ABSOLUTE RATE CONSTANTS FOR SILYLENE REACTIONS WITH DIATOMIC MOLECULES

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Absolute rate constants have been determined for the reaction of SiH_2 with the diatomics HCl, Cl_2, NO and O_2. Upper limits are reported for rate constants for the reaction of SiH_2 with N_2 and CO. Comparisons are made between the reactivity of silylene, singlet methylene and halogenated silylenes.

1. Introduction

Absolute rate constants for the gas phase reactions of silylene, SiH_2, are crucial to understanding the chemistry of silicon hydride and organosilicon compounds. Silylene is a key reactive intermediate in the decomposition chemistry of silicon hydrides and organosilicon molecules [1–3], yet, until very recently, no absolute rate data were available for its reactions. In the past two years, several absolute rate studies of silylene reactions have been performed [4–8]. The results demonstrate that silylene is much more reactive with hydrogen, silanes, olefins, dienes and acetylenes than was previously thought.

In this paper we report rate constants for the reaction of silylene with a series of diatomic molecules, HCl, Cl_2, NO, O_2, CO and N_2. The results provide information which is relevant to mechanistic studies of chemical vapor deposition (CVD) [9] and relevant to radical scavenging in previous mechanistic studies of silicon CVD [10]. In addition, the data can be compared with studies of the reactivity of singlet methylene to provide information on periodic trends, and can be compared with the results of increasingly accurate ab initio calculations on silylene reactivity. Rate constants have been determined at 5 Torr total pressure and ambient temperature by directly monitoring silylene removal rates using laser resonance absorption flash kinetic spectroscopy (LRAFKS).

2. Experimental

The experimental apparatus, general experimental procedures, and data acquisition and analysis techniques have been described in detail [5,6,8]. Briefly, transient concentrations of silylene are created by pulsed excimer laser photolysis of phenylsilane at 193 nm or iodosilane at 248 nm. Bimolecular removal rate constants for silylene are determined from the decay of the silylene concentration under pseudo-first-order conditions at constant total pressure in helium buffer gas. The silylene concentration is measured directly in real time by high-resolution transient absorption spectroscopy using a single-frequency ring-dye laser tuned to single rotational lines of the $\tilde{A}\,{}^1B_1\,(0,2,0) \leftarrow \tilde{X}\,{}^1A_1\,(0,0,0)$ transition of silylene [11]. The experiment is performed under slowly flowing conditions in a 1 m long gas cell equipped with a capacitance manometer, electronic mass flow controllers and an automatic throttle valve. This configuration allows kinetic data to be obtained under conditions of constant total gas flow and constant total pressure.

Reactant gases used were HCl (Matheson, 99.995%), Cl_2 (Matheson, 99.99%), O_2 (MG Scientific, 99.95% and 99.999%), NO (Liquid Carbonic, 99%), CO (Matheson, 99.5%) and N_2 (Liquid Carbonic, 99.999%). Nitric oxide was passed through a trap held at −130°C by a pentane slush to remove the ≈1% SO_2 impurity in the sample. Analysis of a sample of NO treated in this way revealed no de-

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tectable (< 100 ppm) impurities by gas chromatography/mass spectrometry. All other gases were used as received. Iodosilane was prepared by HI cleavage of phenylsilane or chlorophenylsilane [12].

In experiments with HCl, Cl_2, O_2, CO and N_2, photolysis of phenylsilane at 193 nm was used to generate silylene. Carbon monoxide and nitrogen are transparent at this wavelength. We estimate that under the experimental conditions about 0.1% of the HCl, Cl_2 and O_2 were excited by the excimer laser pulse. Some experiments with O_2 and all experiments with NO were performed with 248 nm photolysis of iodosilane as the silylene source to check for artifacts in the O_2 reaction and to avoid possible complications due to NO photochemistry at 193 nm. Both O_2 and NO are transparent at 248 nm.

