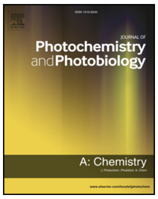
Journal of Photochemistry & Photobiology A: Chemistry 360 (2018) 145–151

Contents lists available at ScienceDirect

Journal of Photochemistry & Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Ultraviolet photolysis of 1,2-Dimethyldisilane in the gas phase

Najem Al-Rubaiey

Petroleum Technology Department, University of Technology, Baghdad, Iraq

ARTICLE INFO

Keywords:
Dimethyldisilane
Methylsilylene
Photolysis
Rate constants
UV

ABSTRACT

The formation of MeSiH is the primary process in the photolysis of 1,2-dimethyldisilane at 193 nm that are analogues of carbenes. Gas chromatographic technique was used with a flame ionization detector as an analysis tool to identify the products mixture. The photolysis light at 193 nm was provided by an Oxford KX2 pulsed laser operated with rare-gas halide (known as an excimer laser) as the gain medium to provide ultraviolet (UV) radiation. This work has confirmed that radical processes are not important in the photolysis of 1,2-dimethyldisilane. A method for the determination of rate constants for MeSiH reactions relative to the rate constants of 1,2-dimethyldisilane has been formulated. This has been used to determine some relative rate constants of MeSiH insertions with methylsilanes. The insertion reactions of MeSiH with SiH_4 and Methysilanes have shown to be fast and closer in reactivity to SiH_2 than to $SiMe_2$, whereas PhSiH looks to be slightly more reactive than MeSiH.

1. Introduction

The calculation of chemical reaction rate constants is of importance to chemistry and biology. Related studies carried out by our group concentrated on using time resolved spectroscopic studies [1–6]. In the same time and for gaseous reactions, gas chromatography is one of the most common and versatile methods of product analysis. This is because it can provide a separation and quantitative measurements of complex gaseous mixtures.

Silylene can be considered as very reactive intermediates. They have a very important role in the chemical vapor deposition of many thin films that contain silicon compounds. These species have technological importance in microelectronics industry besides the dry etching process of silicon wafers [7,8].

Providing the reaction system is carefully selected, and the conditions are well-defined, product yields can provide a mean of measuring relative rate constants of many chemical intermediate species in the presence of selected substrates.

This technique was employed in this research in order to:

(i) determine the primary processes and mechanism of the photolysis of 1,2-dimethyldisilane (DMDS) using 193 nm excimer laser,

(ii) study the rate of trapping of MeSiH by SiH_4, $MeSiH_3$, and Me_2SiH_2.

2. Material and methods

2.1. Apparatus

A Pyrex glass, static, high vacuum system has been used. The line was pumped by a mercury diffusion pump backed by a single stage rotary oil pump. A pre-calibrated MKS Baratron (type 170 M) was used to measure the pressure. An Edward speedivac gauge model B5 in conjunction with a Pirani gauge head model G6A was employed to monitor the pressure in the line continuously.

Two gas chromatographs were used for the analysis, both of which were equipped with gas sampling valve. Most of the analysis of the runs in this work was carried out using a Perkin-Elmer model 8310 gas chromatograph with flame ionization detector (FID) connected to Hewlett-Packard 3390 integrator. In addition a Perkin-Elmer model F33 gas-liquid chromatography with an FID was also used for some analyses. Several types of columns were employed for analytical purposes, the packing materials and operating conditions of which were dependent on the reaction under investigation. The main columns were of 15% PPG on 80–100 mesh chromosorb W (4.5m), 10% OV101 on chromosorb W-HP 80/100 (4m), Porapak T (4m) and Porapak Q (3m).

Five main cylindrical reaction cells were used for the kinetic runs. Two of these cells were constructed of spectrosil quartz tubing of length

---

E-mail address: 100108@uotechnology.edu.iq.

https://doi.org/10.1016/j.jphotochem.2018.04.041
Received 8 February 2018; Received in revised form 20 April 2018; Accepted 20 April 2018

6.5 cm and internal diameter 2.8 cm to be used at high temperature. The two other cells were built from Pyrex glass with silica windows fixed by using black wax. These cells were suitable for possible cleaning of the windows. These windows easily became covered with thin solid films after a number of experiments. One cell was constructed of spectrosil quartz tubing and wrapped (except for the window) in "electro-thermal" heating tape and maintained at 343 K during the time of experiments.

The furnace consisted of a horizontal silica tube (4 cm in diameter), wound with nichrome resistance wire as a heater and contained in a box packed with asbestos fiber. The furnace electrical supply was controlled by using a Variac. Temperatures were measured using a chrome-alumel thermocouple, located near the center of the furnace.

The photolysis light was provided by an Oxford KX2 pulsed laser operated with rare-gas halide (known as an excimer laser) as the gain medium to provide ultraviolet (UV) radiation. It was usually used with Ar/F_2 mixtures to provide a wavelength of 193 nm. Discharge efficiencies were around 1–5% and emitted pulses have 0.1 to 1 J of energy in the time range of 10–100 ns. Average powers are normally in the 10 to 100 MW range.

2.2. Source and purity of materials

1,2-Dimethyldisilane, DMDS, was kindly obtained from Professor E. Hengge (University of Graz/Austria), and found to be about 85% pure. The purity was improved to better than 95%, by low temperature distillation using a dry-ice slush technique (DMDS has a vapor pressure of 0.3 mm at 195 K). Unfortunately amongst the remaining traces of other compounds ($MeSiH_3$, Me_2SiH_2, Me_3SiH, SiH_4, $Me_2SiHSiH_3$ and $MeSiH_2SiHMeSiH_2Me$) were two of the main products *viz*, methylsilane and 1,2,3-trimethyltrisilane. This means that correction had to be applied to the yields of these compounds in the photolysis runs.

