

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

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The interaction of  $\text{SiF}_4$ ,  $\text{Si}_2\text{F}_6$ ,  $\text{SiCl}_4$ ,  $\text{Si}_2\text{Cl}_6$ ,  $\text{SiH}_3\text{I}$ ,  $\text{SiH}_3\text{Br}$ ,  $\text{SiF}_3\text{I}$  and  $p\text{-ClC}_6\text{H}_4\text{SiH}_3$  with nitrogen oxides chosen from  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_4$ , and  $\text{N}_2\text{O}_5$  has been studied with and without u.v. irradiation. There is very little reaction between  $\text{SiF}_4$  and  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}_4$ , or  $\text{N}_2\text{O}_5$  at room temperature. Below ca.  $-60^\circ$ ,  $\text{SiF}_4$  reacts with  $\text{N}_2\text{O}_3$  (but not with  $\text{N}_2\text{O}_4$  or  $\text{N}_2\text{O}_5$ ) to give a 1:1 adduct, probably  $\text{NO}^+(\text{SiF}_4, \text{NO}_2)^-$ , which dissociates and decomposes above  $0^\circ$ . Both  $\text{NO}$  and  $\text{N}_2\text{O}_4$  react with  $\text{Si}_2\text{F}_6$  to produce  $(\text{SiF}_3)_2\text{O}$  and its disproportionation products, but  $\text{Si}_2\text{Cl}_6$  with  $\text{NO}$ ,  $\text{N}_2\text{O}_3$ , or  $\text{N}_2\text{O}_4$ , and  $\text{SiCl}_4$  with  $\text{NO}$  usually give  $\text{NOCl}$  and polychloro-siloxanes or -silanes. The iodo-derivatives  $\text{SiF}_3\text{I}$  and  $\text{SiH}_3\text{I}$  chiefly form disiloxanes and  $\text{N}_2\text{O}$  or  $\text{N}_2$  with  $\text{NO}$ , but in the former case some oligomeric fluorosiloxanes including cyclic  $(\text{SiF}_2\text{O})_n$  are produced with irradiation;  $\text{SiH}_3\text{Br}$  and  $\text{NO}$  yield  $\text{SiH}_2\text{Br}_2$  and  $(\text{SiH}_2\text{O})_n$  (especially  $n = 4$ ) under similar conditions. The reaction of  $\text{SiHCl}_3$  and  $\text{NOCl}$  produces  $\text{HCl}$ ,  $\text{N}_2\text{O}$ , 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<sup>1</sup> that  $\text{SiF}_4$  reacted with  $\text{NO}$ ,  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_4$ , and  $\text{N}_2\text{O}_5$ , Caillat<sup>2</sup> found that  $\text{N}_2\text{O}_4$  and  $\text{N}_2\text{O}_5$  were without effect on  $\text{SiF}_4$  under a variety of conditions. Also  $\text{N}_2\text{O}_4$  and  $\text{NOCl}$  did not react<sup>3-5</sup> with  $\text{SiCl}_4$ , but  $\text{N}_2\text{O}_5$  did,<sup>6</sup> while  $\text{SiHCl}_3$  and  $\text{N}_2\text{O}_4$  rapidly produced  $\text{NOCl}$  and  $\text{HCl}$ .<sup>7</sup> In a comparative study, Spialter and Austin<sup>8</sup> 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:  $\text{N}_2\text{O}_4 > \text{N}_2\text{O}_3 > \text{NO} \gg \text{N}_2\text{O}$ . Brief preliminary reports<sup>9,10</sup> have stated that photolysis with  $\text{NO}$  results in oxidation of  $\text{SiH}_4$ ,  $\text{Si}_2\text{Cl}_6$ ,  $\text{SiHCl}_3$ , or  $\text{Me}_3\text{SiCl}$  and formation of  $\text{NOCl}$  (in the last three cases),  $\text{N}_2\text{O}$ , and possibly  $\text{N}_2$ .

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<sup>10</sup> describes the characterization of  $\text{SiCl}_3\text{NO}$  from the brief reaction of  $\text{SiCl}_4$  or  $\text{Si}_2\text{Cl}_6$  with  $\text{NO}$  under u.v. irradiation; the other products were  $(\text{SiCl}_3)_2\text{O}$ ,  $\text{NOCl}$ ,  $\text{N}_2\text{O}$ , and  $\text{N}_2$ . Two Si-nitroso-compounds,  $\text{R}_3\text{SiNO}$  ( $\text{R} = \text{Ph}$  or  $\text{SiMe}_3$ ), have been isolated<sup>11</sup> from the reaction of  $\text{R}_3\text{SiLi}$  and  $\text{NOCl}$ , 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  $\text{SiF}_2$  with  $\text{NO}$ ,<sup>12</sup>  $(\text{SiMe}_3)_n\text{-NMe}_{3-n}$  ( $n = 1-3$ ) with  $\text{NOCl}$ ,<sup>13</sup> and  $(\text{SiH}_3)_2\text{NMe}$  with  $\text{NOCl}$ .<sup>14</sup> Finally, in a thorough study of the mercury-sensitized photolysis of methylsilanes, Nay *et al.*<sup>15</sup> found that added  $\text{NO}$  resulted in the formation of disiloxanes; with  $\text{MeSiH}_3$ , they were able to isolate a compound formulated as  $\text{MeSiH}_2\text{ON}(\text{SiH}_2\text{Me})\text{N}(\text{SiH}_2\text{Me})\text{-OSiH}_2\text{Me}$ , and it was suggested that this arose from  $(\text{MeSiH}_2\text{ON}=\text{N})_2$ , itself formed by the addition of  $\text{NO}$  to  $\text{MeSiH}_2\cdot$  radicals and subsequent dimerization. Decomposition of  $(\text{MeSiH}_2\text{ON}=\text{N})_2$  provided a route to the observed  $(\text{MeSiH}_2)_2\text{O}$ ,  $\text{N}_2$ , and  $\text{N}_2\text{O}$ .

