Matrix Reactions of Silane and Oxygen Atoms. Infrared Spectroscopic Evidence for the Silanol, Silanone, and Silanolc and Silicic Acid Molecules

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Matrices formed by the cocondensation of SiH₄ and O₃ in argon at 17 K were irradiated by a high-pressure mercury arc. Photoproducts include the silicon-oxygen double bond containing species SiO, H₂SiO, H(HO)SiO, and (HO)₂SiO. HSiOH was prepared in high yield by the reaction of SiH_4 with O atoms from the microwave discharge of O_2 in excess argon. In both photolysis and discharge experiments, SiH₃OH is proposed as a primary reaction product formed by insertion of O atoms into an Si-H bond of SiH₄.

Introduction

Although silicon is the second most abundant element in the earth's crust, much less is known about the chemistry of silicon than the chemistry of its group 4^{27} relative, carbon. Moreover, the chemistry of silicon and carbon is quite different. For example, silicon, unlike carbon, does not easily form double bonds, but Si–O–Si bonds are more stable than C–O–C bonds due to $d\pi$ –p π overlap.¹ Thus, there has hitherto been no direct spectroscopic observation of the silicon analogues of some commonly occurring carbon-containing molecules such as CH₃OH, CH₂O, and HCOOH.

This argon matrix study of reactions of O atoms with SiH4 was undertaken to develop a better understanding of silicon chemistry. In the first section, O atoms were generated from the photolysis of O₃ isolated in solid argon. In the second section, O atoms were prepared from microwave discharge of O_2 in an argon stream. Some of the reaction products have been observed spectroscopically for the first time and include three new species containing silicon-oxygen double bonds, which is of considerable current interest.²⁻⁴ This work may also help in understanding the mechanism of the gas-phase reaction of O₃ with SiH₄, which shows chemiluminescence⁵ and may proceed via some of the intermediates which are discussed below.

Experimental Section

Apparatus. The cryogenic refrigeration system and vacuum vessel have been described elsewhere.⁶ Spectra were recorded on a Beckman IR-12 spectrophotometer over the range 4000-200 cm⁻¹. Regions of interest were recorded on an expanded wavenumber scale, which allowed the measurement of band positions to an accuracy of better than ± 1 cm⁻¹. Additionally, spectra of products of the reaction of SiH₄ and O atoms, produced by microwave discharge, were recorded on a Nicolet 7199 FTIR spectrometer over the frequency region 4000-400 cm⁻¹ at a spectral resolution of 1 cm⁻¹. The frequency accuracy of both spectrometers was calibrated by using the vibration-rotation lines of standard gas-phase molecules. The temperature of the CsI cold window in the range 15-25 K was determined by using a H₂ vapor pressure gauge attached to the second stage of the refrigerator cold tip, and in the range above 25 K it was determined by using a chromel/gold thermocouple. The temperature was varied by adjusting the voltage applied to three heater buttons (Minco Products, Inc., Minneapolis, MN) mounted on the copper window support. Ozone/silane samples were photolyzed for periods up to 150 min by using the 220-1000-nm output of a BH-6 high-

pressure mercury arc lamp (1000 W, Illumination Industries, Inc.). A 10-cm water filter reduced the amount of infrared radiation incident upon the matrix during photolysis while replacement with an aqueous $NiSO_4/CoSO_4$ solution afforded selective transmission of near-ultraviolet light (240-400 nm).

Chemicals. Ozone was generated by a static discharge (Tesla coil) of oxygen in a Pyrex tube and condensed with liquid N_2 ; residual O₂ was removed by pumping at 77 K.⁷ Normal isotopic O₂ was obtained from Burdett, U.S.P. grade. Two samples enriched in ¹⁸O to 50% and 95%, respectively, were supplied by Yeda (Israel). Silane (Matheson) was degassed by freezing, thawing, and pumping at 77 K; only the middle fraction was kept. Isotopically enriched silane SiD_4 (98% D), supplied by MSD Isotopes (Canada), was used without purification. Si_2H_6 was prepared by the addition of $LiAlH_4$ to Si_2Cl_6 (Pfaltz and Bauer) in ether at 273 K and collected at 77 K;8 the sample was purified by vacuum distillation.

