

Theoretical Studies of Reactions of Silanes

Paul Marshall

Department of Chemistry, University of North Texas

P.O. Box 5068, Denton, Texas 76203-5068, USA

Abstract

Computational investigations of abstraction reactions of the form $X + \text{SiR}_3\text{H} \rightarrow \text{XH} + \text{SiR}_3$ are reviewed, where $X = \text{H}, \text{O}, \text{F}$ and Cl and SiR_3H represents SiH_4 , Si_2H_6 and $(\text{CH}_3)_n\text{SiH}_{4-n}$ ($n = 1-3$). Si-H bond dissociation enthalpies and energy barriers for the formation of transition states can be calculated to within 5 kJ mol^{-1} using e.g. Gaussian 2 theory. Analysis of isodesmic reactions provides a route to reliable thermochemistry for systems too large for Gaussian 2 theory. Expressions for rate constants calculated *ab initio* using transition state theory are given; they are in generally good agreement with experimental measurements.

1. INTRODUCTION

The gas-phase kinetics of silanes, especially SiH_4 , are important in chemical vapor deposition of silicon and silicon compounds such as the oxide and nitride, and in silane combustion. In this paper computational investigations of H-atom abstraction from Si-H bonds in silanes will be summarized. The overall goal is reliable prediction of the thermochemistry and reactivity of silanes so as to be able to model their gas-phase chemistry. To test these predictions we have carried out laboratory measurements of individual elementary reactions; quantitative comparisons with theory will be presented. Silanes are valence-isoelectronic with alkanes, which have been extensively studied in the context of hydrocarbon combustion and whose properties can be rationalized according to simple semi-empirical principles including e.g. the Polanyi-Semenov [1][2] and Bond-Order Bond-Energy (BEBO) [3] relationships. Important differences between Si-H and C-H bonds include the greater charge separation in the former, because Si is more electropositive than C, and the possibility of formation of pentacoordinated Si species by participation of low-lying d-orbitals on Si. Here it will be demonstrated that, although semi-empirical methods break down for silanes, usefully accurate results may be obtained via *ab initio* methods.

The focus is on SiH_4 and substituted silanes where H atoms are replaced by CH_3 or SiH_3 . Computational investigations of Si-H bond dissociation enthalpies and reactivity towards atomic H, O and halogens in reactions of the type



carried out by our group and others will be discussed.

2. COMPUTATIONAL APPROACH

Quantitative molecular orbital theory is applied using methods detailed elsewhere [4][5], implemented with the GAUSSIAN series of programs [6]. Briefly, the atomic orbitals are represented mathematically by a selected basis set. Molecular orbitals are constructed from linear combinations of the atomic orbitals, optimized variationally to give the lowest energy at a selected geometry. The geometry is then varied, using analytical gradients, to obtain the stationary points on the potential energy surface (PES). Harmonic vibrational frequencies are calculated at each stationary point to verify it as a true minimum, with all real frequencies, or a transition state with a single imaginary frequency that corresponds to motion along the reaction coordinate. Typically these geometry and frequency calculations are carried out with the split-valence 3-21G(*) and/or 6-31G* atomic basis sets, using self-consistent field Hartree-Fock theory. For closed-shell singlet species spin-restricted RHF theory is applied, and unrestricted UHF theory for open-shell species. For some species a partial correction for electron correlation effects is obtained using Møller-Plesset perturbation theory to second-order (MP2). HF frequencies are scaled by a factor of 0.89 and MP2 frequencies by a factor of 0.95.

Next, single-point energies at these geometries are obtained using larger basis sets and better corrections for correlation such as MP4 and QCISD(T) theory. The highest level of theory applied here is the Gaussian-2 (G2) methodology of Pople *et al.* [7][8][9], which *approximates* a complete QCISD(T)/6-311+G(3df,2p) calculation with a series of additive corrections to the MP4/6-311G** energy. In some cases an extra term has been added to correct for spin-contamination (this is larger for transition states than most bound molecules), defined as the energy change upon projecting-out spin contamination [10] at the PMP4/6-311G**

level, and the results are denoted as P-G2 [11]. When zero-point vibrational energies are included, the energy difference between the reactants and products corresponds to the reaction enthalpy at 0 K, ΔH_0 . The enthalpy difference between reactants and the transition state (TS) at 0 K, E_0^\ddagger , represents the barrier to reaction and controls the kinetics, and is usually similar but not identical to the empirical activation energy, E_a . The second-order rate constants for the bimolecular abstraction reactions considered here (reaction 1) are obtained via conventional transition state theory (TST) [12]:

$$k_{\text{TST}} = \Gamma \ell^\ddagger \frac{k_B T}{h} \frac{Q_{\text{TS}}^\ddagger}{Q_X Q_{\text{silane}}} \exp\left(-\frac{E_0^\ddagger}{RT}\right) \quad (2)$$

