J. Phys. Chem. **1988**, *92*, 4025–4027 **4025**

Temperature Dependence of the Reaction of SiH_2 with D_2

J. E. Baggott,* H. M. Frey, K. D. King,† P. D. Lightfoot,‡ R. Walsh, and I. M. Watts

Department of Chemistry, University of Reading, Whiteknights, P.O. Box 224, Reading RG6 2AD, U.K.
(Received: April 11, 1988)

A laser flash photolysis/laser absorption technique has been used to generate and monitor SiH_2 radicals in real time. We present preliminary results of a study of the rate of removal of SiH_2 radicals in the presence of D_2 in the temperature interval 268–330 K. The removal rate coefficient is found to be temperature independent in this range with a value (1.88 ± 0.17) $\times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. The implications of this result for the temperature dependence of the reaction of SiH_2 with H_2 are discussed.

1. Introduction

The reaction of silylene, SiH_2, with molecular hydrogen is one of the key reactions of silylene chemistry. The central role played by SiH_2 in the mechanism of the pyrolysis of silane[1-4] and in modern methods of vapor deposition of thin films of amorphous silicon[5] has prompted much recent experimental and theoretical interest in the stability and chemical reactivity of this species.

A quantitative estimate of the rate coefficient for the reaction of SiH_2 with H_2 was first attempted by John and Purnell,[6] based on competitive kinetic studies combined with other rate coefficient estimates derived from studies of silane and disilane pyrolyses. They proposed an activation energy of 5.5 ± 1.0 kcal mol^{-1} (and a related value for $\Delta H_f°(SiH_2,298\ K)$ of 58 ± 1 kcal mol^{-1}). A number of subsequent ab initio theoretical calculations of the barrier to SiH_2 insertion into H_2 were in reasonable agreement with this activation energy.[7-10] However, other theoretical studies[11,12] aimed more specifically at calculations of $\Delta H_f°(SiH_2,298K)$, gave values between 63 and 68 kcal mol^{-1}, well in excess of John and Purnell's estimate.

The situation has been considerably clarified by the application of time-resolved techniques, which enable direct monitoring of SiH_2 and the measurement of absolute rate coefficients for its removal.[13,14] In particular, Jasinski[14] reported a room temperature rate coefficient for the removal of SiH_2 by D_2 which is 4 orders of magnitude larger than John and Purnell's earlier estimate for the rate coefficient for the reaction of SiH_2 with H_2. This was interpreted as evidence for a small barrier to insertion, and offered support for the higher values for $\Delta H_f°(SiH_2,298\ K)$. Reanalysis[15,16] of the earlier data on disilane pyrolysis and its subsequent experimental reinvestigation[17] have come down in favor of the higher value of $\Delta H_f°(SiH_2,298\ K)$.[18-22]

In his note, Jasinski[14] argued that the measured room temperature rate coefficient for SiH_2 removal in the presence of D_2, combined with an estimate for the value of the Arrhenius preexponential factor for the insertion of SiH_2 into H_2, suggested an activation energy for the insertion reaction of ≤ 1 kcal mol^{-1}. The $SiH_2 + D_2$ removal rate coefficient was taken as an estimate of the $SiH_2 + H_2$ reaction rate coefficient at the high-pressure limit. A more recent ab initio study of the $SiH_2 + H_2$ potential energy surface by Gordon et al.[23] gives an activation energy of 1.7 kcal mol^{-1}, in tolerable agreement with Jasinski's estimate. In addition, the theoretical studies indicate the presence of a long-range weakly bound $SiH_2 \cdots H_2$ complex. As part of a research program designed to characterize the reactivities of a number of silylenes, we have studied the temperature dependence of the $SiH_2 + D_2$ removal process and report here the preliminary results over the temperature interval 268–330 K. We also describe related transition-state theory calculations of the effects of isotopic substitution on the rate coefficients of the $SiH_2 + H_2/D_2$ insertion reactions.

