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REACTIONS OF SILICON MONOXIDE WITH ORGANIC COMPOUNDS

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SUMMARY

Silicon monoxide has been shown to be a very reactive silylene. The gas has been condensed with organic compounds at −196° to give a direct synthesis of silicones. The products are thermally stable, infusible solids in which the silicon monoxide has added across multiple C–C bonds and inserted into C–H, C–halogen, O–H, or N–H bonds. Some of the reactions suggest that diradical intermediates may be formed in the polymerization of silicon monoxide.

INTRODUCTION

Chemical reactions of several silylenes such as SiF_2, $SiCl_2$ and $SiMe_2$ have been reported and reviewed[1] but the chemistry of the well known gaseous species silicon monoxide has not previously been described.

The monomeric gaseous compound is formed[2,3] by heating mixtures of silicon and silica under vacuum at temperatures above 1200°, a convenient source being commercially available solid "silicon monoxide" which is made by condensation of the gas. Recently the infrared spectrum of silicon monoxide condensed in inert gas matrixes has been studied[4,5]. This shows that silicon monoxide polymerizes rapidly even at −243° forming oxygen bridged dimers, trimers and higher polymers, apparently all retaining silylene character. The polymers seem to be more reactive in further polymerization than the monomer.

In this work, it seemed practicable to study reactions of gaseous silicon monoxide with volatile organic compounds by cocondensing the reactants at −196°, a technique of wide application for high temperature species[6]. It was hoped that such reactions would give a new, direct synthesis of silicones.

RESULTS AND DISCUSSION

Gaseous silicon monoxide was made by heating commercial solid "silicon monoxide" under high vacuum at 1200–1400°. The vapor was condensed on a liquid nitrogen cooled cold surface together with a six- to twenty-fold mole excess of the vapor of an organic or inorganic compound. Reaction between silicon monoxide and the other compound occurred on the cold surface and the product was collected after the surface had been warmed to room temperature.

All the reaction products obtained were solids which were infusible, generally insoluble in inert solvents, but often rather hygroscopic. The composition of the solids was slightly variable from run to run but it seemed to be independent of the ratio of the reactants provided that there has been at least a six-fold mole excess of the compound condensed with the silicon monoxide.

Some information about the structure of the solids was obtained from their infrared spectra. However, the spectra were often diffuse and were dominated by very strong broad Si–O bands centered around 1050, 870 and 440 cm^{-1}. If the samples were exposed to air strong O–H bands appeared. A better method for structure determination was quantitative hydrolysis or deuterolysis using 10 *M* NaOH or NaOD at 100–150° which broke all Si–C, Si–N or Si–H bonds. Table 1 summarizes the reactions studied, the composition of the resulting solids, and their hydrolysis or their deuterolysis products.

Reactions with alkenes and alkynes

Silicon monoxide formed white or colorless solids with propene, 1-pentene, and cyclohexene which could be heated in air to 350° before decomposition was detectable and which were completely decomposed only above about 550°. Complete hydrolysis gave a mixture of the original alkene, the corresponding alkane, plus a little hydrogen, as shown in Table 1. The propene/SiO solid was partially hydrolyzed by 2*M* HF and gave some propene plus a little hydrogen. The infrared spectra of the solids showed, in addition to SiO bands, C–H stretching and deformation bands in the ranges of 2850–3020 cm^{-1} and 1370–1450 cm^{-1} respectively, and bands at 2240 cm^{-1} and 2170 cm^{-1} indicating the presence of Si–H bonds.

The results suggest that silicon monoxide attacks alkenes in two ways, adding across the C=C double bond and inserting into the olefinic C–H bonds. It seems likely that silacyclopropane derivatives are first formed in the addition reaction and that these polymerize to six-membered or more complex rings. In this respect silicon monoxide probably behaves like dichlorosilylene which is known to form 1,4-disilacyclohexane derivatives with alkenes[7] and these yield two molecules of the alkanes corresponding to the alkene on vigorous hydrolysis. Moreover, mild hydrolysis of the reaction product of propene and $SiCl_2$ gave a solid with an infrared spectrum identical with that of the propene/SiO polymer except in the Si–H stretch region, strongly suggesting the presence of 1,4-disilacyclohexane rings in the latter.