Other compounds, such as SiH_4 (> 99.9 purity, BOC Ltd. Electra-II grade), $MeSiH_3$ (99.6% purity, prepared in our lab.), Me_2SiH_2 (99.5% purity, prepared in our lab.), and Me_3SiH (99.8% purity, Fluorochem Ltd.) were degassed by freezing down (77 K) in liquid nitrogen and were used in this work. Electra-II grade Nitrogen (oxygen free, 99.9% purity) was supplied by BOC Ltd.

2.3. Experimental procedure

Samples for photolysis were prepared by putting the required pressure of precursor into the reaction cell then adding the other reacting substrate (if required) and finally making the reaction mixture up with nitrogen to the required pressure. Every precaution was made to reduce the adsorption of the silicon compounds on the walls of the gas line, the reaction cell and the gas sampling loop of the GC by heating. After the photolysis, the mixture of gases in the cell was analyzed by gas chromatography. Kinetic experiments were carried out with mixtures containing 50–100 mTorr precursor with partial pressures of the reacting substrate in the range of 50–2000 mTorr and total pressure ca, 200 Torr (made with nitrogen). An average of 2–10 laser shots was used which was indicated by the amount of the product peaks by GC. The number of shots was chosen as small as possible to keep the conversion low. The procedure for a particular substrate gas was to vary the ratio of precursor to the gas added and monitor the change in the ratio of products produced by gas chromatography.

3. Discussion

3.1. Results and discussion

3.1.1. Experiments with DMDS alone

The first set of experiments indicated that the major products were methylsilane (MS) and 1,2,3-trimethyltrisilane (TMTS). The MS peak was identified by comparison of its retention time with that of an authentic sample. As will be seen, this photolysis provides a relatively clean source of methylsilylene (MeSiH). MeSiH reacts with the precursor, DMDS to produce TMTS:

$$MeH_2SiSiH_2Me\ (DMDS) + h\nu \rightarrow MeSiH + MeSiH_3$$

$$MeSiH + DMDS \rightarrow MeSiH_2SiMeHSiMeH_2\ (TMTS)$$

To start with, the measurement of TMTS was a problem. Chromatographic peaks were irreproducible and had rather small yields which made them difficult to analyze. However there were several unrecorded, small peaks in the region where these molecules could be expected. After heating the sample loop of the gas chromatograph the peaks become reproducible. Because of the absence of TMTS authentic sample, TMTS was identified by comparing its retention time with those of other available trimethyltrisilane samples (*ie.* $H_3SiSiH_2MeSiH_2Me$ and $HSiMe_2SiMeHSiH_2Me$) [9,10]. Its identity was supported by other experiments [11]. The area for this peak was found to increase with the number of shots and decrease in the presence of another substrate under fixed photolysis conditions. TMTS was also observed as one of the main products in the pyrolysis of DMDS by Ring et al. [10]. In the Ring et al. work, the reaction was studied over the temperature range 295–573 K.

Small traces of other compounds such as SiH_4 and Me_2SiH_2 (in addition to $MeSiH_3$ and TMTS) have also been observed. The most obvious suggestion for the formation of those compounds was due to the presence of about 4% of the 1,1-dimethyldisilane impurity in DMDS. This impurity was identified by comparing its retention time with that of an authentic sample but under different GC conditions [11]. At 193 nm the photodecomposition of this impurity may lead to the formation of SiH_4 and Me_2SiH_2 as follows:

$$Me_2SiHSiH_3 \rightarrow Me_2SiH_2 + SiH_2$$

$$Me_2SiHSiH_3 \rightarrow SiH_4 + SiMe_2$$

Me_2SiH_2 and SiH_4 were identified by comparison of their retention times with those of authentic samples. Me_2SiH_2 was also detected by gas chromatography in the work of Davidson et al. [9] on the pyrolysis of DMDS. SiH_2 and $SiMe_2$ probably react with DMDS to give other products ($H_3SiSiH_2MeSiH_2Me$ and $HSiMe_2SiMeHSiH_2Me$) but these will have rather small yields which makes them difficult to analyze. However there were several unrecorded, small peaks in the region where these molecules could be expected.

Preliminary experiments indicated the formation of an opaque solid film which covered the walls of the cell, particularly when high laser pulse energies were employed. The production of such films reduced the transmission of laser radiation and also could lead to product coming from direct photolysis of the adsorbed material. Usually those compounds if produced were in small yields compared to those produced by the homogenous photolysis of DMDS in the gas phase. Many efforts were made to reduce the effect of this film by using a low pressure of DMDS and low conversion (a few numbers of shots). Regular cleaning of the cell after five runs and leaving it overnight in an oven to 830 K prevented film build up.

DMDS photochemistry was explored by investigating the experimental effects of the number of laser shots, DMDS pressure, total pressure, added oxygen and temperature. In order to assess the effects, The GC peaks ratio $[MeSiH_3]/[DMDS]$ was measured. This ratio gives an indication of the photochemical conversion. TMTS was not identified (and therefore not monitored) at the beginning of the work. The results of these preliminary investigations are shown in Figs. 1–5. A number of points can be extracted from this study:

1) The results in Fig. 1 show the linear dependence of the ratio with the number of shots. This suggests a well behaved reaction with product yields proportional to absorbed photons.