Procedure. (i) Ozone Photolysis Experiments. Ozone and silane were diluted with argon and codeposited through two separate spray-on lines at equal rates of 1.4 mmol h^{-1} for 10 h. The matrix ratio for the Ar/O_3 gas mixture was varied between 100/1 and 300/1 and the matrix ratio for the Ar/SiH₄ gas mixture was varied between 100/1 and 600/1. Samples were photolyzed after deposition.

(ii) Microwave Discharge Experiments. O atoms were generated by the microwave discharge (Burdick, 2450 MHz) of an Ar/O_2 stream in a 6-mm-o.d. quartz tube directed at the cold window using Ar/O_2 gas mixtures of 50/1 or 100/1. The argon/O₂/O atom stream was codeposited with Ar/SiH₄ samples for a maximum of 20 h.

Results

 $SiH_4 + O_3$. Samples of silane (Ar/SiH₄ = 200) and ozone $(Ar/O_3 = 200)$ were codeposited at 17 K for 10 h. The infrared spectrum was recorded immediately after deposition, and the 300-1300-cm⁻¹ region (Figure 1a) shows absorptions due to the precursors SiH_4 and O_3 . The additional weak absorption at 1283 cm^{-1} is probably due to N₂O made from nitrogen impurity in the oxygen used to prepare ozone. After 30 min of photolysis with the full output of the high-pressure mercury arc (220-1000 nm), approximately 40% of the ozone was decomposed, based on the decrease in intensity of the 704-cm⁻¹ O₃ absorption (see Figure 1b). The infrared spectrum was rich in new absorptions, the peak locations and intensities of which are listed in Table I. On warming to 25 K for 10 min and then recooling to 17 K, the intensities of the absorptions centered on 746, 961, and 1101 cm⁻¹ (labeled E) increased by a factor of 2, while the absorptions marked with an asterisk in Table I (which include those labeled A, B, SiO, and H in Figure 1b) disappeared. The other absorptions decreased in intensity but did not disappear on warming. In a similar experiment, Pyrex-filtered photolysis (290-1000 nm)

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Figure 1. Infrared spectra of a sample of $Ar/SiH_4/{}^{16}O_3 = 400/1/1$ (a) immediately after deposition at 17 K and (b) after 220–1000-nm photolysis for 30 min.



Figure 2. Infrared spectra of a sample of $Ar/SiH_4/{}^{18}O_3 = 400/1/1$ (a) immediately after deposition at 17 K and (b) after 220–1000-nm photolysis for 30 min.

gave 10-20% of the product absorbance observed with a subsequent full-arc irradiation.

The dependence of the intensities of the bands listed in Table I on the SiH₄ concentration was also studied, keeping the O₃ concentration constant (Ar/O₃ = 200). In a silane-rich experiment (Ar/SiH₄ = 100), the intensities of the absorptions centered on 746, 834, 839, 951, 961, 986, and 1101 cm⁻¹ were doubled while H₂O bands at 1591, 1610, 1624, and 3727 increased dramatically in intensity. In a silane lean experiment (Ar/SiH₄ = 600), very little H₂O was produced, and the absorptions at 746, 834, 839, 951, 961, 986, and 1101 cm⁻¹ were weak. Of the four product absorptions in the 1200-cm⁻¹ Si=O stretching region, those at 1222 and 1270 cm⁻¹ were favored by high SiH₄/O₃ ratios.

