

to spectral data prior to irradiation.

Direct Photolysis of 3 at 185 nm. VPC-purified **3** (342 mg, 2.76 mmol) in 100 mL of pentane was irradiated in a reactor with a Suprasil immersion well and Osram Hg lamp. Aliquots were monitored by VPC (50–120 °C program) as a function of the time of irradiation. At 10% conversion or less, (*Z*)-3-methylhex-3-ene was the only photofragmentation product observed. However, at conversions higher than 10%, both the *Z* and *E* isomers are observed. After 3 h of irradiation (50% conversion of **3** by VPC), the photolysate was concentrated by careful distillation in a water bath (40 °C). Photoproducts were isolated by preparative VPC and identified. Recovered starting material was examined by 300-MHz proton NMR to determine the extent of geometrical isomerization of **3** to **2**. The photolysis was calibrated by a 0.01 M pentane solution of (*Z*)-3-methylhex-3-ene.

Direct Photolysis of 2 at 185 nm. VPC-purified **2** (205 mg, 1.65 mmol) in 70 mL of pentane was irradiated in a reactor with a Suprasil immersion well and Osram Hg lamp. Aliquots were monitored as a function of the time of irradiation by VPC (50–120 °C program). At 10% conversion or less, (*E*)-3-methylhex-3-ene was the only photofragmentation product observed. However, at conversions higher than 10%, both *Z* and *E* isomers were present. After 3 h of irradiation (50% conversion of **2** by VPC) the photolysate was concentrated by careful distillation in a water bath (40 °C). The photoproducts were isolated by preparative VPC and identified. Recovered starting material was examined by 300-MHz proton NMR to determine the extent of geometrical isomerization of **2** to **3**. The photolysis was also calibrated with a 0.01 M pentane solution of (*E*)-3-methylhex-3-ene.

Quantitative Photolysis of 2 at 185 nm. VPC-purified **2** (181 mg, 1.46 mmol) in 50 mL of pentane was irradiated in a reactor with a Suprasil immersion well and Osram Hg lamp. The photolysis was conducted in the same manner as the preparative photolysis at 185 nm. After calibration by cyclooctene actinometry,¹⁷ a quantum yield of 0.29 was calculated for the photoreaction of **2** at 185 nm. (This calculated quantum yield does not account for the geometrical isomerism that is shown to occur, and, therefore, the actual quantum yield would be slightly higher.)

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Photolysis Products. (*Z*)-3-Methylhex-3-ene (**5**) was identified by comparison of its IR, PMR, mass spectrum, and VPC retention time with that of an authentic sample (Wiley 99%). The authentic compound was also used to calibrate the quantitative photolysis of **2** for the photofragmentation process.

(*E*)-3-methylhex-3-ene (**4**) was identified by comparison of its IR, PMR, mass spectrum, and VPC retention time with that of an authentic sample (Wiley 98%).

1-Isobutylidene-2-ethylcyclopropane (**8** + **9**) was identified by the following: IR 3025, 1770, 1452, 1372, 1180, 1067, 955 cm⁻¹; PMR δ 2.03 (2 H, m), 1.70 (br s, 3 H), 1.5–0.2 (11 H); MS, *m/z* 67 (base), 41, 27, 39, 29, 53, 55, 81, 109, 95; mol wt by mass spectrum 124.

syn-1-Ethyl-1-methyl-2-propylidenecyclopropane (**7**) was identified by the following: IR 3030, 1458, 1372, 1128, 1105, 1083, 1053 cm⁻¹; PMR δ 5.55 (m, 1 H), 2.02 (2 H, m), 1.28 (2 H, m), 1.1–0.7 (11 H); MS, *m/z* 67 (base), 41, 27, 39, 29, 53, 55, 81, 109, 96; mol wt by mass spectrum 124.

anti-1-Ethyl-1-methyl-2-propylidenecyclopropane (**6**) was identified by the following IR 3030, 1760 (w), 1455, 1372, 1287, 1052, 1000, 978, 942 cm⁻¹; PMR δ 5.64 (m, 1 H), 2.01 (2 H, m), 1.22 (2 H, m), 1.05–0.7 (11 H); MS, *m/z* 67 (base), 41, 27, 39, 29, 55, 53, 81, 109, 96; mol wt by mass spectrum 124, and from its predominance in the pyrolysis reaction.