2) Fig. 2 demonstrates that the more DMDS in the cell, the less is the $[MeSiH_3]/[DMDS]$ ratio. A possible explanation is that most of the

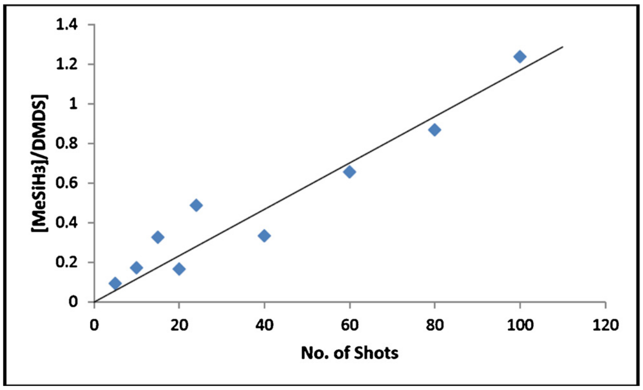


Fig. 1. Dependence of $[MeSiH_3]/[DMDS]$ on number of shots.

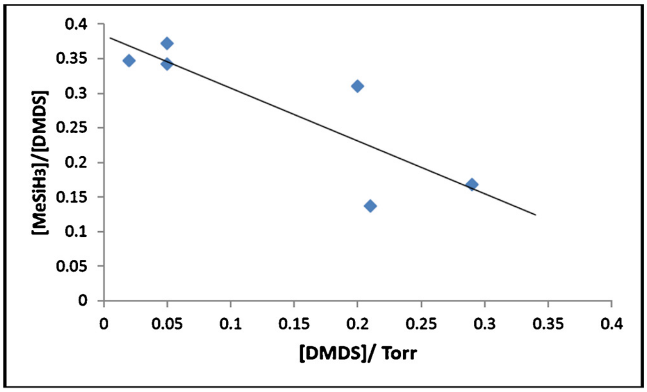


Fig. 2. Dependence of $[MeSiH_3]/[DMDS]$ on DMDS pressure.

193 nm radiation light is absorbed by the DMDS at the front end of the cell. Therefore, the more DMDS in the cell the more $MeSiH_3$ formed is diluted in unphotolysed DMDS. Another possible explanation is related to the film build up which has similar effect by reducing the amount of radiation going through the cell. To minimize difficulties of high light absorption or film formation, the pressure of DMDS was kept as low as possible. In practice the pressure range was 50–100 mTorr.

3) The results in Fig. 3 confirm that the ratio $[MeSiH_3]/[DMDS]$ did not vary beyond experimental error, with change in total pressure. This suggests that the reaction is pressure independent within the scatter.

4) The results in Fig. 4 show that adding oxygen does not affect the ratio of $[MeSiH_3]/[DMDS]$ within experimental error which suggests that the primary process is not radical process but rather molecular extrusion process. No mechanistic information is available at present concerning the reaction of MeSiH with O_2, however Becerra et al. [12] reported the time-resolved kinetic studies of the reaction of SiH_2, with O_2 over the pressure range 1–100 Torr and temperature range 297–600 K. Becerra et al. reported that the reaction of $SiH_2 + O_2$ was almost pressure independent over the temperature range studied. In order to reduce the effect of such reaction, many efforts have been made in this work to prevent the contamination of reaction system with oxygen.

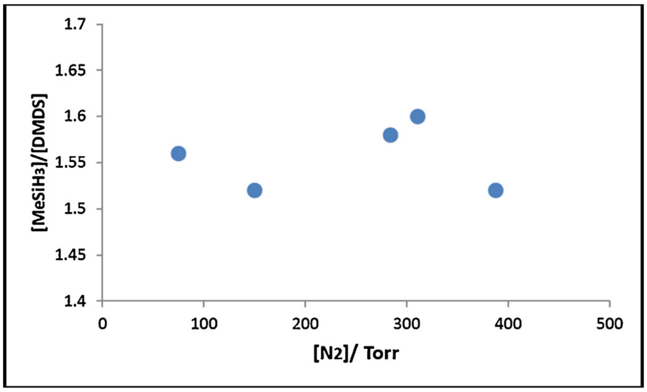


Fig. 3. Dependence of $[MeSiH_3]/[DMDS]$ on total pressure.

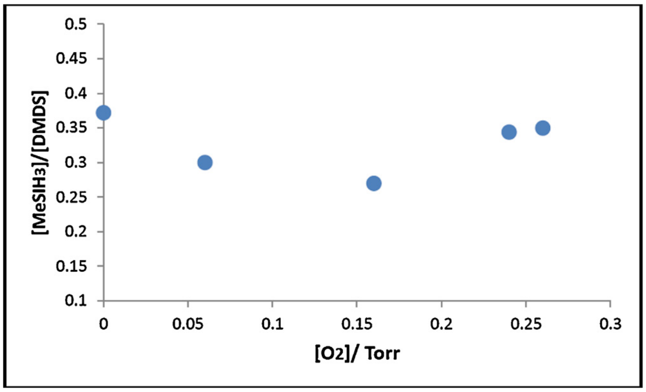


Fig. 4. Dependence of $[MeSiH_3]/[DMDS]$ on oxygen.