The insertion reaction is indicated by the presence of Si–H bonds in the products and the reformation of alkenes on hydrolysis. The liberation of hydrogen on hydrolysis is not conclusive proof of the presence of Si–H bonds as unreacted, polymeric silicon monoxide would also liberate hydrogen when dissolved. Insertion into C–H bonds is not a common reaction with silylenes. Dimethylsilylene does give products containing Si–H bonds on reaction with alkenes under some conditions[8] but the mechanism of the $SiMe_2$/alkene reaction may be different from the SiO/alkene reaction. With the former, in addition to small yields of 1,4-disilacyclohexanes and products containing

TABLE 1

SiO CONDENSATES AND THEIR DEUTEROLYSIS OR HYDROLYSIS PRODUCTS

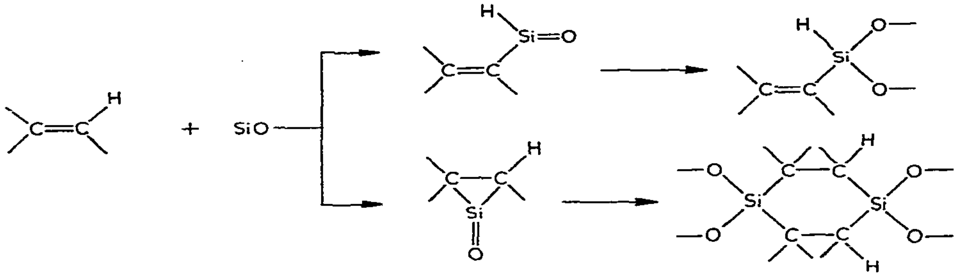
Organic reactant	Approximate composition of solid	Hydrolysis or deuterolysis products	
Propene	$C_3H_6(SiO)_3$	C_3H_5D	(15%)
		CH_3CHDCH_2D	(85%)
1-Pentene	$C_5H_{10}(SiO)_2$	C_5H_9D	(~20%)
		$C_3H_7CHD{-}CH_2D$	(~80%)
Cyclohexene	$C_6H_{10}(SiO)_3$	1-Deuterocyclohexene	(20%)
		1,2-Dideuterocyclohexane	(80%)
Acetylene	$C_2H_2(SiO)_3$	$CH{\equiv}CD$, $DC{\equiv}CD$	(25%)
		$CHD{=}CHD$	(61%)
		CHD_2CHD_2	(14%)
Diphenylacetylene	$C_{14}H_{10}(SiO)_2$	*cis*-PhCD=CDPh	
2,3-Dimethyl-1,4-butadiene	$C_6H_{10}(SiO)_2$	$CH_2DC(CH_3){=}C(CH_3)CH_2D$	
Benzene	$C_6H_6(SiO)_3$	1,4-Dideutero-1,4-cyclohexadiene	(50%)
		C_6H_5D	(50%)
Anthracene	$C_{14}H_{10}(SiO)_2$	$C_{14}H_9D$	(~75%)
		$C_{14}H_{10}D_2$	(~25%)
2,2-Dimethylpropane	$C_5H_{12}(SiO)_{10}$	$C_5H_{11}D$	
Cyclohexane	$C_6H_{12}(SiO)_8$	$C_6H_{11}D$	
1-Chlorobutane	$C_4H_9Cl(SiO)_6$	$C_3H_6DCH_2D$	(~10%)
		C_4H_9D	(~90%)
1-Bromobutane	$C_4H_9Br(SiO)_4$	$C_3H_6DCH_2D$	(10%)
		$C_3H_7CH_2D$	(90%)
Chlorobenzene	$C_6H_5Cl(SiO)_6$	$C_6H_4D_2$	(~10%)
		C_6H_4DCl	(10%)
		C_6H_5D	(~80%)
Bromobenzene	$C_6H_5Br(SiO)_5$	$C_6H_4D_2$	(~5%)
		C_6H_4DBr	(~5%)
		C_6H_5D	(~90%)
Ethanol	$C_2H_5OH(SiO)_4$	C_2H_5OD	
Ammonia	$NH_3(SiO)_4$	ND_3	
		ND_2H	
		NDH_2	
1-Aminobutane	$C_4H_9NH_2(SiO)_4$	C_4H_9NHD	
		$C_4H_9ND_2$	

All SiO condensates (except the condensates of SiO with diphenylacetylene and 2,3-dimethyl-1,4-butadiene), yielded some hydrogen in addition to the listed deuterolysis products.