Pyrolysis. Pyrolysis of 3 at 198 °C. VPC-purified **3** (200 mg, 1.61 mmol) was divided into three Pyrex tubes. The tubes were evacuated (with liquid nitrogen cooling), sealed with an oxygen–propane torch, and immersed in a heated silicon oil bath (198 °C). The pyrolysis samples were monitored by VPC (50–120 °C program) at 30, 60, and 90 min and compared to a *t* = 0 sample of **3**. The relative product ratios were calculated by VPC and were invariant (within experimental error) for each time interval of the pyrolysis.

Pyrolysis of 2 at 198 °C. VPC-purified **2** (193 mg, 1.56 mmol) was pyrolyzed exactly according to the procedure given above.

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A Theoretical Study of Fluorine Atom and Fluoride Ion Attack on Methane and Silane

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Abstract: We have performed MNDO and ab initio calculations for reactions of fluorine atom attack on methane and silane and, in addition, fluoride ion attack on the same molecules in the case of MNDO. We modeled both substitution and abstraction reactions in each case. Results were compared with experimental data, where available. Comparisons show that MNDO usually does as well as the ab initio methods in reproducing experimental values for ΔE 's of these reactions, but MNDO predicts activation barriers too high in most cases. Nevertheless, MNDO does qualitatively agree with the ab initio result that, while carbon undergoes abstraction much more easily than substitution, silicon can undergo either substitution or abstraction quite easily. The analysis in the case of fluoride ion attack on silane is complicated by the predicted ease of formation of a stable trigonal-bipyramidal intermediate.

Silicon chemistry is increasingly important to many products of materials science including catalysts, semiconductors, organosilicon polymers, ceramics, glasses, and composites. Our special interest is silica surfaces and their interactions with organic molecules. In all of these applications an efficient, accurate, theoretical model for predicting silicon chemistry could produce

a great economy of effort. In particular, a detailed model of the mechanisms and products for silica polymerization would be of great help in tailoring silica materials for specific purposes. To this end, we began a combined theoretical and experimental program to study silicon reactions and silica surfaces several years ago.

Our goal is to perform theoretical calculations for rather large molecular systems without resorting to theoretical models which are expensive, time-consuming, and, thus, self-defeating for our

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Table I. Heats of Formation of Reactants and Products

| molecule | ΔH_f° (25 °C) (MNDO), kcal mol ⁻¹ | ΔH_f° (25 °C), (exptl), ^a kcal mol ⁻¹ |
|--------------------|--|---|
| H | 52.1 | 52.103 |
| H ⁻ | 73.8 | 33.2 |
| F | 18.9 | 18.86 |
| F ⁻ | -17.1 | -61.08 |
| H ₂ | 0.7 | 0.0 |
| HF | -59.7 | -65.14 |
| CH ₃ | 25.8 | 34.82 |
| CH ₄ | -11.9 | -17.895 |
| CH ₃ F | -60.9 | -56 |
| CH ₃ | 56.8 | |
| SiH ₃ | 38.2 | 49.2, ^b 46.4 ^c |
| SiH ₄ | 11.4 | 8.2 |
| SiH ₃ F | -85.8 | -90 |
| SiH ₃ | -12.4 | |

^aAll experimental values, unless otherwise indicated, are obtained from: "JANAF Thermochemical Tables"; Dow Chemical Company: Midland, MI, 1965, and updates. ^bSteele, W. C.; Stone, F. G. A. *J. Am. Chem. Soc.* **1962**, *84*, 3599-3600. ^cWalsh, R. *Acc. Chem. Res.* **1981**, *14*, 246-252.

purposes. At the same time, we needed a theoretical model that could produce approximate geometries for transition states and products and yield good energies of reaction and energies of activation (to within about 10 kcal mol⁻¹) for these processes.

