Available online at www.sciencedirect.com
SCIENCE DIRECT®

Chemical Physics Letters 413 (2005) 194–200

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

Direct detection of chlorosilylene and time resolved study of some of its reactions in the gas-phase using a new photochemical precursor

R. Becerra [a], S.E. Boganov [b], M.P. Egorov [b], I.V. Krylova [b], O.M. Nefedov [b], R.Walsh [c,*]

[a] *Instituto Quimica Fisica 'Rocasolano', C.S.I.C., C/Serrano 119, 29006 Madrid, Spain*
[b] *N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Prospekt 47, 119991 Moscow, Russian Federation*
[c] *School of Chemistry, University of Reading, Whiteknights, P.O. Box 224, Reading RG6 6AD, UK*

Received 10 May 2005; in final form 20 July 2005
Available online 15 August 2005

Abstract

Chlorosilylene, ClSiH, was prepared by 193 nm laser flash photolysis of 1-chloro-1-silacyclopent-3-ene in the gas phase. ClSiH was monitored in real time at 457.9 nm using a CW argon ion laser. The kinetics of reactions of ClSiH with C_2H_4, $CH_2{=}CHCMe_3$, C_2H_2, Me_2O, SO_2, HCl, $MeSiH_3$, Me_2SiH_2, Me_3SiH, $MeGeH_3$, Me_2GeH_2 and precursor have been studied at ambient temperatures for the first time. Addition reactions of ClSiH and reactions with lone pair donors are faster than insertion reactions. Surprisingly ClSiH inserts faster into Si–H than Ge–H bonds. ClSiH is intermediate in reactivity between SiH_2 and $SiCl_2$. Relative reactivities of ClSiH and SiH_2 vary considerably.

1. Introduction

Silylenes are of importance because they are implicated in the thermal and photochemical breakdown mechanisms of silanes and organosilanes [1] as well as being key intermediates in CVD [2]. Time-resolved studies, carried out in recent years [3–5] have helped establish a growing database of gas-phase rate constants for these species. While the parent silylene, SiH_2, reacts very rapidly (at close to the collisional rate) with many different molecules, substituted silylenes such as $SiMe_2$ and $SiCl_2$ react more slowly, indicating the significantly deactivating effects of both methyl- and chloro- substitution. Very little attention has been paid to the monosubstituted silylenes, XSiH, although it is known from studies of MeSiH [6] that substitution by a single methyl group is much less deactivating than by two. In order to probe the question of single chlorine substitution on silylene reactivity, we turn our attention to the kinetics of chlorosilylene reactions. Chlorosilylene, ClSiH, is known to be an important intermediate in the pyrolysis of chlorosilanes [7].

ClSiH, was first obtained by flash photolysis of SiH_3Cl by Herzberg and Verma [8] who observed its UV-visible absorption spectrum as a series of highly resolved rovibrational lines of the $\widetilde{A}(^1A'') \leftarrow \widetilde{X}(^1A')$ electronic transition. Using laser-excited fluorescence (LEF) on the 482 nm emission line of this system, Ho, Breiland and Carr [9] were able to monitor ClSiH, formed by 193 nm excimer laser photolysis of SiH_2Cl_2 and obtain rate constants (in $cm^3 molecule^{-1} s^{-1}$) for its gas-phase reactions with SiH_2Cl_2 ($(4.1 \pm 0.3) \times 10^{-15}$) and SiH_4 ($(5.3 \pm 0.1) \times 10^{-15}$). These are the only published rate constants for ClSiH. While these values indicate that ClSiH is much less reactive than SiH_2 in these cases, it seemed to us worthwhile to extend the range of substrates for this important silylene. Preliminary attempts in our laboratory [10] to obtain ClSiH from SiH_2Cl_2 by laser flash photolysis were unsuccessful due to difficulties in handling the precursor, although ClSiH was observed [10] as a product of the reaction of SiH_2 + HCl

---

[*] Corresponding author. Fax: +44 0 118 378 6331.
E-mail address: r.walsh@reading.ac.uk (R.Walsh).

0009-2614/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2005.07.079

previously studied by some of us [11]. By analogy with photochemical sources of other heavy carbenes, we decided to explore the UV photodecomposition of a new precursor, 1-chlorosilacyclopent-3-ene, synthesised by us. This Letter reports the first use of this molecule to generate ClSiH in a time resolved experiment and a study of the kinetics of its further reactions.