Under the deuterolysis conditions there was apparently no hydrogen–deuterium exchange of C–H hydrogen atoms.

an $Me_2SiH{-}C{=}C$ group, silacyclopentanes and polymers containing long carbon chains are also produced. On complete hydrolysis these must yield butanes or high alkanes whereas only alkanes containing the same number of carbon atoms as the alkene have been found from hydrolysis of SiO/alkene polymers.

The reaction between an alkene and silicon monoxide can perhaps be represented schematically thus:



It is almost certain that Si=O groups polymerize immediately to form Si–O–Si linked products.

The above scheme implies that the products should have one mole of SiO per mole of alkene, but the observed products contain 2–3 moles of SiO per mole of alkene. Polymerization of the silicon monoxide probably competes with its reaction with the alkene. The polymers first formed are presumably oxygen bridged rings as found in the matrix studies[4,5] but these are still silylenes and may also react with the alkene. As further discussed below, there is a possibility that some of the polymers of silicon monoxide are diradicals of much greater reactivity than the singlet state monomer. The hygroscopic nature of the products suggests they may contain small silicon–oxygen rings derived from silicon monoxide polymers which are unstable and liable to hydrolysis.

The composition and to some extent the structure of the products, is clearly critically dependent on the rate of polymerization of the silicon monoxide relative to the rate of attack of silicon monoxide and its polymers on the alkene. Slight variability in the composition of the solids from run to run and marked differences in the SiO/alkene ratio in the solids with different alkenes are thus to be expected.

Silicon monoxide gave a pyrophoric solid with acetylene. On mild hydrolysis this material liberated acetylene, and under vigorous conditions it formed ethylene and some ethane. Both insertion of silicon monoxide into the C–H bond and addition across the multiple bond must occur as with alkenes.

Diphenylacetylene and silicon monoxide formed two products, a little hexaphenylbenzene and a yellow solid of great thermal stability which decomposed only above 400° in air. The infrared spectrum of the solid showed Si–O and phenyl bands but no Si–H band. Part of the solid dissolved on boiling with wet diethyl ether, dioxane or dimethylformamide. When the solvent was evaporated from the ether solution a fine yellow powder was left which would not redissolve in ether. This had an infrared spectrum similar to the original solid. Analysis of this powder showed a Si/C mole ratio of 1/14 corresponding to one molecule of SiO per molecule of diphenylacetylene. In the original solid this latter ratio was about 2/1. Partial hydrolysis of the original solid presumably formed a soluble silanol which lost water and became insoluble again on removal of the solvent. The exact nature of the species in solution is still being investigated.

Reaction with dienes and aromatic hydrocarbons; *1,4-addition*

The yellow solid formed from silicon monoxide and 2,3-dimethyl-1,3-butadiene was less hygroscopic than most of the reaction products. It showed no Si–H band in the infrared spectrum and gave only one product, 2,3-dimethyl-2-butene on hydrolysis.

The reaction with silicon monoxide is thus formally a 1,4-addition. Atwell and Weyenberg[9] found a similar reaction between 2,3-dimethyl-1,3-butadiene and dimethylsilylene, but they proposed the initial formation of a vinylsilacyclopropane derivative followed by an intramolecular rearrangement to the observed product, a 1-sila-3-cyclopentene. This seems a possible mechanism for the reaction of silicon monoxide with the diene, although the important rearrangement step must have a very low activation energy to occur at the low reaction temperature.

The reaction product between silicon monoxide and benzene was a faintly yellow solid which decomposed only above 500° in air. The infrared spectrum showed Si–H bands at 2240 cm^{-1} and 2180 cm^{-1}. Deuterolysis gave monodeuterobenzene and 3,6-dideutero-1,4-cyclohexadiene. Anthracene and silicon monoxide formed a yellow solid which gave mainly monodeuteroanthracene on deuterolysis.