Recently, theoretical methods have become available to study reactions of silicon-containing compounds. Dewar's MNDO method¹ has now been parameterized for silicon,² and his MINDO/3 program has included silicon parameters for a number of years.³ Unfortunately, only a few MNDO studies of silicon reactions have appeared,^{4,5} probably due to the poorer agreement with experimental data for silicon-containing compounds compared with second-row elements.⁶ MINDO/3 cannot be used for studies involving silicon-fluorine compounds, since the pair parameters for this combination of elements are not available in MINDO/3.³ Good ab initio calculations on simple silicon systems have also recently appeared.⁷⁻⁹ The current work extends these calculations to abstraction reactions involving fluorine.

Our initial goal in these calculations was to evaluate silica polymerization mechanisms, both in acidic and basic media. That goal remains and will be addressed in later publications. In this initial paper, we focus on the general question of the applicability and reliability of MNDO calculations to simple silane reactions and their comparison with the analogous methane reactions. Since MNDO has already been shown to be generally quite useful in the study of reaction mechanisms in carbon systems,¹⁰ this comparison will give us some indication of the reliability of the silicon parameters for these types of reactions. Future work will address the reliability of MNDO for compounds which contain pentavalent and hexavalent silicon.

Calculations

The semiempirical calculations were performed with the MNDO method developed by Dewar and co-workers.¹ The silicon parameters were obtained from a later communication by Dewar.² All stationary points on the potential surface were optimized with procedures supplied with the MOPAC package of programs available through QCPE.¹¹

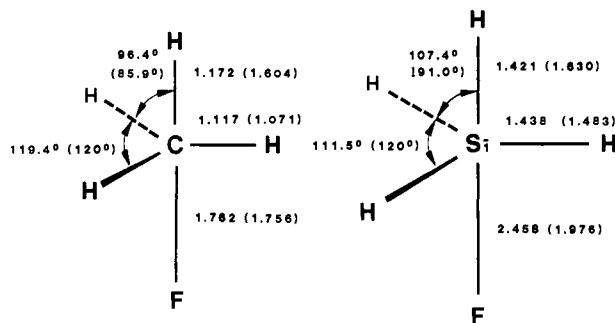


Figure 1. Comparison of MNDO geometries with 3-21G geometries (in parentheses) for the transition states of fluorine atom substitution onto methane and silane. The MNDO geometries are slightly distorted trigonal bipyramids, so the distances and angles given are the average values for the equatorial hydrogens. All bond distances are in angstroms.

The ab initio geometries were predicted at the 3-21G¹² SCF level. For energy comparisons single-point calculations were performed with MP3¹³/6-31G**¹⁴ and MP3/EXT wave functions, where EXT refers to 6-311G**¹⁵ in the C-F case and to 6-31G**^{14,15} for Si-F.

Cartesian force constant calculations were carried out on all suspected transition states. In each case, diagonalization of the force constant matrix yielded one, and only one, negative eigenvalue, thereby verifying the transition states.

Results and Discussion

Reactants and Products. In order to test the validity of using MNDO for these calculations, we first need to consider how well it predicts heats of formation for our reactants and products. These results are given in Table I. The agreement between the calculated heats of formation and the experimental ones is reasonable (better than 10 kcal mol⁻¹) for all species except the anions F⁻ and H⁻, both of which MNDO predicts to be about 40 kcal mol⁻¹ too unstable. This failure of MNDO is typical of its inability to reproduce the stability of small anions in which the charge is highly localized on one atom. This discrepancy will affect our calculated energies of reaction only slightly, however, since the errors will almost cancel for reactions in which one of the anions is a reactant and the other is a product. We note that there is some uncertainty in the experimental data for some of the silicon compounds, most notably SiH₃. The calculated results support the lower of the two experimental values cited, the result of 46.4 kcal mol⁻¹ determined by Walsh. In addition, the higher value was determined by electron impact, which may yield slightly high values for heats of formation. Still, the good agreement for all of the species displayed in the table (except H⁻ and F⁻) supports the conclusion that MNDO should be useful for these types of reactions.