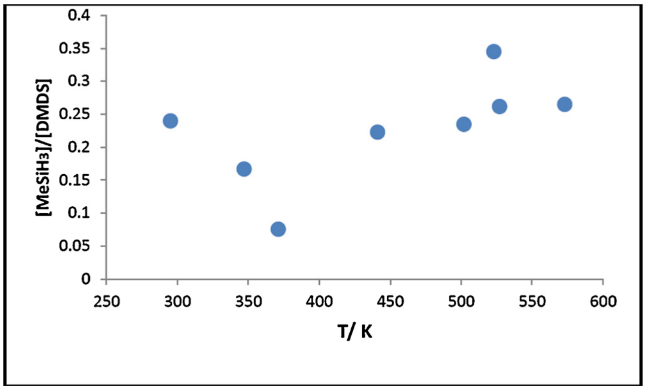


Fig. 5. Dependence of $[MeSiH_3]/[DMDS]$ on temperature.

5) The effect of increasing the reaction temperature is shown in Fig. 5.

6) In addition to $MeSiH_3$, TMTS, Me_2SiH_2 and SiH_4, no other products were detected at 298 K or higher temperatures.

3.1.2. *Experiments with added gases*

The second set of experiments was carried out with added SiH_4, Me_2SiH_2, and Me_3SiH in order to confirm the production of MeSiH (by scavenging it *via.* Si-H insertion processes). All the expected products were detected. The stoichiometric equations are presented as follows:

$$SiH_4 + MeSiH \rightarrow H_3SiSiMeH_2$$

$$Me_2SiH_2 + MeSiH \rightarrow Me_2SiHSiMeH_2$$

$$Me_3SiH + MeSiH \rightarrow Me_3SiSi\ MeH_2$$

The observation of these products provides strong evidence for the intermediacy of methylsilylene, MeSiH. These products, $H_3SiSiMeH_2$, $Me_2SiHSiMeH_2$ and $Me_3SSiMeH_2$ have been identified by comparing their GC retention times with those from previous studies on the same molecules [11]. It was also found that addition of these gases did not deplete the observed amount of MS but it did reduce the amount of TMTS relative to $MeSiH_3$ which suggested that they were competing with the DMDS for the methylsilylene.

It was subsequently found that by using a heated sample loop, the peak area of TMTS increased and now became reproducible and formed in fixed ratio to the quantity of MS. The ratio of peak areas $[MeSiH_3]/$

[TMTS] = 1.5 ± 0.5 is constant for the initial DMDS in the range of 50–100 mTorr, total pressure 160–200 Torr and 1–10 shots/80 mJ pulse^{-1}. This suggests that the FID is more sensitive to MS than to TMTS. However it is still possible that some TMTS is lost in the system.

These experiments give an indication that relative rate studies can be carried out to obtain rate constants of MeSiH removal with SiH_4, Me_2SiH_2 and Me_3SiH at 298 K. These were carried out by monitoring both the depletion of TMTS and by the increase of the insertion product ($H_3SiSiMeH_2$, $Me_2SiHSiMeH_2$ and $Me_3SiSiMeH_2$) as substrate pressure was varied.

In order to get reliable results it was important to select the lowest conversion but at the same time suitable experimental conditions in which the product peaks could be observed and monitored.

When DMDS is photolysed in the presence of added gas then the latter will compete with the unphotolysed DMDS to trap the methylsilylene formed. A depletion in the amount of TMTS will be observed, and thus will be an increase in the ratio of MS to TMTS.

For the experiments in the presence of SiH_4, MeSiH would react as follows:

$MeSiH + SiH_4 \rightarrow MeSiH_2SiH_3$ (MDS)

By following the procedure explained in Ref. [13], the following expressions have been obtained:

(1) $[MeSiH_3]/[TMTS] = 1 + (k_{SiH4}/k_{DMDS})\,([SiH_4]/[DMDS])$

(2) $[MDS]/[TMTS] = (k_{SiH4}/k_{DMDS})\,([SiH_4]/[DMDS])$

(3) $[MeSiH_3]/[MDS] = 1 + (k_{DMDS}/k_{SiH4})\,([DMDS]/[SiH_4])$

For reactions of MeSiH with Me_2SiH_2 and Me_3SiH, similar expressions are obtained. Gaseous mixtures involving the additives SiH_4, Me_2SiH_2, and Me_3SiH were made up and studied over a suitable range of starting pressures for each added gas. These gases were picked out as examples to illustrate the insertion reaction of methylsilylene.

$MeSiH + Me_2SiH_2 \rightarrow MeSiH_2SiMe_2H$ (TMDS)

$MeSiH + Me_3SiH \rightarrow MeSiH_2SiMe_3$ (TTMS)

In this study (to improve analysis) different columns were used from the preliminary study. The experiments with silane, dimethylsilane and trimethylsilane (which do not absorb significantly at 193 nm) were carried out at room temperature. In these, partial pressures in the range of 50–100 mTorr of DMDS were photolysed in the presence of varying partial pressures of the added reactant gases at 0.05–2 Torr (in the presence of nitrogen to a total pressure of 200 Torr), 1–5 shots (60–80 mJ per pulse energy of the laser) were used. These conditions were chosen to keep conversions low (≈10%) and to minimize film formation.

The results of these experiments are shown in Figs. 6–8. It is worth mentioning here that only equations (1) and (3) have been used to plot the data in Figs. 6–8. For example, in Fig. 6, it has been shown that plot 6a represents equation (1) and plot 6b represents equation 3. Thus both plots (6a and 6b) should give the same relative rate value (k_{SiH4}/k_{DMDS}). Substrate to DMDS ratios in all cases show that these results confirm to the relationship determined here. Applying the relative rate procedure described previously, the relative rate constants can now be calculated with two values for each reaction.

