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The reactions of silylenes on the chemically activated silica surface

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Abstract

The reactions of silylene centres (SC) on the surface of a chemically activated silica (reactive silica, RSi), characteristic of silylenes and carbenes under homogeneous conditions, have been explored by IR and luminescence spectroscopy. SC were found to insert into the H–S bond of H_2S and the C–S bond of Me_2S with rate constants of $4.5 \cdot 10^{-17}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ and $8.3 \cdot 10^{-18}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$, respectively. The reaction of SC with ethylene oxide proceeds via ring-opening with a further cyclization to give presumably a 5-membered surface siladioxolane heterocycle. The thermal reaction between SC and ethylene is shown to be very slow and not to yield products of addition or insertion. Ethylene appears to quench both fluorescence and phosphorescence of SC with almost gasokinetical quenching constants, but photoreaction between SC and ethylene was not observed.

Keywords: Silicon; Silylene; Kinetics; Mechanism

1. Introduction

The chemistry of silylenes has increasingly gained attention in recent years [1]. Silylene centres (SC) on a reactive silica (RSi) surface obtained by SiO_2 methoxylation and subsequent high temperature pyrolysis [2–4] or by milling of SiO_2 [5] are interesting examples of such species. SC are ground state singlets with an intensive absorption band at 240 nm ($S_0 \rightarrow S_1$) and two luminescence bands at 290 ($S_1 \rightarrow S_0$) and 460 nm ($T_1 \rightarrow S_0$) [3] with lifetimes of 5.6 ns [6] and 10.2 ms [7]. These properties are close to those for gaseous F_2Si: [8], but the chemical similarity of SC and this or other silylene-like intermediates has not yet been shown experimentally. The chemical properties of SC, other than some reactions with simple inorganic molecules [6] as well as their reactivity when in the excited state practically have not been investigated. In the present work the behaviour of SC in main reactions, typical for silylenes and carbenes (a general term for which is carbenoids) under homogeneous conditions, is explored.

2. Experimental section

A commercially available aerosil with a specific surface area of 170 m^2/g was used. Ethylene oxide, ethylene, hydrogen sulphide and dimethyl sulphide were purified by a low temperature trap-to-trap distillation and several freeze-pump-thaw cycles prior to use for oxygen removal. A high-vacuum technique ($P = 10^{-6}$ Torr) was used for the preparation of RSi samples and volumetric measurements. The pressure was measured using a calibrated Pirany manometer. RSi samples were prepared using a method described elsewhere [2–4]. Aerosil samples (0.5 g) were annealed in oxygen at 1220 K for 30 min, then pumped, stored in methanol vapour at 720 K for 15 min and, after thorough pumping, were subjected to pyrolysis at 1220 K under pumping. RSi samples thus obtained were stored in hydrogen ($P = 10^{-2}$ Torr) at 720 K for 10 min in order to remove surface paramagnetic centres, if this was required.

IR spectra of RSi samples were recorded in a 2 mm quartz cuvette on a Specord M80 spectrophotometer with a spectral slit width not more than 6 cm^{-1}. In some cases the triple spectrum accumulation was used to improve the signal/noise ratio. Luminescence spec-

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tra were obtained using a Perkin-Elmer LS-50 spectrofluorimeter. A low pressure resonance mercury lamp was used as a 253.7 nm radiation source.

3. Results and discussion

3.1. Insertion of SC into S–H and C–S single bonds

The insertion into single bonds is characteristic of carbenoids [9,10]. It may proceed either via a synchronous one-stage mechanism or by formation of an ylide $=E^{-}-X^{+}-Y$ (where E: C or Si, X–Y is a molecule into which a carbenoid is inserted) as an intermediate [9,10]. Silylenes, in contrast to carbenes, are considered to form not ylides but more weakly bound donor–acceptor complexes [10] that might have been spectroscopically detected in low temperature matrices [11,12]. Silylenes are known to react under homogeneous conditions with alcohols, ethers [13,14], H_2O [15] etc. being inserted into single bonds.