The 3-21G geometries for all closed-shell reactants and products have been published previously.¹² The MNDO geometries for these same species give the expected tetrahedral geometries for the tetravalent carbon and silicon species. The 3-21G geometry for the methyl radical is planar (*D*_{3h}) with C-H bond lengths of 1.072 Å. The MNDO geometry for the methyl radical is quite similar (planar *D*_{3h}) with C-H bond lengths of 1.078 Å. The 3-21G geometry for the silyl radical is a trigonal pyramid (*C*_{3v}) with Si-H bond lengths of 1.486 Å and HSiH angles of 111.7°. MNDO predicts the same shape (*C*_{3v}) with Si-H bond lengths of 1.432 Å and HSiH angles of 110.0°. MNDO predicts the CH₃⁻ anion to have the same basic structure as the methyl radical (*D*_{3h}), with slightly shorter C-H bond lengths of 1.077 Å. This is in contrast to predictions of both MINDO/3 and ab initio calculations, all of which predict the methyl anion to be a *C*_{3v} pyramidal

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Table II. Results for Fluorine Atom Reactions

| $\Delta E(\text{reaction}), \text{kcal mol}^{-1}$ | | | | $E_a, \text{kcal mol}^{-1}$ | | |
|---|------------|----------------------|--|-----------------------------|------------|----------------------|
| MNDO | MP3/6-31G* | MP3/Ext ^b | exptl ^a | MNDO | MP3/6-31G* | MP3/Ext ^b |
| -15.8 | -1.4 | 2.4 | F + CH ₄ → CH ₃ F + H -4.9 | 57.7 | 47.5 | 48.8 |
| 64.0 | -54.0 | -50.4 | F + SiH ₄ → SiH ₃ F + H -65.0 | 20.2 | 1.5 | 5.2 |
| -40.9 | -15.2 | -24.3 | F + CH ₄ → CH ₃ + HF -31.1 | 27.3 | 3.3 | 6.5 |
| -51.8 | -33.7 | -35.6 | F + SiH ₄ → SiH ₃ + HF -45.8 ^c -43.0 ^d | 23.3 | 0 | 0 |

^aAll experimental values calculated from: "JANAF Tables", footnote *a* to Table I, unless otherwise noted. ^bExt means a basis set for carbon of 6-311G** and for silicon 6-31**. ^cValue calculated from Walsh's heat of formation for SiH₃, footnote *c* to Table I. ^dValue calculated from Steele et al.'s heat of formation for SiH₃, footnote *b* to Table I.

structure. We believe that the ab initio predicted C_{3v} structure is correct, in agreement with what one would expect from a simple VSEPR treatment. The SiH₃⁻ anion is predicted by MNDO to be C_{3v}, with Si-H bond distances of 1.472 Å and HSiH bond angles of 94.1°.

Fluorine Atom Substitution Reactions. We next consider reactions of the type F + AH₄ → AH₃F + H, in which A stands for either C or Si. The results of these calculations and experimental results, where available, are presented in Table II. Both the MNDO and ab initio results for ΔE of the reactions are reasonably close to the experimental values, with MNDO doing somewhat better for the silicon case and the ab initio results slightly better for the carbon case. The ab initio results are too endoergic while the MNDO results are too exoergic in the carbon case, but nearly correct in the silicon case.