 $SiH_4 + {}^{16,18}O_3$. The band at 1283 cm⁻¹, which was present after deposition, was shifted by 37 cm⁻¹ to 1246 cm⁻¹ with ${}^{18}O_3$ (95%)

TABLE I: Absorptions (cm⁻¹) Appearing on Photolysis of Silane and Ozone in Solid Argon^{α}

¹⁶ O ₃	¹⁸ O ₃	identification
359 (0.03)	353 (0.04)	S
	423 (0.02)	?
453 (0.20)	451 (0.16)	S
596 (0.03)*	594 (0.02)	Н
697 (0.08)*	694 (0.07)	В
723 (0.02)*	720 (0.02)	Н
746 br (0.05)	740 br (0.13)	E
759 (0.02)		?
764 (0.05)	758 (0.03)	?
813 (0.05)*	800 (0.10)	?
834 (0.17)	834 (0.25)	Si ₂ H ₆
839 (0.19)	839 (0.25)	(Si_2H_6)
847 (0.03)*	820 (0.02)	Н
859 (0.08)	851 (0.08)	H₃SiOH
938 (0.03)*	933 (0.06)	Н
951 (0.62)	949 (0.67)	$H_x Si_v O_z$
961 br (0.26)	960 br (0.26)	E
986 (0.22)	b	$H_x Si_v O_z$
995 (0.14)*	Ь	?
1023 (0.09)	b	S
1027 (0.02)	b	S
1101 br (0.10)	1060 br (0.15)	E
1202 (0.07)*	1162 (0.06)	В
1222 (0.08)*	1179 (0.06)	SiO
1249 (0.07)*	1211 (0.10)	Α
1270 (0.13)	1232 (0.08)	S
1276 (0.05)	1235 (0.03)	S
1591 (0.05)	1585 (0.03)	H_2O
1846 (0.02)*	1842 (0.02)	Н
1882 (0.03)*	1878 (0.03)	Н
3677 (0.13)	3667 (0.13)	S
3682 (0.12)	3670 (0.07)	S
3727 br (0.18)	3711 br (0.15)	H ₂ O ^c

^aAbsorbances given parenthetically. Asterisks denote bands that disappear upon sample warming. ? denotes unidentified absorption, br = broad. Weak 1283- and 1246-cm⁻¹ bands observed before photolysis are due to N₂O and N₂¹⁸O, respectively. Withnall, R. Ph.D. Thesis, University of East Anglia, Norwich, England, 1984. ^{b18}O counterparts presumably hidden by ¹⁸O₃ which absorbs at 983 cm⁻¹. The 995-cm⁻¹ band is not due to SiH₂ since the stronger Si-H stretching modes were not observed: see Fredin, L.; Hauge, R. H.; Kafafi, Z.; Margrave, J. L. J. Chem. Phys. **1985**, 82, 3542. ^c Perturbed water.

¹⁸O). The 300–1300 cm⁻¹-region of the infrared spectra taken before and after 30-min photolysis with the full mercury arc are shown in parts a and b of Figure 2, respectively; the peak locations and intensities of absorptions appearing on photolysis are listed in Table I. The bands at 1202, 1222, 1249, and 1270 cm⁻¹ in the Si=O stretching region were shifted to 1162, 1179, 1211, and 1232 cm⁻¹, respectively. The broad E absorption centered at 1101 cm⁻¹ also showed a large ¹⁸O shift to 1060 cm⁻¹. Many of the other bands showed smaller ¹⁸O shifts as can be seen from Table I.

Argon matrices containing SiH₄ and scrambled ^{16,18}O₃ (50% ¹⁸O) were also irradiated for 30 min with the full mercury arc. In these experiments the absorption at 1270 cm⁻¹ gave rise to a doublet of triplets, one component of which was centered on 1268 cm⁻¹ and had satellites at 1270 and 1266 cm⁻¹, and the other component was centered on 1235 cm⁻¹ and had satellites at 1232 and 1237 cm⁻¹. A weak unresolved multiplet was also observed between 353 and 359 cm⁻¹. All the other multiplets were doublets with components of equal intensity and centered on the same frequencies as in the pure ¹⁶O₃ and ¹⁸O₃ samples, as is illustrated in Figure 3 for three different isotopic ozone samples.

