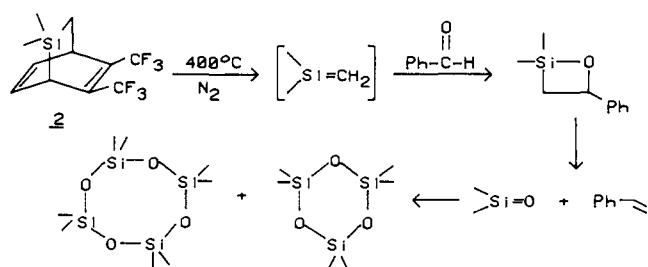
theoretical¹⁰⁻¹⁵ papers on this subject have appeared recently in the literature. The growing body of known chemistry of the silenes

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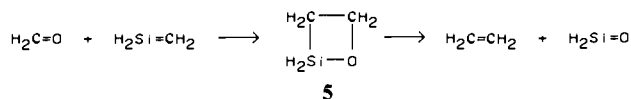
(7) Barton, T. J.; Hussmann, G. P. *Organometallics* **1983**, *2*, 692.

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Scheme II

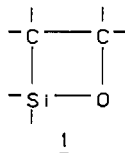


Scheme III



includes some interesting features. In particular, the reaction of silenes with ketones to give alkenes (Scheme I) is known, yet the mechanism remains essentially speculation. This reaction is of interest since any new method for joining two carbon atoms may be of synthetic value.

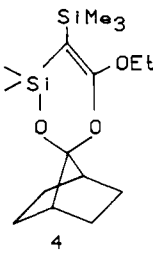
Ando^{2,3,6} and Barton^{4,5,8} have each reported a number of reactions of this type and have postulated a reaction mechanism, analogous to the Wittig reaction, which invokes a silaoxetane (**1**) intermediate. For example, Barton⁴ reported the pyrolysis of **2**



in the presence of benzaldehyde to give styrene and the trimer of dimethylsilanone (Scheme II). Since these reactions are carried out at high temperature (>200 °C) in order to generate the silene, it is possible that silaoxetane is not thermally stable at these temperatures. Barton⁵ has attempted a variety of alternative



pathways to the silaoxethane, such as silylene insertion into an epoxide, but has as yet been unsuccessful in obtaining a stable



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Table I. Calculated Geometrical Parameters for 1,2-Silaoxetane at Various Basis Sets

parameter	3-21G	3-21G(*)	3-21G*
Bond Distances, Å			
Si-O	1.713	1.653	1.643
O-C1	1.480	1.491	1.444
C1-C2	1.573	1.575	1.564
C2-Si	1.919	1.881	1.873
Si-H	1.479	1.464	1.466
C1-H	1.078	1.077	1.087
C2-H	1.080	1.082	1.086
Bond Angles, deg			
Si-O-C1	95.4	94.94	94.52
O-C1-C2	100.0	98.99	100.98
C1-C2-Si	84.7	83.77	82.16
C2-Si-O	80.0	82.31	82.34
energy ^a	-440.636 504	-440.706 456	-440.806 842
rel E ^b	106.89	62.99	0.0

^aIn hartrees. ^bIn kcal mol⁻¹.

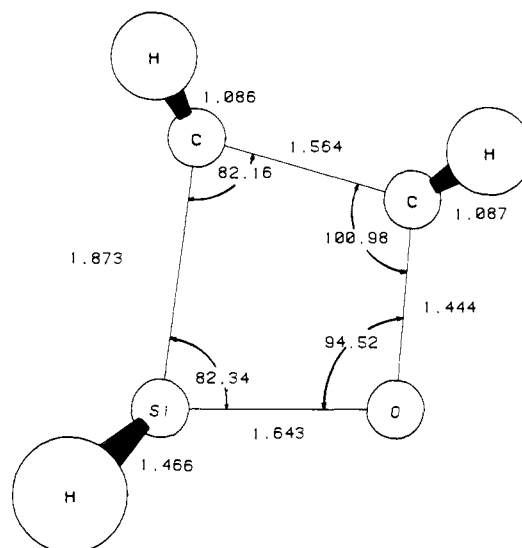


Figure 1. Optimized geometry of 1,2-silaoxetane at 3-21*. All distances in angstroms, and all angles in degrees.

silaoxetane. Recently, Ando⁶ has reported the synthesis of a compound that he suggests is the silaoxetane **3**. Barton, however, has interpreted the evidence as being more consistent with compound **4**. If Barton is correct, no silaoxetane has yet been detected. Additionally, no silanone has been isolated, but rather the trimer or higher oligomers of silanone are the recovered products.