Both methods predict a trigonal-bipyramidal five-coordinate transition state for both reactions, shown in Figure 1. MNDO predicts the CH₄ + F transition state to be slightly distorted from the ideal trigonal bipyramid, with a C-F distance of 1.76 Å and a C-H distance of 1.17 Å for the leaving hydrogen. For simplicity, the figure shows average C-H distances and bond angles, but there are variations in these average distances of a few hundredths of an angstrom and in the angles of a few degrees. The fluorine is slightly close to one equatorial hydrogen than the other two. The force constant calculation gave the required one, and only one, negative force constant, with an imaginary frequency along the reaction coordinate of 1136i cm⁻¹. The 3-21G C-F distance was practically identical with the MNDO C-F distance (1.76 Å), but the C-H distance for the leaving hydrogen was appreciably more stretched (1.60 Å). The 3-21G imaginary frequency is 1645i cm⁻¹.

MNDO predicts the SiH₄ + F transition state to be more distorted from the ideal trigonal bipyramid, with a Si-F distance of 2.46 Å and a Si-H distance of 1.44 Å. In this transition state, there is very little Si-H bond breaking. In fact, the fluorine is so far away from the silane molecule this calculated transition state appears very much like a tetrahedral silane perturbed only slightly by the fluorine atom in the vicinity. The force constant calculation gives a single negative force constant, with imaginary frequency along the reaction coordinate of 335i cm⁻¹. The 3-21G geometry has a much shorter Si-F distance (1.98 Å) and a considerably longer Si-H distance (1.63 Å) than MNDO. It appears that in this case MNDO is predicting a much-too-long bond length because of spuriously large core-core repulsions, as have been observed in previous calculations as well.¹⁶ The 3-21G imaginary frequency is 1950i cm⁻¹, slightly larger than the carbon frequency. The MNDO value is much smaller due to the very long Si-F distance.

The activation energies (Table II) predicted by both methods are relatively high for the carbon-substitution reaction. The ab initio values are about 10 kcal mol⁻¹ lower than the MNDO value and are probably more accurate given the tendency of MNDO

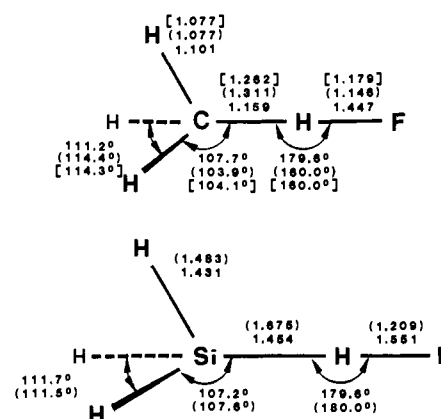


Figure 2. Comparison of the MNDO geometries with 3-21G geometries (in parentheses) for the transition states of fluorine atom abstraction from methane and silane. For the methane case, the transition-state geometry from ref 17 (in brackets) is also included for comparison. All bond distances are in angstroms.

to overestimate activation energies.¹⁶ The latter occurs particularly for cases in which abnormally high repulsions result from transition-state geometries in which there is a distance(s) of approximately van der Waals length. This effect is even more pronounced for the silicon substitution reaction, for which the ab initio results indicate a very small activation barrier, but MNDO predicts a barrier of 20 kcal mol⁻¹. Note that the overprediction of the barrier is more pronounced in the silicon case, because a larger proportion of the MNDO-calculated activation energy is due to these spuriously large core-core repulsions. In the carbon case, the barrier is substantial anyway due to steric crowding of the required five atoms in the transition state around the smaller carbon atom. Also note that the greater error in barrier height corresponds to the case in which the C-F bond length is predicted to be considerably too long, at least in comparison with the ab initio result. Still, the trend in both methods indicates a much easier substitution reaction at silicon than at carbon.

Fluorine Atom Abstraction Reactions. These reactions are of the type AH₄ + F → AH₃ + HF, in which A is either carbon or silicon. The results for these reactions are also given in Table II. In the carbon case, MNDO predicts the ΔE about as well as the more accurate ab initio procedure, but in the opposite direction. In the silicon case, both methods do reasonably well, although the experimental value is not certain due to the two different values in the literature for the heat of formation of SiH₃.