2. Experimental Method and Results

Transient concentrations of SiH_2 radicals were produced by 193-nm flash photolysis of phenylsilane using an Oxford Lasers KX2 ArF exciplex laser. We have previously verified using end product analysis[24] that both SiH_2 and PhSiH are produced by laser photolysis at this wavelength. The SiH_2 radical concentrations were monitored in real time by using a multipass absorption arrangement similar to the one we have described in earlier publications,[25] and our methods are very similar to those employed by Jasinski.[14] The output of a Coherent Innova 90-5 Ar^+ laser-pumped 699-21 single-mode dye laser operating with rhodamine 6G was multipassed through a purpose-built variable-temperature cell at right angles to the photolysis radiation. A total of 36 passes gave an optical path length for SiH_2 radical detection of 1.8 m. The monitoring laser was tuned to the maximum of the ${}^{r}Q_{0,J}(5)$ rotational line of the $\tilde{A}^1B_1(0,2,0) \leftarrow \tilde{X}^1A_1(0,0,0)$

---

† Permanent address: Department of Chemical Engineering, The University of Adelaide, Box 498, G.P.O. Adelaide, South Australia 5001.

‡ Present address: Laboratoire de Chimie Physique A, Université de Bordeaux I, 33405 Talence Cedex, France.

(1) Purnell, J. H.; Walsh, R. *Proc. R. Soc. London* **1966**, *A293*, 543.

(2) Newman, C. G.; O'Neal, H. E.; Ring, M. A.; Leska, F.; Shipley, N. *Int. J. Chem. Kinet.* **1979**, *11*, 1167.

(3) Neudorfl, P.; Jodhan, A.; Strausz, O. P. *J. Phys. Chem.* **1980**, *84*, 338.

(4) Jasinski, J. M.; Estes, R. D. *Chem. Phys. Lett.* **1985**, *117*, 495.

(5) Jasinski, J. M.; Meyerson, B. S.; Scott, B. A. *Annu. Rev. Phys. Chem.* **1987**, *38*, 109.

(6) John, P.; Purnell, J. H. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 1455.

(7) Gordon, M. S. *J. Chem. Soc., Chem. Commun.* **1981**, 890.

(8) Grev, R. S.; Schaeffer, H. F., III *J. Chem. Soc., Chem. Commun.* **1983**, *14*, 785.

(9) Gordon, M. S.; Gano, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 5421.

(10) Sax, A.; Olbrich, G. *J. Am. Chem. Soc.* **1985**, *107*, 4868.

(11) Pople, J. A.; Luke, B. T.; Frisch, M. J.; Binkley, J. S. *J. Phys. Chem.* **1985**, *89*, 2198.

(12) Ho, P.; Coltrin, M. E.; Binkley, J. S.; Melius, C. F. *J. Phys. Chem.* **1985**, *89*, 4647.

(13) Inoue, G.; Suzuki, M. *Chem. Phys. Lett.* **1985**, *122*, 361.

(14) Jasinski, J. M. *J. Phys. Chem.* **1986**, *90*, 555.

(15) Frey, H. M.; Walsh, R.; Watts, I. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1189.

(16) Roenigk, K. F.; Jensen, K. F.; Carr, R. W. *J. Phys. Chem.* **1987**, *91*, 5726.

(17) Martin, J. G.; Ring, M. A.; O'Neal, H. E. *Int. J. Chem. Kinet.* **1987**, *19*, 715.

(18) There remains some spread in experimental values within the range 64–69 kcal mol^{-1} with figures based on the chemistry of neutrals at the lower end (ref 15–17), and those derived from ion chemistry at the higher end (ref 19–21). A very recent theoretical calculation (ref 22) gives 64.5 ± 0.9 kcal mol^{-1}.

(19) Shin, S. K.; Beauchamp, J. L. *J. Phys. Chem.* **1986**, *90*, 1507.

(20) Berkowitz, J.; Greene, J. P.; Cho, H.; Ruscic, B. *J. Chem. Phys.* **1987**, *86*, 1235.