We report here a theoretical study of the energetics of the parent reaction (Scheme III) in an attempt to gain some knowledge of the mechanism of this reaction. In addition, we report some structural information on 1,2-silaoxetane and cyclodisiloxane as an aid in identifying these species.

Computational Methods

The geometries for all compounds were obtained at the SCF level by fully optimizing the coordinates to minimize the energy. All calculations were run by using either GAUSSIAN 80 UCSF^{16a} or GAUSSIAN 82^{16b} with the 3-21G,^{17a} 3-21G(*),^{17b} and 3-21G*^{17c} bases. Gordon and George¹⁵ have recently rejected the contention¹³ that diffuse functions are necessary for adequate description of the Si-O bond; hence, such diffuse functions are not employed here. In addition, the calculations do not include correlation effects, but it will be shown that the reaction energetics are relatively insensitive to correlation. Electron density analysis was performed

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(17) (a) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. *J. Am. Chem. Soc.* **1982**, *104*, 2797. (b) d functions on silicon only ($\alpha_d(\text{Si}) = 0.6$). (c) d functions on all heavy centers ($\alpha_d(\text{C}) = 0.75$, $\alpha_d(\text{O}) = 0.8$).

Table II. Calculated Vibrational Frequencies of 1,2-Silaoxetane at 3-21G (cm⁻¹)^a

frequency	type	frequency	type
147	ring vibration	1132	H-C-H bend
451	H-Si-H bend	1152	H-C-H bend
550	ring vibration	1210	H-C-H bend
651	H-Si-H bend	1311	C-H stretch
688	ring vibration	1441	C-H stretch
741	C-H stretch	1516	C-H stretch
786	C-O stretch	2091	H-Si-H bend
831	Si-O stretch	2101	H-Si-H bend
862	C-C stretch	2928	C-H stretch
914	H-C-H bend	2939	C-H stretch
948	C-O stretch	2971	C-H stretch
992	H-Si-H bend	2992	C-H stretch

^a Corrected by 10%; see text.**Table III.** Optimized Energies^a and Reaction Energetics^b of the Reactant and Product Species in Scheme III at Various Basis Sets^a

	3-21G	3-21G(*)	3-21G*
Reactants			
formaldehyde	-113.221 820	-113.221 820	-113.303 539
silene	-327.301 663	-327.349 970	-327.377 256
total	-440.523 483	-440.571 790	-440.680 795
Products			
silanone	-362.955 895	-362.996 146	-363.061 966
ethylene	-77.600 988	-77.600 988	-77.664 963
total	-440.556 883	-440.597 134	-440.726 929
reactants 1,2-silaoxetane products			
3-21G	70.92	0.0	49.96
3-21G(*)	84.50	0.0	68.60
3-21G*	79.90	0.0	50.14

^a In hartrees. ^b Relative energies in kcal mol⁻¹.with the PROJ¹⁸ program to yield both integrated spatial electron populations (ISEP) and electron density maps.**Structure of 1,2-Silaoxetane, 5**

1,2-Silaoxetane was optimized with all three basis sets, yielding in each case a molecule with C_s symmetry. Although four-membered ring systems may be puckered, oxetane¹⁹ and a substituted 1,2-disilacyclobutane²⁰ are nearly planar. Previous calculations²¹ of oxetane and 1,3-dioxetane found these to be planar also. The geometrical parameters of interest are presented in Table I, and a drawing of the structure of 1,2-silaoxetane at 3-21G* is given in Figure 1.