2. Experimental

The apparatus and equipment for these studies have been described in detail previously [12,13]. Only essential and brief details are therefore included here. ClSiH was produced by flash photolysis of 1-chlorosilacyclopent-3-ene (CSCP) using a Coherent Compex 100 exciplex laser operating at 193 nm (ArF fill). Photolysis laser pulses (energies ca. 50–70 mJ) were fired into a variable temperature quartz reaction vessel with demountable windows, at right angles to its main axis. ClSiH concentrations were monitored in real time via their absorbances by means of a Coherent Innova 90-5 argon ion laser. The monitoring laser beam was multipassed 36 times along the vessel axis, through the reaction zone, to give an effective absorption path length of ca. 1.5 m. A portion of the monitoring beam was split off before entering the vessel for reference purposes. The monitoring laser was tuned to the 457.9 nm line, co-incident with the known transition, $\widetilde{A}^1A''(0,2,0) \leftarrow \widetilde{X}^1A'\ (0,0,0)$, in the ClSiH vibronic band [8]. Light signals were measured by a dual photodiode/differential amplifier combination, and signal decays were stored in a transient recorder (Datalab DL 910) interfaced to a BBC microcomputer. This was used to average the decays of typically three photolysis laser shots (at a repetition rate of 1 Hz or less). The averaged decay traces were processed by fitting the data to an exponential form using a non-linear least-squares package. This analysis provided the values for the first-order rate coefficients, k_{obs}, for removal of ClSiH in the presence of known partial pressure of substrate gas. This was always in excess of that of ClSiH thereby ensuring pseudo-first-order conditions.

Gas mixtures for most photolysis experiments were made up containing 10–30 mTorr of the transient precursor, CSCP, variable pressures of reactive substrates with total pressures made up to 10 Torr with inert diluent (SF_6). For the least reactive substrates, pressures went as high as 30 Torr. In these experiments, SF_6 was not added and total pressures were not constant. For the specific study of ClSiH with its precursor, pressures of CSCP from 9 to 63 mTorr were used. Pressures were measured with capacitance manometers (MKS Baratron). All measurements were made at room temperature of 299 ± 2 K.

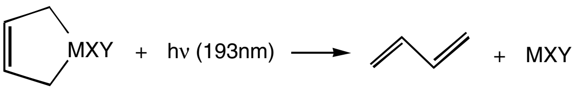
1-Chlorosilacyclopent-3-ene was prepared by the reaction of silacyclopent-3-ene with $SnCl_4$ according to the published procedure [14]. Silacyclopent-3-ene was obtained by reduction of 1,1-Dichlorosilacyclopent-3-ene with $LiAlH_4$ [15]. 1,1-dichlorocyclopent-3-ene was prepared by a two-step synthesis from 1,4-dichlorobutene-2 and trichlorosilane as described in [16]. All compounds were fully characterized by mass spectrometry and by ^1H and ^{13}C NMR.

All gases used in this work were deoxygenated thoroughly prior to use. Commercial samples of reactive substrates used in this work were obtained as follows. C_2H_4 and C_3H_8 were from Cambrian gases. C_6H_{12} (3,3-dimethylbutene-1) was from Ralph Emanuel. C_2H_2 was from BOC and was distilled to remove acetone stabiliser. All hydrocarbons were >99% pure as checked by gas chromatographic (GC). HCl (99+%) and Me_2O (99+%) were from Aldrich. SO_2 (99.5%) was from BDH. Me_3SiH (99.5%) was from Fluorochem. Me_2SiH_2 (99.0%)and $MeSiH_3$ (99.4%) were prepared previously [17] as were Me_2GeH_2 (99.2%) [18] and $MeGeH_3$ (99.3%) [19]. GC analyses of reactant and product mixtures were carried out using a Perkin–Elmer 8310 chromatograph equipped with a flame ionization detector. A 3 m silicone oil (OV101) column operated at 60 °C (or higher) was used to analyse most of the reagents investigated, although other columns, such as Porapak Q were also used when necessary (for light hydrocarbons). Retention times and peak sensitivities (GC response factors) were calibrated with authentic samples where possible.