In the present work the kinetics of the reactions between SC and H_2S, SC and Me_2S has been studied by monitoring SC fluorescence intensity at 290 nm with the gas reagent pressure kept constant. RSi samples free of paramagnetic centres were used to exclude the possibility of chain processes being initiated by free radicals. The pressures applied ($P_{Me_2S} = 10^{-2}$ Torr, $P_{H_2S} = 6 \cdot 10^{-2}$ Torr) were too low for SC fluorescence quenching to occur. Under these conditions, SC fluorescence intensity decreased exponentially (Fig. 1), SC disappearing completely and irreversibly in the course of the reaction. Bimolecular rate constants were evaluated as a ratio of the pseudo-first order rate constants and H_2S (Me_2S) concentrations in gaseous phase:

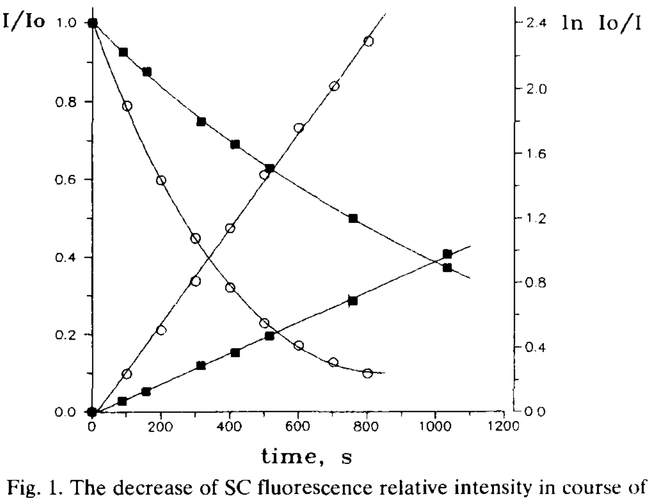


Fig. 1. The decrease of SC fluorescence relative intensity in course of the reactions of SC with gaseous H_2S (○) and Me_2S (■) at 295 K and their first order plots. Excitation: 240 nm; registration: 290 nm. H_2S and Me_2S pressures $6 \cdot 10^{-2}$ and 10^{-2} Torr, respectively.

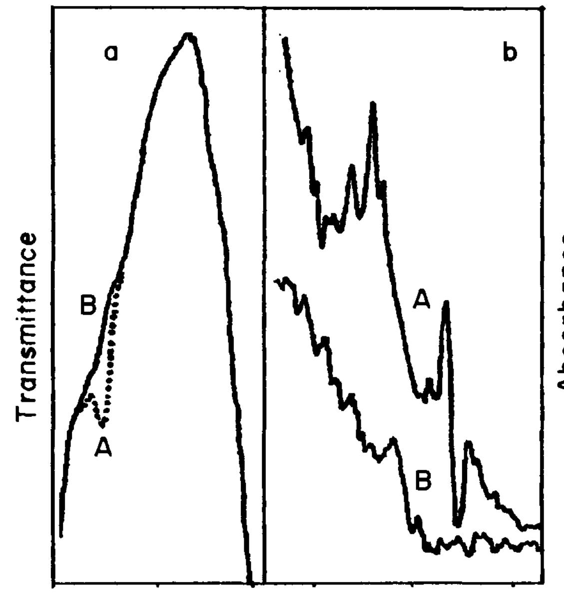
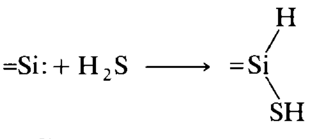


Fig. 2. The IR spectra of aerosil surface products obtained in course of the reactions of SC with gaseous H_2S (a) and Me_2S (b). A—the spectra recorded upon completion of the reactions. B—the spectra recorded with RSi samples before reagent admission. H_2S and Me_2S pressures are as in Fig. 1.

$k_{H_2S} = 4.5 \cdot 10^{-17} \mathrm{cm^3 molecule^{-1} s^{-1}}$;

$k_{Me_2S} = 8.3 \cdot 10^{-18} \mathrm{cm^3 molecule^{-1} s^{-1}}$.