Silicon monoxide seems to attack benzene and anthracene by inserting into the C–H bonds. With benzene, apparent 1,4-addition occurs as with a diene. However, the type of mechanism suggested above for 1,4-addition to a diene seems less probable with the aromatic compounds. With benzene it would involve a sigmatropic 1,3-shift to give a 7-silanorbornadiene derivative, a reaction unlikely to occur at very low temperatures. Dimethylsilylene does not react with aromatic hydrocarbons but difluorosilylene, which is thought to react via polymeric diradicals[10], adds 1,4 to benzene[11]. Thus, it is very possible that benzene and other aromatic hydrocarbons do not undergo addition reactions with monomeric silicon monoxide but only with its polymers formed in triplet states. Insertion into C–H bonds probably occurs with either monomeric or polymeric silicon monoxide.

Reactions with alkanes

Condensation of silicon monoxide with 2,2-dimethylpropane or cyclohexane gave a white solid in each case, far richer in SiO than corresponding products with unsaturated hydrocarbons. The products were very stable thermally with decomposition starting above 400° for the SiO/cyclohexane condensate and above 500° for the SiO/2,3-dimethylpropane condensate. The infrared spectrum of the solids showed a prominent Si–H band at 2240 cm^{-1} and a weaker band at 2160 cm^{-1}. Vigorous hydrolysis regenerated the hydrocarbon.

Insertion into the C–H bonds of alkanes is a reaction shown by no other silylene. The low efficiency of the insertion suggests again that diradical species possibly formed during the polymerization of silicon monoxide are more likely to be the active molecules than monomeric silicon monoxide.

Reaction with organic halides

The white solids formed from silicon monoxide and 1-bromobutane or bromobenzene were very moisture sensitive, evolving hydrogen bromide. The corresponding products from 1-chlorobutane or chlorobenzene were less rapidly decomposed by moist air. These latter solids were also richer in SiO than the solids derived from the organic bromides indicating a less efficient reaction with silicon monoxide. No bands could be ascribed unambiguously to Si–Cl or Si–Br stretching modes in the infrared spectra of the solids, but each of the solids showed bands at 2240 cm^{-1} and 2160 cm^{-1} indicating the presence of Si–H bonds.

The hydrolysis and deuterolysis products suggest that the main reaction in each case is insertion of silicon monoxide into the carbon–halogen bond. This is accompanied by varying amounts of insertion into a C–H bond of either an unchanged molecule of halide (as with bromo- and chlorobenzene) or a molecule where carbon–halogen insertion of silicon monoxide also occurs.

Condensation of silicon monoxide with tetrafluoroethylene, hexafluorobenzene, or carbon tetrachloride gave products which exploded as they were being warmed to room temperature. The energy for the explosions is undoubtedly supplied by transfer of halogen from carbon to silicon with a large gain in bond energy. Mild explosions have been reported in the reaction of difluorosilylene with hexafluorobenzene[11].

Reactions with compounds containing –OH and –NH– groups

The product from co-condensing water vapor and silicon monoxide was an exceptionally white solid of approximate composition $H_2O(SiO)_3$. No hydrogen or silanes[12] were evolved while the condensate was being warmed to room temperature. The product from methanol and silicon monoxide was a glassy, colorless solid, and ethanol and silicon monoxide formed a white solid. The infrared spectrum of each of these products showed a strong Si–H band at 2240–2250 cm^{-1}.

Ammonia and 1-aminobutane gave white solids with silicon monoxide which were very easily hydrolyzed in air, ammonia or the amine being released. The infrared spectra of the solids showed strong Si–H bands at 2240 cm^{-1} and N–H stretching bands, partly overlapped by O–H bands, around 3360 cm^{-1}.

Insertion of silicon monoxide into O–H or N–H bonds is consistent with its ability to insert into normally much less active C–H bonds. Other silylenes, in general, behave similarly towards compounds containing –NH– or –OH groups.

EXPERIMENTAL

Reagents

Silicon monoxide gas was formed by heating solid "silicon monoxide" (Union Carbide, vacuum outgassed). Organic or inorganic compounds used were at least 99% pure and were outgassed before evaporation into the vacuum system.

Apparatus

Two forms of apparatus were used for the vaporization and reaction of silicon monoxide gas with volatile compounds at $-196°$. These are shown in Fig. 1 and 2.