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  $\text{SiF}_4$  was compared with that of the more studied  $\text{BF}_3$ ,<sup>16</sup> and the possibility that silicon might form analogues of C-nitroso-compounds such as  $\text{CX}_3\text{NO}$  ( $\text{X} = \text{H}, \text{F}, \text{or Cl}$ ) 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,<sup>17</sup> 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

<sup>12</sup> J. M. Bassler, P. L. Timms, and J. L. Margrave, *Inorg. Chem.*, 1966, **5**, 729.

<sup>13</sup> J. E. Byrne and C. R. Russ, *J. Organometallic Chem.*, 1970, **22**, 357; F. A. Lavallee and C. R. Russ, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 527.

<sup>14</sup> C. Glidewell and D. W. H. Rankin, *J. Chem. Soc. (A)*, 1970, 279.

<sup>15</sup> M. A. Nay, G. N. C. Woodall, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, 1965, **87**, 179.

<sup>16</sup> (a) G. B. Bachman, H. Feuer, B. R. Bluestein, and C. M. Vogt, *J. Amer. Chem. Soc.*, 1955, **77**, 6188; (b) G. B. Bachman and J. Hokama, *ibid.*, 1957, **79**, 4370; (c) G. B. Bachman and J. L. Dever, *ibid.*, 1958, **80**, 5871; (d) R. W. Sprague, A. B. Garrett, and H. H. Sisler, *ibid.*, 1960, **82**, 1059; (e) J. C. Evans, H. W. Rinn, S. J. Kuhn, and G. A. Olah, *Inorg. Chem.*, 1964, **3**, 857; (f) A. B. Ray, *ibid.*, 1967, **6**, 110; (g) S. Ikawa and S. Maeda, *Bull. Chem. Soc. Japan*, 1969, **42**, 1462.

<sup>17</sup> (a) G. E. Coates, *J. Chem. Soc.*, 1951, 2003; (b) B. J. Aylett, I. A. Ellis, and J. R. Richmond, *J.C.S. Dalton*, 1973, 981.

<sup>1</sup> F. Kuhlmann, *Annalen*, 1841, **39**, 319; *Ann. Chim. Phys.*, 1841, [3], **2**, 116.

<sup>2</sup> R. Caillat, *Bull. Soc. chim. France*, 1944, [5], **11**, 453; *Ann. Chim. (France)*, 1945, [11], **20**, 367.

<sup>3</sup> R. Weber, *Pogg. Ann.*, 1863, **118**, 471.

<sup>4</sup> J. F. X. Harold, *J. Amer. Chem. Soc.*, 1898, **20**, 13.

<sup>5</sup> I. R. Beattie and K. M. Livingston, *J. Chem. Soc. (A)*, 1969, 859.

<sup>6</sup> M. Schmeisser, *Angew. Chem.*, 1955, **67**, 493.

<sup>7</sup> A. Besson and L. Fournier, *Compt. rend.*, 1909, **148**, 1192.

<sup>8</sup> L. Spialter and J. D. Austin, *J. Amer. Chem. Soc.*, 1966, **88**, 1828.

<sup>9</sup> K. R. Prasad, B. K. Sahay, A. K. Ray, A. Signorelli, and R. Varma, Abstracts 4th International Conference on Organometallic Chemistry, Bristol, 1969, M10; R. H. Kagann, A. K. Ray, and R. Varma, *ibid.*, M11.

<sup>10</sup> R. Varma and K. H. Kagann, Abstracts 163rd. American Chemical Society National Meeting, Boston, Mass., U.S.A., 1972, INOR 138; R. Varma and P. Orlander, *ibid.*, INOR 139.

<sup>11</sup> J. Jappy and P. N. Preston, *J. Organometallic Chem.*, 1969, **19**, 196.

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

Tetrafluorosilane,<sup>18</sup> (*p*-chlorophenyl)silane,<sup>19</sup> iodosisilane,<sup>19</sup> and di-iodosisilane<sup>19</sup> were prepared by literature methods, and the last two were converted into bromo- and dibromosilane by passage over dry mercuric bromide. Trifluoroiodosisilane resulted from the reaction<sup>17b</sup> of hydrogen iodide with SiF<sub>3</sub>NMe<sub>2</sub>. Fluorination of hexachlorodisilane with antimony trifluoride below room temperature yielded crude

mixture at 254 nm for 15 min, the only new products were N<sub>2</sub> and (SiF<sub>3</sub>)<sub>2</sub>O, corresponding to about 0.2% reaction. Representative reactions with other oxides are summarized in Table 1. SiF<sub>4</sub> alone was unaffected by long irradiation.

*Reaction of Tetrafluorosilane with 'Lithium Nitrosyl.'*—SiF<sub>4</sub> (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<sub>2</sub> (0.3 mmol), N<sub>2</sub>O (0.2 mmol) and NO (3.9 mmol). The dark grey solid