(21) Boo, B. H.; Armentrout, P. B. *J. Am. Chem. Soc.* **1987**, *109*, 3549.

(22) Curtis, L. A.; Pople, J. A. *Chem. Phys. Lett.* **1988**, *144*, 38.

(23) Gordon, M. S.; Gano, D. R.; Binkley, J. S.; Frisch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 2191.

(24) Baggott, J. E.; Frey, H. M.; Lightfoot, P. D.; Walsh, R. *Chem. Phys. Lett.* **1986**, *125*, 22.

(25) Baggott, J. E.; Blitz, M. A.; Frey, H. M.; Lightfoot, P. D.; Walsh, R. *Chem. Phys. Lett.* **1987**, *135*, 39. Baggott, J. E.; Frey, H. M.; Lightfoot, P. D.; Walsh, R. *J. Phys. Chem.* **1987**, *91*, 3386.

0022-3654/88/2092-4025$01.50/0

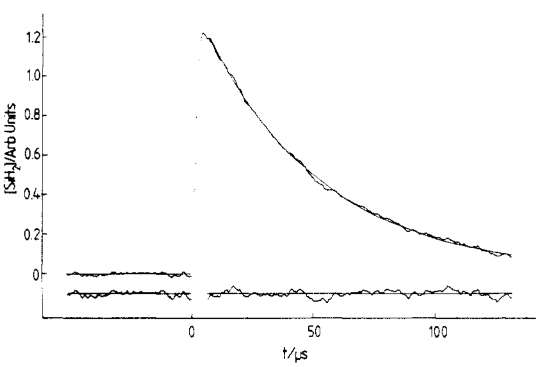

Figure 1. Concentration–time profile obtained from the photolysis of 1.5 mTorr phenylsilane in 5.0 Torr of SF_6 at 296 K. The decay represents an average of 32 photolysis shots. A single-exponential fit to the data is shown, with $k_{obsd} = 2.03 \times 10^4$ s^{-1}.

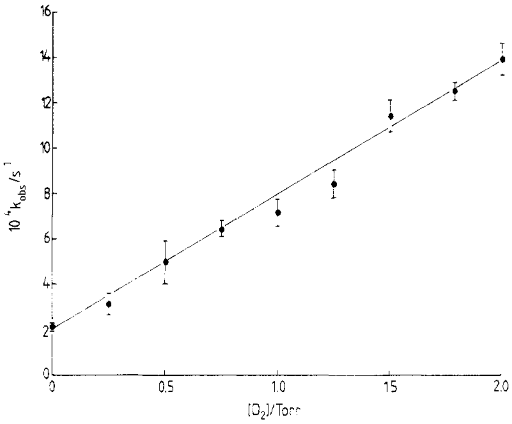

Figure 2. Plot of k_{obsd} for SiH_2 removal vs D_2 pressure at 299 K. The total pressure was 5.0 Torr, using SF_6 as diluent. Least-squares analysis gives $k_{bi} = (1.81 \pm 0.14) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Two standard deviations are quoted.

transition at 17 259.52 cm^{-1}.[26] The wavelength was set by reference to a coincident transition in the visible spectrum of I_2 vapor and was checked at frequent intervals during the experiments. In a typical experiment, we used 1.5 mTorr partial pressure of $PhSiH_3$, pressures of D_2 in the range 0–2 Torr, total pressures of 5.0 Torr (remainder SF_6) and ArF laser pulse energies of 70–80 mJ. Identical results were obtained from experiments performed with both static and slowly flowing gas samples. The SiH_2 concentration–time curves were captured by a transient recorder interfaced to a BBC microcomputer. The latter was used to signal average the decays from between 16 and 64 photolysis laser shots. In Figure 1 we show a typical example of an averaged SiH_2 decay trace.

