Reaction of Oxides of Nitrogen with Some Silicon Halides and Hydride-halides

By **Bernard J. Aylett,* Ian A. Ellis,** and **John R. Richmond,** Chemistry Department, Westfield College, Hampstead, London NW3 7ST

The interaction of SiF_4, Si_2F_6, $SiCl_4$, Si_2Cl_6, SiH_3I, SiH_3Br, SiF_3I and p-$ClC_6H_4SiH_3$ with nitrogen oxides chosen from N_2O, NO, N_2O_3, N_2O_4, and N_2O_5 has been studied with and without u.v. irradiation. There is very little reaction between SiF_4 and N_2O, NO, N_2O_4, or N_2O_5 at room temperature. Below *ca.* −60°, SiF_4 reacts with N_2O_3 (but not with N_2O_4 or N_2O_5) to give a 1 :1 adduct, probably $NO^+(SiF_4,NO_2)^-$, which dissociates and decomposes above 0°. Both NO and N_2O_4 react with Si_2F_6 to produce $(SiF_3)_2O$ and its disproportionation products, but Si_2Cl_6 with NO, N_2O_3, or N_2O_4, and $SiCl_4$ with NO usually give NOCl and polychloro-siloxanes or -silanes. The iodo-derivatives SiF_3I and SiH_3I chiefly form disiloxanes and N_2O or N_2 with NO, but in the former case some oligomeric fluorosiloxanes including cyclic $(SiF_2O)_2$ are produced with irradiation; SiH_3Br and NO yield SiH_2Br_2 and $(SiH_2O)_n$ (especially $n = 4$) under similar conditions. The reaction of $SiHCl_3$ and NOCl produces HCl, N_2O, and chloro-siloxanes. No clear evidence for isolable Si-nitroso-compounds was obtained in any system.

THERE have been few comprehensive studies of the reactions of nitrogen oxides with simple silicon compounds. Despite early reports [1] that SiF_4 reacted with NO, N_2O_3, N_2O_4, and N_2O_5, Caillat [2] found that N_2O_4 and N_2O_5 were without effect on SiF_4 under a variety of conditions. Also N_2O_4 and NOCl did not react [3-5] with $SiCl_4$, but N_2O_5 did,[6] while $SiHCl_3$ and N_2O_4 rapidly produced NOCl and HCl.[7] In a comparative study, Spialter and Austin [8] showed that a variety of compounds containing Si–H, Si–Si, and Si–C bonds were oxidized by nitrogen oxides at room temperature, and that the general order of reactivity was: $N_2O_4 > N_2O_3 > NO \gg N_2O$. Brief preliminary reports [9,10] have stated that photolysis with NO results in oxidation of SiH_4, Si_2Cl_6, $SiHCl_3$, or Me_3SiCl and formation of NOCl (in the last three cases), N_2O, and possibly N_2.

The silicon-containing product in those cases where reaction occurs is normally silica or a siloxane. In a few cases, however, it has been possible to isolate intermediates. A recent preliminary report [10] describes the characterization of $SiCl_3NO$ from the brief reaction of $SiCl_4$ or Si_2Cl_6 with NO under u.v. irradiation; the other products were $(SiCl_3)_2O$, NOCl, N_2O, and N_2. Two Si-nitroso-compounds, R_3SiNO (R = Ph or $SiMe_3$), have been isolated [11] from the reaction of R_3SiLi and NOCl, but they decompose well below room temperature, probably forming disiloxanes. Intermediates with Si–N bonds have also been proposed (but not isolated) for the siloxane-forming reactions of SiF_2 with NO,[12] $(SiMe_3)_nNMe_{3-n}$ ($n = 1$—3) with NOCl,[13] and $(SiH_3)_2NMe$ with NOCl.[14] Finally, in a thorough study of the mercury-sensitized photolysis of methylsilanes, Nay *et al.*[15] found that added NO resulted in the formation of disiloxanes; with $MeSiH_3$, they were able to isolate a compound formulated as $MeSiH_2ON(SiH_2Me)N(SiH_2Me)OSiH_2Me$, and it was suggested that this arose from $(MeSiH_2ON=)_2$, itself formed by the addition of NO to $MeSiH_2\cdot$ radicals and subsequent dimerization. Decomposition of $(MeSiH_2ON=)_2$ provided a route to the observed $(MeSiH_2)_2O$, N_2, and N_2O.