3. Results

3.1. Identity of the transient

There is little doubt that the transient generated in this study is ClSiH. The precursor, CSCP, was chosen because of the well established photochemical generation process



where MXY represents a Group 14 heavy carbene. This pathway has been used to generate GeH_2 [20], $GeMe_2$ [21] and $SnMe_2$ [22] in the gas phase as well as several other heavy carbenes in solution [22]. CSCP was found to possess a UV absorption at wavelengths below 210 nm and preliminary experiments using GC analysis established that butadiene was the only hydrocarbon product of the 193 nm gas phase photolysis.

The transient species was detected in absorption by means of the 457.9 nm line of our argon ion laser. This coincides with the known $\widetilde{A}^1A''(0,2,0) \leftarrow \widetilde{X}^1A'(0,0,0)$ transition [8]. The vibronic spectrum of ClSiH is characterised by a well resolved set of bands constituting a vibrational progression in the bending mode of the excited state. Rotational fine structure has also been observed but the strongest absorption lines lie close to each band origin. Table 1 shows the wavelengths of the first four vibrational bands. The argon ion laser possesses nine lines in the green to violet region of the spectrum, but the 457.9 nm line provides the only coincidence with any of the ClSiH vibronic bands. As a check the search for transient signals was carried out at each of the known argon ion laser lines (λ/nm: 514.5, 501.7, 496.5, 488.0, 476.5, 472.7, 465.8, 457.9, 454.0). No signals were found at any other line apart from 457.9 nm. This check had been carried out previously in our laboratory [10] using both SiH_2Cl_2 as a photochemical source and the reaction of $SiH_2 + HCl$ as a thermal source [11]. Although ClSiH was detected is these earlier tests, neither of these sources were suitable for kinetic studies.

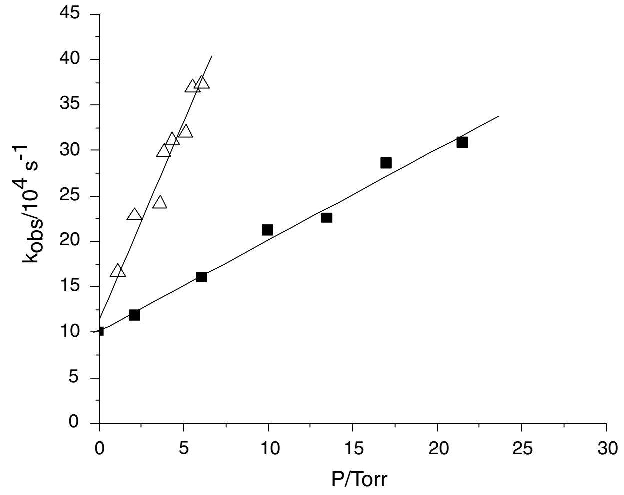


Fig. 1. Second-order plots for reactions of ClSiH at 299 K: (△) Me_2SiH_2 in 10 Torr (SF_6); (■) $MeSiH_3$.

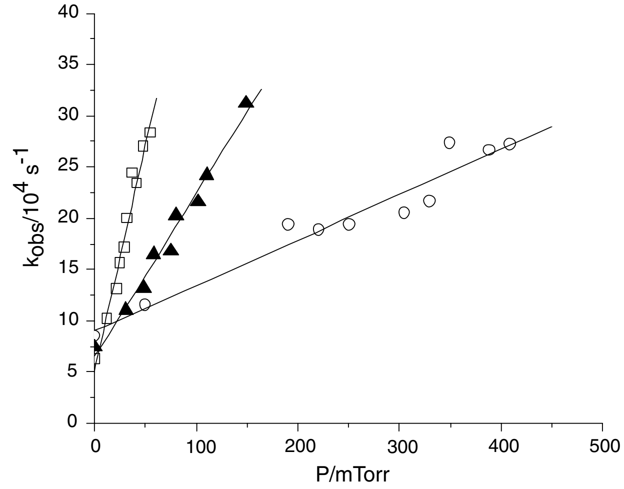


Fig. 2. Second-order plots for reactions of ClSiH at 299 K and 10 Torr (SF_6): (□) C_2H_2; (▲) C_2H_4; (○) Me_2O.