The averaged decay traces were transferred to the University mainframe computer and analyzed by using a numerical integration/nonlinear least-squares package written by Lightfoot. Single-exponential decays were obtained in all cases. These analyses returned the values of the observed pseudo-first-order rate coefficients, k_{obsd}, for the removal of SiH_2 in the presence of a given partial pressure of D_2. A plot of k_{obsd} vs D_2 partial pressure at $T = 299$ K is shown in Figure 2. The error bars attached to each determination of k_{obsd} represent external standard deviations obtained by repeating the measurements under identical conditions. The data of Figure 2 were analyzed by linear least-squares fitting to give a value for the bimolecular rate coefficient, k_{bi}, of $(1.81 \pm 0.14) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for SiH_2 removal by D_2 at 299 K, where the quoted error represents two standard deviations.

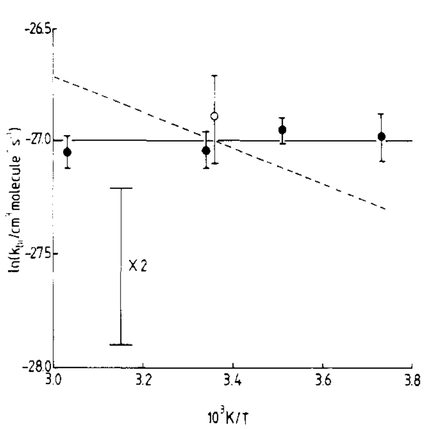

Figure 3. Arrhenius plot for k_{bi} over the temperature range 268–330 K: (●) present work; (○) Jasinski and Chu, ref 26. In both cases the error bars represent two standard deviations. Also indicated (dashed line) is the expected temperature variation for a reaction with an A factor of 2 × 10^{-11} cm^3 molecule^{-1} s^{-1} and an activation energy of 1.57 kcal mol^{-1}, and the expected change in ln (k_{bi}/cm^3 molecule^{-1} s^{-1}) for a factor of 2 change in k_{bi}.

Using a variable-temperature cell, we repeated the measurements of k_{obsd} and hence k_{bi} over the temperature interval 268–330 K. Cooling was achieved by circulating cold nitrogen gas through the body of the cell. The temperature was measured by using a thermocouple connected to a digital thermometer and was stable to ±3 K. Crude calculations indicate an instantaneous temperature rise of ca. 5 K resulting from the absorption of photolysis radiation in a single laser pulse under our experimental conditions (5 Torr total pressure), which increases further the uncertainty in the absolute temperature. For measurements above ambient temperatures, the cell was heated electrically. After correcting for the variation of gas density with pressure, we found that the bimolecular rate coefficient *remained effectively constant over the temperature range of the experiments.* The data are shown in the form of an Arrhenius plot in Figure 3, where the temperature variation is compared with that expected of a reaction with a preexponential factor of 2 × 10^{-11} cm^3 molecule^{-1} s^{-1} and an activation energy of 1.57 kcal mol^{-1} (dashed line). Also shown is the difference between the values of ln k_{bi} for a factor of 2 change in k_{bi}. Since the data show virtually no variation with temperature, and the temperature range is limited, we prefer to report an average value of $(1.88 \pm 0.17) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for k_{bi} for the range 268–330 K. The largest positive activation energy which can be accommodated within the 2σ errors of the measured rate coefficients at 268 and 330 K is ca. 0.3 kcal mol^{-1}.

Following the reasoning outlined by Jasinski[14] we may assume that the observed bimolecular rate coefficient for SiH_2 removal by D_2 closely approximates the high-pressure limiting rate coefficient for SiH_2 insertion into D_2:

$$SiH_2 + D_2 \rightarrow [SiH_2D_2]^\dagger \qquad (1)$$

First, unlike CH_2, the SiH_2 ground state is a singlet state and so problems of collision-induced intersystem crossing do not arise in the evaluation of kinetic data obtained for SiH_2 removal. Second, although redissociation of the vibrationally excited adduct formed in reaction 1, $[SiH_2D_2]^\dagger$, is likely to occur with high probability under our conditions of total pressure (collisional stabilization is estimated to be fairly inefficient), the fractional probability for regeneration of SiH_2 is only one-sixth of that for the generation of all isotopic species (i.e., including SiHD and SiD_2) and is indicated to be even lower from a consideration of kinetic isotope effects.[27] Since we observe only SiH_2 removal, and the removal is dominated by the initial insertion process, k_{bi} should be a good approximation to k_1. To a certain extent, this was confirmed by the fact that at the highest temperature of the present study (330 K) k_{bi} was observed to exhibit no significant pressure dependence on doubling the pressure from 5 to 10 Torr.