The geometries of the transition states are shown in Figure 2, along with the geometry predicted by another recent ab initio calculation for this system.¹⁷ Overall, the geometries are similar, particularly when we compare the two ab initio results. All of the calculations predict a transition state of C_{3v} symmetry. The

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Table III. Results for Fluoride Ion Reactions

| $\Delta E(\text{reaction}), \text{kcal mol}^{-1}$ | | $E_a, \text{kcal mol}^{-1}$ MNDO |
|---|---|-------------------------------------|
| MNDO | exptl ^a | |
| 41.9 | $\text{F}^- + \text{CH}_4 \rightarrow \text{CH}_3\text{F} + \text{H}^-$ 56.2 | 40.6 |
| -6.3 | $\text{F}^- + \text{SiH}_4 \rightarrow \text{SiH}_3\text{F} + \text{H}^-$ -3.9 | |
| 26.1 | $\text{F}^- + \text{CH}_4 \rightarrow \text{CH}_3^- + \text{HF}$ | 7.3 |
| -66.4 | $\text{F}^- + \text{SiH}_4 \rightarrow \text{SiH}_3^- + \text{HF}$ | 4.7 |

^aAll experimental values calculated from: "JANAF Tables", footnote *a* to Table I.

MNDO H-F distance is much greater than that of the ab initio calculations, 1.45 Å compared with 1.15 Å for our ab initio result. The C-H bond breaking is much less developed in MNDO, with a C-H distance of 1.16 Å compared to our ab initio value of 1.31 Å. Thus the MNDO transition state occurs much earlier, leading us to suspect that spuriously large repulsions are distorting the transition-state geometry and producing an inordinately large activation energy. The activation energies are about 20 kcal mol⁻¹ higher for MNDO than the ab initio results shown in the table. Sana et al.¹⁷ calculated values ranging from 2.2 to 3.1 kcal mol⁻¹, depending on the ab initio method they used. They also give an experimental value of 1.15 kcal mol⁻¹. Thus it does appear that MNDO overpredicts the activation energy by about 20 kcal mol⁻¹. Note again that this overprediction occurs for a case in which there is a bond being formed in the transition state that MNDO predicts to be far too long. The predicted transition state for this reaction (MNDO) was confirmed with a force constant calculation, with the imaginary frequency along the reaction coordinate calculated to be 1090i cm⁻¹. The 3-21G imaginary frequency for this transition state is 2897i cm⁻¹.

The geometry of the transition state for the silicon analogue was qualitatively similar to the carbon case as calculated with MNDO, again with a fairly long H-F distance of 1.56 Å compared to our ab initio distance of 1.21 Å. The Si-H bond is predicted to be barely stretched by MNDO, from 1.43 Å in the reactant to 1.45 Å in the transition state. In contrast, the ab initio Si-H distance is 1.68 Å. In both cases the transition state has C_{3v} symmetry. The process is predicted to occur without activation according to the ab initio results, but MNDO predicts a barrier of 23 kcal mol⁻¹, again about 20 kcal mol⁻¹ greater than the ab initio results. Once again, MNDO has overpredicted the activation energy in a case that it also predicts the bond being formed in the transition state to be too long. It is interesting to note, however, that both methods predict the barrier to be about 4 to 6 kcal mol⁻¹ lower for the silicon reaction as compared with the carbon case. The MNDO transition state was confirmed with a force constant calculation, the imaginary frequency along the reaction coordinate being 1100i cm⁻¹, about the same as for the carbon case. The 3-21G imaginary frequency here is 2449i cm⁻¹.