The present work was undertaken to gain a clearer understanding of reactions of oxides of nitrogen with simple Si–H and Si–halogen compounds. In particular the behaviour of SiF_4 was compared with that of the more studied BF_3,[16] and the possibility that silicon might form analogues of C-nitroso-compounds such as CX_3NO (X = H, F, or Cl) was explored.

EXPERIMENTAL

All reactions were carried out using high-vacuum or dry-box techniques. Pressures were measured with sensitive glass spiral or spoon gauges, and i.r. spectra were recorded on a Perkin-Elmer 337 spectrometer. Products were separated by trap-to-trap distillation or with a 5 ft, jacketed, low-temperature fractionation column,[17] then generally characterized by measurement of vapour density, vapour pressures at various temperatures, and i.r. spectra. For u.v. irradiation, either 150 W or 1 kW sources were used, together with a quartz reaction tube and mercury

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sensitization in most cases: variations are indicated in the Tables.

Tetrafluorosilane,[18] (*p*-chlorophenyl)silane,[19] iodosilane,[19] and di-iodosilane [19] were prepared by literature methods, and the last two were converted into bromo- and dibromosilane by passage over dry mercuric bromide. Trifluoroiodosilane resulted from the reaction [17b] of hydrogen iodide with SiF_3NMe_2. Fluorination of hexachlorodisilane with antimony trifluoride below room temperature yielded crude hexafluorodisilane, which was purified by repeated fractionation from the column at −85°. Oxides of nitrogen were prepared by standard routes and then rigorously dried and fractionated. Reaction of the stoicheiometric quantity of nitric oxide with 1% lithium amalgam with shaking for 40 min led to its complete absorption and formation of a mixture of 'lithium nitrosyl' and mercury.[20]

TABLE 1

Reactions of SiF_4 with nitrogen oxides

SiF_4 mmol	Oxide mmol	Temp. °C	Pressure atm	Irradiation [a]	Time h	Products/mmol
19·5	NO, 39	25	15(g) [b]	No	15	No reaction [e]
19·5	NO, 39	25	6(g)	Yes. P/Hg	0·2	NO; SiF_4; $(SiF_3)_2O$ (0·01)
19·5	NO, 39	25	10(g)	Yes. Q/Hg	0·2	N_2O (trace); NO; SiF_4; $(SiF_3)_2O$ (0·05)
19·0	NO, 38	25	5(g)	No	6550	N_2O (trace); NO; SiF_4; $(SiF_3)_2O$ (1·0)
6·3	N_2O_4, 5·2	25	3(1)	No	120	N_2O_4; SiF_4 (6·2); $(SiF_3)_2O$ (0·05) [e]
12·8	N_2O_5, 7·4	5	3(1)	No	84	O_2 (0·5); N_2O_4; N_2O_5; SiF_4 (12·4); $(SiF_3)_2O$ (0·2)
2·98	N_2O_3, 3·70	−84	−(1)	No	1	Solid adduct; N_2O_3 (0·78) [d]

[a] P, Pyrex reaction vessel. Q, quartz reaction vessel. [b] Phase present during reaction. [c] Red colour below *ca.* −150°. BF_3–NO mixtures are similarly orange at low temperatures (ref. 16*f*). [d] Combining ratio ($SiF_4 : N_2O_3$) 1 : 0·98. Similar stoicheiometry when SiF_4 in excess. I.r. (thin film, −80°): 2120w [$\nu(NO^+)$]; 1380vs, 1290s, 1250s [all $\nu(NO_2^-)$]; 1100w; 1030vs (SiF_4); 1020sh; 750vs,br cm^{-1}. The adduct decomposed at room temperature to give NOCl, SiF_4, and a solid {i.r.: 1370vs [$\nu(NO_2^-)$]; 1100m,br (SiO_2); 1025m; 836w; 824w; 720s,br (SiF_6^{2-}) cm^{-1}}, partly involatile at 300°. [e] Gas-liquid titrations showed no interactions at −64°.