 $SiD_4 + {}^{16}O_3$. Samples of deuterated silane (Ar/SiD₄ = 200) and ozone (Ar/O₃ = 200) were codeposited at 17 K. The 300– 1300-cm⁻¹ region of the infrared spectrum recorded before photolysis is shown in Figure 4a; the absorptions are due to the precursors SiD₄ and O₃ as well as SiHD₃ which was present as an impurity in the sample. Figure 4b shows the spectrum recorded after 30-min photolysis with the full arc. The peak locations and intensities of product absorptions are listed in Table II. Two very



Figure 3. Infrared spectra of silane-ozone-argon samples after 220-1000-nm photolysis for 30 min at 17 K. (a) $Ar/SiH_4/^{16}O_3 = 200/1/1$ (b) $Ar/SiH_4/^{16}O_3 = 200/1/1$, (c) $Ar/SiH_4/^{18}O_3 = 500/3/2$. Spectra were plotted on a common transmittance scale; for example the band labeled B in trace (a) had an intensity of 0.08 absorbance units. Bands marked with an "o" were present before photolysis and are due to N₂O.



Figure 4. Infrared spectra of a sample of $Ar/SiD_4/{}^{16}O_3 = 400/1/1$ (a) immediately after deposition at 17 K and (b) after 220–1000-nm photolysis for 30 min.

intense absorptions were present at 868 and 874 cm⁻¹. These absorptions showed a 24-cm⁻¹ shift on ¹⁸O substitution, which is considerably higher than the ¹⁸O shift on any of the bands in this spectral region in the natural isotope experiments, with the exception of the weak feature at 846 cm⁻¹. With scrambled ^{16,18}O₃, the bands at 868 and 874 cm⁻¹ each gave a doublet, the former having components of equal intensity at 868 and 844 cm⁻¹ and the latter having equal intensity components at 874 and 850 cm⁻¹.

The absorptions in the 1150–1300-cm⁻¹ region were less intense than in the natural isotope experiments, and all but SiO showed a deuterium shift. The absorptions which occurred at 1276 and 1270 cm⁻¹ in the SiH₄/¹⁶O₃ experiments had two counterparts at 1267 and 1273 cm⁻¹ in the SiD₄/¹⁶O₃ experiments. These gave way to two adsorptions at 1229 and 1236 cm⁻¹ with ¹⁸O₃. In

TABLE II: Absorptions (cm⁻¹) Appearing on Photolysis of SiD₄ and Ozone in Solid Argon^{*a*}

¹⁸ O ₃	identification
	S
368 (0.12)	S
445 (0.01)	н
	?
503 (0.06)	?
530 (0.07)	В
550 br (0.06)	?
620 br (0.10)	Si ₂ D ₆
	?
696 (0.25)	$D_x Si_y O_z$
703 (0.42)	E
809 (0.04)	H ^b
817 (0.05)	H ^b
844 (0.15) ^c	SiOD or D ₂ SiOD
850 (0.21)	D₃SiOD
866 (0.02)	Α
896 (0.03)	S
902 (0.01)	S
969 (0.08)	S
972 (0.02)	S
d	S
1039 br (0.20)	E
1166 (0.02)	D ₂ O
1147 (0.03)	В
1179 (0.02)	SiO
1210 (0.02)	Α
1229 (0.03)	S
1236 (0.04)	S
$1359 (0.04)^{e}$	н
2694 (0.09)	S
2698 (0.08)	S
2726 br (0.14)	D ₂ O ⁷
	 ¹⁸O₃ 368 (0.12) 445 (0.01) 503 (0.06) 530 (0.07) 550 br (0.06) 620 br (0.10) 696 (0.25) 703 (0.42) 809 (0.04) 817 (0.05) 844 (0.15)^c 850 (0.21) 866 (0.02) 896 (0.03) 902 (0.01) 969 (0.08) 972 (0.02) <i>d</i> 1039 br (0.20) 1166 (0.02) 1147 (0.03) 1179 (0.02) 1210 (0.02) 1236 (0.04) 1359 (0.04)^e 2694 (0.09) 2698 (0.08) 2726 br (0.14)