The partition functions Q are calculated from the *ab initio* geometries and frequencies [13]. Rotational symmetry factors are ignored and symmetry is taken into account by the reaction path degeneracy ℓ^\ddagger . Γ represents a correction factor for quantum mechanical tunneling which is ≥ 1 , although for most of the reactions considered here E_0^\ddagger is small enough to neglect any enhancement of reactivity by tunneling i.e. $\Gamma \approx 1$. An exception is $\text{H} + \text{SiH}_4$ for which the Wigner approximation [14] is employed,

$$\Gamma = 1 + \frac{1}{24} \left(\frac{h\nu^*}{k_B T}\right)^2 \quad (3)$$

where ν^* is the conjugate of the complex frequency of the TS.

3. RESULTS AND DISCUSSION

3.1 Si-H Bond Dissociation Enthalpies

There have been numerous theoretical investigations of the Si-H bond strength in silanes.

Several have been summarized by Apeloig [15] while halogenated species were recently reviewed by Gordon *et al.* [16]; some recent studies of $D_0(\text{SiH}_3\text{-H})$ include those by Ho *et al.* ($377.0 \text{ kJ mol}^{-1}$) [17], Curtiss and Pople ($383.8 \text{ kJ mol}^{-1}$) [18], Curtiss *et al.* ($382.0 \text{ kJ mol}^{-1}$) [9], Grev and Schaefer ($376.6 \text{ kJ mol}^{-1}$) [19] and Maître and Ohanessian ($377.4 \text{ kJ mol}^{-1}$ once zero-point vibrational energies are included) [20]. These values compare well to the best experimental estimate derived from the ratio of the forward and reverse rate constants for [21]



that imply [19] $D_0 = 377.8 \pm 2 \text{ kJ mol}^{-1}$.

The effect of methyl substitution in SiH_4 has been studied computationally. Trimethylsilane is too large for high-level calculations such as G2, but the bond strength can be related to that in SiH_4 by analysis of the *isodesmic* reaction



which conserves the number and type of each bond [22]. ΔH can be reliably calculated even at modest levels of theory because errors arising from deficient basis sets and incomplete corrections for electron correlation largely cancel. This ΔH equals the *difference* between $D((\text{CH}_3)_3\text{Si-H})$ and $D(\text{SiH}_3\text{-H})$. MP3/6-31G* results indicate that trimethyl substitution increases the Si-H bond dissociation enthalpy by 13.5 kJ mol^{-1} [23], in excellent accord with experimental data that show an increase of $14 \pm 3 \text{ kJ mol}^{-1}$ [24]. For monomethylsilane and dimethylsilane experiments suggest smaller increases of 4 ± 5 and $7 \pm 5 \text{ kJ mol}^{-1}$, respectively, over $D_0(\text{SiH}_3\text{-H})$ [25]. Isodesmic reactions at up to MP4/6-31G* theory show no significant increase in $D(\text{Si-H})$ for these two molecules [25], but the discrepancies are close to the

experimental uncertainty. BAC-MP4 results do show a steady rise of $D(\text{Si-H})$ with the degree of methyl substitution, of about 4 kJ mol^{-1} per methyl group [17][26].

Analysis of $D(\text{Si-H})$ in disilane via



at the MP4/6-31G* level indicates that silyl substitution in SiH_4 weakens the Si-H bonds by 12 kJ mol^{-1} [27]. This change is in excellent accord with an experimental reduction of $12 \pm 5 \text{ kJ mol}^{-1}$ [27] and earlier computational values [28][29][30].