Fluoride Ion Substitution Reactions. Next we consider reactions of the type $\text{F}^- + \text{AH}_4 \rightarrow \text{AH}_3\text{F} + \text{H}^-$, in which A stands for either C or Si. Our results, along with the available experimental results are given in Table III. Dewar and Healy⁴ addressed these types of reactions and concluded that the silicon reaction differs from the carbon reaction in that the trigonal-bipyramidal 5-coordinate adduct is a stable intermediate in the silicon case, but it is a transition state for the carbon substitution. They explained the difference on the basis of the larger size of silicon, making it possible to accommodate a 5-coordinate structure as a stable intermediate. Our results agree with theirs, and their explanation seems quite reasonable, since neither set of calculations included orbitals in the basis set. We calculate an activation energy for the fluoride attack on methane of 40.6 kcal mol⁻¹. This is less than the endoergic energy change for the reaction (to isolated products) of 41.9 kcal mol⁻¹. The actual minimum along the

reaction path after the transition state is a charge-dipole complex in which the hydride ion has separated by a distance of 2.5 Å, and it lies about 7 kcal mol⁻¹ lower than the transition state. The transition state was confirmed by a force constant calculation, with a single negative force constant whose imaginary frequency was 489i cm⁻¹. The large activation energy and endoergic ΔE of reaction will not make the process very favorable. The calculated ΔE of reaction is less than the experimental value by 15 kcal mol⁻¹.

In the silicon case, the fluoride ion falls into silane without activation to form a stable trigonal-bipyramidal intermediate which is more stable than the reactants by about 75 kcal mol⁻¹. The structure is more stable with the fluoride in an equatorial position by about 4 kcal mol⁻¹. If we take either of these structures and pull off a hydride ion, the energy increases monotonically to the energies of the isolated products. An interesting feature is the conversion of the hydride from an equatorial to an axial position as it leaves from an equatorial position in the complex. The overall energy change for the reaction is calculated to be exoergic by 6.3 kcal mol⁻¹, in good agreement with the experimental value. Thus, in the gas phase, we would expect the substitution reaction to proceed readily, but in solution, the trigonal-bipyramidal structure could quite possibly persist because of dissipation of the initial energy to the solvent.

Fluoride Ion Abstraction Reactions. Finally we consider reactions of the type $\text{F}^- + \text{AH}_4 \rightarrow \text{AH}_3^- + \text{HF}$, in which A is again either silicon or carbon. Results of the calculations are given in Table III. No experimental comparisons can be made because of the lack of data for CH₃⁻ and SiH₃⁻. Again the analysis is complicated by the appearance of a charge-dipole complex of the type AH₃⁻-HF. In the fluoride attack on one of the hydrogens of methane, a transition state was located at an energy only 7.3 kcal mol⁻¹ above the reactants, but the overall energy change for the reaction is endoergic by 26.1 kcal mol⁻¹. The charge-dipole complex, however, is only endoergic by 4.1 kcal mol⁻¹ compared with the reactants. The transition state was confirmed with a force constant calculation, with the imaginary frequency along the reaction coordinate being 621i cm⁻¹. We feel that the value for the overall energy change may be higher than we calculate, since MNDO predicts one of the reactants, F⁻, to be far too unstable. There will likely be a partially compensating error for CH₃⁻, but probably not of the same magnitude due to the larger size of CH₃⁻. An experimental value for the heat of formation of CH₃⁻ would settle this question. Thus, while the abstraction reaction should be much more likely than the substitution reaction at carbon, neither reaction would be predicted to be very fast.

Attack of F⁻ on a hydrogen of silane provides an interesting contrast. In this case, the fluoride attack preferentially forms the trigonal-bipyramidal intermediate by attaching to the silicon, but the abstraction can be forced to take place by continuing to shorten the F-H bond. A transition state was obtained at an energy only 4.7 kcal mol⁻¹ above that of the isolated reactants, but it is about 80 kcal mol⁻¹ above that of the stable trigonal-bipyramidal intermediate. In addition, the 4.7 kcal mol⁻¹ is probably much too low, again because of the fluoride ion being predicted far too unstable. The force constant calculation produced an imaginary frequency along the reaction coordinate being 3097i cm⁻¹. The reaction may proceed in the gas phase, but at least in solution the trigonal-bipyramidal intermediate probably will form and remain.