^aAbsorbances given parenthetically. ? denotes unidentified absorption, br = broad. ^b cis- and trans-DSiOD. ^cSiHD₃ absorbance subtracted out. ^d¹⁸O counterpart presumably hidden by ¹⁸O₃ absorption. ^ePositive ¹⁸O shift due to resonance interaction with overtone of the DSiO bend of DSiOD; see ref 10. ^fPerturbed D₂O.

addition the absorptions located at 1249 and 1202 cm⁻¹ in the SiH₄ experiments also showed deuterium shifts to 1245 and 1189 cm⁻¹, respectively. Furthermore, the absorptions which occurred at 839, 834, and 453 cm⁻¹ in the protonated samples showed large shifts on deuteration, the first two moving to 620 and the third to 376 cm⁻¹. The broad absorption, which occurred at 1101 cm⁻¹ in the SiH₄/¹⁶O₃ experiments, was also shifted on deuterium enrichment, moving to 1087 cm⁻¹.

 $SiH_4 + O$. Figure 5 shows important regions of the infrared spectrum taken after 10 h of deposition of samples of silane $(Ar/SiH_4 = 200)$ and oxygen $(Ar/O_2 = 100)$ passed through a microwave discharge tube. Most of the absorptions with the notable exception of those labeled as HO₂ in Figure 5 were also observed in the ozone photolysis experiments, but the major difference is that the bands labeled H were markedly stronger in intensity in discharge experiments. The peak locations and intensities of the product absorptions together with their counterparts on ¹⁸O substitution, from a similar $Ar/^{18}O_2$ discharge experiment, are listed in Table III. After 320-1000-nm photolysis of these matrices for 30 min, absorptions due to species H disappeared and a new absorption appeared at 1222 cm⁻¹ (1179 cm⁻¹ in the ¹⁸O experiment). When a more concentrated Ar/O_2 gas mixture was employed (typically $Ar/O_2 = 50/1$), 320-1000-nm irradiation of the matrix produced new infrared absorptions at 453, 1023, 1270, and 3677 cm⁻¹ belonging to species S in addition to the band at 1222 cm⁻¹. The deep yellow color of the matrix also disappeared on photolysis; attempts to observe a structured electronic absorption of HSiOH in the visible and near-ultraviolet were not successful.

 $SiD_4 + O$. On reaction of SiD₄ with O atoms from the microwave discharge, a strong 868-cm⁻¹ absorption was observed, which gave rise to a sharp doublet at 868 and 844 cm⁻¹ with isotopically scrambled ^{16,18}O₃. Again HO₂ was observed, and DO₂ was not found, which suggests that HO₂ is produced in the dis-



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Figure 5. Selected spectral regions for $Ar/SiH_4 = 200/1$ sample codeposited at 17 K with $Ar/{^{16}O_2} = 100/1$ sample passed through a microwave discharge. The 3600-3800-cm⁻¹ region was recorded with a Nicolet 7199 FTIR spectrometer.

TABLE III:	Absorptions (cm ⁻¹)	Appearing on	Codeposition of Silar	e with Oxygen	Atoms Produced by	Microwave Discharge of	f an Argon/Oxy	gen
Stream ^a								