Coolidge and Borden [31] drew attention to the application of Bent's Rule [32] to rationalize the influence of substituents on the Si-H bond strengths. Because CH_3 is more electronegative than H, which is more electronegative than Si, bonding in trimethylsilane from Si to C would be expected to involve hybrid orbitals with greater p character than in the sp^3 Si-H bonds of SiH_4 , and thus the remaining Si-H bond would have greater s character, better overlap and stronger bonding. In disilane, the Si-Si bond would have more s character and thus the remaining Si-H bonds less, relative to sp^3 in SiH_4 , and therefore the Si-H bonds are weakened. However, the CSiC angle of 110.4° in trimethylsilane (HF/6-31G* calculation) contradicts this explanation, and apparently the steric repulsion between the CH_3 groups leads to *less* p character in the C-Si bonds than sp^3 . An alternative explanation is based on the inductive effect. The electron-withdrawing methyl groups will destabilize $(\text{CH}_3)_3\text{Si}\cdot$ over $\text{SiH}_3\cdot$, thus raising the bond dissociation enthalpy, whereas the electron-donating SiH_3 group stabilizes $\text{Si}_2\text{H}_5\cdot$ and reduces the Si-H bond dissociation enthalpy in Si_2H_6 , similar to the lowering of $D(\text{C-H})$ in C_2H_6 as compared to CH_4 .

In summary, computational chemistry yields Si-H bond strengths in silanes with an

accuracy comparable to experiment.

3.2 *The Reaction of H Atoms with Silanes*

Two initial computational investigations of the transition state for H-atom abstraction yielded barriers of 32 and 45 kJ mol⁻¹ [33][34], higher than is consistent with laboratory measurements [35]. Recently, it was shown that G2 theory predicts $E_0^\ddagger = 20.7$ kJ mol⁻¹, and 15.1 kJ mol⁻¹ at the P-G2 level, results that are close to the experimental value of 17.1 ± 3 kJ mol⁻¹ [36]. Table 1 summarizes values of ΔH_0 and E_0^\ddagger for



at selected levels of theory. It may be seen that ΔH_0 is calculated accurately more easily, i.e. at lower levels of theory, than E_0^\ddagger . We observe similar patterns of decreasing barrier height with increasing sophistication of the calculations for other silane abstraction reactions discussed below. The P-G2 barrier height was combined with MP2/6-31G* information about the geometry and frequencies of the TS to calculate rate constants using TST (equation 2) with a Wigner tunneling correction. The results may be described by $k_7 = 2.44 \times 10^{-16} (\text{T/K})^{1.90} \exp(-860 \text{ K/T})$ cm³ s⁻¹ and are plotted in Arrhenius form on Figure 1. Also shown there are measurements from our laboratory [36]: agreement is seen to be satisfactory, with the difference arising almost entirely from a 2 kJ mol⁻¹ discrepancy between theory and experiment for E_0^\ddagger . No computational evidence for a neutral bound SiH₅ intermediate has been obtained, and it appears plausible that direct abstraction dominates the reactivity of SiH₄.

The reaction of H with Si₂H₆ has been studied at the G2 level by Dobbs and Doren [37]. They predict that E_0^\ddagger for abstraction is about 14 kJ mol⁻¹, which would be similar to

that found in SiH₄. The weak Si-Si bond opens the possibility of a substitution reaction



where the most energetically favorable substitution pathway had about the same barrier as abstraction. Thus for disilane abstraction and substitution are predicted to be competitive [37], which is consistent with experiments indicating that substitution accounts for around 20% of the total reactivity at room temperature [38].

3.3 *The Reactions of O Atoms with Silanes*

Horie *et al.* have noted that the BEBO method "fails completely" for the reactions of ground-state O(³P₁) atoms with SiH₄ and methylsilanes [39]. The reactivity trend is for the rate constant at room temperature to increase with the number of CH₃ groups [39], even as the Si-H bond energy goes up (see Section 3.1) and thus in contradiction to the Polanyi-Semenov rule. The calculated P-G2 barrier for



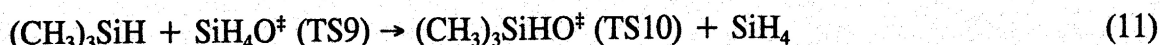
of $E_0^\ddagger = 11.3 \text{ kJ mol}^{-1}$ is in excellent accord with our experimental value of $11.8 \pm 3 \text{ kJ mol}^{-1}$ [11]; the agreement between TST rate constants ($k_0 = 5.17 \times 10^{-17} (\text{T/K})^{2.15} \exp(-1000 \text{ K/T}) \text{ cm}^3 \text{ s}^{-1}$) and measurements [11] may be seen in Figure 2. As in the case of reaction 7, no evidence was found for a bound pentacoordinate intermediate on the triplet PES.