TABLE 2

Reactions of Si_2X_6 (X = F or Cl) with nitrogen oxides

Disilane mmol	Oxide mmol	Temp. °C	Pressure atm	Irradiation [a]	Time h	Products/mmol
Si_2F_6 (5·0)	NO (10·6)	25	4(1) [b]	No	72 [c]	SiF_4; N_2O; NO (0·2); Si_2F_6 (trace); $(SiF_3)_2O$; $(SiF_2O)_n$ [d]· solid $(SiF_2O)_x$ [e]
Si_2F_6 (5·3)	NO (10·6)	25	0·2(g)	Yes. Q/Hg	0·15	SiF_4; N_2O (trace); NO (10·5); Si_2F_6 (5·2); solid (trace)
Si_2F_6 (1·6)	NO (3·3)	25	0·2(g)	Yes. Q/I_2	0·15	N_2O (trace); NO (3·3); Si_2F_6 (1·6)
Si_2F_6 (1·5)	N_2O_4 (1·6)	5	1(g)	No	17	SiF_4 (trace); NO; N_2O_4; Si_2F_6 (0·9); $(SiF_3)_2O$ (trace); solid $(SiF_2O)_x$ (0·0985 g) [e]
Si_2F_6 (1·4)	N_2O_4 (2·6)	25	2(1)	No	12	SiF_2 (trace); N_2O; NO; N_2O_4; $(SiF_3)_2O$ (trace); solid $(SiF_2O)_x$ [e]
Si_2Cl_6 (5·2)	NO (30·3)	25	5(1)	No	16	N_2O; NO (28·7); Si_2Cl_6; $(SiCl_3)_2O$; liquid chlorosiloxanes (0·020 g) [f]
Si_2Cl_6 (4·3)	NO (4·9)	25	1(1)	No	6040	N_2O (2·0); NO (0·8); Si_2Cl_6; $(SiCl_3)_2O$
Si_2Cl_6 (5·0)	NO (4·9)	25	5(1)	Yes. P	0·25	NO (3·7); NOCl; Si_2Cl_6; $(SiCl_3)_2O$; liquid chlorosiloxanes (0·005 g) [f]
Si_2Cl_6 (7·4)	NO (9·3)	25	1·5(1)	Yes. Q/Hg	18	NOCl (9·3); Si_2Cl_6; $(SiCl_3)_2O$ (trace); solid chloro-polysilanes and -siloxanes [g]
Si_2Cl_6 (5·8)	N_2O_4 (0·30)	−3	0·5(1)	No	6000	Incondensible gas (0·30) NOCl (0·59); Si_2Cl_6 (5·3); solid (0·0482 g) [h]
Si_2Cl_6 (5·4)	'N_2O_3' (1·25)	5	1(1)	No	6000 [i]	NOCl (2·4); $SiCl_4$; solid [j]

[a] Pyrex vessel; Q, quartz vessel. [b] Phase present. [c] A red colour appeared after some hours, but disappeared with longer reaction times. The compound responsible for this colour could not be isolated. [d] Refers to volatile oligomers. [e] The solid appeared inert towards hot alkali. On heating to 350° *in vacuo*, it evolved traces of SiF_4 and $(SiF_3)_2O$, but the i.r. spectrum was unchanged. [f] Purple liquid, partly held at −23°. V.P.: 6 mmHg/25°. I.r. (gas) showed bands at 1120, 1082, 808, 765, and 718 cm^{-1}. [g] Involatile at 350° *in vacuo*. [h] Equivalent to 0·24 mmol of 'Si_2Cl_4'. [i] Reaction appeared complete after 5 min. [j] Involatile at 300° *in vacuo*; slowly hydrolysed, giving SiO_2 and HCl.

Reactions of Tetrafluorosilane with Nitrogen Oxides.—SiF_4 and N_2O did not react in the gas phase at 25° even after 10 weeks; after mercury-sensitized irradiation of the mixture at 254 nm for 15 min, the only new products were N_2 and $(SiF_3)_2O$, corresponding to about 0·2% reaction. Representative reactions with other oxides are summarized in Table 1. SiF_4 alone was unaffected by long irradiation.