The bond lengths calculated at 3-21G* are all in good agreement with analogous known bond lengths. The Si-O bond lengths in disiloxane²² and octaphenylcyclotetrasiloxane²³ are 1.631 and 1.615 Å, respectively. The calculated Si-O bond distance of 1.643 Å in 1,2-silaoxetane is slightly longer, but this is not unexpected for such a small ring. The Si-C bond length in methylsilane¹⁴ of 1.867 Å is in excellent agreement with the 1,2-silaoxetane value of 1.873 Å. The C-O and C-C bond lengths in oxetane¹⁹ are 1.549 and 1.449 Å, which correspond very well with the calculated bond lengths in silaoxetane. There are no good systems in the literature for comparison of bond angles in 1,2-silaoxetane; however, as a rough guide, the C-O-C and C-C-C angles in oxetane¹⁹ are 92.0° and 84.5°, respectively. The highly strained Si-C-C angle of 82.16° in 1,2-silaoxetane corresponds well with the comparably strained C-C-C angle in oxetane. The calculated vibrational frequencies at 3-21G are listed in Table II. It is well established that vibrational frequencies calculated at the SCF level are in general approximately 10% too large.²⁴ The frequencies

Table IV. Geometrical Parameters and Energies of Cyclodisiloxane

parameter	3-21G	3-21G(*)	3-21G*	expt ^a
Bond Distance, Å				
Si-O	1.717	1.666	1.653	1.66, 1.72
Si-Si	2.539	2.420	2.359	2.31
O-O	2.312	2.290	2.313	2.47
Bond Angle, deg				
Si-O-Si	95.4	93.2	91.1	86
O-Si-O	84.6	86.8	88.8	94
energy ^b	-726.131 706	-726.298 447	-726.262 679	
rel E ^c	144.94	40.31	0.0	

^a See ref 29. ^b In hartrees. ^c In kcal mol⁻¹.

reported here have been scaled down by 10% so as to give a better estimate of the actual values. Overall, it must be stated that the structure of 1,2-silaoxetane is by no means unusual.

From Table I it is clear that d functions on silicon are critical. The bonds to silicon calculated at 3-21G are far too long, but the 3-21G(*) results are quite reasonable. The addition of d functions to oxygen and carbon shortens all bond lengths but not by large amounts. Interestingly, the bond angles appear to be rather insensitive to d functions.

Reaction Energetics

The energies of the products and reactants of the parent reaction at the three basis sets are given in Table III. Note that there is little difference in the exothermicity of the reaction when using the various basis sets, indicating that larger, more complete basis sets will probably yield similar reaction energetics. This is especially true since the 3-21G* basis set incorporates polarization functions on all heavy centers and should be sufficient to describe all of the major electronic features of these systems. At the 3-21G* level, the reaction is exothermic by 29.8 kcal mol⁻¹. Gordon and George¹⁵ have calculated the exothermicity of this reaction by using 6-31G**/3-21G²⁵ at the MP3 level to be 24.9 kcal mol⁻¹. These two energies agree quite well and indicate that for net reaction energetics, correlation effects are relatively unimportant. Correlation is certainly important to obtain accurate energetics of the individual species as Gordon and George¹⁵ have shown, but apparently the correlation effects on both sides of the reaction essentially cancel.

Perhaps the most interesting feature of the energetics is that 1,2-silaoxetane is stable to both the forward and backward reaction by at least 50 kcal mol⁻¹ at all basis sets used. There are two approximations at this level of calculation which may be causing this extreme stability. First, superposition²⁶ has been neglected. Superposition error results when comparing energies of species which have not been calculated by using equivalent functional space. The superposition error involved in the present case is probably small since neither reactants nor products are grossly underdescribed at these basis set levels and, thus, are not in great need of additional functional space.²⁷ Correcting for superposition would lower the energies of both the reactants and products with respect to 1,2-silaoxetane but by a rather small amount. Second, correlation effects have been neglected. Correlation has been shown above to be relatively unimportant for comparing reactants and products, but this may not be true in comparisons with the silaoxetane intermediate. Nevertheless, since all the species involved are normal closed shell compounds, it is unlikely that correlation would effect the energies by a great margin, let alone cause 1,2-silaoxetane to become less stable than the products.