TABLE 1  
Reactions of SiF<sub>4</sub> with nitrogen oxides

SiF <sub>4</sub> mmol	Oxide mmol	Temp. °C	Pressure atm	Irradiation *	Time h	Products/mmol
19.5	NO, 39	25	15(g) <sup>b</sup>	No	15	No reaction *
19.5	NO, 39	25	6(g)	Yes. P/Hg	0.2	NO; SiF <sub>4</sub> ; (SiF <sub>3</sub> ) <sub>2</sub> O (0.01)
19.5	NO, 39	25	10(g)	Yes. Q/Hg	0.2	N <sub>2</sub> O (trace); NO; SiF <sub>4</sub> ; (SiF <sub>3</sub> ) <sub>2</sub> O (0.05)
19.0	NO, 38	25	5(g)	No	6550	N <sub>2</sub> O (trace); NO; SiF <sub>4</sub> ; (SiF <sub>3</sub> ) <sub>2</sub> O (1.0)
6.3	N <sub>2</sub> O <sub>4</sub> , 5.2	25	3(1)	No	120	N <sub>2</sub> O <sub>4</sub> ; SiF <sub>4</sub> (6.2); (SiF <sub>3</sub> ) <sub>2</sub> O (0.05) *
12.8	N <sub>2</sub> O <sub>5</sub> , 7.4	5	3(1)	No	84	O <sub>2</sub> (0.5); N <sub>2</sub> O <sub>4</sub> ; N <sub>2</sub> O <sub>5</sub> ; SiF <sub>4</sub> (12.4); (SiF <sub>3</sub> ) <sub>2</sub> O (0.2)
2.98	N <sub>2</sub> O <sub>3</sub> , 3.70	-84	-(1)	No	1	Solid adduct; N <sub>2</sub> O <sub>3</sub> (0.78) <sup>d</sup>

\* P, Pyrex reaction vessel. Q, quartz reaction vessel. <sup>b</sup> Phase present during reaction. \* Red colour below ca. -150°. BF<sub>3</sub>-NO mixtures are similarly orange at low temperatures (ref. 16f). <sup>d</sup> Combining ratio (SiF<sub>4</sub>:N<sub>2</sub>O<sub>3</sub>) 1:0.98. Similar stoichiometry when SiF<sub>4</sub> in excess. I.r. (thin film, -80°): 2120w [ν(NO<sup>+</sup>)]; 1380vs, 1290s, 1250s [all ν(NO<sub>2</sub><sup>-</sup>)]; 1100w; 1030vs (SiF<sub>4</sub>); 1020sh; 750vs, br cm<sup>-1</sup>. The adduct decomposed at room temperature to give NOCl, SiF<sub>4</sub>, and a solid {i.r.: 1370vs [ν(NO<sub>2</sub><sup>-</sup>)]; 1100m, br (SiO<sub>2</sub>); 1025m; 836w; 824w; 720s, br (SiF<sub>6</sub><sup>2-</sup>) cm<sup>-1</sup>}, partly involatile at 300°. \* Gas-liquid titrations showed no interactions at -64°.

TABLE 2  
Reactions of Si<sub>2</sub>X<sub>6</sub> (X = F or Cl) with nitrogen oxides

Disilane mmol	Oxide mmol	Temp. °C	Pressure atm	Irradiation *	Time h	Products/mmol
Si <sub>2</sub> F <sub>6</sub> (5.0)	NO (10.6)	25	4(1) <sup>b</sup>	No	72 <sup>c</sup>	SiF <sub>4</sub> ; N <sub>2</sub> O; NO (0.2); Si <sub>2</sub> F <sub>6</sub> (trace); (SiF <sub>3</sub> ) <sub>2</sub> O; (SiF <sub>2</sub> O) <sub>n</sub> <sup>d</sup> solid (SiF <sub>2</sub> O) <sub>x</sub> <sup>e</sup>
Si <sub>2</sub> F <sub>6</sub> (5.3)	NO (10.6)	25	0.2(g)	Yes. Q/Hg	0.15	SiF <sub>4</sub> ; N <sub>2</sub> O (trace); NO (10.5); Si <sub>2</sub> F <sub>6</sub> (5.2); solid (trace)
Si <sub>2</sub> F <sub>6</sub> (1.6)	NO (3.3)	25	0.2(g)	Yes. Q/I <sub>2</sub>	0.15	N <sub>2</sub> O (trace); NO (3.3); Si <sub>2</sub> F <sub>6</sub> (1.6)
Si <sub>2</sub> F <sub>6</sub> (1.5)	N <sub>2</sub> O <sub>4</sub> (1.6)	5	1(g)	No	17	SiF <sub>4</sub> (trace); NO; N <sub>2</sub> O <sub>4</sub> ; Si <sub>2</sub> F <sub>6</sub> (0.9); (SiF <sub>3</sub> ) <sub>2</sub> O (trace); solid (SiF <sub>2</sub> O) <sub>x</sub> (0.0985 g) <sup>e</sup>
Si <sub>2</sub> F <sub>6</sub> (1.4)	N <sub>2</sub> O <sub>4</sub> (2.6)	25	2(1)	No	12	SiF <sub>4</sub> (trace); N <sub>2</sub> O; NO; N <sub>2</sub> O <sub>4</sub> ; (SiF <sub>3</sub> ) <sub>2</sub> O (trace); solid (SiF <sub>2</sub> O) <sub>x</sub> <sup>e</sup>
Si <sub>2</sub> Cl <sub>6</sub> (5.2)	NO (30.3)	25	5(1)	No	16	N <sub>2</sub> O; NO (28.7); Si <sub>2</sub> Cl <sub>6</sub> ; (SiCl <sub>3</sub> ) <sub>2</sub> O; liquid chlorosiloxanes (0.020 g) <sup>f</sup>
Si <sub>2</sub> Cl <sub>6</sub> (4.3)	NO (4.9)	25	1(1)	No	6040	N <sub>2</sub> O (2.0); NO (0.8); Si <sub>2</sub> Cl <sub>6</sub> ; (SiCl <sub>3</sub> ) <sub>2</sub> O
Si <sub>2</sub> Cl <sub>6</sub> (5.0)	NO (4.9)	25	5(1)	Yes. P	0.25	NO (3.7); NOCl; Si <sub>2</sub> Cl <sub>6</sub> ; (SiCl <sub>3</sub> ) <sub>2</sub> O; liquid chlorosiloxanes (0.005 g) <sup>f</sup>
Si <sub>2</sub> Cl <sub>6</sub> (7.4)	NO (9.3)	25	1.5(1)	Yes. Q/Hg	18	NOCl (9.3); Si <sub>2</sub> Cl <sub>6</sub> ; (SiCl <sub>3</sub> ) <sub>2</sub> O (trace); solid chloro-poly- silanes and -siloxanes <sup>g</sup>
Si <sub>2</sub> Cl <sub>6</sub> (5.8)	N <sub>2</sub> O <sub>4</sub> (0.30)	-3	0.5(1)	No	6000	Incondensable gas (0.30) NOCl (0.59); Si <sub>2</sub> Cl <sub>6</sub> (5.3); solid (0.0482 g) <sup>h</sup>
Si <sub>2</sub> Cl <sub>6</sub> (5.4)	'N <sub>2</sub> O <sub>3</sub> ' (1.25)	5	1(1)	No	6000 <sup>i</sup>	NOCl (2.4); SiCl <sub>4</sub> ; solid <sup>j</sup>