In the apparatus shown in Fig. 1 the solid "SiO" was heated in an alumina boat inside a 50 mm bore mullite tube furnace with a background pressure of less than 5×10^{-5} mm. In passing down the tube much of the silicon monoxide vapor condensed on the walls of the tube, but about 10% was condensed on a liquid nitrogen cooled cold finger at the end of the tube. Reactants to be condensed with the silicon monoxide were sprayed on to the cold finger from tubes placed near the mouth of the furnace tube. In a typical run 25 mmoles of silicon monoxide was deposited in 5 h and this was co-condensed with a twenty-fold excess of an organic compound.

In the apparatus shown in Fig. 2 the silicon monoxide was vaporized from a resistively heated, molybdenum wire wound, alumina crucible mounted inside a 250 mm diam. stainless steel vacuum chamber, the walls of which were cooled in liquid nitrogen. The background pressure was kept below 5×10^{-6} mm. About 70% of the

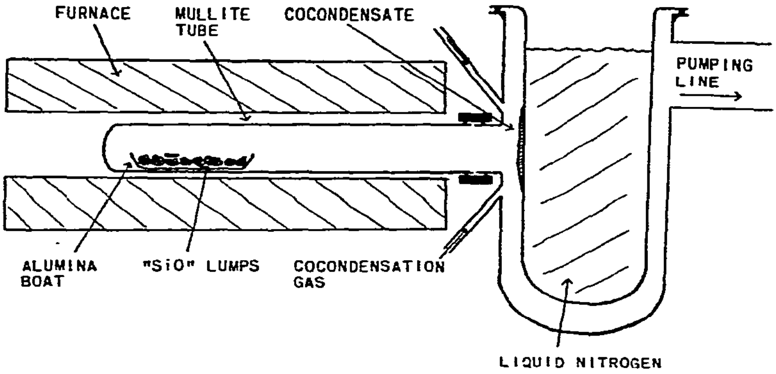


Fig. 1. Apparatus used for the vaporization and reaction of silicon monoxide gas with volatile compounds at −196°.

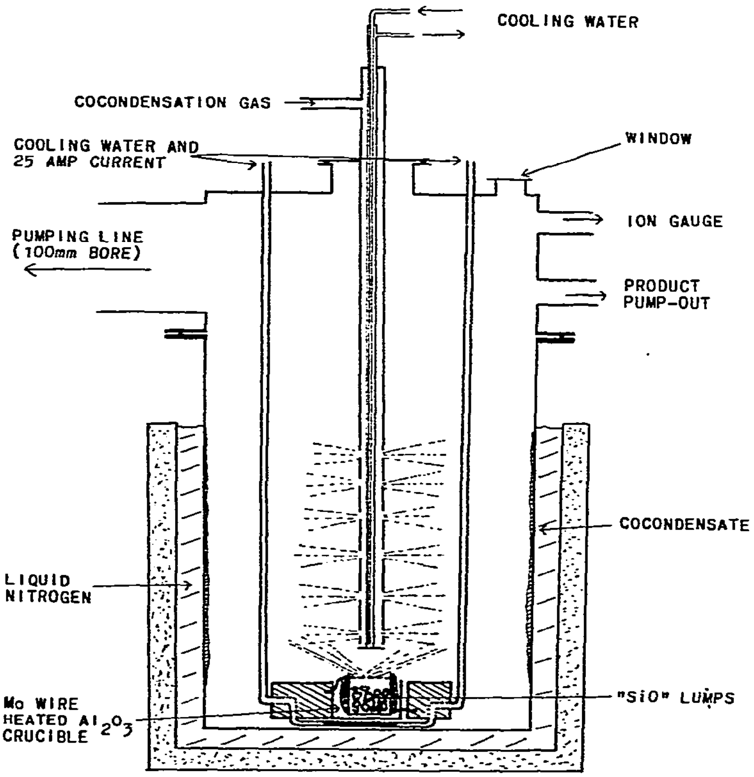


Fig. 2. Apparatus used for the vaporization and reaction of silicon monoxide gas with volatile compounds at −196°.

silicon monoxide evaporated was condensed on the liquid nitrogen cooled walls. In a typical run, 50 mmoles of silicon monoxide were deposited in 15 min along with a six- to twenty-fold excess of another compound sprayed from the center of the vacuum chamber.