3.2. Kinetic studies

Preliminary checks showed that the values for the decay constants, k_{obs}, were not dependent on the excimer laser energy or the number of photolysis shots. None of the substrates absorbed at 457.9 nm, the transient monitoring wavelength, nor produced products which absorbed. For each substrate a set of runs was carried out with varying substrate pressures but a fixed pressure of precursor made up to a total pressure of 10 Torr with SF_6. The substrates were chosen to explore the various known reaction types open to silylenes. The substrate pressures were varied over suitable ranges to explore the systematic dependences of k_{obs} upon them. The results of a representative set of these experiments are shown in Figs. 1 and 2. Good linear fits were obtained, as expected for second order kinetics. The second order rate constants derived from the gradients of these plots by least squares fitting, are shown in Table 2, along with the known rate constants for the analogous SiH_2 reactions [11,17,23–26] for comparison purposes. The error limits are single standard deviations. The table includes one substrate, C_3H_8, for which no sign of reaction could be obtained up to a total (substrate) pressure of 32 Torr. Only an upper limit for the rate constant could be set in this case. We tried experiments with methanol as a plausible scavenger for ClSiH, but these were unsuccessful because MeOH reacted with the precursor, CSCP. Experiments with silane were not attempted because (based on the published rate constant [9]) pressures of ca. 1 atm would have been required to obtain reasonable decays, and such pressures of SiH_4 would have been unsafe in our system.

Experiments in this exploratory Letter were limited, for the most part, to a fixed total pressure, although it is likely that some of the reactions investigated will exhibit rate constant pressure dependences. For the least reactive substrates ($MeGeH_3$, Me_2GeH_2, $MeSiH_3$) substrate pressures up to 30 Torr were used, and total pressures were not constant. If these reactions had been pressure dependent (not expected: see Section 4)

Table 1
Origins of the lower energy vibrational bands in the $\tilde{A}(^1A'') \leftarrow \tilde{X}(^1A')$ electronic transition of ClSiH[a]

$v_1' v_2' v_3'$	$v_1'' v_2'' v_3''$	λ/nm
000	000	482.68
010	000	469.90
020	000	457.94
030	000	446.74
001	000	470.58
011	000	458.52

[a] From [8].

Table 2
Measured second-order rate constants for reactions of ClSiH at 299 ± 2 K (in SF_6; 10 Torr)

Substrate	k(ClSiH)[a]	$k(SiH_2)$[a]
$MeSiH_3$	$(3.16 \pm 0.14)\times10^{-13}$	4.08×10^{-10} [b]
Me_2SiH_2	$(1.43 \pm 0.09)\times10^{-12}$	3.51×10^{-10} [b]
Me_3SiH	$(1.77 \pm 0.11)\times10^{-12}$	2.55×10^{-10} [b]
$MeGeH_3$	$(6.61 \pm 0.80)\times10^{-14}$	–
Me_2GeH_2	$(3.49 \pm 0.12)\times10^{-13}$	–
C_3H_8	$<2.9\times10^{-14}$	–
CSCP	$(1.19 \pm 0.04)\times10^{-10}$	–
C_2H_4	$(4.95 \pm 0.27)\times10^{-11}$	1.58×10^{-10} [c]
$H_2C{=}CHCMe_3$	$(1.13 \pm 0.07)\times10^{-10}$	–
C_2H_2	$(1.37 \pm 0.09)\times10^{-10}$	3.21×10^{-10} [d]
Me_2O	$(1.38 \pm 0.12)\times10^{-11}$	2.8×10^{-11} [e]
SO_2	$(8.77 \pm 0.62)\times10^{-11}$	3.14×10^{-10} [f]
HCl	$(9.01 \pm 0.34)\times10^{-13}$	7.23×10^{-12} [g]

Values for analogous reactions of SiH_2 shown for comparison.
[a] Units $cm^3\,molecule^{-1}\,s^{-1}$.
[b] Ref. [17].
[c] Ref. [23].
[d] Ref. [24].
[e] Ref. [25].
[f] Ref. [26].
[g] Ref. [11].

curvatures in the second order plots would have been seen. Temperature dependences were not investigated at this stage.