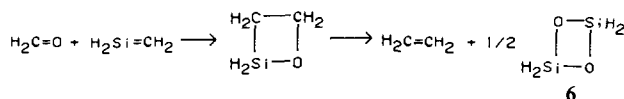
Experimental and theoretical dissociation energies confirm the stability of 1,2-silaoxetane. Using the dissociation energies from Walsh²⁸ for the Si-O and Si-C bonds, the theoretical estimates¹⁴ of the Si-C and Si-O π bonds of 40 and 45 kcal mol⁻¹, respec-

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(25) This notation indicates a calculation using the 6-31* basis set on the 3-21 optimized geometry.

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Scheme IV

Table V. Reaction Energetics for Scheme IV^a

	reactants	1,2-silaoxetane	products
3-21G	89.96	19.04	0.0
3-21G(*)	111.96	27.46	0.0
3-21G*	103.86	24.76	0.0

^aRelative energies in kcal mol⁻¹.

tively, the four-membered ring strain of 25 kcal mol⁻¹, and standard dissociation energies for all other bonds, one can estimate the energetics of this reaction. This crude method shows 1,2-silaoxetane to be approximately 60 kcal mol⁻¹ more stable than the reactants and 20 kcal mol⁻¹ more stable than the products.

The above analysis indicates that the parent reaction will not go to completion and that 1,2-silaoxetane or some substituted silaoxetane should be isolable. The experimental evidence is completely contrary yet also provides the clue to understanding this reaction. The product obtained in all cases has been the trimer (or higher oligomer) of silanone. The great stability of the Si-O bond is the driving force for trimerization, and perhaps trimerization is the driving force for the entire reaction. Calculation of the trimer of silanone is too large and costly for our resources. Instead, the silanone dimer cyclodisiloxane, **6**, was optimized at all three basis sets with the hope that extrapolation to the trimer would be possible.

The geometrical parameters and energies of cyclodisiloxane at the three basis sets are listed in Table IV. All three optimized structures are planar and have *C_s* symmetry; however, they are all slightly distorted from both *C_{2v}* and *D_{2h}* geometries. Recently, West and co-workers²⁹ have reported the crystal structure of tetramesitylcyclodisiloxane. Their experimental data for the ring parameters are listed in Table IV. Complete comparison is not possible since our calculation is of the unsubstituted compound in the gas phase while the reported structure is for the crowded tetramesityl compound as a crystal, but certain features are quite similar. In particular, the highly strained Si-O-Si angle and short cross-ring distances appear in both the calculation and experiment. In addition, the experimental structure is nearly planar, which agrees well with the calculated *C_s* symmetry.

The energetics for the reaction shown in Scheme IV are listed in Table V. We write the reaction to produce half a mole of cyclodisiloxane so that direct comparison to the parent reaction (where the product is silanone) is possible. At all three basis sets, the reaction is strongly exothermic. Furthermore, 1,2-silaoxetane is intermediate in energy between reactants and products. Since the dimerization of silanone is sufficient to push the product energy below 1,2-silaoxetane, trimerization is expected to further stabilize the products. It is clear that trimerization of silanone is the driving force or this reaction.

The large energy difference between the reactants and 1,2-silaoxetane suggests a method for preparing a silaoxetane. The back reaction of trisiloxane and alkene at high temperature should be sufficient to form silaoxetane. However, for silaoxetane to continue on to silene and ketone would require gaining an additional 80 kcal mol⁻¹. The activation barrier for this reaction would be still larger. Therefore, it is unlikely that the silaoxetane would degrade to silene and ketone. To our knowledge, this reaction has not been reported.

Electron Density Analysis

West and co-workers²⁹ noted an unusually short Si-Si distance of 2.31 Å in the crystal structure of tetramesitylcyclodisiloxane. The normal Si-Si single bond length is 2.34 Å, only slightly longer than this formally nonbonded Si-Si distance. West proposed two possible models to explain this short distance: (1) severe lone-pair-lone-pair repulsions between the oxygens, forcing a lengthened