$^{16}O + SiH_4$	$^{18}O + SiH_4$	$^{16}O + SiD_4$	$^{18}O + SiD_4$	identification	
350 (0.03)	347 (0.06)			?	
453 (0.04)	450 (0.03)			S	
596 (0.72)	594 (0.44)	448 (0.16)	445 (0.08)	Н	
<i>c, c</i> (<i>c</i> , <i>c</i>)		496 br (0.05)	496 br (0.05)	?	
		620 (0.05)	620 (0.03)	Si_2D_6	
		(665–680)	. ,	SiD₄	
		(692)		SiHD ₃	
		533 (0.03)	533 (0.02)	?	
698 (0.08)	697 (0.07)			В	
705 (0.03)		705 (0.06)		O3	
723 (0.48)	720 (0.41)	523 (0.04)		н	
751 (0.03)				?	
,		868 (0.37)	844 <i>b</i>	D ₂ SiOD or SiOD	
		874 (0.04)		D ₃ SiOD	
814 (0.13)	800 (0.07)			?	
837 (0.32)	837 (0.13)			Si ₂ H ₆	
847 (0.39)	820 (0.25)	837 (0.12)	809 (0.05)	H^{b}	
		843 (0.25)	817 (0.12)	H ^b	
		(844)		SiHD ₃	
(895-920)	(895-920)			SiH4	
938 (0.25)	933 (0.20)	716 (0.08)		Н	
951 (0.26)	949 (0.09)			H _x Si _v O _z	
961 (0.07)				E	
986 (0.24)				H _x Si _y O _z	
	978 (0.17)			¹⁸ O ₃	
	984 (0.42)			¹⁸ O ₃	
	992 (0.05)			¹⁸ O ¹⁸ O ¹⁶ O	
	1018 (0.05)			¹⁸ O ¹⁶ O ¹⁸ O	
1034 (0.32)		1034 (0.33)		¹⁶ O ₃	
1040 (0.62)		1040 (0.60)		¹⁶ O ₃	
1101 (0.10)	1040 (0.04)	1101 (0.05)		HO ₂ ^c	
1202 (0.07)	1162 (0.05)			В	
1249 (0.03)				Α	
1270 (0.03)				H_2O_2	
1389 (0.16)	1381 (0.16)			HO ₂ ^c	
1846 (0.30)	1842 (0.16)	1352 (0.23)	1359 (0.13)	H	
1882 (0.28)	1878 (0.23)		A < 81	H	
3661	3649	2667	2651	H"	

^aAbsorbances given parenthetically. ? denotes unidentified absorption. br = broad. ^b cis- and trans-DSiOD. ^cTraces of HO₂ have been observed from passing Ar/O_2 and Ar only through microwave discharge tubes in this laboratory. Ever present traces of H₂O provide the needed elements. ^aThese peak locations were taken from IR spectra recorded in separate experiments using a Nicolet 7199 FTIR spectrometer.

charge tube.⁹ Table III also lists bands from these SiD_4 reactions. After 60 min of photolysis with the full high-pressure Hg arc, absorptions identified as belonging to species H were reduced in intensity by approximately 50%. Again, a new absorption appeared at 1222 cm⁻¹ (1179 cm⁻¹ in the ¹⁸O experiments).

 $Si_2H_6 + O$. Four experiments were run with Si_2H_6 and O atoms. The only product absorptions, other than those of HO₂ at 1389 and 1101 cm⁻¹, belonged to species H.

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TABLE IV: Infrared Absorption (cm⁻¹) for Isotopic Hydroxysilylene Species in Argon Matrices

vibrational	HS	SiOH	HS	i ¹⁸ OH	DS	SiOD	DS	i ¹⁸ OD
mode	a	b	a	Ь	a	<u>b</u>	а	b
ν ₁ (H-O)	3661	3650	3649		2667		2651	
$\nu_2(H-Si)$	1846 1882 ^c	1847.1 1881.9°	1842 1878°	1841.8 1880.0 ^c	1352	1354.5	1359	1362.2
$\nu_3(\mathrm{HSiO})$	938	937.0	933	932.1	716	700.7° 715.1 ^d		695.3 ^e 706.2 ^d
<i>ν</i> ₄(Si−O)	847	850.6	820	823.1	837 ^d 843 ^e	840.7 ^d 847.0 ^e	809 ^d 817 ^e	812.3 ^d 820.9 ^e
$\nu_{5}(SiOH)$	723	722.6	720	720.0	523	521.2		
v_6 (torsion)	596	595.2	594	593.6	448	447.3	445	444.0

^a This work, microwave discharge experiments. ^bReference 10. ^cA doublet is observed on account of Fermi resonance interaction between ν_2 and $2\nu_3$. ^d Trans isomer. ^e Cis isomer.