The appearance of a narrow band at 2254 cm^{-1}, characteristic of the Si–H stretching mode, was detected in the IR-spectrum of RSi as a result of SC reaction with H_2S (Fig. 2a). The shift of the Si–H vibrational energy to lower values when compared to the $(-O)_3SiH$ surface silanes (2280 cm^{-1}) is indicative of a silicon atom bonded to a substituent less electronegative than a lattice oxygen. These data evidence that SC insertion into the S–H bond takes place:

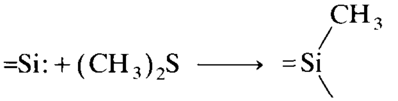


$$=Si: + H_2S \longrightarrow =Si(H)(SH) \qquad (1)$$

However, our attempts to detect an S–H vibrational band in the IR spectrum of the reaction product have failed. This does not exclude the reaction mechanism proposed as vibrations of this type are known to have usually low intensity in IR spectra.

The IR spectrum of an RSi sample containing the surface products of the reaction SC–Me_2S shows the bands at 2865 cm^{-1}, 2838 cm^{-1}, 2950 cm^{-1} and 2972

cm^{-1} (Fig. 2b). The first two have been assigned to symmetric vibrations of the CH_3-group, the latter two to asymmetric vibrations. The presence of band pairs in the region of symmetric and asymmetric vibrations allows to suppose the existence of two types of methyl groups in the surface product. The bands attributable to Si–H group vibrations are absent. These data indicate the insertion into the C–S bond rather than the C–H one in course of the reaction:

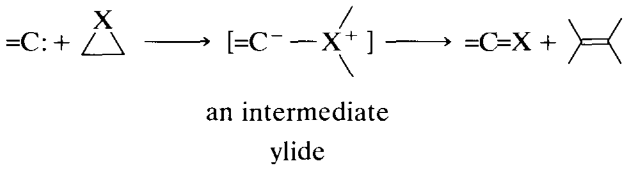


$$=Si: + (CH_3)_2S \longrightarrow =Si(CH_3)(S{-}CH_3) \qquad (2)$$

Thus, these experimental data show that SC insert into single bonds of simple molecules in a similar manner to silylenes under homogeneous conditions. Data on the mechanism of SC insertion and formation of intermediates have not been obtained either by kinetic methods or by using IR-spectroscopy. We can only show that stable intermediates like ylide or a donor–acceptor complex do not form.

3.2. *The reactions of SC with three-membered heterocycles*

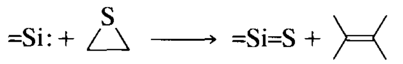
The reactions of carbenes with strained three-membered heterocycles are known to proceed via the ring opening [16]:



(3)

where X = 0 or S.

Recently ethylene sulphide was found to react with SC. The rate constant has been evaluated by following the SC phosphorescence intensity of $1 \cdot 10^{-16}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ [17]. Gaseous ethylene was shown to be the reaction product via its trapping by surface paramagnetic centres $\equiv Si^{\bullet}$ with the formation of surface-bound $\equiv SiCH_2CH_2^{\bullet}$ free radicals, detected by ESR. The formation of thiosilanone groups has been proposed according to reaction scheme (4), analogous to reaction (3):

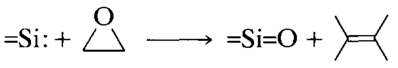


(4)

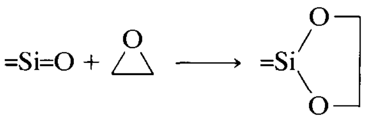
In the present work the mechanism of reaction of SC with ethylene oxide (EO) has been tested. Rapid chemisorption of EO at the initial pressure of approximately 10^{-2} Torr is followed by the irreversible disappearance of SC luminescence. The reaction rate was found to be limited by diffusion of EO into an aerosil layer, and thus, the rate constant for this reaction could not be detected. As in our previous work [17], the surface paramagnetic centres $\equiv Si^{\bullet}$ were used for trapping reaction products from the gaseous phase. The interaction of $\equiv Si^{\bullet}$ with EO was tested using an RSi sample free of SC (the procedure of preparation of an RSi sample, where SC are eliminated and only surface paramagnetic centres are present, is described in [18]) and resulted in the formation of the surface-bound $\equiv SiOCH_2CH_2^{\bullet}$ radicals detected by ESR (a_α = 23.5 Gs (2H), a_β = 26.7 Gs (2H) [19]). On the contrary, the products of ethylene addition, the $\equiv SiCH_2CH_2^{\bullet}$ radicals (a_α = 23 Gs (2H), a_β = 21.5 Gs (2H) [19]) were detected by ESR in the course of the reaction between SC and EO. Thus, evolution of ethylene takes place in the course of this reaction as in the above mentioned case with ethylene sulphide.