---

(26) Jasinski, J. M.; Chu, J. O. In *Silicon Chemistry*; Corey, J. Y.; Corey, E. R.; Gaspar, P. P., Eds.; Ellis Horwood: Chichester, U.K., 1988.

(27) Baggott, J. E.; Frey, H. M.; Lightfoot, P. D.; Walsh, R., unpublished results.

3. Discussion

The rate data obtained in this work are consistent, within experimental error, with the room-temperature (298 K) values reported by Jasinski[14] [$(2.6 \pm 0.7) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}] and by Jasinski and Chu[26] [$(2.1 \pm 0.4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}]. Although the Arrhenius parameters for reaction 1 have not previously been reported, the effectively zero activation energy *implied* by the results of the present study supports Jasinski's earlier suggestion[14] of a value ≤ 1 kcal mol^{-1}. The Arrhenius A factor implied by our measurements, 1.88×10^{-12} cm^3 molecule^{-1} s^{-1}, may be compared with an estimated value for the high-pressure limiting rate coefficient, k_2^∞, for the insertion of SiH_2 into H_2:

$$SiH_2 + H_2 \rightarrow SiH_4 \qquad (2)$$

Jasinski and Chu[26,28] have recently obtained $k_2^\infty = 3.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} from experimental studies of the pressure dependence of k_2 in the range 1–100 Torr, combined with RRKM theoretical modelling. The value for k_2^∞ may be identified with A_2^∞ on the reasonable presumption that reaction 2, like reaction 1, has a zero activation energy.

Some further information concerning A_2^∞ comes from a consideration of the reverse reaction, viz., SiH_4 dissociation. Experimental studies[1,2,29] have shown that reaction −2 is also in the unimolecular falloff regime under the conditions of its investigation (38–4000 Torr, 650–1200 K). RRKM modelling of reaction −2 suggests[2,16,29] that its high-pressure limiting A factor, A_{-2}^∞, lies in the range $10^{15.2}$–$10^{16.0}$ s^{-1}. By use of published standard entropies for H_2,[30] SiH_2,[31] and SiH_4,[30] and the standard relationship linking A_2 and A_{-2} through $\Delta S_{2,-2}^\circ$,[32] we estimate that A_2^∞ should lie in the range 2×10^{-11} to 1.2×10^{-10} cm^3 molecule^{-1} s^{-1}. Thus, the value for A_2^∞ is apparently at least a factor of 6 higher than that which may be inferred from Jasinski and Chu's data.[26,28] At this stage it is important to point out that this comparison depends on the assumption that the Arrhenius parameters for SiH_4 pyrolysis apply at temperatures close to ambient. Unfortunately, this is difficult to verify by experiment and the temperature extrapolation via RRKM theory depends on the choice of transition-state model.

In light of the above discrepancy, we were prompted to investigate more closely the comparison between reactions 1 and 2 by means of a calculation of the expected kinetic isotope effect. For the reasons already given, the measured values for k_{bi} are thought to represent a good approximation to the high-pressure limiting rate coefficient for reaction 1. It may readily be shown, using transition-state theory, that

$$\frac{k_2^\infty}{k_1^\infty} = \frac{q_{SiH_4}^\ddagger}{q_{SiH_2D_2}^\ddagger} \frac{q_{D_2}}{q_{H_2}} \exp[-(\Delta\epsilon_{H_2} - \Delta\epsilon_{D_2})/kT] \qquad (3)$$

where q_X is the total partition function for species X, the ‡ refers to the transition state, and $\Delta\epsilon_{X_2}$ is the activation barrier for the reaction $SiH_2 + X_2$. The experimental finding here of an essentially zero barrier for reaction 1 suggests that the only significant contributions to the term $\Delta\epsilon_{H_2} - \Delta\epsilon_{D_2}$ will arise from differences in the zero-point vibrational energies.