CH₃ is more electronegative than H, so that the central Si atom is expected to be more positive in trimethylsilane than in SiH₄. This is consistent with the Mulliken charges calculated from the HF/6-31G* wavefunction: the charges on Si and H in SiH₄ are +0.41 and -0.10, respectively, and change to +1.16 and -0.15 in (CH₃)₃SiH. The effect of increased polarization

on the reactivity of the Si-H bond has been investigated through consideration of the TS for



at the MP2/6-31G**//HF/3-21G* level [40]. At this level of theory E_0^\ddagger is very inaccurate (for reaction 9 the error was 39 kJ mol⁻¹, which corresponds to a factor of more than 10⁶ in k_9 at 298 K [11]), but trimethylsilane is too large for e.g. a G2 analysis. Instead, E_0^\ddagger for reaction 10 can be derived from the isodesmic reaction



for which $\Delta H_0 = E_{0,10}^\ddagger - E_{0,9}^\ddagger = -13.0$ kJ mol⁻¹ at the MP2/6-31G**//HF/3-21G* level. This is in qualitative agreement with the lower barrier measured for reaction 10 [40], although the reduction in E_0^\ddagger is slightly overestimated: fitting to experimental k_9 and k_{10} data indicates that methylation reduces the barrier by 10.5 kJ mol⁻¹ rather than 13.0 kJ mol⁻¹ [40]. Using the latter purely theoretical value together with $E_{0,9}^\ddagger = 11.3$ kJ mol⁻¹ discussed above implies an unphysically *negative* value for $E_{0,10}^\ddagger$ of -1.7 kJ mol⁻¹; the corresponding TST rate constant of $k_{10} = 1.87 \times 10^{-17} (\text{T/K})^{2.13} \exp(+360 \text{ K/T}) \text{ cm}^3 \text{ s}^{-1}$ agrees with experimental measurements to within an order of magnitude [40] as shown on Fig. 2. The difference corresponds to an underestimation of only 4.5 kJ mol⁻¹ in the theoretical $E_{0,10}^\ddagger$, and presumably indicates an incomplete accounting for basis set size and changes in electron correlation in the calculation of ΔH_0 for reaction 11.

The reduction in barrier to O-atom abstraction with alkylation of the silane is interesting because it violates the Polanyi-Semenov rule. A qualitative rationalization is that the bonding σ orbital between Si and H is distorted towards the H atom, because of the latter's greater electronegativity, and thus the corresponding σ^* orbital is distorted towards the Si atom. This

antibonding MO accepts an electron from the attacking O atom in the TS, and is stabilized by other electron-withdrawing groups on Si such as CH₃. Thus the energy of the TS is lowered by alkylation of the central Si atom.

3.4 The Reactions of Halogen Atoms with Silanes

Sato *et al.* have studied the reaction



and obtained a significant barrier of about 15 kJ mol⁻¹ at the MP4/6-21G**//HF/6-21G** level of theory [41]. However, available experimental evidence suggests an effectively zero barrier for reaction 12 because $k_{12} \approx 3 \times 10^{10} \text{ cm}^3 \text{ s}^{-1}$ at room temperature [42][43] which implies that F and SiH₄ react at every collision. Results from our own laboratory are summarized in Table 2 [44], and it may be seen as the calculations are improved the predicted E_0^\ddagger and ΔH_0 decrease, similar to the pattern noted above for reaction 7. HF theory gives a very poor estimate of the overall ΔH_0 for reaction 12, while the G2 result is in excellent accord with experiment. The MP2/6-31G* potential energy surface has a saddle point (see Table 2), but at this geometry the G2 energy lies *between* that of the reactants and products i.e. E_0^\ddagger is negative. This is suggestive of a purely attractive interaction between F and SiH₄ with no barrier to reaction.

The TS for the reaction



shows similar behavior (Table 2). At the G2 level of theory the energy at the MP2/6-31G* TS geometry is again *below* that of the reactants, so there is apparently no barrier to reaction [44].

