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THE PHOTOLYSIS OF 1,1-DIMETHYLSILACYCLOBUTANE IN THE GAS PHASE

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Summary

The gas phase photolysis of 1,1-dimethylsilacyclobutane (DMSCB) has been carried out at wavelengths 185 nm $< \lambda <$ 210 nm. The major products of the photodissociation are ethylene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane (TMDSCB). The relative quantum yield $\Phi(C_2H_4)/\Phi(\text{TMDSCB}) = 8.0 \pm 0.5$ in neat DMSCB is independent of the initial pressure but decreases to a limiting value of ca. 4.5 in the presence of H_2. The silicon mass deficit is accounted for, qualitatively, by the production of an involatile polymeric material, of approximate composition -$(Me_2SiCH_2)_x$-, on photolysis. Under these conditions, $Me_2Si{=}CH_2$ undergoes an oligomerisation reaction in addition to the established homogeneous dimerisation reaction to form TMDSCB.

Introduction

Multiple bonded intermediates have been previously invoked in the mechanism of the gas phase photolysis of $MeSiH_3$ [1], Me_2SiH_2 [2], Me_4Si [3], Me_3SiCMe_3 and Me_6Si_2 [4] and 1,1-dimethylsilacyclobutane [5]. Quantitative photochemical studies [3—5] of these silicon containing molecules are bedevilled by the non-establishment of a mass balance. The silicon mass deficits and concomitant low quantum yields of TMDSCB, observed by Koob et al. [5] on photolysis of 1,1-dimethylsilacyclobutane (DMSCB) at 147.0 nm, arise from poorly characterised reactions of $Me_2Si{=}CH_2$. Interpretation of gas phase vacuum ultraviolet photolyses is complicated by multiple primary photodissociation channels and subsequent fragmentation or isomerisation of vibrationally excited products [6]. Additional evidence supports the view, however, that reactions competing with the established "head to tail" dimerisation of $Me_2Si{=}$

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CH_2 predominate in gas phase [1—4] and solution [7,8] photolyses.

The need to establish the nature of the hitherto ill-defined reactions of $Me_2Si{=}CH_2$ stimulated the present investigation of the gas phase photolysis of DMSCB.

Experimental

Photolyses were carried out in a cylindrical quartz reaction vessel 10 cm × 4.5 cm diameter. The irradiation source was a 150 W Xe arc lamp (Oriel Corp.), fitted with suprasil quartz optics, with the collimated output passed along the cell axis.

DMSCB was purchased from Silar Ltd., fractionally distilled until gas chromatographically pure and used after degassing by the simple freeze-thaw-pump technique. Hydrogen (BOC) was deoxygenated and dried, prior to use, by passage over a catalytic "deoxo unit" (Englehard Ind.) and 5A molecular sieve.

Analysis of the photolysis products was carried out by gas chromatography (Carle micro-thermistor katharometer) using a 2 m squalene (20%) on Chromosorb P-AW 80-100 mesh at 60°C. Accurately determined pressure of each component were injected into the chromatograph, using a heated (60°C) greaseless gas sampling valve (Varian Ltd.), for calibration purposes.