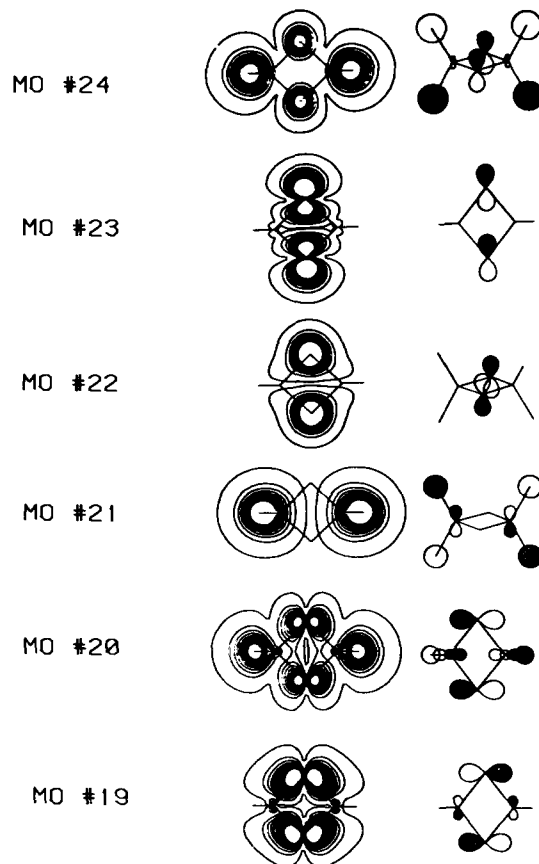


Figure 2. Projected electron density maps and schematic diagrams of the highest six MOs of cyclodisiloxane at 3-21G(*). Contour levels for the density maps are from 0.001 to 0.101 by 0.01 e au⁻².

Table VI. Net Charge Derived from ISEPs on Fragments of 1,2-Silaoxetane

	3-21G	3-21G(*)
H ₂ Si	1.51	1.54
O	-1.31	-1.32
CH ₂	0.46	0.44
CH ₂	-0.64	-0.67

Si-O bond and contracted Si-O-Si angle, or (2) a localized two-electron Si-Si bond with four-center six-electron delocalized bonding about the periphery.

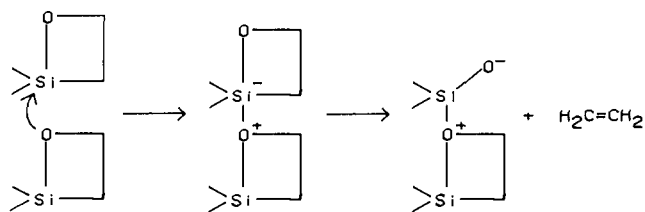
To test these hypotheses, the electron density of cyclodisiloxane at 3-21G(*) was calculated by projecting the density onto the plane of the heavy centers. The projected electron density maps of the highest six occupied molecular orbitals (MOs) along with schematic drawings of the atomic orbitals (AOs) comprising these MOs are shown in Figure 2. There is no MO which is a Si-Si bonding orbital. Rather, the interactions of the two silicon AOs with each other are primarily nonbonding or antibonding. Only in the HOMO (MO 24, 3b₂₁³⁰) is there a bonding interaction between the two silicon atoms, but this is a very small π-type interaction. Slight π-type Si-Si interaction is also present in MO 18 (2b_{2u}). MOs 23 (4b_{3u}) and 22 (1b_{1g}) clearly show large oxygen-oxygen lone-pair repulsions, one in the plane and one perpendicular to the symmetry plane. There are four MOs (24, 20, 19, and 18) which comprise the bonds in the ring. All of these are two-electron bonds, indicating that the periphery is not electron deficient. The unusual structure of cyclodisiloxane arises from this extreme oxygen-oxygen lone-pair repulsions coupled with a slight silicon-silicon attraction. A similar conclusion was reached by Jemmis based on qualitative EHT considerations.³¹

The projected electron density analysis was also carried out on 1,2-silaoxetane at 3-21G and 3-21G(*). Integrations of the

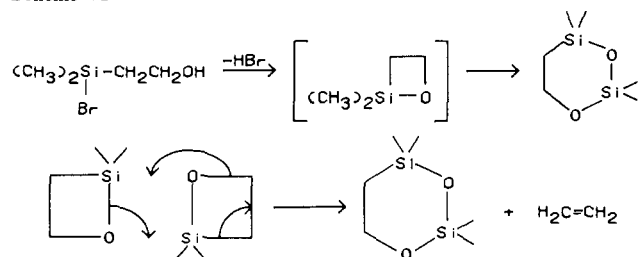
(30) Although cyclodisiloxane is of *C_s* symmetry, it is quite close to *D_{2h}* symmetry and, therefore, *D_{2h}* point group designations for the MOs are used.