4. Discussion

The results reported here represent only the second direct kinetic study of ClSiH and the first measurements of the rate constants for all of the substrates investigated. Because of experimental limitations (vide supra) we were not able to confirm the rate constant values for ClSiH with SiH_4 or SiH_2Cl_2, obtained by Ho et al. [9]. However the results obtained do allow us to make some interesting comparisons. First the lack of reactivity with C_3H_8 indicates that ClSiH does not readily insert in C–H or C–C bonds, which is similar to the behaviour of SiH_2 [3,4]. The remaining discussion is based on the general belief that the mechanistic behaviour of ClSiH is similar to that of SiH_2 and other silylenes [1,3–5]. This is supported in the case of the Si–H insertion reaction by end product studies by Jenkins et al. [27] who detected $EtSiH_2SiH_2Cl$ from reaction of ClSiH + $EtSiH_3$ and by Chernyshev and co-workers [28] who found Cl_3SiSiH_2Cl from ClSiH + $SiHCl_3$. The discussion is sub-divided according to reaction type.

4.1. Insertion reactions

For comparison purposes relative rate constants for reactions of SiH_2, ClSiH, MeSiH and $SiMe_2$ with the methylsilanes are listed in Table 3. These processes all involve Si–H bond insertion [1]. The table contains absolute rate constants for SiH_2 reactions[1] and rate constant ratios, k_{rel}, which were calculated using the rate constants of Table 2 and previous studies [6,9,29]. The values for k_{rel} signify the deactivating factors of the particular substituents compared with H– for each silylene. It is clear that ClSiH is very much less reactive than SiH_2 in the Si–H insertion reaction. The factors are large, lying between 2 and 5 orders of magnitude! Cl– is clearly more deactivating than Me–. Indeed a single chlorine substituent is more deactivating than <u>two</u> methyl groups. Unfortunately the effect of double Cl– substitution is unknown because the analogous $SiCl_2$ reactions have not yet been studied. It is interesting to note that methyl substitution in the substrate is significantly activating. On a per H-atom basis, for ClSiH, insertion into Me_3SiH is 1320 times faster than into SiH_4.

Table 3
Some relative rate constants for Si-H insertion reactions of SiH_2 compared with other silylenes at 10 Torr total pressure

Molecule	$k(SiH_2)$[a]	k_{rel}[d]		
		ClSiH	MeSiH[g]	$SiMe_2$[h]
SiH_4	4.0[b]	75,500[e]	4.9	2000
$MeSiH_3$	4.08[c]	1290[f]	2.0	215
Me_2SiH_2	3.51[c]	245[f]	2.1	64
Me_3SiH	2.55[c]	144[f]	0.90	57

[a] Units $10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$.
[b] Ref. [12].
[c] Ref. [17].
[d] $k(SiH_2)/k$(silylene).
[e] Based on data from [9].
[f] Based on this work.
[g] Based on data from [6].
[h] Based on data from [29].

The mechanism of silylene insertion has been established to occur via an intermediate complex [3,4] viz

$$R_3Si{-}H + SiXY \rightarrow R_3Si{-}H\cdots SiXY \rightarrow R_3SiSiHXY$$

where R = H or Me; X and Y may be any of H, Me or Cl.

For ClSiH, the overriding consideration is the stabilising interaction of the Cl atom lone pairs with the silicon empty p orbital by p_π–p_π overlap. This will make ClSiH much less electrophilic than SiH_2 and almost certainly weaken the binding energy of the complex. This in turn will make the overall process more sensitive to the secondary energy barrier for rearrangement of the complex to the product disilane. Thus while secondary barrier effects on the Si–H insertion reactions of SiH_2 are small and fairly insignificant, they could well dominate in the case of ClSiH insertions and account for the large rate reductions. This will also help explain why methyl substitution in the substrate silane enhances reaction

---

[1] The data used here are from the more recent [12,17] rather than the older [3,4], but differences are quite small.

by making the recipient silicon atom more electropositive and thereby lowering the secondary barrier which is associated with the nucleophilic interaction of the lone pair on the inserting silylene [3,4].