\* Pyrex vessel; Q, quartz vessel. <sup>b</sup> Phase present. \* A red colour appeared after some hours, but disappeared with longer reaction times. The compound responsible for this colour could not be isolated. <sup>d</sup> Refers to volatile oligomers. \* The solid appeared inert towards hot alkali. On heating to 350° *in vacuo*, it evolved traces of SiF<sub>4</sub> and (SiF<sub>3</sub>)<sub>2</sub>O, but the i.r. spectrum was unchanged. <sup>f</sup> Purple liquid, partly held at -23°. V.P.: 6 mmHg/25°. I.r. (gas) showed bands at 1120, 1082, 808, 765, and 718 cm<sup>-1</sup>. <sup>g</sup> Involatile at 350° *in vacuo*. <sup>h</sup> Equivalent to 0.24 mmol of 'Si<sub>2</sub>Cl<sub>4</sub>'. <sup>i</sup> Reaction appeared complete after 5 min. <sup>j</sup> Involatile at 300° *in vacuo*; slowly hydrolysed, giving SiO<sub>2</sub> and HCl.

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 stoichiometric 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.<sup>20</sup>

*Reactions of Tetrafluorosilane with Nitrogen Oxides.*—SiF<sub>4</sub> and N<sub>2</sub>O did not react in the gas phase at 25° even after 10 weeks; after mercury-sensitized irradiation of the

product was shown (qualitative analysis, i.r.) to contain Li<sup>+</sup>, SiF<sub>6</sub><sup>2-</sup>, and fluorosiloxane polymers, together with finely divided mercury.

*Reactions of Hexafluoro- and Hexachloro-disilane with Nitrogen Oxides.*—Si<sub>2</sub>F<sub>6</sub> 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<sub>2</sub>F<sub>6</sub>, Si<sub>2</sub>Cl<sub>6</sub>, and NO, alone and under the same conditions, were essentially unaffected by gas-phase irradiation.

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

<sup>18</sup> B. J. Aylett, I. A. Ellis, and C. J. Porritt, *J.C.S. Dalton*, 1972, 1953.

<sup>19</sup> B. J. Aylett and I. A. Ellis, *J. Chem. Soc.*, 1960, 3415.

<sup>20</sup> H. Hohn, V. Gutmann, and O. Sova, *Monatsh.*, 1957, 88, 502.

*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<sub>4</sub> and NO produced only a trace of NOCl after 72 h at room temperature; when irradiated for 1.5 h, SiCl<sub>4</sub> (7.6 mmol) and NO (8.4 mmol), yielded N<sub>2</sub> (trace), N<sub>2</sub>O, NO (6.5 mmol),

SiF<sub>4</sub> at low temperatures, while gas-liquid titrations of the N<sub>2</sub>O<sub>4</sub>-SiF<sub>4</sub> system at -64° showed no interaction. The normal decomposition of N<sub>2</sub>O<sub>5</sub> to N<sub>2</sub>O<sub>4</sub> and oxygen was unaffected by the presence of SiF<sub>4</sub>, confirming ref. 2.

With N<sub>2</sub>O<sub>3</sub> 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.

TABLE 3

Reactions of SiF<sub>3</sub>I, SiH<sub>3</sub>I, and SiH<sub>3</sub>Br with nitric oxide <sup>a</sup>