Reaction of Tetrafluorosilane with 'Lithium Nitrosyl.'—SiF_4 (4·9 mmol) was shaken at 60° for 17 h with the solid derived from 4·9 mmol each of lithium and NO. The nitrogen-containing volatile products were N_2 (0·3 mmol), N_2O (0·2 mmol) and NO (3·9 mmol). The dark grey solid product was shown (qualitative analysis, i.r.) to contain Li^+, SiF_6^{2-}, and fluorosiloxane polymers, together with finely divided mercury.

Reactions of Hexafluoro- and Hexachloro-disilane with Nitrogen Oxides.—Si_2F_6 and NO did not react after 72 h in the gas phase at 25°; systems in which reaction occurred are summarized in Table 2. Control experiments showed that Si_2F_6, Si_2Cl_6, and NO, alone and under the same conditions, were essentially unaffected by gas-phase irradiation.

Reactions of Bromo-, Iodo-, and Trifluoroiodo-silane with

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Nitric Oxide.—There was no reaction after 20 min between these halogenosilanes and nitric oxide at low pressure (*ca.* 0·2 atm) and room temperature. At higher pressures (with a liquid phase present) or with irradiation, reaction proceeded to give the products shown in Table 3. Control experiments showed that irradiation of the halogenosilanes alone under similar conditions merely led to slight (*ca.* 1%) disproportionation.

Other Reactions.—(*a*) An equimolar mixture of $SiCl_4$ and NO produced only a trace of NOCl after 72 h at room temperature; when irradiated for 1·5 h, $SiCl_4$ (7·6 mmol) and NO (8·4 mmol), yielded N_2 (trace), N_2O, NO (6·5 mmol), NOCl (1·3 mmol), $SiCl_4$ (7·2 mmol), $(SiCl_3)_2O$ (trace), and solid (shown by i.r. to be chlorosiloxanes and/or silica).

TABLE 3

Reactions of SiF_3I, SiH_3I, and SiH_3Br with nitric oxide[a]

Silyl derivative mmol	NO mmol	Pressure atm	Irradiation[c]	Time h	Products/mmol
SiF_3I (4·6)	24·4	4(l)[b]	No	720	N_2O; NO (20·6); SiF_4; SiF_3I; SiF_2I_2; I_2; solid fluorosiloxanes.
SiF_3I (2·2)	2·2	1(g)[b]	Yes. Q/Hg	0·25	N_2 (0·4); N_2O; NO; SiF_4; SiF_3I; SiF_2I_2 (trace); $(SiF_3)_2O$; $(SiF_2O)_n$[d]; HgI_2
SiH_3I (7·5)	78	10(l)	No	20[e]	N_2O; NO; SiH_3I (3·0); $(SiH_3)_2O$; Compound *A*[f]; solid siloxanes; I_2
SiH_3I (9·8)	10·0	5(l)	Yes. Q	0·1	N_2O (0·1); NO (9·8); SiH_3I (9·6); $(SiH_3)_2O$ (0·1); I_2
SiH_3I (0·4)	0·6	0·1(g)	Yes. Q/Hg	0·25	H_2 (trace); N_2O; NO; SiH_3I; $(SiH_3)_2O$ (trace); $(SiH_2O)_n$ (trace); HgI_2
SiH_3Br (4·7)	23·2	7(l)	No	2	N_2O; NO; SiH_3Br; $(SiH_3)_2O$; $(SiH_2O)_n$[g]
SiH_3Br (5·9)	13·0	4(l)	No	106	N_2/H_2 (0·2); N_2O; NO (10·5); SiH_3Br (4·6); SiH_2Br_2; $(SiH_3)_2O$ (trace); $(SiH_2O)_n$[g]; solid
SiH_3Br (6·2)[h]	25·9	8(l)	No	21	N_2/H_2 (0·25); N_2O; NO (24·1); SiH_3Br; $(SiH_2O)_n$; solid
SiH_3Br (5·8)	12·2	1·5(g)	Yes. P	0·2	N_2/H_2; N_2O; NO; SiH_3Br; SiH_2Br_2 (0·4); $(SiH_3)_2O$ (trace); $(SiH_2O)_n$[g,i]
SiH_3Br (3·9)	11·1	1(g)	Yes. Q	0·1	N_2/H_2; N_2O; NO; SiH_3Br; SiH_2Br_2; $(SiH_3)_2O$; $(SiH_2O)_n$[g]; solid