An examination of Table 2 reveals the surprising fact that ClSiH is 3.9 times less reactive towards Me_2GeH_2 than Me_2SiH_2. It is assumed by analogy that reaction here involves Ge–H insertion, since alternative mechanisms seem unlikely. There is no doubt that Ge–H bonds are weaker than Si–H bonds and so this is a counter-intuitive result. To demonstrate that this was not an isolated (or erroneous) result, we also studied the reaction with $MeGeH_3$. A similar outcome was obtained. ClSiH is 4.7 times less reactive with $MeGeH_3$ than with $MeSiH_3$. The explanation for this is again likely to turn on the magnitude of secondary barriers to insertion. Theoretical calculations for the reaction of GeH_2 with GeH_4 [30] indicated that the secondary barrier was responsible for the rate reduction compared with the reaction of $SiH_2 + SiH_4$ [12]. The situation is not straightforward, however, because GeH_2 reacts faster with GeH_4 than with SiH_4 [31]. It seems to us probable that unexpected rate effects are more likely to arise with stabilised (or less reactive) heavy carbenes (silylenes or germylenes) than with the prototype species, SiH_2 or GeH_2. The known insertion reactions of SiH_2 with methylsilanes are not pressure dependent [4,17] and from the admittedly limited evidence of a factor of three it appears that their ClSiH counterparts (with both methylsilanes and methygermanes) are also pressure independent.

4.2. Addition reactions

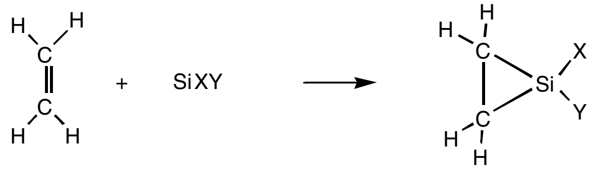
For comparison purposes relative rate constants for reactions of SiH_2, ClSiH, $SiCl_2$ and $SiMe_2$ with ethene and ethyne are listed in Table 4. These processes all involve π-type additions [1]. The table contains absolute rate constants for SiH_2 reactions and rate constant ratios, k_{rel}, which were calculated using the rate constants of Table 2 and previous studies [5,32,33]. The values for k_{rel} once again signify the deactivating factors of the particular substituents compared with H– for each silylene. Once again there is a clear cut indication that ClSiH is less reactive than SiH_2, although the deactivating factors are much smaller than those for the Si–H insertions. It is noteworthy that for double chlorine substitution, the effect is much larger, whereas for double methyl substitution it is more modest. There is no data for MeSiH with which to extend this comparison. It should be borne in mind that the rate constants for these reactions are known to be pressure dependent in some cases [23,24,32], and so these numbers may not represent the true relative addition factors. The pressure dependences for ClSiH additions remain to be investigated. However, some idea about them may be obtained from the rate constant of addition to 3,3-dimethylbutene-1 (*t*-butylethene) in Table 2. The addition process to a large alkene is expected to be much less prone to pressure dependence and therefore this rate constant should be close to the true addition rate constant. If we assume that this represents the limiting value for ClSiH addition to C_2H_4, then the rate constant at 10 Torr is only a factor of 2.3 below its high pressure limit. This involves the assumption that the true bimolecular addition rate constant to 1-alkenes is independent of the specific alkene. This is true for SiH_2 additions [32]. Taking the high pressure limiting value for $SiH_2 + C_2H_4$ ($3.5 \times 10^{-10}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$ [23]) and comparing it with rate constant for ClSiH addition to $H_2C{=}CHCMe_3$, gives a k_{rel} value of 3.1, hardly different from the value of Table 4.

Table 4
Some relative rate constants for π-type addition reactions of SiH_2 compared with other silylenes at 10 Torr total pressure (where recorded)

Molecule	$k(SiH_2)$[a]	k_{rel}[d]		
		ClSiH[e]	$SiCl_2$[f]	$SiMe_2$
C_2H_4	1.58[b]	3.2	1220	6.3[g]
C_2H_2	3.21[c]	2.3	4500	6.9[h]

[a] Units $10^{-10}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$.
[b] Ref. [23].
[c] Ref. [24].
[d] $k(SiH_2)/k(\text{silylene})$.
[e] Based on this work.
[f] Based on data from [5].
[g] Based on data from [32].
[h] Based on data from [33].

The mechanism of the silylene addition reaction to alkenes is well known [1,3–5] to lead to formation of siliranes (or silirenes in case of addition to alkynes), viz



What is less clear is whether this reaction occurs via an intermediate π-complex. For the SiH_2 + alkene reactions there seems to be no evidence for involvement of such a complex [23,32], although for $SiMe_2$ addition to C_2H_4 the high negative activation energy ($-8.5\,\mathrm{kJ\,mol^{-1}}$) suggests that a complex might be involved [32]. Pressure and temperature dependence studies of ClSiH + alkene reactions, as well as theoretical calculations, would help to throw some light on whether π-complexes are involved here. Such studies are planned.