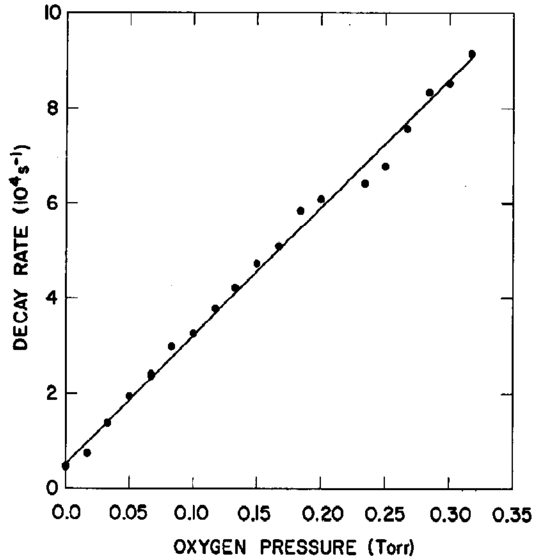

Fig. 1. Silylene decay rate as a function of oxygen partial pressure at 5 Torr total pressure. The line is a least-squares fit to the data.

3. Results and discussion

Bimolecular rate constants were determined from least-squares fits to pseudo-first-order rate plots of silylene removal rate versus reactant gas pressure. A typical plot is shown in fig. 1 for reaction with oxygen. Pseudo-first-order decay rates were obtained from single-exponential fits to the decay of the silylene transient absorption signal. Reactant partial pressures were calculated from the total pressure, total flow and reactant gas flow rates. Absolute rate constants for silylene removal by HCl, Cl_2, NO, O_2, N_2 and CO are presented in table 1. The rate constants for silylene removal by N_2 and CO are upper limits only, since these reactions are too slow to be accurately studied with our present technique at room temperature. These limits are determined by impurities in the gas handling system and the ability to maintain a sufficiently constant partial pressure of silylene precursor. The error bars are estimated from uncertainty in partial pressures of the reactant gases and the reproducibility of replicate rate constant determinations and are in the range ±10–20%. The scatter in pseudo-first-order rate plots was significantly less than this (typically ±2–4%, one standard deviation). For comparison, the rate constant for removal of silylene by hydrogen at 5 Torr is also shown in table 1, as are available data [13] for reactions of singlet methylene with many of the diatomics. Absolute rate data for some other silylenes, such as SiF_2,

Table 1
Absolute rate constants for the reaction of $SiH_2\ \tilde{X}\ ^1A_1$ and $CH_2\tilde{a}\ ^1A_1$ with diatomics

Reactant	$k(SiH_2)$ [a] (cm^3 $molecule^{-1}$ s^{-1})	Ref.	$k(CH_2)$ [b] (cm^3 $molecule^{-1}$ s^{-1})	Ref.
H_2	$(4.5\pm0.9)\times10^{-13}$	[8]	$(1.05\pm0.05)\times10^{-10}$	[13]
HCl	$(6.8\pm1.0)\times10^{-12}$	this work	–	–
Cl_2	$(1.4\pm0.2)\times10^{-10}$	this work	–	–
NO	$(1.7\pm0.2)\times10^{-11}$	this work	$(1.60\pm0.15)\times10^{-10}$	[13]
O_2	$(7.7\pm1.0)\times10^{-12}$	this work	$(7.4\pm0.5)\times10^{-11}$	[13]
CO	$<10^{-13}$	this work	$(4.9\pm0.4)\times10^{-11}$	[13]
N_2	$<10^{-13}$	this work	$(1.1\pm0.1)\times10^{-11}$	[13]

[a] Silylene rate constants at 5 Torr total pressure in helium buffer gas at ambient temperature.

[b] Methylene rate constants at 4 or 6 Torr total pressure in helium buffer gas at ambient temperature.

$SiCl_2$ and SiHCl, reacting with some of the diatomics have also recently become available and are discussed below. A full comparison among silylenes is not yet possible, however, because time-resolved kinetic studies of the reactions of other silylenes with most of the diatomics listed in table 1 remain to be carried out.