With both apparatus the condensate was warmed to room temperature at the end of a run with continuous vacuum pumping to remove unreacted substrate. The product was left on the surface as an involatile solid which has to be scraped off, preferably in a dry nitrogen atmosphere.

In the case of diphenylacetylene and anthracene, organic reactants of low volatility, removal of unreacted substrate was carried out later by extraction with pentane or hexane in a Soxhlet extractor.

Despite the different conditions and rates of deposition of silicon monoxide in the two apparatus the composition and properties of the products obtained in each were very similar.

Characterization of products

The solids scraped off the cold-finger or off the walls of the vacuum chamber (Figs. 1 and 2) were lightly crushed with a pestle and mortar. Any visible pieces of black silicon monoxide which had been blown from the hot zone during the deposition of the solids, were rejected. The resulting ungraded powdered solids proved to be fairly homogeneous in chemical composition. The Si/C mole ratios on different samples of the same solid were reproducible to within ±3%. The solids were very hygroscopic and were exposed to the atmosphere as little as possible before analysis. Carbon, hydrogen, and nitrogen in the samples were analyzed by combustion in oxygen at 1200°. For

TABLE 2

CHARACTERISTIC INFRARED FREQUENCIES OF THE REACTION PRODUCTS OF SILICON MONOXIDE

Reaction product of SiO with:	Infrared frequencies (cm^{-1})
Propene	3020sh, 2960s, 2875s, 2240w, 2170w, 1450m, 1400w, 1370w, 1050vs(b), 880s, 440m.
1-Pentene	3020sh, 2950s, 2240w, 2160w, 1450m, 1400vw, 1375vw, 1050vs(b), 900s, 780s, 420s.
Cyclohexene	2925s, 2850m, 2240w, 2150w, 1450m, 1050vs(b), 900m, 450m.
Diphenylacetylene	3030m, 3020w, 1590m, 1565w, 1485m, 1435m, 1070vs(b), 1025vs(b), 685s.
2,3-Dimethyl-1,4-butadiene	2920s, 2850m, 1450m, 1370m, 1050vs(b), 870w, 450m.
Benzene	3020vw, 2920vw, 2240m, 2180w, 1600m, 1510vw, 1490w, 1430m, 1050vs(b), 690m, 440m.
Anthracene	3050w, 2930w, 2240w, 1600m, 1440w, 1060vs(b), 880m, 750m, 450m.
2,2-Dimethylpropane	2960s, 2885m, 2240m, 2170w, 1460m, 1360m, 1050vs(b), 870m, 800w, 430m.
Cyclohexane	2920s, 2240m, 2170vw, 1450m, 1060vs(b), 870w, 810w, 450m.
1-Chlorobutane	2960s, 2930s, 2870m, 2240m, 2150vw, 1460m, 1400vw, 1380w, 1050vs(b), 870s, 400m.
Chlorobenzene	2240m, 2160vw, 1050vs(b), 870m, 735m, 690m, 430s.
1-Bromobutane	2960s, 2930s, 2870m, 2240m, 2160w, 1460w, 1400vw, 1375w, 1050vw(b), 870m, 410s.
Bromobenzene	2240m, 2160w, 1430w, 1050vs(b), 870m, 725m, 690w.
Water	2250s, 1150sh, 1050vs(b), 820vs, 450m.
Ethanol	3400s, 2980s, 2925m, 2895w, 2240s, 2140w, 1440vw, 1390w, 1050vs(b), 820vs, 450m.
Ammonia	3360m, 2230s, 2160m, 1050vs(b), 860s, 740w, 440m.
1-Aminoburane	3360w, 2980s, 2920s, 2860m, 2230s, 1460m, 1375w, 1050vs(b), 860m, 720w, 430m.

vw = very weak, w = weak, m = medium, s = strong, vs = very strong, b = broad, sh = shoulder.

silicon analysis, samples were fused with Na_2CO_3 and silicon was determined by atomic absorption. Samples for halogen analysis were fused with Na_2O_2 and halogens were determined by the Volhard method. Oxygen was estimated by difference.