4.3. Reactions with lone pair donors

In this class of processes we have studied the reactions of ClSiH with Me_2O, SO_2 and HCl. From Table 2 we can calculate that these reactions are slower by factors of 2.0, 3.6 and 8.0 than their SiH_2 counterpart reactions. As with the previous reaction types, Cl– for –H replacement in the silylene has a deactivating effect. Also, as with the π-type additions, rate constants for these reactions can, in some cases (e.g., Me_2O [25]), show pressure dependences which may modify these effects somewhat.

There is little doubt that these reactions proceed via the formation of zwitterionic donor–acceptor complexes, the stabilities of which can vary widely [11,25]. Overall reaction rates will be affected by both the stabilities of these complexes and the barriers to their further rearrangement. For some SiH_2 reactions, rearrangement barriers can be so high that the donor acceptor complexes are effectively the end products [34]. Further studies are needed to enable us to learn how Cl– for –H substitution will affect these detailed considerations. Again such studies are planned.

For the ClSiH + HCl reaction, theoretical calculations [35] have found the overall energy barrier to lie in the range 11–40 $kJ\,mol^{-1}$. To have been able to observe this reaction here suggests that the actual barrier, if there is one, must be small and probably below the minimum value given so far by theory.

5. Conclusion

Chlorosilylene has been observed, via its 457.9 nm absorption, as a primary product of the 193 nm photolysis of 1-chlorocyclopent-3-ene and 12 of its rate constants have been measured in the gas phase for the first time at ambient temperature. Chlorosilylene is less reactive than silylene in all of the reactions investigated here. It shows no propensity to insert into C–H or C–C bonds, and its insertion rate constants into Si–H bonds vary over a range of ca. 1320 (on a per bond basis). Unexpectedly insertion into Ge–H bonds is slower than into Si–H bonds. Most of the reactions with molecules containing π-bonds or lone pairs are faster than all the insertion reactions studied so far. The deactivating effect of Cl– for –H replacement in silylene is more pronounced in its reactions with σ-bonded electron pairs than with π-bonded or lone pairs of electrons. On the limited evidence available, ClSiH is still much more reactive than $SiCl_2$.

Acknowledgements

We thank the following for financial support: RFBR (Project No. 04-03-32838), the Russian Federation Presidential Program for support of leading Research schools (Grant NSh-1987.2003.3), the Russian Academy of Sciences (programs OX-1 and P-18) (S.E.B., M.P.E., I.V.K. and O.M.N.); the DGICYT (Spain) (project BQU2002-03381) (R.B.); the Royal Society (Great Britain) for a Spain-UK joint project grant (No. 15636) (R.W.).