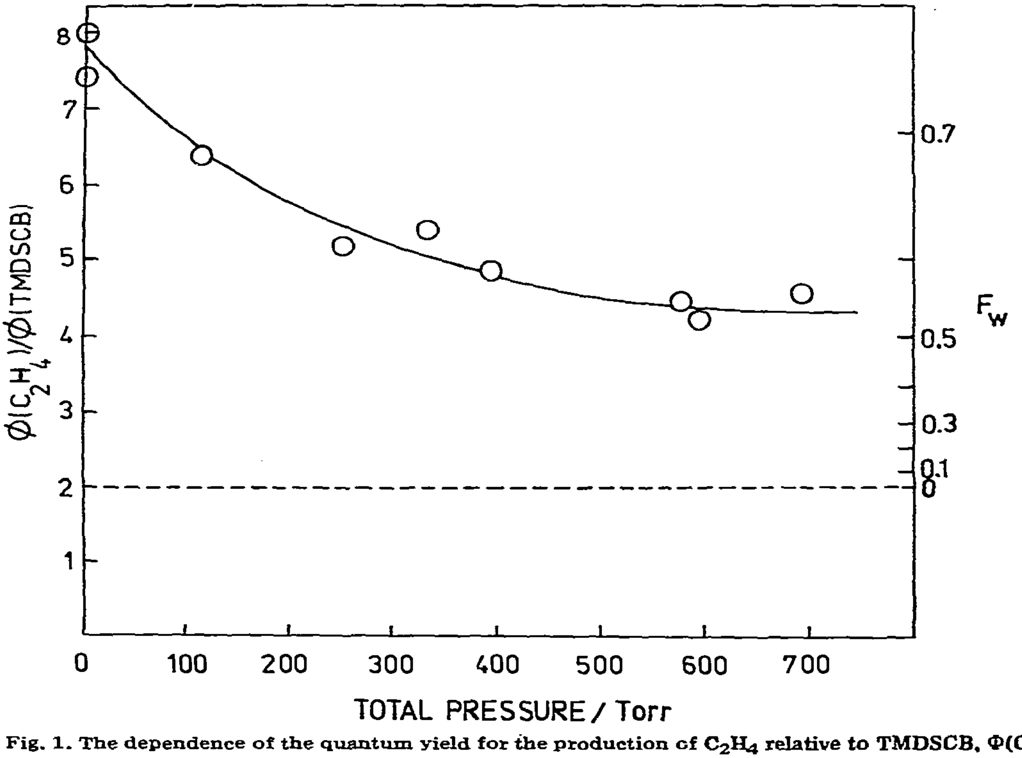

Fig. 1. The dependence of the quantum yield for the production of C_2H_4 relative to TMDSCB, $\Phi(C_2H_4)/\Phi(TMDSCB)$, on H_2 pressure. Partial pressure of DMSCB = 50.0 mmHg. The dashed line represents $\Phi(C_2H_4)/\Phi(TMDSCB) = 2.0$ at which stoichiometry $F_w = 0$.

Results

The ultraviolet absorption spectrum of DMSCB has been previously measured [9] with the onset of absorption occurring at ca. 210 nm ($\epsilon_{195} = 850$). The volatile products of photolysis at room temperature in this absorption band were identical to those observed on pyrolysis of DMSCB [10], namely ethylene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane together with a very minor amount of propylene (<0.05% of C_2H_4). Quantum yield ratios of C_2H_4 to TMDSCB were independent, within experimental error, of the initial pressure of DMSCB in the range 10 mmHg to 50 mmHg and the mean value of $\Phi(C_2H_4)/\Phi(\text{TMDSCB}) = 8.0 \pm 0.5$ is significantly higher than the stoichiometric ratio of 2.0 ± 0.2 cited by Gusel'nikov and Flowers [10] on thermal decomposition of DMSCB. Conversions were limited to 0.1%; under these conditions secondary photolysis of TMDSCB is negligible. The implied mass deficit was accounted for, qualitatively, by the observation of an involatile polymeric material (vide infra) deposited on the walls of the photolysis cell. Photolysis of the polymeric substance did not yield volatile products when irradiated, in vacuo, under the same conditions.

Further photolyses were performed with a constant partial pressure of DMSCB (50.0 mmHg) in the presence of varying amounts of H_2. The relative