Complete hydrolysis or deuterolysis of the Si–C bonds in the products was achieved by heating 100–500 mg samples of the solids with 2–5 ml of a 10 *M* solution of NaOH or NaOD, in a sealed glass ampoule at 150° for up to 4 h. The volatile hydrolysis and deuterolysis products were separated from H_2O or D_2O on a vacuum line or by extraction with solvents, and were then identified and their relative amounts estimated from their mass spectra. The spectra were taken on a Varian M66 or AE1 MS10c2 instrument over a range of electron voltages to aid in the interpretation. Additional information was obtained by infrared spectroscopy (using Perkin–Elmer 257 or GP2 instruments) or by proton NMR spectroscopy at 100 MHz as discussed for specific cases below.

Infrared spectra of the solids were mostly obtained using mulls, but in a few cases transparent flakes of solid could be used. Spectra taken by the two methods were in good agreement. The observed frequencies are listed in Table 2.

Thermogravimetric and differential thermal analysis were carried out on a DuPont 950 Thermogravimetric Analyzer and a Dupont 900 Differential Thermal Analyzer respectively.

Analysis of the solids and their hydrolysis products

SiO + propene. (Found: C, 19.20; H, 3.42; O, 29.36; Si, 48.02%.) Volatile deuterolysis products were separated from D_2O on a vacuum line. The mass spectrum of the volatiles indicated the presence of only dideuteropropane and monodeuteropropene. A pressure of 50 mm of the volatiles was measured out in a constant volume (approx. 30 ml) portion of the vacuum line. This sample of gas was shaken with 3 ml of concentrated H_2SO_4 for 20 min. The unreacted gas then gave a pressure of 43.5 mm. The mass spectrum of this gas was identical with that of 1,2-dideuteropropane formed by deuterolysis of the reaction product of $SiCl_2$ and propene. The infrared spectrum of the original crude mixture of deuterolysis products, after subtraction of the 1,2-dideuteropropane spectrum, was still quite complex and suggested the presence of all three possible monodeuteropropene isomers.

SiO + 1-pentene. (Found: C, 33.61; H, 5.78; O, 22.40; Si, 38.21%.) The volatile deuterolysis products were examined directly by mass spectrometry. The abundance of the ions at *m/e* 29, 30 and 31 suggested a 1,2-dideuteropentene was the main component. An estimated 20% of monodeuteropentene was also present.

SiO + cyclohexene. (Found: C, 34.81; H, 4.94; O, 21.95; Si, 38.30%.) The deuterolysis products were separated into two fractions by GLC using 15% w/w tritolyl phosphate on Chromasorb at 25°. The gas phase infrared spectrum of the smaller fraction showed it to be 1-deuterocyclohexene. The mass spectrum of the larger fraction was clearly that of a dideuterocyclohexane, the abundance of the ions at *m/e* 29 and 30 corresponding to $C_2HD_2^+$ and $C_2H_2D_2^+$ suggesting it was the 1,2-dideutero-isomer.

SiO + acetylene. (Found: C, 15.51; H, 1.42; O, 30.72; Si, 52.35%.) Mono- and dideuteroacetylene were separated from more volatile deuterolysis products by low temperature distillation on the vacuum line. They were identified by their infrared spectrum and mass spectrum. The mass spectrum of the remaining volatiles suggested they were 1,2-dideuteroethylene and 1,1,2,2-tetradeuteroethane. A portion of the gas giving a pressure of 42 mm on the vacuum line was shaken with 2 ml concentrated H_2SO_4; 34 mm was recovered unreacted and its infrared spectrum showed it to be 1,1,2,2-tetradeuteroethane.

SiO + diphenylacetylene. (Found: C, 59.98; H, 3.61; O, 13.86; Si, 22.55%.) The solid obtained by boiling the diphenylacetylene + SiO reaction product with wet diethyl ether and evaporating to dryness, had the following analysis: C, 68.2; Si, 11.5%. The infrared spectrum of the product of complete hydrolysis, taken in CCl_4 solution, showed it to be *cis* 1,2-diphenylethylene. Comparison of this spectrum with the spectrum of the deuterolysis product suggested the latter was the 1,2-dideutero analogue.