This is in accord with experiments that show a high rate constant, around $3 \times 10^{10} \text{ cm}^3 \text{ s}^{-1}$, and a slightly negative activation energy of $E_a \approx -2 \text{ kJ mol}^{-1}$ [45]. One interpretation is that the mechanism involves formation of an adduct between Cl and SiH_4 , which preferentially dissociates back to reactants [46]. However, searches of the HF and MP2 PES revealed no bound species, except for a very loose van der Waals-like complex between $\text{SiH}_3 + \text{HCl}$ which is bound by about RT or less [44] and is therefore unlikely to affect the kinetics significantly. An alternative explanation of the negative E_a is based on TST [46], where if $E_{0,13}^\ddagger \approx 0$ and the temperature dependences of Q_{vib}^\ddagger and $Q_{\text{vib},\text{SiH}_4}$ cancel, then E_a is expected to approach $-RT/2$ i.e. about -1.6 kJ mol^{-1} for the experiments, close to that observed [45].

4. CONCLUSIONS

Transition states for the reactions of atoms with SiH_4 are well-characterized at the G2 level of theory, to within 5 kJ mol^{-1} , and rate constants derived via TST are in accord with experimental results. The properties of more complicated silanes, that are too large for the application of G2 theory, may be related to those of SiH_4 through isodesmic reactions. This analysis at the MP2/6-31G* and/or MP4/6-31G* levels of theory yields good results for the variation of the Si-H bond dissociation enthalpy with methyl and silyl substitution. Isodesmic reactions also seem promising for analysis of transition states, and give a reasonable estimate of the relative reactivities of SiH_4 and $(\text{CH}_3)_3\text{SiH}$ towards O atoms. All these reactions have been interpreted in terms of direct H-atom abstraction, and so far no theoretical evidence for participation by bound pentacoordinate intermediates has been found.

5. ACKNOWLEDGMENTS

Special thanks are due to members of my research group who carried out much of the work reviewed here: L. Ding, Dr. A. Goumri, A. Misra and W.-J. Yuan. This work has been supported by Texas Instruments, Inc., the Robert A. Welch Foundation (Grant B-1174) and the UNT Organized Research Fund.

REFERENCES

1. M.G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 34 (1938) 11.
2. N.N. Semenov, *Some Problems in Chemical Kinetics and Reactivity Vol. 1*, Princeton, 1958, p. 30.
3. H.S. Johnston and C. Parr, *J. Am. Chem. Soc.*, 85 (1963) 2544.
4. W.J. Hehre, L. Radom, P.v.R. Schleyer and J.A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986.
5. J.B. Foresman and Æ. Frisch, *Exploring Chemistry with Electronic Structure Methods*, Gaussian, Pittsburgh, 1993.
6. M.J. Frisch, G.W. Trucks, M. Head-Gordon, P.M.W. Gill, M.W. Wong, J.B. Foresman, B.G. Johnson, H.B. Schlegel, M.A. Robb, E.S. Replogle, R. Gomperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzalez, R.L. Martin, D.J. Fox, D.J. DeFrees, J. Baker, J.J.P. Stewart, J.A. Pople, *Gaussian 92*, Gaussian, Pittsburgh, 1992.
7. J.A. Pople, M. Head-Gordon, D.J. Fox, K. Raghavachari and L.A. Curtiss, *J. Chem. Phys.*, 90 (1989) 5622.
8. L.A. Curtiss, C. Jones, G.W. Trucks, K. Raghavachari and J.A. Pople, *J. Chem. Phys.*, 93 (1990) 2537.
9. L.A. Curtiss, K. Raghavachari, G.W. Trucks and J.A. Pople, *J. Chem. Phys.* 94 (1991) 7221.
10. H. B. Schlegel, *J. Chem. Phys.*, 84 (1986) 4530.
11. L. Ding and P. Marshall, *J. Chem. Phys.*, 98 (1993) 8545.
12. K. J. Laidler, *Theories of Chemical Reaction Rates*, McGraw-Hill, New York, 1969, Chapters 4 and 5.
13. G. N. Lewis and M. Randall, *Thermodynamics*, 2nd ed., revised by K. S. Pitzer and L. Brewer, McGraw-Hill, New York, 1961, Chapter 27.
14. M.F.R. Mulcahy, *Gas Kinetics* (Nelson, London, 1973).