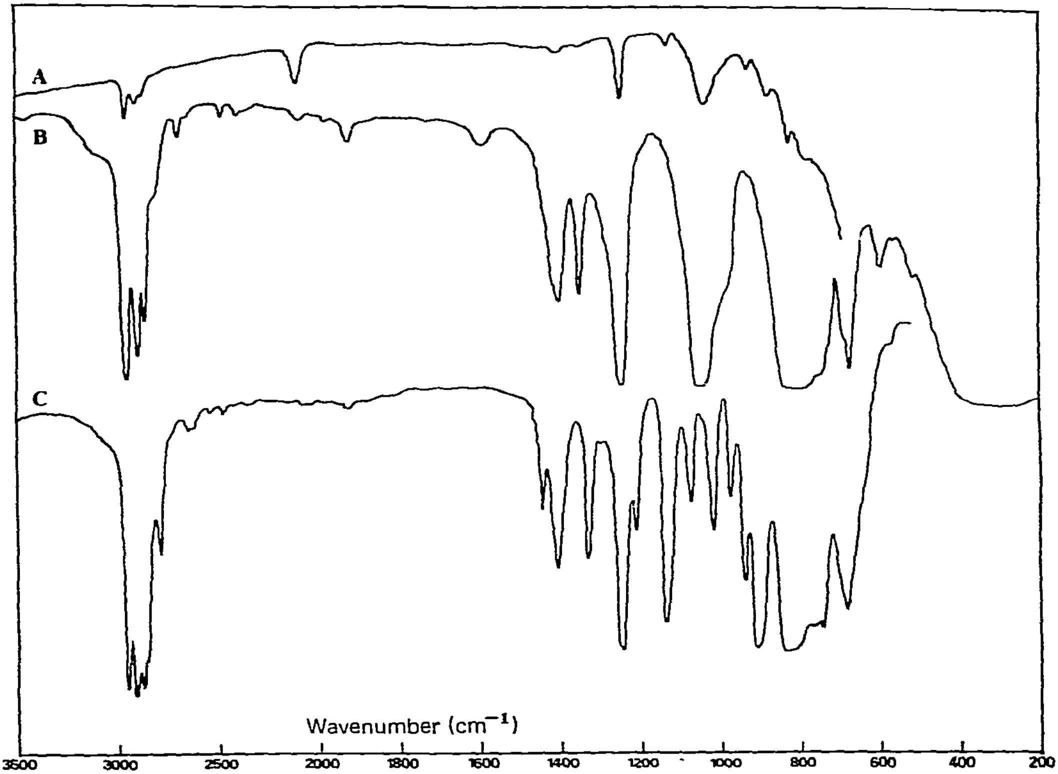

Fig. 2. Comparison of the infrared spectra of A, oligomerisation product of $Me_2Si{=}CH_2$; B, $-[CH_2SiMe_2]_x-$ and C, $-[CH_2CH_2CH_2SiMe_2]_x-$.

quantum yield, $\Phi(C_2H_4)/\Phi(\text{TMDSCB})$ exhibited a monotonic decrease on increasing the hydrogen pressure as shown in Fig. 1. At the largest $[H_2]/[\text{DMSCB}]$ ratio employed the value of $\Phi(C_2H_4)/\Phi(\text{TMDSCB})$ attained a value of ca. 4.5. No photolysis products other than C_2H_4, C_3H_6 or TMDSCB were observed in the presence of H_2.

The infrared spectrum of the solid material, produced on photolysis of neat DMSCB and deposited in situ on a NaCl plate, is shown in Fig. 2. The solid material was laid down by successive photolyses carried out to low extents of conversion. Samples of polymers $-[CH_2Si(CH_3)_2]_x-$ (I) and $-[CH_2CH_2CH_2Si(CH_3)_2]_x-$ (II) were prepared, independently, by the liquid phase thermal polymerisation of TMDSCB and DMSCB respectively according to the method of Nametkin and Vdovin [11a]. The synthesis of polymer I has been reported previously [11b]. The wave numbers, >950 cm^{-1}, of the absorption bands in the solid photolysis product and a thin film of polymer I were as follows: photolysis product, 2960s, 2910m, 2870m, 2160s, 1410w, 1360w, 1260s, 1150w, 1100s, 1020(sh) and 950w; polymer I, 2947s, 2893m, 2853m, 1427m, 1373m, 1253s, 1053s and ~1000(sh). The mass spectrum of the photolysis product exhibited a complex fragmentation pattern extending to large *m/e* values >400. A detailed interpretation of the spectrum in terms of the nature of the fragment ions was not attempted but the major *m/e* peaks are common to both, but not derived exclusively, from polymers I and II.