[a] All experiments carried out at 25°. [b] Phase present. [c] P, Pyrex vessel. Q, quartz vessel. [d] Pumped from column at −128°, slightly less volatile than $(SiF_3)_2O$; *M*, 170 ± 20; decomposed to solids with essentially no evolution of SiF_4; i.r. (gas): 1170s,br, 1020sh, 990vs,br, 881sh, 875m, 870sh, 425w cm^{-1}. [e] Even after 48 h, $\not> 60\%$ of SiH_3I was oxidized. [f] I.r. (gas): 2210s, 1660s, 1460w, 1295s, 1280sh, 1190m,br, 940vs, 750m,br cm^{-1}. Passed −46°, held at −96°. [g] Chiefly $n = 4$; see text. [h] With tin foil (10 mmol). [i] Found: *M*, 188. Calc. for $(SiH_2O)_4$, 184.

(*b*) When NOCl and an excess of $SiHCl_3$ were irradiated for 1 h, all NOCl was consumed and the products were HCl, N_2O, $SiHCl_3$, $(SiCl_3)_2O$ (trace), and a mixture of chlorosiloxanes. Under similar conditions, $SiHCl_3$ alone was essentially unchanged: after irradiation for 20 h, more than 90% of the starting material was recovered, together with small amounts of H_2 and an almost involatile yellow oil.

(*c*) An equimolar mixture of (chlorophenyl)silane and NO was unchanged after 192 h at room temperature.

RESULTS AND DISCUSSION

Reactions with SiF_4.—Generally, SiF_4 was rather unreactive towards oxides of nitrogen (Table 1); only with N_2O_3 did more than 5% react, even after long reaction times or with irradiation. Small amounts of $(SiF_3)_2O$ no doubt resulted from attack on walls of the vessel by SiF_4, but the formation of some N_2O from NO suggests reaction (1). No NOF was detected: it is

$$2SiF_4 + 4NO \longrightarrow (SiF_3)_2O + N_2O + 2NOF \quad (1)$$

reported [21] to react with glass or silica, forming SiF_4 and N_2O_3. Neither N_2O_4 nor N_2O_5 gave solid adducts with SiF_4 at low temperatures, while gas–liquid titrations of the N_2O_4–SiF_4 system at −64° showed no interaction. The normal decomposition of N_2O_5 to N_2O_4 and oxygen was unaffected by the presence of SiF_4, confirming ref. 2.

With N_2O_3 at −84°, there was immediate formation of a 1 : 1 solid adduct, involatile at that temperature, when either component was initially in excess. At room temperature, the vapour pressure of the adduct exceeded 1 atm; at first, it re-formed unchanged on cooling, but after several such cycles irreversible changes gave a solid, involatile at room temperature. These changes were conveniently followed by observing the i.r. spectrum of a thin film of adduct inside a cooled cell.

A 1 : 1 adduct, possibly NO^+BF_3,ONO^-, is reported between BF_3 and N_2O_3 at low temperatures,[16b] although the final products are given by equation (2).[16e,f] In

$$3N_2O_3 + 8BF_3 \longrightarrow 6NOBF_4 + B_2O_3 \quad (2)$$

this case, the 1 : 1 adduct at −84° is formulated as NO^+SiF_4,ONO^-, with NO_2^- possibly bidentate.[22] The solid decomposition product contains NO_2^- and SiF_6^{2-} (refs. 22 and 23) as well as SiO_2; $(NO)_2SiF_6$, expected by analogy with equation (2) dissociates rather readily,[24] and NOF thus produced can react further with the glass. The observed anions in the solid and NOCl [*] in the volatile products probably arise by reaction with cell windows (*cf.* ref. 25).

