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Photolysis of $(Me_2Si)_6$ in argon matrices doped with high concentrations (ca. 20%) of N_2O or C_2H_4O: formation of $(Me_2SiO)_6$

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Abstract

Irradiation using a low pressure mercury lamp ($\lambda =$ ca. 250 nm) of argon matrices containing ca. 1% $(Me_2Si)_6$ and ca. 20% ethylene oxide (C_2H_4O) or nitrous oxide (N_2O) for a period of ca. 20 h leads to the formation of the cyclic compound $(Me_2SiO)_6$. This has a 12-membered ring with alternating Si and O atoms. It is identified by comparison of its infrared spectrum with a spectrum of an authentic sample. The reaction appears to proceed by stepwise insertion of O atoms into Si–Si bonds. © 2001 Published by Elsevier Science B.V.

Keywords: Photolysis; Matrix isolation; $(Me_2Si)_6$; Oxidation

1. Introduction

There has been considerable interest in the matrix chemistry of reactive silicon-containing species [1–3]. Much of this work has focused on the silylenes—compounds of general formula R_2Si, and a convenient route to dimethylsilylene has been found to be the photolysis of the cyclic compound $(Me_2Si)_6$. This extrudes Me_2Si upon irradiation around $\lambda = 250$ nm to yield $(Me_2Si)_5$ [4]. Upon irradiation at longer wavelengths ($\lambda = 450$ nm) Me_2Si is slowly isomerised to $MeSi(H){=}CH_2$ [5a]; a reaction that can be reversed either by photolysis at $\lambda = 250$ nm or by annealing. The thermal reaction only proceeds at temperatures above 100 K [5b], so it is only possible to observe it in involatile media such as a 3-methylpentane glass [5a]. If an argon matrix containing $MeSi(H){=}CH_2$ is heated above 50 K, all of the argon evaporates and the product is the σ-bonded cyclic dimer [5a].

In argon matrices doped with low concentrations (ca. 0.5–1%) of the O-donors ethylene oxide (C_2H_4O) or nitrous oxide (N_2O) the observed chemistry is somewhat different. When $(Me_2Si)_6$ is irradiated using a low-pressure mercury lamp with output centred around $\lambda = 254$ nm in 0.5–1% N_2O-doped argon matrices, Me_2Si is generated [6]. Upon annealing to 35 K the bands of Me_2Si decay and new bands are seen at 1186 and 1204 cm^{-1}. It is concluded that the band at 1204 cm^{-1} is the ν(Si=O) mode of Me_2SiO while that at 1186 cm^{-1} is ν(Si=O) of Me_2SiO complexed to N_2O. When the experiment is repeated using C_2H_4O in place of N_2O, one band in this region—at 1193 cm^{-1} is seen—and this is assigned to the complex of Me_2SiO with C_2H_4O [6]. In both cases the initial product therefore appears to be the monomeric silanone $Me_2Si{=}O$ [6]. Unfortunately other infrared bands of $Me_2Si{=}O$ or of its complexes could not be identified probably because the bands are weak and likely to overlap with bands of starting materials. Intriguingly, the silene $MeSi(H){=}CH_2$ yields the same products as Me_2Si upon annealing an N_2O-doped argon matrix at 35 K although the silene does not convert to the silylene at such low tempera-

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tures. It is suggested that the H atom migration is promoted by the O-donor. In the work reported here we have studied the photochemistry of $(Me_2Si)_6$ in argon matrices doped with 2–20% of the O-donors C_2H_4O or N_2O and we find that at these higher O-donor concentrations very different chemistry is observed from that seen at low O-donor concentrations.