Discussion

Ethylene is the major product formed in the photolysis of DMSCB at wavelengths in the range 210 nm $< \lambda <$ 185 nm. The congenitic formation of $Me_2Si{=}CH_2$ is implied by the characteristic production of TMDSCB previously observed in both the pyrolytic [10] and photochemical [3] decomposition of DMSCB in the gas phase. The primary photochemical pathway is thus

$$\text{DMSCB} \rightarrow C_2H_4 + Me_2Si{=}CH_2^{+} \qquad (1)$$

where $Me_2Si{=}CH_2^{+}$ represents a vibrationally or electronically excited molecule. The yield of propylene is sufficiently small to exclude the extrusion of dimethylsilylene, $SiMe_2$, as a major pathway at these wavelengths.

Reaction 1 has been cited by Koob et al. [3] as the major primary photodissociative path on photolysis of DMSCB at 147.0 nm. At this wavelength the ionisation cross section of DBSCB has not been measured but the reported [12] ionisation potential (8.33 ± 0.07 eV) is less than the photon energy (8.38 eV). The role of ionisation and concomitant ion-molecule reactions requires careful assessment in the vacuum ultraviolet region [6].

The incident photon energy (136.1 kcal mol^{-1} $< h\nu <$ 178.6 kcal mol^{-1}) in the present work and the thermochemistry of reaction 1 implies that the maximum excess energy, E^{+}, in $Me_2Si{=}CH_2^{+}$ is $81 < E^{+} < 124$ kcal mol^{-1}. The value of the heat of formation of $Me_2Si{=}CH_2$, $\Delta H_f^0(Me_2Si{=}CH_2) = 22.7 \pm 5.4$ kcal mol^{-1}, is based on a recent determination [13] whereas $\Delta H_f^0(\text{DMSCB}) = 19.8 \pm 1.4$ kcal mol^{-1} [14] and $\Delta H_f^0(C_2H_4) = 12.5$ kcal mol^{-1} [15] are currently accepted literature data. Thus the nascent $Me_2Si{=}CH_2$ is probably formed with an internal energy in excess of the silicon—carbon π-bond energy, $D_\pi^0(Si{=}C) =$

23 kcal mol^{-1} [13]. The reactions of vibrationally excited $Me_2Si{=}CH_2^{+}$ produced on photolysis may differ from thermally generated species.

Recent theoretical calculations [16] of the ground closed shell singlet state of $CH_2{=}SiH_2$ demonstrate that methylsilylene, CH_3SiH: is the most thermodynamically stable isomer in comparison with the parent silaethylene and the corresponding silacarbene SiH_3CH:. The calculated [16,17] thermodynamic stabilities of methylsilylene and silylcarbene in the lowest triplet state is reversed. The accuracy of the calculations is insufficient to assess the activation energy of isomerisation of singlet $Me_2Si{=}CH_2$ to CH_3SiH: with confidence. Spin conservation rules favour production of the singlet state in the photodissociative step. There is a measure of agreement that $CH_2{=}SiH_2$, at least, has a singlet ground state [18,19] although the exact value of the singlet—triplet energy separation is in dispute [18a,19,20]. If isomerisation of the vibrationally excited $Me_2Si{=}CH_2$ to methylsilylene occurs, then the fate of CH_3SiH: is probably polymerisation since insertion reactions of simple silylenes [21] into H_2 and carbon—hydrogen bonds has not been observed.