The strong interaction between SiF_4 and N_2O_3 and lack of it between SiF_4 and N_2O_4 or N_2O_5 at −64° may be rationalized by noting that these oxides tend to ionize as $NO^+NO_2^-$, $NO^+NO_3^-$, and $NO_2^+NO_3^-$ respectively,[26] and that NO_3^- is a poorer electron donor

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[*] No interaction between NOCl and SiF_4 was observed down to −96°; *cf.* M. E. Peach and T. C. Waddington, *J. Chem. Soc.*, 1963, 799, and ref. 5.

[21] C. Woolf, *Adv. Fluorine Chem.*, 1965, **5**, 1.

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[24] F. Seel and H. Massat, *Z. anorg. Chem.*, 1955, **280**, 186. But see also: A. Chrétian and P. Bouy, *Compt. rend.*, 1958, **246**, 2493 and S. J. Kuhn, *Canad. J. Chem.*, 1967, **45**, 3207.

[25] *Cf.* ref. 16*e*.

[26] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Interscience, New York, 3rd edn., 1972; C. B. Colburn, 'Developments in Inorganic Nitrogen Chemistry,' vol. I, Elsevier, Amsterdam, 1966.

than NO_2^-. Only with more powerful electron acceptors than SiF_4 may adducts such as $NO^+(SnX_4,NO_3)^-$ (X = F or Cl) be isolated.[27]

Lithium nitrosyl, $(LiNO)_x$, now considered[28] to be a *cis*-hyponitrite rather than Li^+NO^-, reacted readily with SiF_4 at 60°. All of the NO was displaced, some 12% having been reduced to nitrogen and 8% to N_2O. The SiF_4 was partly converted into fluorosiloxane polymers and SiF_6^{2-}, but no evidence for SiF_3NO was found. Few reactions of lithium derivatives with SiF_4 have been attempted,[29] but some are thermodynamically favoured and should be useful in synthesis.

Reactions with Si_2X_6 (X = F *or* Cl).—It was hoped that Si_2F_6 might react with NO after photolytic cleavage of the Si–Si bond to give SiF_3NO. In the event, gaseous mixtures were almost unaffected by irradiation in the presence of either mercury or iodine (Table 2). Formation of small amounts of N_2O gave some evidence for reaction according to equation (3), X = F. When a liquid phase was present, almost all Si_2F_6 was consumed, and *ca.* 2 mol of NO were used per mol of Si_2F_6. Besides the products required by equation (3), SiF_4 and fluorosiloxane oligomers arose from disproportionation[30] of $(SiF_3)_2O$; control experiments showed that Si_2F_6 alone yielded only small amounts of SiF_4.

$$Si_2X_6 + 2NO \longrightarrow (SiX_3)_2O + N_2O \qquad (3)$$

By contrast, reaction between Si_2F_6 and N_2O_4 followed equation (4), X = F, in either gaseous or gas-liquid systems. As before, $(SiF_3)_2O$ reacted further to give SiF_4 and $(SiF_2O)_n$; additional reduction of NO to N_2O was observed when a liquid phase was present.

$$Si_2X_6 + \tfrac{1}{2}N_2O_4 \longrightarrow (SiX_3)_2O + NO \qquad (4)$$

With Si_2Cl_6 and NO, relatively brief reaction times led to the formation of a rather involatile purple liquid; under irradiation, some NOCl was also formed. The i.r. spectrum of the liquid showed bands consistent with the formation of $SiCl_3O(SiCl_2O)_nSiCl_3$ and $(SiCl_2O)_n$ species, but gave no indication of any nitrogen-containing product; the origin of the colour is not known. Longer reaction times without irradiation led to products in amounts consistent with equation (3), X = Cl; with long irradiation, almost all NO was converted into NOCl, and the solid product was chiefly chloropolysilanes. Similarly, after prolonged reaction of Si_2Cl_6 with NO + $\tfrac{1}{2}N_2O_4$ (*viz.* 'N_2O_3') or N_2O_4 below room temperature, essentially all nitrogen was present as NOCl (equation 5).

$$Si_2Cl_6 + N_2O_x \longrightarrow 2NOCl + \text{solids} \qquad (5)$$
$$(x = 3 \text{ or } 4)$$

All excess of Si_2Cl_6 disproportionated with N_2O_3, and this may be related to the superior Lewis base strength of NO_2^- referred to earlier.