Silyl derivative mmol	NO mmol	Pressure atm	Irradiation <sup>c</sup>	Time h	Products/mmol
SiF <sub>3</sub> I (4.6)	24.4	4(1) <sup>b</sup>	No	720	N <sub>2</sub> O; NO (20.6); SiF <sub>4</sub> ; SiF <sub>3</sub> I; SiF <sub>2</sub> I <sub>2</sub> ; I <sub>2</sub> ; solid fluorosiloxanes.
SiF <sub>3</sub> I (2.2)	2.2	1(g) <sup>b</sup>	Yes. Q/Hg	0.25	N <sub>2</sub> (0.4); N <sub>2</sub> O; NO; SiF <sub>4</sub> ; SiF <sub>3</sub> I; SiF <sub>2</sub> I <sub>2</sub> (trace); (SiF <sub>3</sub> ) <sub>2</sub> O; (SiF <sub>2</sub> O) <sub>n</sub> <sup>d</sup> ; HgI <sub>2</sub>
SiH <sub>3</sub> I (7.5)	78	10(1)	No	20 <sup>e</sup>	N <sub>2</sub> O; NO; SiH <sub>3</sub> I (3.0); (SiH <sub>3</sub> ) <sub>2</sub> O; Compound A <sup>f</sup> ; solid siloxanes; I <sub>2</sub>
SiH <sub>3</sub> I (9.8)	10.0	5(1)	Yes. Q	0.1	N <sub>2</sub> O (0.1); NO (9.8); SiH <sub>3</sub> I (9.6); (SiH <sub>3</sub> ) <sub>2</sub> O (0.1); I <sub>2</sub>
SiH <sub>3</sub> I (0.4)	0.6	0.1(g)	Yes. Q/Hg	0.25	H <sub>2</sub> (trace); N <sub>2</sub> O; NO; SiH <sub>3</sub> I; (SiH <sub>3</sub> ) <sub>2</sub> O (trace); (SiH <sub>2</sub> O) <sub>n</sub> (trace); HgI <sub>2</sub>
SiH <sub>3</sub> Br (4.7)	23.2	7(1)	No	2	N <sub>2</sub> O; NO; SiH <sub>3</sub> Br; (SiH <sub>3</sub> ) <sub>2</sub> O; (SiH <sub>2</sub> O) <sub>n</sub> <sup>g</sup>
SiH <sub>3</sub> Br (5.9)	13.0	4(1)	No	106	N <sub>2</sub> /H <sub>2</sub> (0.2); N <sub>2</sub> O; NO (10.5); SiH <sub>3</sub> Br (4.6); SiH <sub>2</sub> Br <sub>2</sub> ; (SiH <sub>3</sub> ) <sub>2</sub> O (trace); (SiH <sub>2</sub> O) <sub>n</sub> <sup>g</sup> ; solid
SiH <sub>3</sub> Br (6.2) <sup>h</sup>	25.9	8(1)	No	21	N <sub>2</sub> /H <sub>2</sub> (0.25); N <sub>2</sub> O; NO (24.1); SiH <sub>3</sub> Br; (SiH <sub>2</sub> O) <sub>n</sub> ; solid
SiH <sub>3</sub> Br (5.8)	12.2	1.5(g)	Yes. P	0.2	N <sub>2</sub> /H <sub>2</sub> ; N <sub>2</sub> O; NO; SiH <sub>3</sub> Br; SiH <sub>2</sub> Br <sub>2</sub> (0.4); (SiH <sub>3</sub> ) <sub>2</sub> O (trace); (SiH <sub>2</sub> O) <sub>n</sub> <sup>g</sup> ; <sup>i</sup>
SiH <sub>3</sub> Br (3.9)	11.1	1(g)	Yes. Q	0.1	N <sub>2</sub> /H <sub>2</sub> ; N <sub>2</sub> O; NO; SiH <sub>3</sub> Br; SiH <sub>2</sub> Br <sub>2</sub> ; (SiH <sub>3</sub> ) <sub>2</sub> O; (SiH <sub>2</sub> O) <sub>n</sub> <sup>g</sup> ; solid

<sup>a</sup> All experiments carried out at 25°. <sup>b</sup> Phase present. <sup>c</sup> P, Pyrex vessel. Q, quartz vessel. <sup>d</sup> Pumped from column at -128°, slightly less volatile than (SiF<sub>3</sub>)<sub>2</sub>O; *M*, 170 ± 20; decomposed to solids with essentially no evolution of SiF<sub>4</sub>; i.r. (gas): 1170s,br, 1020sh, 990vs,br, 881sh, 875m, 870sh, 425w cm<sup>-1</sup>. <sup>e</sup> Even after 48 h, >60% of SiH<sub>3</sub>I was oxidized. <sup>f</sup> I.r. (gas): 2210s, 1660s, 1460w, 1295s, 1280sh, 1190m,br, 940vs, 750m,br cm<sup>-1</sup>. Passed -46°, held at -96°. <sup>g</sup> Chiefly *n* = 4; see text. <sup>h</sup> With tin foil (10 mmol). <sup>i</sup> Found: *M*, 188. Calc. for (SiH<sub>2</sub>O)<sub>4</sub>, 184.

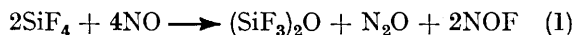
NOCl (1.3 mmol), SiCl<sub>4</sub> (7.2 mmol), (SiCl<sub>3</sub>)<sub>2</sub>O (trace), and solid (shown by i.r. to be chlorosiloxanes and/or silica).

(b) When NOCl and an excess of SiHCl<sub>3</sub> were irradiated for 1 h, all NOCl was consumed and the products were HCl, N<sub>2</sub>O, SiHCl<sub>3</sub>, (SiCl<sub>3</sub>)<sub>2</sub>O (trace), and a mixture of chlorosiloxanes. Under similar conditions, SiHCl<sub>3</sub> alone was essentially unchanged: after irradiation for 20 h, more than 90% of the starting material was recovered, together with small amounts of H<sub>2</sub> 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<sub>4</sub>.*—Generally, SiF<sub>4</sub> was rather unreactive towards oxides of nitrogen (Table 1); only with N<sub>2</sub>O<sub>3</sub> did more than 5% react, even after long reaction times or with irradiation. Small amounts of (SiF<sub>3</sub>)<sub>2</sub>O no doubt resulted from attack on walls of the vessel by SiF<sub>4</sub>, but the formation of some N<sub>2</sub>O from NO suggests reaction (1). No NOF was detected: it is



reported <sup>21</sup> to react with glass or silica, forming SiF<sub>4</sub> and N<sub>2</sub>O<sub>3</sub>. Neither N<sub>2</sub>O<sub>4</sub> nor N<sub>2</sub>O<sub>5</sub> gave solid adducts with

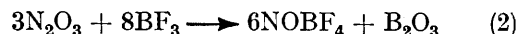
<sup>21</sup> No interaction between NOCl and SiF<sub>4</sub> was observed down to -96°; *cf.* M. E. Peach and T. C. Waddington, *J. Chem. Soc.*, 1963, 799, and ref. 5.

<sup>22</sup> C. Woolf, *Adv. Fluorine Chem.*, 1965, 5, 1.