2. Experimental

Experiments were carried out using the matrix isolation apparatus at University of Reading which has been described elsewhere [7,8]. Gas mixtures were prepared using standard vacuum line techniques. $(Me_2Si)_6$ and $(Me_2SiO)_6$ were deposited by the slow spray-on method with the sample held at room temperature and the matrix gas flowed over the sample at a pressure of ca. 7.5×10^{-5} mmHg. A deposition time of ca. 90 min was employed. The sample was deposited onto a CsI window held at ca. 12 K by means of an Air Products 202OSP "Displex" closed-cycle helium refrigerator. The deposit was irradiated using a low-pressure mercury lamp (Hanovia), which has one very intense line at around 254 nm, lines of moderate intensity at 365, 405, 434, 546 and 577 nm, and weak lines at 248, 265, 297, 302 and 334 nm. In order to cut out most of the longer wavelength emission a filter was employed consisting of two 25 mm quartz cells filled with saturated solutions of $CoSO_4$ and $NiSO_4$. This transmitted in the region 220–300 nm only. Infrared spectra were recorded using a Perkin–Elmer model 983 dispersive spectrometer with a typical accuracy of ± 2 cm^{-1}.

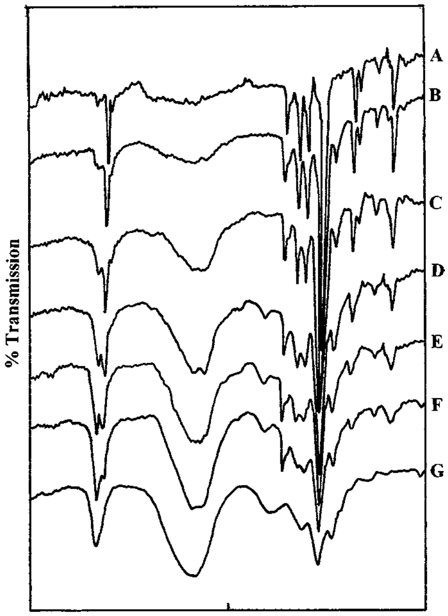

Fig. 1. Infrared transmission spectra in the region 1400–600 cm^{-1} seen upon photolysis of $(Me_2Si)_6$ (at a concentration of ca. 1%) in an argon matrix doped with 20% ethylene oxide. The matrix support was a CsI window at 12 K and the photolysis source used was a low-pressure mercury lamp with output centred at $\lambda = 254$ nm. Spectrum **A**, after deposition; spectrum **B**, after photolysis for 1 h; spectrum **C**, after photolysis for 3 h; spectrum **D**, after photolysis for 7 h; spectrum **E**, after photolysis for 10 h; spectrum **F**, after photolysis for 20 h; spectrum **G**, after allowing the matrix to warm to room temperature over a period of 4 h.

3. Results and discussion

When an argon matrix (at ca. 12 K) doped with ca. 20% ethylene oxide (C_2H_4O) and containing a low concentration (ca. 1%) of the cyclic hexamer $(Me_2Si)_6$ is subject to prolonged irradiation using a low-pressure mercury lamp with output around $\lambda = 250$ nm the infrared bands of the starting compound gradually decay in intensity. At the same time new infrared bands appear and grow. These spectral changes are illustrated in Fig. 1 while the band positions and their assignments are listed in Table 1. It may be seen from Fig. 1 that after about 20 h of photolysis the bands of the starting compound have decayed to about half of their original intensity. Several prominent bands are observed which are assigned to a product **A**. Most striking is a broad band around 1070 cm^{-1} which is likely to arise from a ν(Si–O–Si) mode of a polymeric silicone species [9,10].

Two conclusions may immediately be drawn from these spectra. First, **A** is not the monomeric silanone ($Me_2Si{=}O$) which is generated when $(Me_2Si)_6$ is irradiated in argon matrices doped with 0.5–1% N_2O or C_2H_4O [6]. Second, it would appear that there is only one product (**A**) formed in our experiments. This conclusion may be drawn from the fact that all new bands seen in the infrared spectra (i.e. those not belonging to starting materials) appear and grow at the same rate and there is no *clear* sign of any different bands seen at shorter photolysis times (but see later).