Two methods of calculating the relative rate constants of SiH_4 and methylsilanes offered a good check on the data. Table 1 shows these data at 298 K and about 200 Torr of total pressure. The agreement between the two sets of values for SiH_4 is quite good but for Me_2SiH_2 and Me_3SiH is less good.

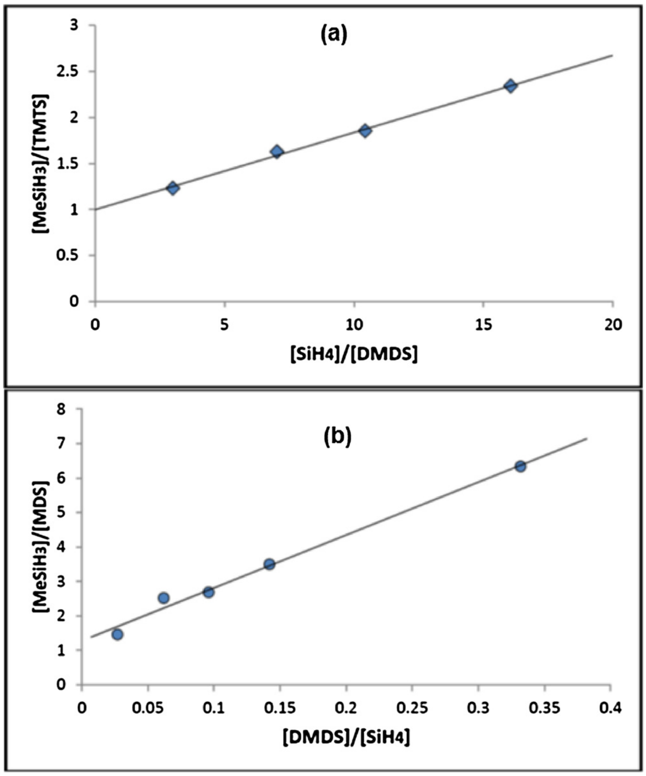


Fig. 6. Dependence of product on added substrate: DMDS + SiH_4.

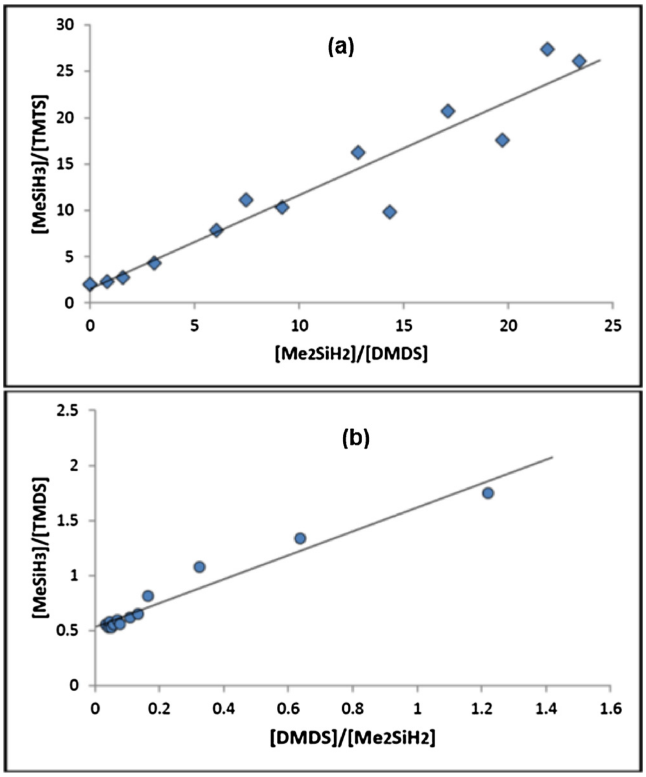


Fig. 7. Dependence of product on added substrate: DMDS + Me_2SiH_2.

3.2. Comparison with other data

There are no other published, room temperature, relative rate studies for methylsilylene to compare with. However there are absolute rate data [6]. An Arrhenius equation for the MeSiH reaction with the precursor, DMDS was obtained by fitting unpublished values from time-resolved studies by Becerra *et al.* [14] at different temperatures.

$\log\ (k/cm^3 molecule^{-1} s^{-1}) = -10.74 \pm 0.1 + 1.93 \pm 0.1\ kcal\ mol^{-1}/2.303\ RT$

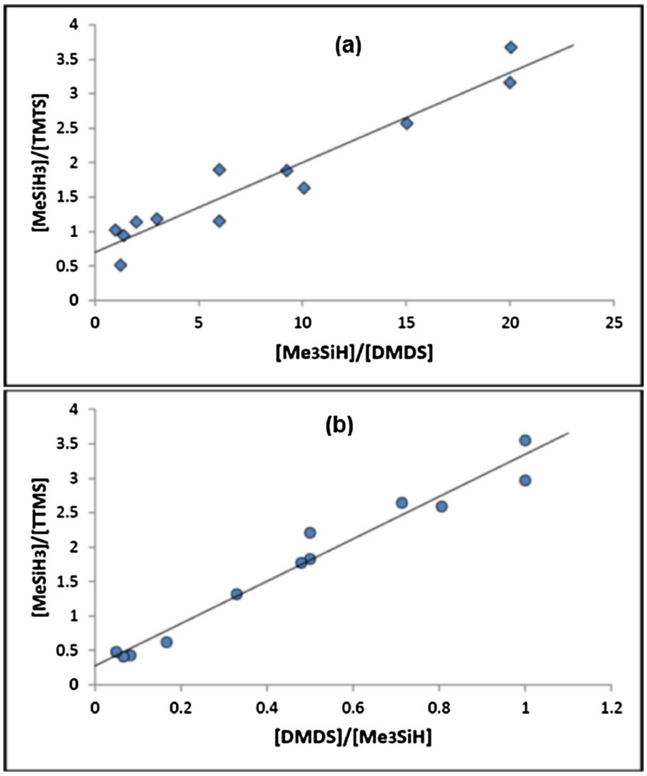


Fig. 8. Dependence of product on added substrate: DMDS + Me_3SiH.