In all cases for which data are available, singlet methylene removal is 1–2 orders of magnitude faster than silylene removal. A direct comparison of singlet methylene data with silylene data must be made carefully, however. Although both species are expected to react with this series of diatomics by initial insertion into single bonds or addition to multiple bonds, two factors complicate rate data comparisons. The singlet methylene removal rates include a contribution from electronic quenching, which is not present in the silylene data, and the silylene reactions may have significant contributions from three-body stabilization effects. Direct electronic quenching contributions to the methylene data are probably small compared to reactive removal rates [13]. Three-body effects on the silylene rate constants are important in the case of reaction with hydrogen [8], but are probably less important for reaction with other diatomics. Such effects may result in the silylene reaction rate constants for reaction with HCl, Cl_2, O_2 and NO reported in table 1 being ≈ 2–5 times smaller than the high-pressure limiting bimolecular rate constants. A further discussion of three-body effects is presented below. Nonetheless, it is qualitatively clear that methylene is significantly more reactive than silylene, and this trend is frequently seen in ab initio calculations which compare potential-energy surfaces for reactions of the two species [14–16].

3.1. HCl

The reaction of SiH_2 with HCl is expected to proceed by insertion to form a highly vibrationally excited SiH_3Cl molecule. This molecule can be collisionally stabilized, re-eliminate HCl, or eliminate H_2. From the available thermochemical information [17,18] we calculate that SiH_3Cl formed by addition of silylene to HCl is chemically activated by at least 77 kcal/mol. Elimination of hydrogen from SiH_3Cl is endothermic by only 51 kcal/mol. However, the insertion of SiHCl into H_2 is unobservably slow at room temperature [19] ($k<3\times10^{-16}$ cm^3 molecule^{-1} s^{-1}), suggesting that there is a significant activation barrier. Without accurate pyrolysis data for SiH_3Cl, it is difficult to quantitatively evaluate the relative importance of collisional stabilization of SiH_3Cl^* and elimination of H_2. We have examined the pressure dependence of the removal rate constant for silylene by HCl, and find that it is weakly pressure dependent over the range 1–10 Torr:

$$k_{1\,\mathrm{Torr}}=(4.3\pm0.6)\times10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\,,$$

$$k_{9.5\,\mathrm{Torr}}=(7.5\pm1.0)\times10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\,.$$

This observation suggests that collisional stabilization is at least competitive with hydrogen elimination under our experimental conditions. If hydrogen elimination were much faster than collisional stabilization, the reaction would exhibit bimolecular kinetics at all pressures and the rate constant would be independent of total pressure.

Moore et al. [20] have measured relative rates for the reaction of silylene generated by infrared multiphoton dissociation (IRMPD) with HCl and silane, and have observed formation of SiH_3Cl, SiH_2Cl_2 and $SiHCl_3$ as stable products. They find that the activation energy for reaction of silylene with HCl is less than or equal to that for reaction with silane. While we cannot accurately evaluate activation energies from our present data, we find that at room temperature and 5 Torr total pressure in helium buffer gas silylene is 20 times more reactive with silane [8] than with HCl. This ratio is unlikely to change by more than a factor of two in the high-pressure bimolecular limit. An ab initio study of the reaction of SiH_2 with HCl finds a potential barrier of ≈ 6 kcal/mol with respect to the isolated reactants [14]. In the absence of large zero-point energy corrections and assuming a reasonable A factor, a potential barrier of this magnitude would render the reaction unobservably slow under our conditions.

3.2. Cl_2

Silylene reacts rapidly with molecular chlorine. The expected product in this case is highly vibrationally excited dichlorosilane. This molecule has available to it two lower-energy decomposition pathways, elimination of HCl and elimination of H_2. Although the pressure dependence of the rate constant was not examined in this case, it is likely to be very weak or not observable. This is because the $SiH_2Cl_2^*$ produced by insertion of silylene into chlorine has at least 100 kcal/mol of excess internal energy with respect to dissociation to $SiCl_2+H_2$.