A likely candidate for **A** is the cyclic siloxane $(Me_2SiO)_6$—known as D_6—which contains a 12-membered ring with alternating Si and O atoms. An experiment was therefore carried out in which an authentic sample of D_6 was isolated in an argon matrix at ca. 12 K. The observed spectrum is illustrated in Fig. 2, while the band positions are listed in Table 1. The strong similarity between this spectrum and the spectrum of **A** confirms that **A** is indeed D_6. Our spectra of **A** are also similar to those previously recorded for *liquid* D_6 [9]. Further evidence for the nature of **A** comes from the result of annealing experiments. No change is seen in the spectrum of **A** upon annealing. Indeed if the matrix is allowed to warm to room temperature over a period of 4 h so that all of the matrix gas is lost, then the only changes to be observed are a broadening of the bands

Table 1
Infrared bands (3000–600 cm^{-1}) [a] seen to appear upon photolysis of $(Me_2Si)_6$ in argon matrices doped with ca. 20% C_2H_4O or N_2O compared with infrared bands of authentic samples of $(Me_2Si)_6$ and $(Me_2SiO)_6$

$(Me_2Si)_6$	$(Me_2SiO)_6$	N_2O 20% product [b]	C_2H_4O 20% product [c]	C_2H_4O 2% product	Approximate description [d,e]
2945 (m)	2945 (m)	[f]	[f]	[f]	$\nu(CH)$
2885 (m)	2883 (m)	[f]	[f]	[f]	$\nu(CH)$
1399 (m)	1399 (w)	[f]	[f]	[f]	$\delta(CH_3)$
	1262 (s)	1261 (s)	1260 (s)	1247 (m)	$\delta(CH_3)$
1249 (m)					$\delta(CH_3)$
1238 (m)					$\delta(CH_3)$
	1063 (vs)	1060 (vs)	1062 (vs)	1038 (s)	$\nu_{as}(SiOSi)$
	880 (m)	885 (m) g	888 (m) [g]	[h]	$\rho(CH_3)$
	860 (m)			[h]	$\rho(CH_3)$
847 (m)					$\rho(CH_3)$
830 (m)					$\rho(CH_3)$
	824 (s)	828 (m) [g]	826 (ms) [g]	823 (m)	$\rho(CH_3)$
	811 (s)				$\rho(CH_3)$
799 (s)					$\nu(SiC)$
	795 (m)	785 (m)	785 (m)	782 (wm)	$\nu(SiC)$
736 (m)					$\nu(SiC)$
	725 (w)	[h]			$\nu(SiC)$
721 (w)					$\nu(SiC)$
	702 (w)	705 (vw)	[h]	[h]	$\nu(SiC)$
686 (m)					$\nu(SiC)$
653 (m)					$\nu(SiC)$
628 (w)					$\nu(SiC)$
	614 (w)	612 (vw)	[h]	[h]	$\nu_{sym}(SiOSi)$

[a] ± 2 cm^{-1}.

[b] Product formed by irradiation of $(Me_2Si)_6$ in 20% N_2O-doped Ar matrices.

[c] Product formed by irradiation of $(Me_2Si)_6$ in 20% C_2H_4O-doped Ar matrices.

[d] References: $(Me_2Si)_6$ [4,6,16]; $(Me_2SiO)_6$ [9,17].

[e] Descriptions are approximate: bands in the fingerprint region results from vibrations which are coupled.

[f] Product bands not observed: obscured by starting material bands.

[g] Broad band–lower frequency component seen for pure $(Me_2SiO)_6$ is not observed.

[h] Not observed probably because of lack of intensity.

of **A** (Fig. 1). The match of band position shows that **A** must be a compound which is stable at room temperature, not prone to polymerisation and quite involatile so that it is not pumped off the matrix window over a period of 4 h. All three of these properties are met by D_6.

We repeated our experiments replacing C_2H_4O by N_2O as the matrix dopant—again at a concentration of ca. 20%. Under these conditions we again observed **A** as the reaction product. The observed bands of **A** from both this experiment and also the experiment using N_2O as the oxidant are listed in Table 1.

As mentioned previously, there is a precedent for our observed matrix chemistry from previous work carried out in solution [10]. Alnaimi and Weber have observed six products upon the oxidation of $(Me_2Si)_6$ using *m*-chloroperbenzoic acid as a source of O atoms. These were cyclic siloxanes containing 1–6 O atoms and were believed to result from the sequential insertion of O atoms into the Si–Si bonds of $(Me_2Si)_6$; the final product being D_6.