Conclusions

Comparisons with ab initio calculations and available experimental data for these simple methane and silane substitution and abstraction reactions show that MNDO can be useful in making predictions for these types of systems. It does have its restrictions, however. One needs to be aware of the gross overprediction of the heats of formation of small anions such as fluoride (by about 40 kcal mol⁻¹) and its tendency to overpredict activation energies (by about 20 kcal mol⁻¹) of strongly exoergic reactions in which spurious core-core repulsions at fairly long distances are a significant fraction of the total activation energy. This situation

occurs for hydrogen abstraction reactions by fluorine and in substitution at silicon. In this case, silicon is large enough to accommodate five atoms around it at the transition state with a minimum of steric repulsion, and thus the actual barrier is fairly low. The spurious repulsions thus result in the bond being formed being much too long at the transition state and the bond being broken being much too short. This distortion of the transition-state geometry appears to occur for many strongly exoergic reactions. In the case of substitution at carbon, there is a substantial actual activation barrier because of its smaller size, so that the spurious repulsions at longer distances do not make much of a contribution to the overall predicted activation energy. Nevertheless, MNDO compares very favorably with good ab initio calculations for predicting reaction energies, particularly in the analysis of trends in related series of compounds. If one is careful to take into account these known discrepancies, MNDO can be useful in modeling large silicon-containing molecules.

For the cases of fluorine atom attack on methane, we predict much easier abstraction to form HF than substitution. For attack on silane, either substitution or abstraction should be quite easy.

For fluoride attack on methane, again abstraction is much more likely, although not as likely as in the neutral fluorine atom case. Fluoride attack on silane is complicated by the formation of a stable, trigonal-bipyramidal intermediate that will persist, at least in solution. If enough energy is available to decompose this complex, both substitution and abstraction should be quite easy. In general, the ease of substitution in the silicon case reflects both the strength of the Si-F bond and the stability of pentacoordinate silicon relative to carbon.

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The Structure Corresponding to the Reference Polynomial of [N]Annulene in the Topological Resonance Energy Theory

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Abstract: A directed weighted graph for [N]annulene, G1', is studied in which directed edge $r \rightarrow s$ is weighted $\exp(iv_{rs})$. It is shown that an appropriate choice of v_{rs} gives "reference" [N]annulene in the topological resonance energy theory. The relationships are discussed between Hückel, "reference", Möbius, and field-perturbed [N]annulenes. The analytical expression for the eigenvalues of the adjacency matrix of G1' is given, which allows one to get a mnemonic device for obtaining the roots of the reference polynomial of [N]annulene.

The topological resonance energy (TRE)¹⁻⁴ is known to be an excellent index for aromaticity of conjugated molecules. The clue to the success of the TRE theory is the mathematical definition of the reference structure. The coefficient of the reference polynomial is computed by dropping all Sachs graphs with cyclic components. So the reference polynomial of a conjugated system is considered to be the characteristic polynomial of the hypothetical "acyclic polyene-like" reference structure. The TRE value of a system, i.e., the difference between the total π -electron energy of the system and that of its reference structure, reflects the degree of π -electron cyclic delocalization arising from the presence of rings in the structure. London susceptibility (and ring current), which has been used as a criterion of aromaticity,^{5,6} is also closely related to the presence of ring.⁷⁻¹⁰

Since the definition of the reference polynomial was purely combinatorial in nature, it was not evident what was the adjacency matrix corresponding to the "structure" of the reference polynomial until Aihara,¹¹ Schaad et al.,¹² and Graovac¹³ obtained the adjacency matrices corresponding to the reference polynomials for a few simple systems. However, their purpose was the proof that the roots of the reference polynomial are real.^{14,15} So the properties of the matrices have not been discussed sufficiently.

All information on the physical property of a system is involved in the adjacency matrix because it reflects the structure of the system. Therefore, it is very important to study the properties of the matrix (and the graph) corresponding to the reference polynomial. In the present paper a directed edge-weighted graph for [N]annulene will be studied in detail, which is slightly more general than the graphs given by Aihara, Schaad et al., and Graovac. The investigation of the graph will clarify some prop-

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