<sup>23</sup> K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' Wiley, New York, 1963; D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 1964, 3, 1389; 1965, 4, 721.

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<sup>+</sup>BF<sub>3</sub>ONO<sup>-</sup>, is reported between BF<sub>3</sub> and N<sub>2</sub>O<sub>3</sub> at low temperatures,<sup>16b</sup> although the final products are given by equation (2).<sup>16c,f</sup> In



this case, the 1:1 adduct at -84° is formulated as NO<sup>+</sup>SiF<sub>4</sub>ONO<sup>-</sup>, with NO<sub>2</sub><sup>-</sup> possibly bidentate.<sup>22</sup> The solid decomposition product contains NO<sub>2</sub><sup>-</sup> and SiF<sub>6</sub><sup>2-</sup> (refs. 22 and 23) as well as SiO<sub>2</sub>; (NO)<sub>2</sub>SiF<sub>6</sub>, expected by analogy with equation (2) dissociates rather readily,<sup>24</sup> 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<sub>4</sub> and N<sub>2</sub>O<sub>3</sub> and lack of it between SiF<sub>4</sub> and N<sub>2</sub>O<sub>4</sub> or N<sub>2</sub>O<sub>5</sub> at -64° may be rationalized by noting that these oxides tend to ionize as NO<sup>+</sup>NO<sub>2</sub><sup>-</sup>, NO<sup>+</sup>NO<sub>3</sub><sup>-</sup>, and NO<sub>2</sub><sup>+</sup>NO<sub>3</sub><sup>-</sup> respectively,<sup>26</sup> and that NO<sub>3</sub><sup>-</sup> is a poorer electron donor

<sup>23</sup> G. M. Begun and A. C. Rutenberg, *Inorg. Chem.*, 1967, 6, 2212 and references therein.

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

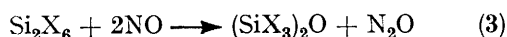
<sup>25</sup> *Cf.* ref. 16e.

<sup>26</sup> 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  $\text{NO}_2^-$ . Only with more powerful electron acceptors than  $\text{SiF}_4$  may adducts such as  $\text{NO}^+(\text{SnX}_4, \text{NO}_3)^-$  ( $X = \text{F}$  or  $\text{Cl}$ ) be isolated.<sup>27</sup>

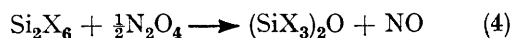
Lithium nitrosyl,  $(\text{LiNO})_x$ , now considered<sup>28</sup> to be a *cis*-hyponitrite rather than  $\text{Li}^+\text{NO}^-$ , reacted readily with  $\text{SiF}_4$  at  $60^\circ$ . All of the  $\text{NO}$  was displaced, some 12% having been reduced to nitrogen and 8% to  $\text{N}_2\text{O}$ . The  $\text{SiF}_4$  was partly converted into fluorosiloxane polymers and  $\text{SiF}_6^{2-}$ , but no evidence for  $\text{SiF}_3\text{NO}$  was found. Few reactions of lithium derivatives with  $\text{SiF}_4$  have been attempted,<sup>29</sup> but some are thermodynamically favoured and should be useful in synthesis.

*Reactions with  $\text{Si}_2\text{X}_6$  ( $X = \text{F}$  or  $\text{Cl}$ ).*—It was hoped that  $\text{Si}_2\text{F}_6$  might react with  $\text{NO}$  after photolytic cleavage of the Si-Si bond to give  $\text{SiF}_3\text{NO}$ . 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  $\text{N}_2\text{O}$  gave some evidence for reaction according to equation (3),  $X = \text{F}$ . When a liquid phase was present, almost all  $\text{Si}_2\text{F}_6$  was consumed, and *ca.* 2 mol of  $\text{NO}$  were used per mol of  $\text{Si}_2\text{F}_6$ . Besides the products required by equation (3),  $\text{SiF}_4$  and fluoro-



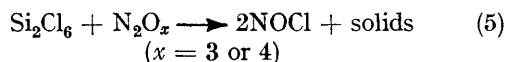
siloxane oligomers arose from disproportionation<sup>30</sup> of  $(\text{SiF}_3)_2\text{O}$ ; control experiments showed that  $\text{Si}_2\text{F}_6$  alone yielded only small amounts of  $\text{SiF}_4$ .

By contrast, reaction between  $\text{Si}_2\text{F}_6$  and  $\text{N}_2\text{O}_4$  followed equation (4),  $X = \text{F}$ , in either gaseous or gas-liquid



systems. As before,  $(\text{SiF}_3)_2\text{O}$  reacted further to give  $\text{SiF}_4$  and  $(\text{SiF}_2\text{O})_n$ ; additional reduction of  $\text{NO}$  to  $\text{N}_2\text{O}$  was observed when a liquid phase was present.

With  $\text{Si}_2\text{Cl}_6$  and  $\text{NO}$ , relatively brief reaction times led to the formation of a rather involatile purple liquid; under irradiation, some  $\text{NOCl}$  was also formed. The i.r. spectrum of the liquid showed bands consistent with the formation of  $\text{SiCl}_3\text{O}(\text{SiCl}_2\text{O})_n\text{SiCl}_3$  and  $(\text{SiCl}_2\text{O})_n$  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),  $X = \text{Cl}$ ; with long irradiation, almost all  $\text{NO}$  was converted into  $\text{NOCl}$ , and the solid product was chiefly chloropolysilanes. Similarly, after prolonged reaction of  $\text{Si}_2\text{Cl}_6$  with  $\text{NO} + \frac{1}{2}\text{N}_2\text{O}_4$  (*viz.* ' $\text{N}_2\text{O}_3$ ') or  $\text{N}_2\text{O}_4$  below room temperature, essentially all nitrogen was present as  $\text{NOCl}$  (equation 5).