Table 1
Relative rate constants of methylsilylene removal by silane, dimethylsilane and trimethylsilane at 298 K (from two different processes).

Substrate	$(k_x/k_{DMDS})_1$	$(k_x/k_{DMDS})_2$
SiH_4	0.08 ± 0.01	0.08 ± 0.01
Me_2SiH_2	0.66 ± 0.47	0.49 ± 0.09
Me_3SiH	0.19 ± 0.04	0.09 ± 0.04

Table 2
Absolute rate constants comparison for thee reaction of MeSiH with monosilanes at 298 K and 200 Torr total pressure.

Substance	$k/10^{-11}$ cm^3 molecule^{-1} s^{-1}		
	Becerra et al. [6]		*This work*
	D (1)	D (2)	
SiH_4	8.1	12.9	3.97
$MeSiH_3$	25.5	19.5	–
Me_2SiH_2	16.9	25.5	23.18
Me_3SiH	27.8	16.3	6.62

Using this equation at 298 K, the absolute rate constant for the reaction of MeSiH + DMDS can now be calculated, to be $k = 4.73 \times 10^{-10}$ cm^{3}molecule^{-1}s^{-1}. This enables the relative rate constants reported (Table 1, average) to be converted to absolute rate constants (see Table 2, column 3). Table 2 shows a comparison of these rate constants between this work and that of Becerra et al. [6]. Two sets of activation of energies were calculated by Becerra et al. First, the Arrhenius parameters were obtained from the directly measured rate constants at each temperature and second by fitting the mid-range rate constants with an assumed A-factor (per Si-H bond) of $10^{-12.4}$ cm^3 molecule^{-1} s^{-1} (average value). The latter values (D1 in Table 2) were preferred because they provide a more constant variation than the apparent best fit values. The uncertainties in the work of Becerra et al. and that described here are big and therefore close agreement cannot be expected. This does suggest, however, that more work is needed to improve these values at 298 K.

Table 3
Absolute rate constant at 298 K, $k/10^{-11}$ cm^3 molecule^{-1} s^{-1}.

Substrate	SiH_2[17]	$SiMe_2$[18]	MeSiH	PhSiH[19]
SiH_4	42	0.02	3.97	5.1
$MeSiH_3$	37	0.19	–	39
Me_2SiH_2	33	0.55	23.18	21
Me_3SiH	25	0.45	6.62	39

In order to examine these results in more detail the rate constants obtained here have been used together with those of earlier studies to make a comparison of reactivity of MeSiH with those of SiH_2[15–17], $SiMe_2$[18], and PhSiH [19]. Table 3 shows these comparison at 298 K in which there are some interesting points worth noting:

(i) MeSiH is much closer in reactivity to SiH_2 than $SiMe_2$. The value of the ratio, $k(SiH_2)/k(MeSiH)$, lies in the range ca. 1–10 whereas the ratio $k(MeSiH)/k(SiMe_2)$, has values in the range ca. −14-200.

(ii) PhSiH looks to be slightly more reactive than MeSiH, although not by much for Me_2SiH_2.

3.3. *Mechanism of the reaction*

In order to explain the type of reaction between MeSiH and the methylsilanes, we need to come back to the theoretical ideas of the nature of insertion process [20] originating with Hoffman [21] (see Scheme 1). This work suggests that the reaction will happen in two stages, the first "electrophilic" stage in which the electrons from the Si-H bond feeds into the empty p orbital on the silylene, then followed by the second "nucleophilic" stage which correspond to donation of the lone-pair on the silylene to make a new Si–Si bond.

The results obtained here suggest that MeSiH has a closer reactivity to SiH_2 than to $SiMe_2$. Previous results also suggest an increase in reactivity with methyl-substitution on the silane substrate. The results here are not clear cut on this point. The sequence of increasing reactivity is SiH_4, Me_3SiH, Me_2SiH_2. It seems probable that this is caused by experimental error and at the same trend is likely as with SiH_2 and $SiMe_2$. These trends have been explained as follows.

There are three possibilities in which silylenes interact with silanes:

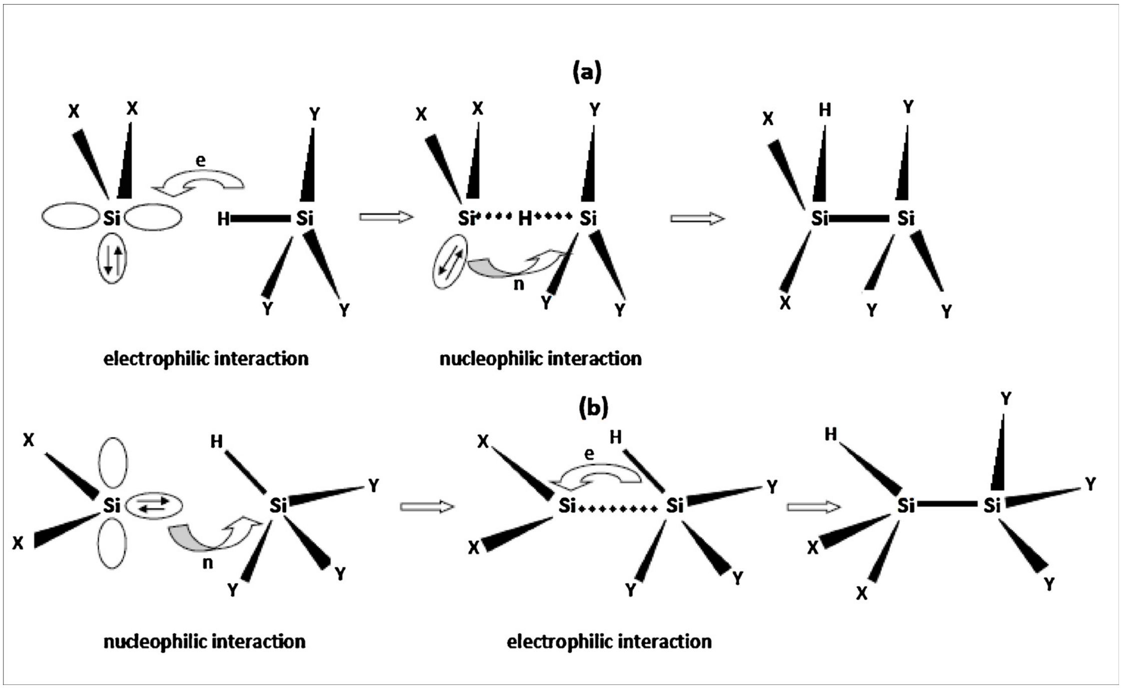
(i) That both "electrophilic" and "nucleophilic" occur simultaneously and at the same time.

(ii) A process led by the "electrophilic" interaction as shown in Scheme 1(a).

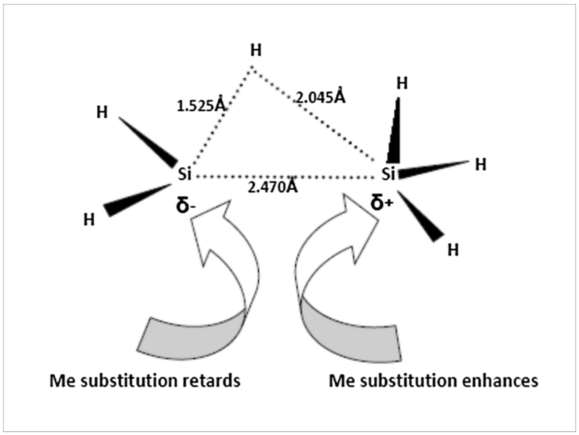
(iii) a process led by "nucleophilic" interaction with a different intermediate complex (see Scheme 1(b)). If the process (ii) was functioning in the Si-H insertion process, then the "electrophilic" stage is unlikely to be rate determining step. Thus the process should not be affected by the methyl substituent.

Reported *ab initio* calculations by Becerra et al. [16,22] (quantum mechanical procedures to calculate the potential energy surface) of SiH_2 insertion into SiH_4 provide support for process (ii). The intermediate complex for this reaction has been illustrated in Scheme 2 where the geometry of the structure has been explained. The bond lengths in this scheme suggest that H transfer from SiH_4 to SiH_2 is considerably more advance than Si–Si bond formation. It may be uncertain whether there is any Si–Si interaction at all. This is clear in the observation of the high entropy requirement (structure looseness) of the complex intermediate. This means that the "electrophilic" interaction may proceed the "nucleophilic" to some degree, although they are evidently coupled.

For mechanism (a) (Scheme 1), where "electrophilic" interaction occurs initially, the effect of an X atom or group which is an electron withdrawing substituent on the silicon center will affect the orbitals.



Scheme 1. Nature of the silylene insertion process.



Scheme 2. Silylene insertion: intermediate complex[22].

They draw off negative charges. However, they resist formation of positive charges at the silicon center. This might appear that they are in disagreement with our study. However, the silylenes are so "electrophilic", it may be assumed that they may have little difficulty in accepting an electron pair whatever the substituent (X = H or Me). The methylsilanes donor character (Y = Me) is also probable not changed much by Me groups. The bond dissociation energies [23–25] gave support for this effect. The effect of methyl substituent on the Si-H bond strength in methylsilanes seems to be very little, whereas the case of the simple alkanes, the effect of methyl substituent on C—H bond strength is to weaken them.

However, it is in the second, "nucleophilic" stage where Me groups that may exert their control. If Me groups are found in the silylene (X = Me) then it will be more disinclined to donate its lone pair. Thus it destabilizes the intermediate and second transition state. On the other hand, if Me groups are found in the silanes (Y = Me) then they will help withdraw charge and make possible the acceptance of the core pair (stabilizing the intermediate). Consequently, if the second stage turns out to be the rate determining step (as with the $SiMe_2$ insertion) or at least rate-influencing (as with the MeSiH insertion), the methyl substituent effect in the silane becomes important.

4. Conclusion

The following points can be concluded:

(i) The primary process for the DMDS decomposition at 193 nm is proposed as follows: $MeH_2SiSiH_2Me + h\nu \rightarrow MeSiH + MeSiH_3$

In the presence of a large amount of DMDS, MeSiH can react to give TMTS:

$MeSiH + DMDS \rightarrow MeSiH_2SiMeHSiMeH_2$ (TMTS)

(ii) The photolysis of DMDS provides a relatively clean source of methylsilylene, MeSiH.