15. Y. Apeloig, in S. Patai and Z. Rappoport (Eds.), *The Chemistry of Organosilicon Compounds*, Wiley, New York, 1989, Chapter 2.
16. M.S. Gordon, J.S. Francisco and H.B. Schlegel, *Adv. Silicon Chem.*, 2 (1993) 137.
17. P. Ho, M.E. Coltrin, J.S. Binkley and C.F. Melius, *J. Phys. Chem.*, 89 (1985) 4647.
18. L.A. Curtiss and J.A. Pople, *Chem. Phys. Lett.*, 144 (1988) 38.
19. R.S. Grev and H.F. Schaefer III, *J. Chem. Phys.*, 97 (1992) 8389.
20. P. Maître and G. Ohanessian, *Chem. Phys.*, 168 (1992) 237.
21. J.A. Seetula, Y. Feng, D. Gutman, P.W. Seakins and M.J. Pilling, *J. Phys. Chem.*, 95 (1991) 1658.
22. A. Greenberg and J.F. Liebman, *Strained Organic Molecules*, Academic, New York, 1978, Chapter 1.
23. L. Ding and P. Marshall, *J. Am. Chem. Soc.*, 114 (1992) 5754.
24. A. Goumri, W.-J. Yuan and P. Marshall, *J. Am. Chem. Soc.*, 115 (1993) 2539.
25. L. Ding and P. Marshall, *J. Chem. Soc. Faraday Trans.*, 89 (1993) 419.
26. M.D. Allendorf and C.F. Melius, *J. Phys. Chem.*, 96 (1992) 428.
27. A. Goumri, W.-J. Yuan, L. Ding and P. Marshall, *Chem. Phys. Lett.*, 204 (1993) 296.
28. P. Ho and C. F. Melius, *J. Phys. Chem.*, 94 (1990) 5120.
29. A. F. Sax and J. Kalcher, *J. Phys. Chem.*, 95 (1991) 1768.
30. L. A. Curtiss, K. Raghavachari, P. W. Deutsch and J. A. Pople, *J. Chem. Phys.*, 95 (1991) 2432.
31. M.B. Coolidge and W.T. Borden, *J. Am. Chem. Soc.*, 110 (1988) 2298.
32. J. E. Huheey, *Inorganic Chemistry*, 2nd Ed., Harper, New York, 1978, p. 145.
33. M.S. Gordon, D.R. Gano and J.A. Boatz, *J. Am. Chem. Soc.*, 105 (1983) 5771.
34. A. Tachibana, Y. Kurosaki, K. Yamaguchi and T. Yamabe, *J. Phys. Chem.*, 95 (1991) 6849.

35. N.L. Arthur, P. Potzinger, B. Reimann and H.P. Steenbergen, *J. Chem. Soc. Faraday Trans. II*, 85 (1989) 1447.
36. A. Goumri, W.-J. Yuan, L. Ding, Y. Shi and P. Marshall, *Chem. Phys.*, 177 (1993) 233.
37. K.D. Dobbs and D.J. Doren, *J. Am. Chem. Soc.*, 115 (1993) 3731.
38. L. Fabry, P. Potzinger, B. Reimann, A. Ritter and H.P. Steenbergen, *Organometallics*, 5 (1986) 1231.
39. O. Horie, R. Taege, B. Reimann, N. L. Arthur and P. Potzinger, *J. Phys. Chem.*, 95 (1991) 4393.
40. A. Misra, L. Ding, P. Marshall, Chr. Buchta, D.-V. Stucken, J.-T. Vollmer and H.Gg. Wagner, *J. Phys. Chem.*, to be published.
41. K. Sato, H. Yamada, S. Iwabuchi, T. Hirano and H. Koinuma, *J. Chem. Phys.*, 98 (1993) 2844.
42. R.K. Pearson, J.O. Cowles, G.L. Hermann, D.W. Gregg and J.R. Creighton, *IEEE J. Quantum Electron.*, 9 (1973) 879.
43. D.J. Smith, D.W. Setser, K.C. Kim and D.J. Bogan, *J. Phys. Chem.*, 81 (1977) 898.
44. A. Goumri, L. Ding and P. Marshall, unpublished work.
45. L. Ding and P. Marshall, *J. Phys. Chem.*, 96 (1992) 2197.
46. A. Fontijn and R. Zellner, in A. Fontijn and M.A.A. Clyne (Eds.), *Reactions of Small Transient Species*, Academic, London, 1983, Chapter 1.

TABLE 1: Enthalpies of the transition state and products relative to reactants at 0 K, E_0^\ddagger , and ΔH_0 , for $\text{H} + \text{SiH}_4 \rightarrow \text{SiH}_5^\ddagger \rightarrow \text{H}_2 + \text{SiH}_3$. Data taken from ref. 36.