All excess of  $\text{Si}_2\text{Cl}_6$  disproportionated with  $\text{N}_2\text{O}_3$ , and this

<sup>27</sup> C. C. Addison and W. B. Simpson, *J. Chem. Soc. (A)*, 1966, 775; R. D. Peacock and I. L. Wilson, *ibid.*, 1969, 2030.

<sup>28</sup> J. Goubeau and K. Laitenberger, *Z. anorg. Chem.*, 1963, **320**, 78; N. Gee, D. Nicholls, and V. Vincent, *J. Chem. Soc.*, 1964, 5897.

<sup>29</sup> U. Wannagat, H. Bürger, and F. Höfler, *Monatsh.*, 1968, **99**, 1198; N. Wiberg and B. Neruda, Abstracts International Symposium Organosilicon Chemistry, Prague, 1965, p. 232.

may be related to the superior Lewis base strength of  $\text{NO}_2^-$  referred to earlier.

*Reactions with  $\text{SiF}_3\text{I}$  and  $\text{SiH}_3\text{X}$  ( $X = \text{Br}$  or  $\text{I}$ ).*—Typical reactions between  $\text{SiF}_3\text{I}$  and  $\text{NO}$  are summarized in Table 3. Equimolar amounts in the gas phase, irradiated in presence of mercury, produced  $(\text{SiF}_3)_2\text{O}$  and fluorosiloxane oligomers from its disproportionation;  $\text{NO}$  was simultaneously reduced to  $\text{N}_2\text{O}$  and nitrogen. It should be noted that the fluorosiloxane oligomers decomposed to give solid polymers with no evolution of  $\text{SiF}_4$ . This fact, and their volatility, molecular weight, and i.r. spectra suggest (on the basis of a recent discussion<sup>17b</sup> of fluorosiloxanes) that they are cyclic  $(\text{SiF}_2\text{O})_n$  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  $\text{SiF}_3\text{I}$  became noticeable. In all cases no evidence for  $\text{SiF}_3\text{NO}$  was found, while the initial reaction could be represented by equation (6) or (7) (with irradiation) ( $X = \text{F}$ ).

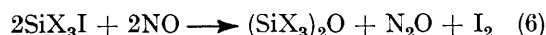
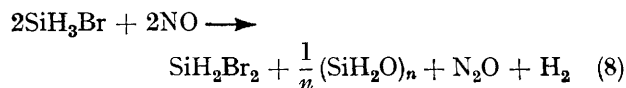


Table 3 shows that  $\text{SiH}_3\text{I}$  also reacted with  $\text{NO}$  according to equation (6) ( $X = \text{H}$ ), either in the liquid phase or in the gas phase with irradiation. In one case, a small amount of liquid was isolated with i.r. absorptions more indicative of a nitrite or nitrate than of a nitroso-derivative.<sup>31</sup> The liquid decomposed readily to  $(\text{SiH}_3)_2\text{O}$ ,  $\text{NO}$ , and  $\text{N}_2\text{O}$ ; 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.<sup>32</sup>

$\text{SiH}_3\text{Br}$  gave small amounts of similar products in the gas phase without irradiation, except that no free halogen was observed. As no  $\text{NOBr}$  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  $\text{SiH}_2\text{Br}_2$ . The i.r. spectra of more volatile samples of  $(\text{SiH}_2\text{O})_n$  (held at  $-96^\circ$ , passed  $-82^\circ$ ) were similar to that reported<sup>33</sup> when  $n = 4$ ; less volatile samples (held at  $-82^\circ$ ) may have corresponded to  $n = 5$  or 6. If tin foil was added to the unirradiated mixture of  $\text{SiH}_3\text{Br}$  and  $\text{NO}$ , some  $(\text{SiH}_2\text{O})_n$  and  $\text{N}_2\text{O}$  (but not  $\text{SiH}_2\text{Br}_2$ ) were slowly formed, analogously to reaction (6).

<sup>30</sup> H. S. Booth and R. S. Osten, *J. Amer. Chem. Soc.*, 1945, **67**, 1091, and other citations in ref. 17b.

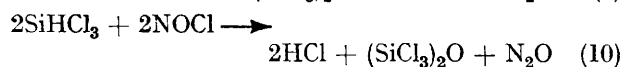
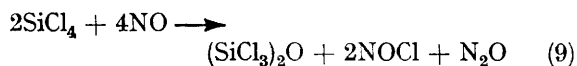
<sup>31</sup> L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Methuen, London, 2nd edn., 1960.

<sup>32</sup> C. Eaborn, *J. Chem. Soc.*, 1950, 3077; M. Schmidt and H. Schmidbaur, *Angew. Chem.*, 1959, **71**, 220.

<sup>33</sup> H. J. Campbell-Ferguson, *J. Inorg. Nuclear Chem.*, 1965, **27**, 2121.

More highly polymerized  $(\text{SiH}_2\text{O})_x$  was formed as a yellow oil from  $\text{SiH}_2\text{I}_2$  and NO after 48 h; iodine was also liberated.

*Other Reactions.*—Neither  $\text{SiCl}_4$  nor *p*- $\text{ClC}_6\text{H}_4\text{SiH}_3$  reacted appreciably with NO without irradiation. When  $\text{SiCl}_4$  and NO were irradiated, however, a complex reaction occurred, represented approximately by equation (9), followed by further abstraction of chlorine from  $(\text{SiCl}_3)_2\text{O}$  by NO, and loss of  $\text{SiCl}_4$  from  $(\text{SiCl}_3)_2\text{O}$  to give chloropolysiloxanes. Also  $\text{SiHCl}_3$  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.