(iii) The data presented here shows that MeSiH is much closer in reactivity to SiH_2 than to $SiMe_2$ whereas PhSiH looks to be slightly more reactive than MeSiH.

(IV) This work also suggests that the reaction will happen in two stages, the first "electrophilic" stage in which the electrons from the Si-H bond feeds into the empty p orbital on the silylene, this follows by the second "nucleophilic" stage which corresponds to donation of the lone-pair on the silylene to make new Si–Si bond.

V) Further work is required on varying the laser energy pulse on the photolysis of 1,2 DMDS. This will determine between one-photon and multiple-photon excitation and may lead to differentiate between photolytic paths.

VI) Investigation of the formation, structure, composition and decomposition of the film formed on the windows during photolysis of DMDS.

VII) Further search for a clean photolysis source of MeSiH.

Acknowledgments

The author would like to express his gratitude to the Department of Chemistry, University of Reading, UK for providing the possibility of completing this work. The author would like also to express his sincere appreciation and thanks to Professor Robin Walsh (Reading University) for his support and advice. A special thanks is given to Professor E. Hengge (University of Graz/Austria) for supplying some chemicals.

References

[1] N. Al-Rubaiey, H. Frey, B. Mason, C. McMahon, R. Walsh, Chem. Phys. Lett. 203 (3–4) (1993) 301–305.
[2] N. Al-Rubaiey, R. Walsh, J. Phys. Chem. 98 (20) (1994) 5303.
[3] N. Al-Rubaiey, I.W. Carpenter, R. Walsh, R. Becerra, M.S. Gordon, J. Phys. Chem. B 102 (44) (1998) 8564–8572.
[4] N. Al-Rubaiey, R. Becerra, R. Walsh, Phys. Chem. Chem. Phys. 4 (20) (2002) 5072–5078.
[5] N. Al-Rubaiey, R. Walsh, EPJ Web Conferences 139 (2017) 1–8, http://dx.doi.org/10.1051/epjconf/201713900004.
[6] R. Becerra, H.M. Frey, B.P. Mason, R. Walsh, J. Chem. Soc. Faraday Trans. 89 (1993) 411–417, http://dx.doi.org/10.1039/FT9938900411.
[7] J.I. Pankove (Ed.), Semiconducators and Semimetals, Academic, New York, 1984(chapter 6–10).
[8] R.A. Morgan, Plasma Etching in Semiconductor Fabrication, Elsevier, Amsterdam, The Netherland, 1985.
[9] I.M.T. Davidson, K.J. Hughes, S. Ijadi-Maghsoodi, Organometallics 6 (3) (1987) 639–643, http://dx.doi.org/10.1021/om00146a034.
[10] M.A. Ring, R.B. Baird, M.D. Sefcik, Inorg. Chem. 10 (5) (1971) 883–886, http://dx.doi.org/10.1021/ic50099a003.
[11] I.M. Watts, H.M. Frey, R. Walsh, Unpublished Results Obtained from Robin Walsh.
[12] R. Becerra, S. Bowes, J.S. Ogden, J.P. Cannady, I. Adamovic, M.S. Gordon, M.J. Almond, R. Walsh, Phys. Chem. Chem. Phys. 7 (2005) 2900, http://dx.doi.org/10.1039/B504760A.
[13] N. Al-Rubaiey, Kinetic Investigation of Some Prototype Silylene Reactions Induced by Laser Flash Photolysis, Doctoral Thesis, ISNI: 0000 0001 3408 1417 University of Reading, Reading, UK, 1994.
[14] R. Becerra, H.M. Frey, B.P. Mason, R. Walsh, unpublished results obtained from Robin Walsh. 2018.
[15] J.E. Baggott, H.M. Frey, P.D. Lightfoot, R. Walsh, I.M. Watts, J. Chem. Soc. Fraday Trans. 86 (1990) 27.
[16] R. Becerra, H.M. Frey, B.P. Mason, R. Walsh, M.S. Gordon, J. Chem. Soc. Faraday Trans. 91 (1995) 2723–2732, http://dx.doi.org/10.1039/FT9959102723.
[17] R. Becerra, I.W. Carpenter, M.S. Gordon, L. Roskop, R. Walsh, Phys. Chem. Chem. Phys. 9 (2007) 2121–2129, http://dx.doi.org/10.1039/B613638A.
[18] J.E. Baggott, M.A. Blitz, H.M. Freyand, R. Walsh, J. Am. Chem. Soc. 112 (1990) 8337.
[19] M.A. Blitz, H.M. Frey, F.D. Tabbutt, R. Walsh, J. Phys. Chem. 94 (1990) 3294.
[20] M.S. Gordon, G. Olbrich, J. Am. Chem. Soc. 106 (1984) 5421.
[21] R.C. Dobson, D.M. Hayes, R. Hoffmann, J. A. Chem. Soc. 93 (1971) 6188.
[22] R. Becerra, H.M. Frey, B.P. Mason, R. Walsh, M.S. Gordon, J. Am. Chem. Soc. 114 (1992) 2751.
[23] R. Walsh, Acc. Chem. Res. 14 (1981) 246.
[24] R. Walsh, S. Patai, Z. Rappoport (Eds.), The Chemistry of Organic Silicon Compounds, Wiley, New York, 1989(page 371).
[25] R. Becerra, R. Walsh, Z. Rappoport, Y. Apeloig (Eds.), Thermochemistry, The Chemistry of Organic Silicon Compounds, Vol. 2 John Wiley and Sons, NY, 1998(Parts 1, 2, and 3,chapter 4, pag 153).