"Head to tail" dimerisation of $Me_2Si{=}CH_2$ to form TMDSCB is observed in thermal reactions, at temperatures in the range 400—460° C, where the stoichiometry is well established [10] with $[C_2H_4] = 2[\text{TMDSCB}]$. The temperature independent second order rate constant ($10^{6.5}$ l mol^{-1} s^{-1}) for this reaction has been experimentally measured [22] although these results have not been substantiated by independent studies [23,24]. Ab initio calculations, restricted to the dimerisation of $CH_2{=}SiH_2$, have indicated that the activation energy is ca. 14 kcal mol^{-1} [19]. The latter figure represents an upper limit to the activation energy [19] and competing reactions of $Me_2Si{=}CH_2$ must, necessarily, be relatively fast. Low quantum yields ($\Phi(\text{TMDSCB} = 0.01$) for the production of TMDSCB, compared to $\Phi(C_2H_4) = 0.86$ have been observed in the photolysis of neat DMSCB [5] at 147 nm. In the presence of 580 mmHg of CF_4 or N_2 the quantum yield for TMDSCB increased but remained <0.1 whilst the quantum yields of other products were virtually unaffected.

A similar phenomena is noted in the present work, as shown in Fig. 1, in which the mass imbalance is reflected in the non-stoichiometric value of $\Phi(C_2H_4)/\Phi(\text{TMDSCB})$. In the presence of H_2, the quantum yield ratio attains a limiting value of ca. 4.5 at high pressures. The following tentative mechanism accomodates the experimental data:

$$\text{DMSCB} \rightarrow C_2H_4 + Me_2Si{=}CH_2^{\ddagger} \qquad \Phi(I)_{abs} \tag{1}$$

$$Me_2Si{=}CH_2^{\ddagger} + M \rightarrow Me_2Si{=}CH_2 + M \tag{2}$$

$$2\, Me_2Si{=}CH_2 \rightarrow \text{TMDSCB} \tag{3}$$

$$Me_2Si{=}CH_2^{\ddagger} \rightarrow \text{isomerisation} \tag{4}$$

$$n\, Me_2Si{=}CH_2 \rightarrow \text{polymerisation} \tag{5}$$

The inclusion of reactions 4 and 5 are required by the following observations. First, the infrared and mass spectra of the solid material is similar to that of polymer I. Such structural similarities would be expected from successive "head to tail" homogeneous or heterogeneous oligomerisation reactions of $Me_2Si{=}CH_2$. The infrared spectrum of the solid material and polymer I exhibit common bands at 1100—1050 cm^{-1} and 1260—1250 cm^{-1}. The former is characteristic of the $SiCH_2Si$ grouping whilst the latter is a CH_2 deformation mode of the same grouping. The additional band at 2160 cm^{-1} is assigned to a Si—H stretching vibration [25]. The per bond silicon—hydrogen oscillator strength in SiH_4 [26] is 3.5 cm^2 $mmol^{-1}$; a value which is similar to silicon—hydrogen stretching modes in the solid phase [27]. Since the carbon—hydrogen oscillator strength in CH_4 is 0.58 cm^2 $mmol^{-1}$ [28] the fraction of Si—H bonds in all configurations, is relatively small in the deposited material and thus reaction 4 is minor. Secondly, although the extent of polymer formation is reduced on addition of an inert gas, cf. Fig. 1, oligomerisation competes with dimerisation even at the highest pressures employed. Thus, formally, the fraction of $Me_2Si{=}CH_2$, F_w, not accounted for in the formation of TBDSCB may be calculated and the results are given in Fig. 1. The present work has not established whether $F_w >$ 0 is due entirely to the formation of the -$[Me_2SiCH_2]_x$- polymer.

It has been tacitly assumed that the oligomerisation reactions denoted simply by equation 5 is preceded by a "head to tail" dimerisation to form the corresponding biradical which adds further to continue chain growth. Conceivably, the oligomerisation reactions may be initiated by free radical addition to Me_2-$Si{=}CH_2$, a reaction which has been postulated previously [29]. The relatively low value of Φ(TMDSCB) at a photolysis wavelength of 147 nm [3] may reflect the greater extent of primary photodissociative channels yielding free radicals in the vacuum ultraviolet region compared to longer wavelengths.

Further work is required to delineate the role of the isomerisation reactions of the electronically or vibrationally excited states of $Me_2Si{=}CH_2$ and to determine the kinetic or thermodynamic reasons for chain, in preference to ring, formation at low temperatures.

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