Discussion

The SiH₄/O₃ photolysis and SiH₄/O reaction products will be identified and mechanisms for these reactions will be proposed.

Identification of the Photoproducts. The group of absorptions labeled H in Figures 1, 2, 4, and 5 are identified as hydroxysilvlene, HSiOH, by comparison with the matrix infrared spectrum of this species produced by the matrix reaction of Si atoms and H_2O^{10} There is good agreement in the observed frequencies of the fundamentals of HSiOH and its isotopes, which were prepared by two different techniques in the present work. Furthermore, the agreement is also good with the frequencies reported for HSiOH by Ismail et al.¹⁰ apart from the ν (O–H) fundamental of HSi¹⁶OH. The conditions of the discharge experiments were more favorable for detecting this fundamental, because H₂O which absorbs in this region was not a precursor here and the signal-to-noise ratio in this frequency region was undoubtedly better owing to the sensitivity of the FTIR spectrometer and the high yield of HSiOH. One other discrepancy is notable: the present v(Si-O) stretch is 3-4 cm⁻¹ lower for each of the isotopes (see Table IV). This reflects the sensitivity of this fundamental to other molecules in the matrix environment of HSiOH such as hydrogen (see pathway (3) in mechanisms below).

The bands labeled E in Figure 1 are assigned to disilyl ether, H₃SiOSiH₃, by comparison with the gas-phase infrared spectrum of Lord, et al.;¹¹ strong bands at 1107, 957, and 764 cm⁻¹ correspond to the bands observed at 1101, 961, and 746 cm⁻¹ in the present natural isotope experiments. Gas-phase D₃SiOSiD₃ has strong absorptions at 1094 and 713 cm⁻¹ compared to absorptions observed in this work at 1087 and 703 cm⁻¹.

The absorption at 1222 cm⁻¹, which showed an ¹⁸O shift of 43 cm⁻¹ but no deuterium shift and did not group with any other absorptions, is assigned to SiO. It lies 4 cm⁻¹ lower than the fundamental absorption frequency for diatomic SiO observed by Anderson and Ogden¹² at 1225.9 cm⁻¹ with an ¹⁸O shift of 43.8 cm⁻¹. The present lower value is due to perturbation of SiO by molecular hydrogen, which is produced and trapped in the same matrix cage (see Mechanism later). This was demonstrated in the most productive discharge experiments, where sharp, weak absorptions were observed at both 1222 and 1226 cm⁻¹ in addition to the bands belonging to HSiOH. On irradiation ($\lambda > 320$ nm) at 11 K, the absorption at 1222 cm⁻¹ grew in intensity whereas that at 1226 cm⁻¹ did not. This is presumably because the sole product of the photolysis of HSiOH is the complex, SiO--- H_2 , under these conditions with no production of isolated SiO. There was no measurable D shift on the ν (Si–O) stretch in the SiO---H₂ complex.

The absorption at 1202 cm⁻¹, which showed a 40-cm^{-1 18}O shift and a 13-cm⁻¹ deuterium shift, is clearly a Si=O stretch, and most

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TABLE V:	Observed Frequencie	s (cm⁻¹) for	Silanone	Isotopes and
Their Calcul	ated Values			

	Si=O stretch, a_1		SiH ₂ wag or rock	SiH ₂ wag, b ₁	SiH ₂ rock, b
	obsd	calcda	obsd	calcd	calcd
H ₂ Si ¹⁶ O	1202	1203	697	721	699
H ₂ Si ¹⁸ O	1162	1162	694	719	695
D ₂ Si ¹⁶ O	1189	1187	533	552	543
$D_2Si^{18}O$	1147	1146	530	551	539

^aReference 4.