We may make some observations regarding the possible mechanism of the reaction in which **A** is formed although our findings do not provide much firm evidence because of the lack of observation of clear bands due to intermediates. The filtered low pressure lamp used in our experiments gives a narrow band output centred around 250 nm. Neither C_2H_4O nor N_2O absorb strongly in this region and irradiation, under these

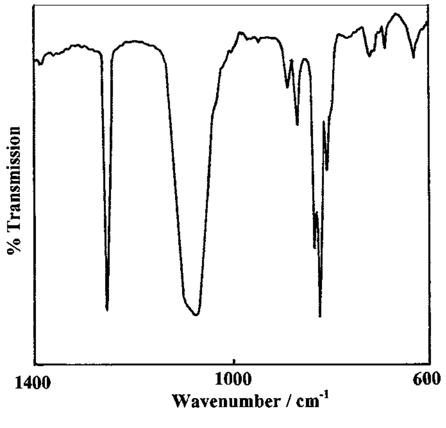

Fig. 2. Infrared transmission spectra in the region 1400–600 cm^{-1} of $(Me_2SiO)_6$ isolated in an argon matrix at a concentration of ca. 1%.

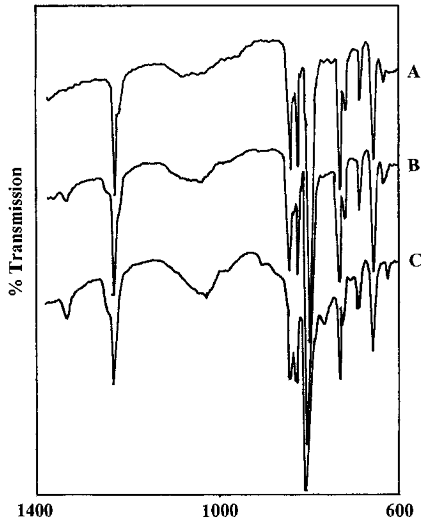

Fig. 3. Infrared transmission spectra in the region 1400–600 cm^{-1} seen upon photolysis of $(Me_2Si)_6$ (at a concentration of ca. 1%) in an argon matrix doped with 2% ethylene oxide. The matrix support was a CsI window at 12 K and the photolysis source used was a low-pressure mercury lamp with output centred at $\lambda = 254$ nm. Spectrum **A**, after deposition; spectrum **B**, after photolysis for 3 h; spectrum **C**, after photolysis for 21 h.

conditions, of argon matrices containing either 20% C_2H_4O or 20% N_2O but no $(Me_2Si)_6$ led to no observable changes in the infrared spectra. However, $(Me_2Si)_6$ is known to absorb at this wavelength resulting in Si–Si bond cleavage [11–13]—probably via σ–σ^* transitions involving electrons in the Si–Si bonds. The first step in the reaction is probably therefore rupture of a Si–Si bond in $(Me_2Si)_6$. In the absence of, or at low concentrations of O-donors the reaction then proceeds to extrude Me_2Si and to form the pentamer $(Me_2Si)_5$ [4]. When low concentrations of O-donors are present this may react to give the silanone $Me_2Si{=}O$ [6]. At higher concentrations of O-donors it is not unreasonable to assume that some form of adduct may be formed between the O-donor and either the starting material or the species with the cleaved Si–Si bond, leading to photosensitisation of the O-donor. This, in turn, may allow insertion of an O atom into the Si–Si bond. That we do not observe any such adduct directly is probably not surprising given (i) that it would doubtless be much more reactive than the starting material or the product, and (ii) that its infrared spectrum would probably be not much different from that of the starting material. We have compared the infrared spectra of $(Me_2Si)_6$ isolated in pure argon and in 20% N_2O- or C_2H_4O-doped argon matrices. These spectra show no significant differences. Although there is a slight broadening of bands in the doped matrices, the band positions are identical to within ± 2 cm^{-1}. Thus there is no direct evidence for the formation of an adduct between $(Me_2Si)_6$ and the O-donor which might account for photosensitisation of the O-donor molecule such as was seen, for example, in the oxidation of $M(CO)_6$ (M = Cr, Mo or W) to metal oxides by CO_2 or N_2O upon photolysis at wavelengths too long for the O-donor to absorb [14].