The reactivity of silylene with H_2, HCl and Cl_2 shows a trend of increasing reactivity with increased electron density and decreased bond strength of the diatomic. This appears to be consistent with the idea that silylene insertion reactions proceed by initial electrophilic attack followed by nucleophilic rearrangement [14,15]. The absolute rate constant for the reaction of SiF_2 with chlorine has been directly determined [21] and is significantly slower than the reaction of SiH_2, with

$$k=(5.1\pm0.6)\times10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ .$$

3.3. NO

Information on the reaction of silylene with nitric oxide is important, since NO has been used as a silyl radical scavenger in a number of mechanistic studies of silicon hydride chemistry [10,22]. We find that SiH_2 reacts rapidly with NO. Therefore, this type of scavenging cannot necessarily be used to distinguish processes proceeding through SiH_2 intermediates from those proceeding through SiH_3, as has been claimed [10]. The reaction is also interesting because the mechanism and reaction products are unknown. An adduct with the chemical formula SiH_2NO and unspecified molecular structure is possible, although no data exist which provide any information on the expected stability or structure of this species. However, production of SiO and NH_2 is ≈63 kcal/mol exothermic, and is therefore possible, at least thermodynamically. The existence of this product channel and its exothermicity may explain the IR laser-induced "explosive" decomposition of SiH_4/NO mixtures which have been observed under some conditions [22,23]. A study of the pressure dependence of the rate constant for the reaction shows that it is again weakly pressure dependent:

$$k_{1\ \text{Torr}}=(1.5\pm0.2)\times10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ ,$$

$$k_{9.5\ \text{Torr}}=(2.1\pm0.2)\times10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ .$$

This suggests that an adduct which can be collisionally stabilized is formed, but does not exclude competitive decomposition of this adduct to other products or the existence of product channels which lead directly to other products. Dohmaru and Lampe have studied the reaction by IRMPD and conclude that NO reacts ≈2 times faster with silylene than does silane [22]. Our results show that silylene is ≈10 times more reactive with silane [8] than with NO. For comparison with other silylenes, Strauz et al. [24] have determined an absolute rate constant of 3.3×10^{-12} cm^3 molecule^{-1} s^{-1} for the reaction of $SiCl_2$ with NO.

3.4. O_2

The reaction of silylene with oxygen is interesting because, again, an adduct of novel and unknown structure may be involved and again, there is an extremely exothermic product channel. The only known structure on the SiH_2O_2 potential surface is silanoic acid, which has been identified in low-temperature matrices [25]. Production of SiO and H_2O is ≈147 kcal/mol exothermic, and the reaction may produce chemiluminescence. Production of electronically excited SiO in the 193 nm photolysis of phenylsilane in the presence of oxygen has been suggested [4]. Our measured rate constant is weakly pressure dependent:

$$k_{1\ \text{Torr}}=(7.5\pm0.8)\times10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ ,$$

$$k_{9.5\ \text{Torr}}=(1.4\pm0.2)\times10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ ,$$

and reasonably rapid, suggesting that an adduct is involved and that there are no significant activation barriers present which might be associated with a spin-forbidden reaction. Our rate constant is ≈6 times faster than a value reported by Eley et al. [26] in a relative rate study. In an effort to reconcile this difference, we have performed several sets of experiments using different oxygen samples and using photolysis of phenylsilane at 193 nm and iodosilane at 248 nm to generate silylene. All of these experiments produce the same rate constant within the quoted error limits. Strauz and co-workers [27] report a rate constant of 5.6×10^{-12} cm^3 molecule^{-1}

s^{-1} for the reaction of $SiCl_2$ with oxygen, while the reaction of SiF_2 with oxygen is unobservably slow [21] ($k < 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}).

3.5. N_2 and CO

Silylene is unreactive with CO and N_2, in contrast to singlet methylene, which reacts reasonably rapidly with these diatomics. Apparently, nothing is known about the expected stability of SiH_2CO species. All possible isomers of SiH_2N_2 are calculated to be unstable with respect to dissociation to silylene and nitrogen [28].

4. Conclusions

Absolute rate constants for the reaction of SiH_2 with a variety of diatomic molecules have been determined. In cases where comparisons can be made with other absolute rate studies, silylene is found to be significantly less reactive than singlet methylene but somewhat more reactive than halogenated silylenes. The reactions of SiH_2 with NO and O_2 are especially interesting, because possible product channels include formation of novel adducts and the production of electronically excited species. Further experimental and theoretical study of the SiH_2NO and SiH_2O_2 potential surfaces is required to elucidate the mechanism of these reactions.

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