The terms in eq 3 were evaluated at 298 K. Only translational and rotational motions contributed to the partition function ratio q_{D_2}/q_{H_2} which was found to have a value of 5.66. For the other terms it was necessary to assume a structure for the transition state. We adopted the geometry and vibration wavenumbers of Roenigk et al.[16] for $SiH_4^\ddagger$. For $SiH_2D_2^\ddagger$ the same geometry was employed, and the vibrational wavenumbers were obtained by modification of the published values for SiH_2D_2[33] by using the same procedure as Roenigk et al.[16] The ratio $q_{SiH_4}^\ddagger/q_{SiH_2D_2}^\ddagger$ was evaluated to be 0.489, the most significant contribution being that of rotation, arising from differences in the moments of inertia of $SiH_4^\ddagger$ and $SiH_2D_2^\ddagger$. The term $\Delta\epsilon_{H_2} - \Delta\epsilon_{D_2}$ was found to have a value of −271 cm^{-1} arising, in significant part, from the difference between the zero-point energies of H_2 and D_2. The combination of all these terms in eq 3 resulted in the value $k_2^\infty/k_1^\infty = 10.24$.

This is a surprisingly high value for an isotopic ratio and yet appears unlikely to be seriously in error. Even though the structure of the transition state obtained from theoretical calculations[23] differs somewhat from that employed here, changes in the magnitudes of the rate coefficients arising from its use would largely cancel in the isotopic ratio. Use of the calculated value for k_2^∞/k_1^∞ in combination with our measured value of k_1 at 298 K suggests a value of ca. 2.0×10^{-11} cm^3 molecule^{-1} s^{-1} for k_2^∞, considerably larger than the value estimated by Jasinski and Chu[26,28] but more consistent with our estimate from the available data on reaction −2. While our own measurements on the pressure dependence of reaction 2 are in good agreement with those of Jasinski and Chu,[26,28] our unimolecular (RRKM) falloff calculations indicate a somewhat higher limiting high-pressure rate coefficient.[27]

We are currently extending the temperature range of our measurements of k_{bi} and hope to approach more closely the temperatures relevant to the SiH_4 pyrolysis studies.

Acknowledgment. We are grateful to Dr. J. M. Jasinski for supplying prepublication copies of manuscripts and for many useful discussions on this and related topics. This work was supported by the S.E.R.C. via the award of research grants (to J.E.B., H.M.F., and R.W.) and a postdoctoral research assistantship (to P.D.L.). K.D.K. thanks the British Council for the award of an A.L.I.S. travel grant.

---

(28) Jasinski, J. M.; Chu, J. O. *J. Chem. Phys.* **1988**, *88*, 1678.

(29) Erwin, J. W.; Ring, M. A.; O'Neal, H. E. *Int. J. Chem. Kinet.* **1985**, *17*, 1067.

(30) *JANAF Thermochemical Tables*, 2nd ed.; U.S. National Bureau of Standards; Washington DC, 1971; NSRDS-NBS-37, and supplements. 1978 supplement, *J. Phys. Chem. Ref. Data*, **1978**, *7*, 793; 1982 supplement, *J. Phys. Chem. Ref. Data*, **1982**, *11*, 695.

(31) Fredin, L.; Mange, R. H.; Kafafi, Z. H.; Margrave, J. L. *J. Chem. Phys.* **1985**, *82*, 3542.

(32) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976.

(33) Meal, J. H.; Wilson, M. K. *J. Chem. Phys.* **1956**, *24*, 385.