Reactions with SiF_3I *and* SiH_3X (X = Br *or* I).—Typical reactions between SiF_3I and NO are summarized in Table 3. Equimolar amounts in the gas phase, irradiated in presence of mercury, produced $(SiF_3)_2O$ and fluorosiloxane oligomers from its disproportionation; NO was simultaneously reduced to N_2O and nitrogen. It should be noted that the fluorosiloxane oligomers decomposed to give solid polymers with no evolution of SiF_4. This fact, and their volatility, molecular weight, and i.r. spectra suggest (on the basis of a recent discussion[17b] of fluorosiloxanes) that they are cyclic $(SiF_2O)_n$ species, where *n* is chiefly 2. Without irradiation, appreciable reaction only occurred if a liquid phase was present. No nitrogen or volatile fluorosiloxanes were observed, but, after some weeks, disproportionation of SiF_3I became noticeable. In all cases no evidence for SiF_3NO was found, while the initial reaction could be represented by equation (6) or (7) (with irradiation) (X = F).

$$2SiX_3I + 2NO \longrightarrow (SiX_3)_2O + N_2O + I_2 \qquad (6)$$
$$2SiX_3I + NO \longrightarrow (SiX_3)_2O + \tfrac{1}{2}N_2 + I_2 \qquad (7)$$

Table 3 shows that SiH_3I also reacted with NO according to equation (6) (X = H), either in the liquid phase or in the gas phase with irradiation. In one case, a small amount of liquid was isolated with i.r. absorptions more indicative of a nitrite or nitrate than of a nitroso-derivative.[31] The liquid decomposed readily to $(SiH_3)_2O$ NO, and N_2O; it may be noted that previous attempts to prepare alkylsilicon nitrites or nitrates from alkyliodosilanes and the appropriate silver salt have also led to disiloxane formation.[32]

SiH_3Br gave small amounts of similar products in the gas phase without irradiation, except that no free halogen was observed. As no NOBr was formed either, it appears that bromine was incorporated into the solid products, no doubt by direct reaction with Si–H bonds. In the liquid phase or with irradiation, the chief products were given by equation (8), in which displaced bromine appears as SiH_2Br_2. The i.r. spectra of more volatile samples of $(SiH_2O)_n$ (held at −96°, passed −82°) were similar to that reported[33] when *n* = 4; less volatile samples (held at −82°) may have corresponded to *n* = 5 or 6. If tin foil was added to the unirradiated mixture of SiH_3Br and NO, some $(SiH_2O)_n$ and N_2O (but not SiH_2Br_2) were slowly formed, analogously to reaction (6).

$$2SiH_3Br + 2NO \longrightarrow SiH_2Br_2 + \frac{1}{n}(SiH_2O)_n + N_2O + H_2 \qquad (8)$$

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More highly polymerized $(SiH_2O)_x$ was formed as a yellow oil from SiH_2I_2 and NO after 48 h; iodine was also liberated.

Other Reactions.—Neither $SiCl_4$ nor *p*-$ClC_6H_4SiH_3$ reacted appreciably with NO without irradiation. When $SiCl_4$ and NO were irradiated, however, a complex reaction occurred, represented approximately by equation (9), followed by further abstraction of chlorine from $(SiCl_3)_2O$ by NO, and loss of $SiCl_4$ from $(SiCl_3)_2O$ to give chloropolysiloxanes. Also $SiHCl_3$ and NOCl on irradiation reacted with elimination of HCl as shown in equation (10).† Other less volatile products with Si–H bonds (i.r.) were also formed.

$$2SiCl_4 + 4NO \longrightarrow (SiCl_3)_2O + 2NOCl + N_2O \quad (9)$$

$$2SiHCl_3 + 2NOCl \longrightarrow 2HCl + (SiCl_3)_2O + N_2O \quad (10)$$

CONCLUSION

Systems without Irradiation.—Reactivity of nitrogen oxides with respect to SiF_4 falls in the order $N_2O_3 > N_2O_5 > N_2O_4 \geqslant NO \geqslant N_2O$, consistent with that determined by Spialter and Austin[8] for other systems.‡ Here N_2O_3 stands apart in that it forms an adduct at low temperatures.§