We attempted to detect the formation of the silanone =Si=O groups in the reaction between SC and EO. The surface silanones are known to react with gaseous CO_2 forming on the surface carbonates [20], but no chemisorption was observed upon treatment of surface products with gaseous CO_2 ($P = 10^{-2}$ Torr) at ambient temperature. As the absence of silanones may result from their high reactivity towards EO, an additional independent test was performed. SC were transformed nearly quantitatively into silanone groups by the well established procedure [18,20], and were then treated with gaseous EO ($P = 10^{-2}$ Torr) at ambient temperature. Fast chemisorption of EO was observed, the concentrations of the surface silanones and EO being in the stoichiometric ratio 1 : 1. The consumption of EO was also found to be approximately one half that observed in its direct reaction with SC. In both cases, the IR spectra obtained contain bands at 3004, 2965, 2925 and 2865 cm^{-1} (Fig. 3a,b), however, the relative intensities of these bands for the reactions of EO with SC or silanones differ somewhat.

Thus, a two-step reaction mechanism between SC and EO with ethylene evolution and formation of intermediate silanone in the first stage (5) can be proposed. One can see this reaction to be analogous to reaction (3). The second stage reaction product is proposed to be a siladioxolane five-membered ring (6):



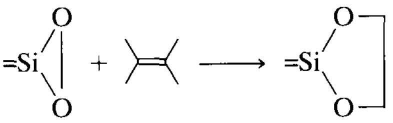
(5)

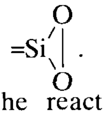


(6)

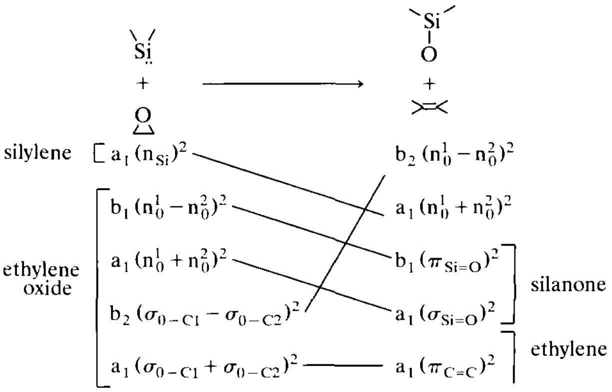
Fig. 3. The IR spectra of aerosil surface products obtained in course of the reactions between (a) SC and ethylene oxide; (b) surface silanones and ethylene oxide; (c) surface sila- dioxiranes and ethylene. Gaseous reagent pressures were no more than $5 \cdot 10^{-2}$ Torr.

The siladioxolanes may be obtained by the reaction of ethylene with the surface siladioxirane groups:


(7)

We found the latter reaction to proceed easily at ambient temperature and an ethylene pressure about 10^{-2} Torr at a nearly 1 : 1 stoichiometric ratio. The IR spectrum of surface products of this reaction show the main bands closely correspond to the IR spectrum bands seen in the EO and SC or silanone reactions (Fig. 3c). Thus, the data suggest the formation of the siladioxolane surface groups in all three cases: (i) ethylene oxide and SC; (ii) ethylene oxide and the silanones =Si=O; (iii) ethylene and the siladioxiranes

$=\mathrm{Si}{<}\overset{O}{\underset{O}{|}}$.