Calculation	E_0^\ddagger , kJ mol ⁻¹	ΔH_0 , kJ mol ⁻¹
HF/6-31G*	66.6	-25.2
MP2/6-31G*	54.8	-34.4
MP4/6-31G*	46.0	-44.8
MP4/6-311G**	29.1	-50.7
G2	20.7	-54.7
P-G2	15.1	-55.5
Expt.	17.1 ± 3.0	-54.0 ± 2.5

TABLE 2: *Ab initio* TS energies and enthalpies of the TS (E_0^\ddagger) and products (ΔH_0) relative to reactants at 0 K for $X + \text{SiH}_4 \rightarrow \text{SiH}_4\text{X}^\ddagger \rightarrow \text{HX} + \text{SiH}_3$ ($X = \text{F}$ and Cl).

Quantity	HF/6-31G** ^a	MP2/6-31G** ^b	G2 ^b	Expt.
$\text{SiH}_4\text{F}^\ddagger$ TS energy (hartrees)	-390.56304	-390.80398	-391.05676	
E_0^\ddagger for $\text{F} + \text{SiH}_4$ (kJ mol ⁻¹)	61.3	4.6	-12.9	
ΔH_0 for $\text{HF} + \text{SiH}_3$ (kJ mol ⁻¹)	-51.4	-166.4	-188.1	-187.8
$\text{SiH}_4\text{Cl}^\ddagger$ TS energy (hartrees)	-750.64849	-750.87300	-751.10390	
E_0^\ddagger for $\text{Cl} + \text{SiH}_4$ (kJ mol ⁻¹)	54.4	5.3	-21.6	
ΔH_0 for $\text{HCl} + \text{SiH}_3$ (kJ mol ⁻¹)	10.4	-27.6	-47.3	-49.7

^aAt the HF/6-31G* geometry. The TS for $\text{F} + \text{SiH}_4$ has $r(\text{F-H}) = 1.26 \text{ \AA}$ and $r(\text{Si-H}) = 1.61 \text{ \AA}$. The TS for $\text{Cl} + \text{SiH}_4$ has $r(\text{Cl-H}) = 1.49 \text{ \AA}$ and $r(\text{Si-H}) = 1.79 \text{ \AA}$. E_0^\ddagger and ΔH_0 include corrections for zero-point vibrational energy.

^bAt the MP2/6-31G* geometry. The TS for $\text{F} + \text{SiH}_4$ has $r(\text{F-H}) = 1.66 \text{ \AA}$ and $r(\text{Si-H}) = 1.51 \text{ \AA}$. The TS for $\text{Cl} + \text{SiH}_4$ has $r(\text{Cl-H}) = 1.58 \text{ \AA}$ and $r(\text{Si-H}) = 1.66 \text{ \AA}$. E_0^\ddagger and ΔH_0 include corrections for zero-point vibrational energy.

FIGURE CAPTIONS

Fig. 1 Comparison of rate constants from *ab initio* theory (dashed line) and experiment (solid line) for $\text{H} + \text{SiH}_4$.

Fig. 2 Comparison of rate constants from *ab initio* theory (dashed lines) and experiment (solid lines) for $\text{O} + \text{SiH}_4$ and $\text{O} + (\text{CH}_3)_3\text{SiH}$.