(31) Jemmis, E. D. Poster session, American Conference of Theoretical Chemistry, Jackson Hole, WY, June 1984.

Scheme V



Scheme VI



projected electron density about each of the heavy centers (and their associated hydrogens) was performed by using lines of demarcation which approximate the virial surfaces.³² These integrations appear in Table VI as net charge on each fragment. Of particular interest is the large negative charge on oxygen. The oxygen atom of 1,2-silaoxetane carries well over a full negative charge. Integration of the electron density in cyclodisiloxane gives a net charge on oxygen of -1.58 and -1.65 at 3-21G and 3-21G(*), respectively. The Si-O bond in cyclic systems is clearly quite polar, with a substantial negative charge centered on oxygen.

This large charge separation suggests a mechanism for the

reaction under study (Scheme V). The oxygen of one silaoxetane molecule can act as a nucleophile toward the silicon of another silaoxetane molecule. This supermolecule can then extrude the alkene, leaving a zwitterion which is capable of forming the silanone oligomers. This mechanism has the benefit of never forming isolated silanone but rather produces directly the oligomers of silanone, a much more energetically feasible route. Barton⁸ has suggested a similar mechanism to explain the reaction of 2-(dimethylsilyl)ethanol with bromine to give 2,2,4,4-tetra-methyl-2,4-disila-1,3-dioxane (Scheme VI). Here two silaoxetane molecules combine directly to yield the alkene and the closed form of the zwitterion intermediate proposed above.

Conclusion

The Si-O bond in cyclic systems is highly polar, with oxygen carrying greater than a full negative charge. This large negative charge coupled with the strong lone-pair repulsions between the oxygens and slight Si-Si attraction accounts for the unusual structure of cyclodisiloxane.

The reaction of silenes with ketones to give alkenes and siloxanes is driven by the great strength of the many Si-O bonds formed in producing the cyclodisiloxanes. Reasonable mechanisms for this reaction must allow for the direct formation of cyclic siloxanes without invoking silanones, since the reaction of silaoxetane to silanone and alkene is strongly endothermic. Silaoxetane has not been isolated due to the large exothermicity involved in proceeding from silaoxetane to alkenes and siloxanes. However, the reverse reaction may allow for the detection of a silaoxetane.

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Registry No. 5, 71814-15-8; formaldehyde, 50-00-0; silene, 51067-84-6; silanone, 22755-01-7; ethylene, 74-85-1; cyclodisiloxane, 34392-10-4.

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Stability of the Reaction Coordinate in the Unimolecular Reaction of Thioformaldehyde

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Abstract: A dynamical aspect of the unimolecular photodissociation reaction of thioformaldehyde is analyzed and compared to the photodissociation reaction of formaldehyde. A characteristic feature of the out-of-plane vibrational mode, which is orthogonal to the reaction coordinate, is revealed. The force constant of the out-of-plane vibrational mode is considerably softened in the neighborhood of the transition state. The electronic structure of this softening mechanism is clarified. This softening may destabilize the reaction coordinate and broaden the area accessible for the reactive flux to pass through the transition state. This may affect the dynamics of the photodissociation reaction considerably.

I. Introduction

One of the principal subjects of recent theoretical chemistry is the study of the dynamical processes in chemical reaction systems. Particularly in photochemical reactions, dynamical processes involving rovibronic energy transfers have recently received much attention.^{1,2} In this field of research, the Born-Oppenheimer adiabatic approximation of electronic motion plays a fundamental role, and certain characteristic features of chemical reaction paths are analyzed by using this approximation. Fukui's

intrinsic reaction coordinate (IRC) approach provides a firm theoretical basis for the study of the chemical reaction paths.³ The

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