The next reaction steps must involve insertion of O atoms into the remaining Si–Si bonds. Here it is known from Alnaimi and Weber's work that Si–Si bonds adjacent to O atoms are significantly more reactive than those not bonded to oxygen; the insertion of one O atom promotes the insertion of other O atoms [10]. Despite this, Alnaimi and Weber were able to observe and record infrared spectra of all the intermediate species $Me_{12}Si_6O_n$ ($n = 1$–6). While in most regions these species show very similar infrared absorptions, for the strongest band, that arising from ν_{asym}(Si–O–Si), there are differences in the band position as follows: $n = 1$, $\nu = 1040$ cm^{-1}; $n = 2$, $\nu = 1030$ cm^{-1}; $n = 3$, $\nu = 1070$ cm^{-1}; $n = 4$, $\nu = 1065$–1075 cm^{-1}; $n = 5$, $\nu =$ 1065–1070 cm^{-1}; $n = 6$, $\nu = 1060$–1090 cm^{-1} [10]. Close inspection of the spectra illustrated in Fig. 1 reveals that the exact position of the broad band in this region does change slightly as photolysis proceeds. After 6–9 h of photolysis, there are two peaks centred at around 1040 and 1070 cm^{-1}; after ca. 20 h of photolysis, the higher wavenumber feature is dominant and the lower wavenumber feature seems to have disappeared completely after the window has been warmed to room temperature. This provides *some* evidence that there are species with different numbers of O atoms present in the matrix, even if only at low concentrations, and that the species with six O atoms predominates only after prolonged photolysis and annealing. We observe no other features which may be assigned to different products, but this is not too surprising given the known similarity in the infrared spectra of these different oxidation products [10].

In order to search more systematically for intermediates in this reaction we carried out experiments in which $(Me_2Si)_6$ isolated in a 2% C_2H_4O-doped argon matrix was photolysed using the low-pressure mercury lamp. The purpose of this experiment was to limit the concentration of the O-donor in order to attempt to generate less oxygen-rich products. The spectral changes observed when the matrix was photolysed for 21 h are shown in Fig. 3. New bands are seen but these are much weaker than in the case of the 20% C_2H_4O-doped matrix. The principal new bands seen upon photolysis are listed in Table 1. These bands are at similar positions to those seen for the product in 20% C_2H_4O- or 20% N_2O-doped argon matrices. The most significant difference is perhaps the position of the broad band arising from ν(Si–O). In the 2% doped matrix this band is centred around 1038 cm^{-1} which is close to the reported positions of the most intense infrared bands of $Me_{12}Si_6O$ and $Me_{12}Si_6O_2$ [10]. This observation suggests that it is possible preferentially to generate intermediates in this reaction sequence by limiting the concentration of the O donor.

This situation, where a complex—clearly multi-step—oxidation reaction proceeds without clear evidence for intermediates is reminiscent of other matrix reactions e.g. the photo-oxidation of $Mn_2(CO)_{10}$ to Mn_2O_7 in O_2-doped argon matrices [15]. It is typical of reactions where the intermediates are much more reactive than starting material so that their concentrations are necessarily low. It is exacerbated when the infrared spectra of starting materials, intermediates and products are all similar.

Our experiments demonstrate that in matrices doped with high concentrations (ca. 20%) of the O donors C_2H_4O and N_2O, photolysis of $(Me_2Si)_6$ proceeds to form $(Me_2SiO)_6$ by O atom insertion into the Si–Si bonds. At lower O-donor concentrations (ca. 2%) it is possible to form less oxygen-rich products, i.e. $(Me_{12}Si_6O)$ or $(Me_{12}Si_6O_2)$. These findings may be contrasted with the situation where even lower concentrations (0.5–1%) of the same O-donors are present, where the principal product is the monomer $Me_2Si{=}O$ [6]. Our findings also demonstrate that the same chemistry may be observed both in low-temperature matrices and in solution. Previous work had shown quite different oxidation products from $(Me_2Si)_6$ in solution [10] or in matrices [6]. It is the specific reaction conditions in the matrix that determine the products; as the O-donor concentration is increased the reaction begins to mirror that seen in solution.

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