#### CONCLUSION

*Systems without Irradiation.*—Reactivity of nitrogen oxides with respect to  $\text{SiF}_4$  falls in the order  $\text{N}_2\text{O}_3 > \text{N}_2\text{O}_5 > \text{N}_2\text{O}_4 \geq \text{NO} \geq \text{N}_2\text{O}$ , consistent with that determined by Spialter and Austin<sup>8</sup> for other systems.‡ Here  $\text{N}_2\text{O}_3$  stands apart in that it forms an adduct at low temperatures.§

Similarly,  $\text{N}_2\text{O}_3$  is much more reactive towards  $\text{Si}_2\text{Cl}_6$  than  $\text{N}_2\text{O}_4$  or, especially, NO. The course of reaction is also different:  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_4$  give NOCl (equations 7 and 8) but NO does not (equation 4). This is reasonably related to the charge separations:  $\text{Si}^{\delta+}\text{Cl}^{\delta-} + \text{NO}^{\delta+}\text{NO}_n^{\delta-}$  ( $n = 2$  or  $3$ ), and it can be predicted that  $\text{Si}_2\text{Cl}_6$ , like  $\text{SiCl}_4$ ,<sup>6</sup> will yield nitryl chloride with  $\text{N}_2\text{O}_5$  ( $\text{NO}_2^{\delta+}\text{NO}_3^{\delta-}$ ).

With  $\text{Si}_2\text{F}_6$ , 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  $\text{Si}_2\text{X}_6$  forms a transient intermediate with the nitrogen oxide dimer,<sup>36</sup> *viz.*  $\text{Si}_2\text{X}_6 \cdot \text{N}_2\text{O}_x$  ( $X = \text{F}$ ,  $x = 2$  or  $4$ ;  $X = \text{Cl}$ ,  $x = 2$ ), which rearranges to  $(\text{SiX}_3)_2\text{O}$  and  $\text{N}_2\text{O}_{x-1}$ .

Both  $\text{SiF}_3\text{I}$  and  $\text{SiH}_3\text{I}$  slowly give free halogen with NO, but with  $\text{SiH}_3\text{Br}$  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

† Irradiated  $\text{CHCl}_3$  and NOCl yield HCl and  $\text{CCl}_3\text{NO}$  (ref. 34).

‡ These authors carried out their experiments at room temperature, when  $\text{N}_2\text{O}_3$  is almost entirely dissociated.<sup>35</sup>

§  $\text{N}_2\text{O}_3$  also forms a white solid with  $\text{SiCl}_4$  at  $-40^\circ$ : B. J. Aylett and J. R. Richmond, unpublished observations.

|| Another clear example of this is provided by the reaction<sup>38</sup> of  $\text{CF}_3\text{NO}$  and  $\text{Me}_3\text{SiH}$ , which yields the Si-O-bonded adduct,  $\text{CF}_3\text{NH}\cdot\text{OSiMe}_3$ .

differences between  $\text{SiH}_3\text{I}$  and  $\text{SiH}_3\text{Br}$  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  $\text{SiX}_3\cdot$  radicals; these then react with NO to give  $\text{SiX}_3\text{NO}$  or (more probably)  $\text{SiX}_3\text{ON}$  diradicals. The former can then decompose or the latter can dimerize (as in the scheme of Nay *et al.*<sup>15</sup>) and then decompose, forming  $\text{N}_2\text{O}$ ,  $\text{N}_2$ , and  $(\text{SiX}_3)_2\text{O}$ . Cleavage of Si-Si bonds in  $\text{Si}_2\text{F}_6$  or Si-I bonds in  $\text{SiF}_3\text{I}$  or  $\text{SiH}_3\text{I}$  is easy,<sup>37</sup> and provides a reasonable route to the observed products. Bond dissociation of  $\text{SiF}_4$  is much more difficult, and little reaction occurs. With  $\text{SiH}_3\text{Br}$ , Si-H, and Si-Br bonds are of comparable energy,<sup>37</sup> and  $\text{SiH}_2\text{Br}\cdot$  radicals may be formed. These, after addition of NO and dimerization, could form  $(\text{SiH}_2\text{BrON})_2$ , which then decomposes to  $\text{N}_2\text{O}$  and  $(\text{SiH}_2\text{Br})_2\text{O}$  [equivalent to  $\frac{1}{n}(\text{SiH}_2\text{O})_n + \text{SiH}_2\text{Br}_2$ ]. The absence of disilanes amongst the products from photolysis of monosilane derivatives suggests that  $\text{SiX}_3\cdot$  reacts much more rapidly with NO than with itself.

Both  $\text{SiCl}_4$  and  $\text{Si}_2\text{Cl}_6$  readily convert NO into NOCl.

It seems reasonable to suppose that reaction of  $\text{NO}$  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.<sup>10</sup> Possibly the compound resulting from  $\text{SiH}_3\text{I}$  and NO was  $\text{SiH}_3\text{NO}_2$  or  $\text{SiH}_3\text{NO}_3$ ; small amounts of coloured products were sometimes observed in reactions between  $\text{Si}_2\text{F}_6$  or  $\text{Si}_2\text{Cl}_6$  and NO, but their properties were not those expected for  $\text{SiX}_3\text{NO}$ . 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.||

We thank the S.R.C. for a studentship (to J. R. R.).

[2/2797 Received, 12th December, 1972]

<sup>34</sup> B. W. Tattershall, *Chem. Comm.*, 1970, 1522; *J. Chem. Soc. (A)*, 1970, 3261.

<sup>35</sup> I. R. Beattie, *Progr. Inorg. Chem.*, 1963, 5, 1.

<sup>36</sup> Cf. ref. 26 and J. E. Williams and J. N. Murrell, *J. Amer. Chem. Soc.*, 1971, 93, 7149.

<sup>37</sup> B. J. Aylett, *Adv. Inorg. Chem. Radiochem.*, 1968, 11, 249.

<sup>38</sup> A. C. Delany, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc. (C)*, 1968, 2537.