Similarly, N_2O_3 is much more reactive towards Si_2Cl_6 than N_2O_4 or, especially, NO. The course of reaction is also different: N_2O_3 and N_2O_4 give NOCl (equations 7 and 8) but NO does not (equation 4). This is reasonably related to the charge separations: $Si^{\delta+}–Cl^{\delta-} + NO^{\delta+}NO_n^{\delta-}$ ($n = 2$ or 3), and it can be predicted that Si_2Cl_6, like $SiCl_4$,[6] will yield nitryl chloride with N_2O_5 ($NO_2^{\delta+}NO_3^{\delta-}$).

With Si_2F_6, it was possible to show that liquid-phase reactions are much faster than gas-phase ones, although the products are generally similar. These observations are consistent with the idea that Si_2X_6 forms a transient intermediate with the nitrogen oxide dimer,[36] *viz.* Si_2X_6,N_2O_x ($X = F$, $x = 2$ or 4; $X = Cl$, $x = 2$), which rearranges to $(SiX_3)_2O$ and N_2O_{x-1}.

Both SiF_3I and SiH_3I slowly give free halogen with NO, but with SiH_3Br any bromine formed rapidly reacts with Si–H bonds. Possibly as a first step, halogen atoms are displaced by NO, since products are generally similar to those from irradiated mixtures. Observed differences between SiH_3I and SiH_3Br are generally consistent with bromine's greater reactivity and the higher Si–Br bond energy (see below).

Systems with Irradiation.—Except in the case of chlorosilanes, results are generally consistent with initial production of $SiX_3\cdot$ radicals; these then react with NO to give SiX_3NO or (more probably) SiX_3ON diradicals. The former can then decompose or the latter can dimerize (as in the scheme of Nay *et al.*[15]) and then decompose, forming N_2O, N_2, and $(SiX_3)_2O$. Cleavage of Si–Si bonds in Si_2F_6 or Si–I bonds in SiF_3I or SiH_3I is easy,[37] and provides a reasonable route to the observed products. Bond dissociation of SiF_4 is much more difficult, and little reaction occurs. With SiH_3Br, Si–H, and Si–Br bonds are of comparable energy,[37] and $SiH_2Br\cdot$ radicals may be formed. These, after addition of NO and dimerization, could form $(SiH_2BrON{=})_2$, which then decomposes to N_2O and $(SiH_2Br)_2O$ [equivalent to $\frac{1}{n}(SiH_2O)_n + SiH_2Br_2$]. The absence of disilanes amongst the products from photolysis of monosilane derivatives suggests that $SiX_3\cdot$ reacts much more rapidly with NO than with itself.

Both $SiCl_4$ and Si_2Cl_6 readily convert NO into NOCl. It seems reasonable to suppose that reaction of $\overset{*}{NO}$ with Si–Cl provides an easy route; NOCl once formed will be stable towards photolysis or further reaction, unlike the corresponding fluoride, bromide, or iodide. Only when NOCl is photolysed with a compound containing Si–H bonds does further reaction occur to give HCl (equation 10).

No clear evidence was obtained for silyl nitrosyls similar to those described by Varma and co-workers.[10] Possibly the compound resulting from SiH_3I and NO was SiH_3NO_2 or SiH_3NO_3; small amounts of coloured products were sometimes observed in reactions between Si_2F_6 or Si_2Cl_6 and NO, but their properties were not those expected for SiX_3NO. In all cases they readily decomposed during attempted separation. Under the conditions used here, the greater Si–O than Si–N bond energy appears decisive in determining the products.‖

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† Irradiated $CHCl_3$ and NOCl yield HCl and CCl_3NO (ref. 34).

‡ These authors carried out their experiments at room temperature, when N_2O_3 is almost entirely dissociated.[35]

§ N_2O_3 also forms a white solid with $SiCl_4$ at −40°: B. J. Aylett and J. R. Richmond, unpublished observations.

‖ Another clear example of this is provided by the reaction[38] of CF_3NO and Me_3SiH, which yields the Si–O–bonded adduct, $CF_3\cdot NH\cdot OSiMe_3$.

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