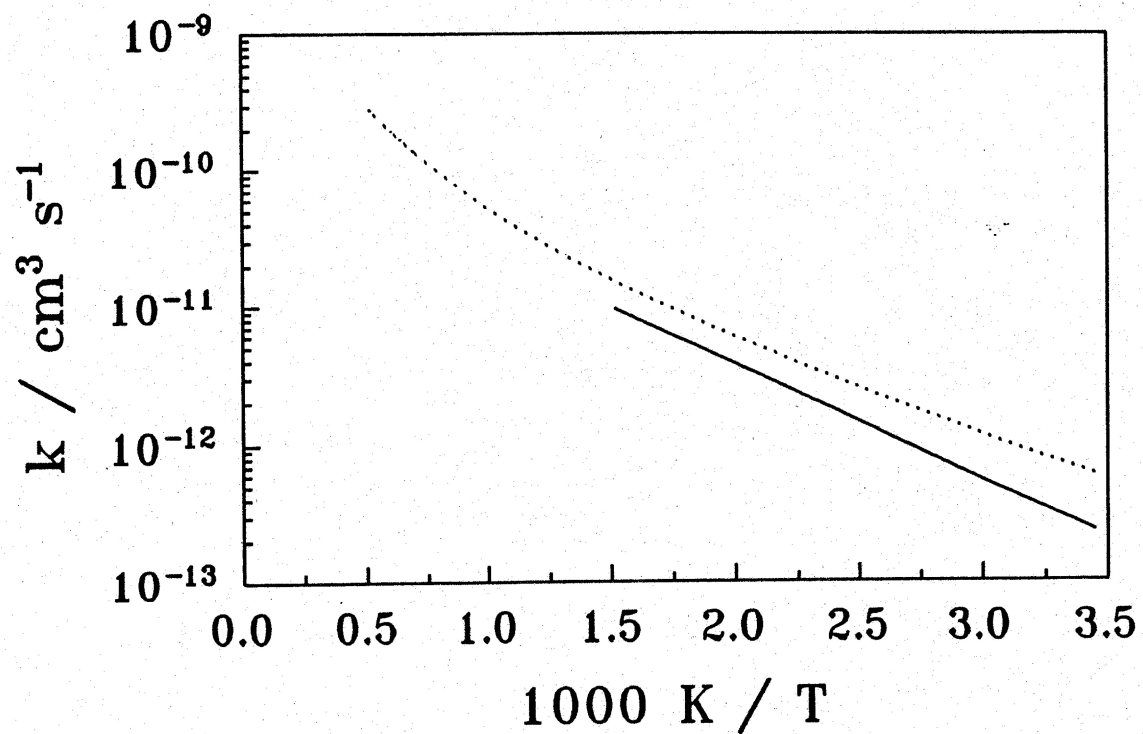


Fig. 1 Comparison of rate constants from *ab initio* theory (dashed line) and experiment (solid line) for $\text{H} + \text{SiH}_4$.

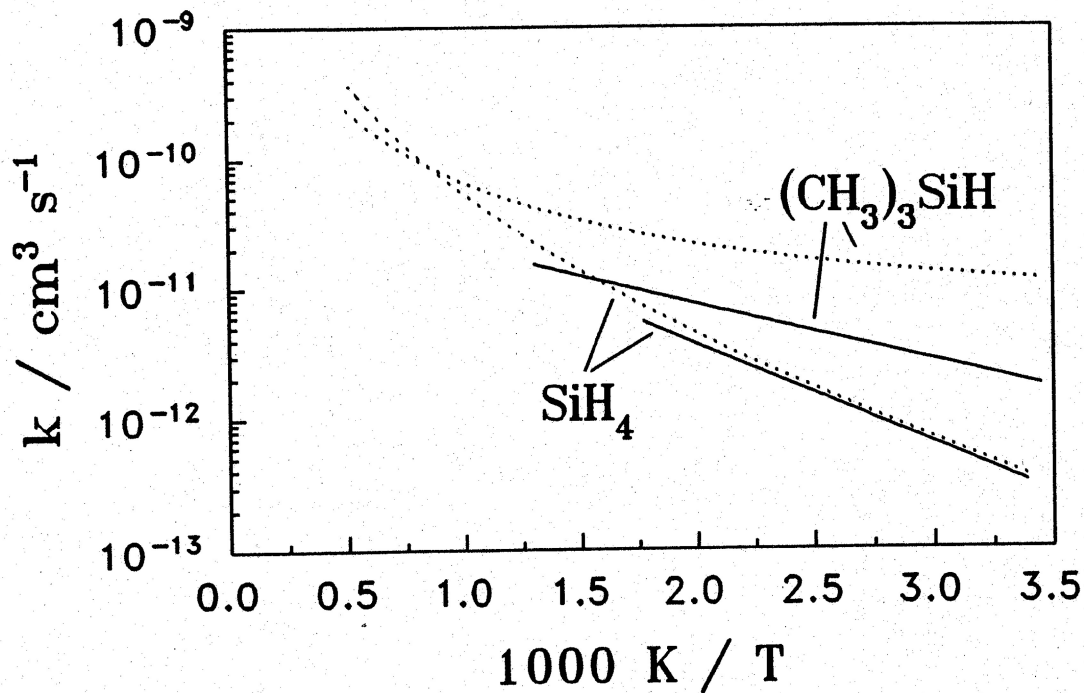


Fig. 2 Comparison of rate constants from *ab initio* theory (dashed lines) and experiment (solid lines) for $\text{O} + \text{SiH}_4$ and $\text{O} + (\text{CH}_3)_3\text{SiH}$.