The question of the mechanism of the reaction between three-membered heterocycles with SC is left open. In accordance with the correlation diagram, the synchronous reaction (5) is thermally allowed at the C_{2v} transition state symmetry:



However, the formation of an intermediate ylide by a reaction analogous to (3) also seemed to be possible.

3.3. Reaction between SC and ethylene

The reactions between ethylene or its derivatives and singlet silylenes in both gaseous and condensed phases are known, in contrast to carbenes, to result in products of insertion rather than addition due to the low stability of the three-membered silacyclopropane cycle [21]. The latter compound is suggested to be an intermediate of the insertion reaction.

The reactivity of silylenes towards olefins strongly depends on their structure and decreases with growing electronegativity of substituents at a silicon centre. The reaction between Cl_2Si: and ethylene [22] is known to proceed very slowly at ambient temperatures and to result effectively in the product of silylene insertion into the C–H bond—vinylsilane—only at 793 K. This reaction is suggested to proceed via the intermediate vibrationally excited silacyclopropane. Thus, a similarly quite low reactivity towards ethylene in the case with SC, where the silicon atom is bound with two oxygens, should be expected. However, the remarkable stability of SC enables us to investigate their very slow bimolecular reactions. The surface may also take part in the effective vibrational activation of the intermediate silacyclopropane possibly formed in the first stage of the reaction, thus providing conditions for its stabilization as final reaction product.

Unfortunately, no reaction was observed by monitoring the SC fluorescence at ambient temperature and ethylene pressures up to 40 Torr. No ethylene consumption has been detected when SC containing RSi samples were treated with ethylene ($P \sim 10^{-2}$ Torr) at temperatures up to 800 K. No IR bands attributable to Si–H vibrations (the surface Si–H bonds emerged as a result of SC insertion into a C–H bond of ethylene) were found after the treatment of SC with ethylene ($P = 20$ Torr) at 800 K during 5 min. We can therefore conclude that SC are remarkably unreactive towards ethylene when compared to other simple silylenes like Cl_2Si:.

Reactivity of the SC excited state towards ethylene has been tested as well. SC phosphorescence was found to be completely quenched by ethylene even at its pressure of 10^{-4} Torr. Assuming SC phosphorescence lifetime as 10.2 ms [7], we can deduce the quenching constant to be no greater than 10^{-11} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$. The quenching of SC fluorescence by ethylene was observed over the ethylene pressure range of 1–40 Torr. With a SC fluorescence lifetime of 5.6 ns [6], the rate constant of SC fluorescence quenching by ethylene was measured from a linear Stern-Volmer plot (data not shown) to be of the order of 10^{-10} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$. Thus, both quenching constants are close to gasokinetical ones. However, no acceleration of SC disappearance rate has been found under continuous 253.7 nm irradiation (SC depletion takes place even in vacuum)in the presence of ethylene. This fact allows us to conclude that SC excited state quenching by ethylene does not yield any chemically stable products. This conclusion is also consistent with the absence of any new IR bands in the spectrum of an SC-containing RSi sample, exposed to 253.7 nm irradiation in the presence of ethylene.

3.4. Conclusions

For the first time SC were shown to participate in the reactions with organic molecules that are characteristic of carbenoids under homogeneous conditions. In spite of the essential difference in the reaction conditions (the reactions were on a silica surface in the case of SC and were homogeneous in the case of carbenoids), the similarity of the chemical properties of SC and other carbenoids is obvious. SC were found to insert into S–H (H_2S) and the C–S (Me_2S) single bonds. The reactions of SC with strained three-membered heterocycles proceed in the same way as in the ring-opening reactions of carbenes. The question on the mechanism of SC insertion and ring-opening still remains obscure as, with kinetic methods, we have not obtained data on the intermediates of these reactions. The thermal reaction between ethylene and SC even at high ethylene pressure and elevated temperature yields neither insertion nor addition products. No photoreaction of SC with ethylene has been found, though quenching of the SC excited state is quite efficient. Thus, SC chemical properties apparently resemble those of other singlet carbenoids, but this similarity appears to be somewhat restricted.

Acknowledgment

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