SiO + 2,3-dimethyl-1,4-butadiene. (Found: C, 38.11; H, 5.37; O, 21.01; Si, 35.51%.) The sole product obtained on hydrolysis was shown by its infrared spectrum in CCl_4 solution to be 2,3-dimethyl-2-butene. The mass spectrum of the deuterolysis product showed it to be the 1,4-dideutero analogue.

SiO + benzene. (Found: C, 32.25; H, 2.79; O, 23.96; Si, 41.00%.) The deuterolysis products were separated by low temperature distillation into two fractions. The less volatile was shown by its infrared and mass spectrum to be monodeuterobenzene. The mass spectrum of the more volatile fraction suggested it was a dideutero-1,4-cyclohexadiene. The ^1H NMR spectrum of the liquid showed allyl protons (doublet τ 7.3) and vinyl protons (broad singlet τ 5.5) with an area ratio of 1 :2.05 showing that the compound was 3,6-dideutero-1,4-cyclohexadiene.

SiO + anthracene. (Found: C, 58.91; H, 3.62; O, 14.08; Si, 23.29%.) Mass spectrometry showed the main deuterolysis product to be a monodeuteroanthracene. The spectrum also showed the presence of a dideutero-substituted dihydroanthracene but the position of substitution was not unambiguously established.

SiO + 2,2-dimethylpropane. (Found: C, 11.98; H, 2.55; O, 32.14; Si, 53.32%.) and *SiO + cyclohexane.* (Found: C, 15.72; H, 2.88; O, 30.42; Si, 50.98%.) Mass spectrometry indicated that in both of these cases only the original hydrocarbon was reformed on hydrolysis. The mass spectra of the deuterolysis products showed they were monodeutero compounds but no prefered positon of substitution was apparent in the branched alkane.

SiO + 1-chlorobutane. (Found: C, 12.65; H, 2.50; Cl, 9.11; O, 28.32; Si, 47.42%.) and *SiO + 1-bromobutane.* (Found: C, 14.21; H, 2.83; Br, 23.35; O, 23.51; Si, 36.10%.) The deuterolysis products were found by mass spectrometry to be the same in both cases. The intensity of ions at *m/e* 43 and 44 showed that the main product was a 1-deuteropropane. A small amount of 1,2-dideuterobutane was also present indicated particularly by the ion at *m/e* 31 ($C_2H_3D_2^+$).

SiO + chlorobenzene. (Found: C, 19.70; H, 1.54; Cl, 9.67; O, 25.84; Si, 43.25%.) The solid (200 mg) yielded a total of 56 mg of volatiles on deuterolysis. Separation on a vacuum line gave two fractions. The smaller (5 mg) was identified by mass spectrometry as a monodeuterochlorobenzene. The larger was shown by mass spectrometry to be mainly monodeuterobenzene with a small amount of a dideuterobenzene.

SiO + bromobenzene. (Found: C, 18.56; H, 1.42; Br, 20.01; O, 22.91; Si, 37.10%.) The volatiles from deuterolysis were put directly into the mass spectrometer. The spectrum was of similar form to those obtained with the chlorobenzene product, but much smaller amounts of monodeuterobromobenzene and of dideuterobenzene relative to monodeuterobenzene were observed.

SiO+ethanol. (Found: C, 11.76; H, 3.08; O, 31.42; Si, 53.74%.) The infrared spectrum of the deuterolysis product, distilled from benzene on the vacuum line, showed it to be C_2H_5OD.

SiO+ammonia. (Found: H, 1.75; N, 7.30; O, 33.97; Si, 56.98%.) and *SiO+1-aminobutane.* (Found: C, 17.81; H, 3.82; N, 5.02; O, 27.43; Si, 45.92%.) Deuterolysis products in both of the above cases were collected and passed into the mass spectrometer. Mixed deutero-substituted ammonias and *N*-deutero-1-aminobutanes were observed.

CONCLUSIONS

Silicon monoxide has proved to be a silylene of exceptional reactivity. Part of this reactivity may be due to the formation of diradical species during polymerization of silicon monoxide at low temperature, but this work provides no conclusive evidence for this. The point can only be proved by a low temperature ESR study of the polymerization.

The reactions of silicon monoxide do indeed provide a one-step synthesis of silicones. However, the products are mostly complex and rather intractable due to simultaneous insertion and addition reactions and uncontrolled polymerization of $>$Si=O groups.

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