References

[1] P.P. Gaspar, R. West, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organosilicon Compounds, vol. 2, Wiley, Chichester, 1998, p. 2463 (Chapter 43).
[2] P. Ho, W.G. Breiland, Appl. Phys. Lett. 43 (1983) 125, and references cited therein.
[3] J.M. Jasinski, R. Becerra, R. Walsh, Chem. Rev. 95 (1995) 1203.
[4] R. Becerra, R. Walsh, in: R.G. Compton, G.M. Hancock (Eds.), Research in Chemical Kinetics, vol. 3, Elsevier, Amsterdam, 1995, p. 263.
[5] J. Safarik, V. Sandhu, E.M. Lown, O.P. Strausz, T.N. Bell, Res. Chem. Int. 14 (1990) 105.
[6] R. Becerra, H.M. Frey, B.P. Mason, R. Walsh, J. Chem. Soc., Faraday Trans. 89 (1993) 411.
[7] K.L. Walker, R.E. Jardine, M.A. Ring, H.E. O'Neal, Int. J. Chem. Kinet. 30 (1998) 69.
[8] G. Herzberg, R.D. Verma, Can. J. Phys. 42 (1964) 395.
[9] P. Ho, W.G. Breiland, R.W. Carr, Chem. Phys. Lett. 132 (1986) 422.
[10] R. Becerra, N. Goldberg, R. Walsh, unpublished studies.
[11] R. Becerra, J.P. Cannady, R. Walsh, J. Phys. Chem. A 108 (2004) 3987.
[12] R. Becerra, H.M. Frey, B.P. Mason, R. Walsh, M.S. Gordon, J. Chem. Soc., Faraday Trans. 91 (1995) 2723.
[13] R. Becerra, S.E. Boganov, M.P. Egorov, V.I. Faustov, I.V. Krylova, O.M. Nefedov, R. Walsh, J. Chem. Am. Soc. 124 (2002) 7555.
[14] V.N. Ushakov, N.A. Pritula, J. Gen. Chem. USSR (English) 62 (1992) 1087;
Zh. Obshch. Khim. 62 (1992) 1318.
[15] E.A. Chernyshev, N.G. Komalenkova, S.A. Bashkirova, V.V. Sokolov, J. Gen. Chem. USSR (English) 48 (1978) 757;
Zh. Obshch. Khim. 48 (1978) 830.
[16] R. Damrauer, R. Simon, A. Laporterie, G. Manuel, Y. Tae Park, W.P. Weber, J. Organomet. Chem. 391 (1990) 7.
[17] I.W. Carpenter, PhD thesis, University of Reading, 1996.
[18] R. Becerra, M.P. Egorov, I.V. Krylova, O.M. Nefedov, R. Walsh, Chem. Phys. Lett. 351 (2002) 47.
[19] R. Becerra, S.E. Boganov, M.P. Egorov, I.V. Krylova, O.M. Nefedov, R. Walsh, paper in preparation.
[20] R. Becerra, S.E. Boganov, M.P. Egorov, O.M. Nefedov, R. Walsh, Chem. Phys. Lett. 260 (1996) 433.
[21] R. Becerra, S.E. Boganov, M.P. Egorov, V.Ya. Lee, O.M. Nefedov, R. Walsh, Chem. Phys. Lett. 250 (1995) 111.
[22] R. Becerra, P.P. Gaspar, C.R. Harrington, W.J. Leigh, I. Vargas-Baca, R. Walsh, D. Zhou, J. Am. Chem. Soc. 127 (2005), submitted.
[23] N. Al-Rubaiey, R. Walsh, J. Phys. Chem. 98 (1994) 5303.
[24] R. Becerra, R. Walsh, Int. J. Chem. Kinet. 26 (1994) 45.
[25] R. Becerra, I.W. Carpenter, G.J. Gutsche, K.D. King, W.D. Lawrance, W.S. Staker, R. Walsh, Chem. Phys. Lett. 333 (2001) 83.
[26] N. Goldberg, Ph.D. Thesis, University of Reading, 2003.
[27] R.L. Jenkins, A.J. Vanderweilen, S.P. Ruis, S.R. Gird, M.A. Ring, Inorg. Chem. 12 (1973) 2968.

[28] T.L. Krasnova, E.S. Abramova, N.V. Alekseev, E.A. Chernyshev, Russ. Chem. Bull. 48 (1999) 1960.

[29] J.E. Baggott, M.A. Blitz, H.M. Frey, R. Walsh, J. Am. Chem. Soc. 112 (1990) 8337.

[30] R. Becerra, S.E. Boganov, M.P. Egorov, V.I. Faustov, O.M. Nefedov, R. Walsh, J. Chem. Am. Soc. 120 (1998) 12657.

[31] R. Becerra, S.E. Boganov, M.P. Egorov, V.I. Faustov, O.M. Nefedov, R. Walsh, Phys. Chem. Chem. Phys. 3 (2001) 184.

[32] N. Al-Rubaiey, I.W. Carpenter, R. Walsh, R. Becerra, M.S. Gordon, J. Phys. Chem. A 102 (1998) 8564.

[33] J.E. Baggott, M.A. Blitz, H.M. Frey, P.D. Lightfoot, R. Walsh, J. Chem. Soc., Faraday Trans. 2 84 (1988) 515.

[34] R. Becerra, J.P. Cannady, R. Walsh, J. Phys. Chem. A 107 (2003) 11048, and references cited therein.

[35] S.P. Walch, C.E. Dateo, J. Phys. Chem. A 105 (2001) 2015, and references cited therein.