TABLE VI: Observed Frequencies (cm⁻¹) for Silicic Acid Isotopes in Solid Argon⁴

	¹⁶ O,H	¹⁸ O,H	¹⁶ O,D	¹⁸ O,D
ν(O-H)	3677	3667	2710	2694
ν (Si=O)	1270	1232	1267	1229
$\nu_{as}(Si-O)$	1023		994	969
$\nu_{s}(Si-O)$			919	896
τ (O-H)	453	451	376	368
δ(OSiO)	359	353	349	

^aAbsorptions due to perturbed silicic acid are not included in this table.

TABLE VII: Observed Frequencies (cm⁻¹) for Silanoic Acid Isotopes in Solid Argon

······································	¹⁶ O,H	¹⁸ O,H	¹⁶ O,H	¹⁸ O,D	-
ν (Si=O) ν (Si-O)	1249ª	1211ª	1245ª 891	1210 866	

^a Absorptions were observed within 1 cm⁻¹ of these values in some of the samples containing SiO that formed the basis for ref 10 (personal communication from the authors).

certainly belongs to a species of the form H_x Si=O (1 $\le x \le 4$) for two reasons, as follows. Firstly, scrambled ^{16,18}O₃ gave rise to a doublet at 1202 and 1162 cm⁻¹ which had no satellite structure, indicating the species contains only one O atom. Secondly, a second electronegative O atom in the species containing a Si=O group would be expected to blue-shift the absorption frequency of the Si=O stretch compared to that of diatomic SiO, as is the case of $OSiCl_2$ and $OSiF_2$.^{15,16} However, the 1202-cm⁻¹ absorption is red-shifted from the SiO fundamental and it lies very close to the 1204-cm⁻¹ fundamental for Me₂Si= O.13 In some of the more productive discharge experiments, a weak absorption was seen at 1205 cm⁻¹ in addition to the band at 1202 cm⁻¹. It is quite possible that this former band is, in fact, due to isolated H₂Si=O formed during deposition, and that the latter band is due to the $H_2Si=O--H_2$ complex, since complexation of SiO diatomic with H₂ was observed to red-shift the ν (Si=O) frequency by a similar amount.

A recent theoretical study of the thermodynamic and kinetic stability of silanone, H₂Si=O, predicted the vibrational frequencies of several isotopic fundamentals.⁴ As can be seen from Table V,

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 J. L. J. Chem. Phys. 1982, 77, 1617.
 (11) Lord, R. C.; Robinson, D. W.; Schumb, W. C. J. Am. Chem. Soc.

^{1955, 78, 1327.}

⁽¹⁵⁾ Schnöckel, H. J. Mol. Struct. 1980, 65, 115

⁽¹⁶⁾ Schnöckel, H. Z. Anorg. Allg. Chem. 1980, 460, 37.

there is excellent agreement between the calculated values for the $\nu(Si=0)$ stretch and the frequencies observed in this work. All of the evidence suggests that the species labeled B in Tables I-III and Figures 1-5 be identified as silanone. In particular, the 13-cm⁻¹ red shift of the $\nu(Si=0)$ stretch of H₂Si¹⁶O on deuteration indicates that there is substantial interaction between the $\nu(Si=0)$ stretch and the symmetric SiH₂ deformation, which was calculated to lie at 1000 cm⁻¹. These calculations strongly support the present identification of silanone, even though the symmetric deformation was not observed here.

The only other band observed for silanone was centered on 697 cm⁻¹ and it is uncertain whether this is the SiH₂ wag or SiH₂ rock. The fact that the CH₂ wag of the carbon analogue of silanone, formaldehyde, is stronger in intensity than the CH₂ rock¹⁴ favors the assignment of the 697-cm⁻¹ band to the SiH₂ wag. However the ¹⁸O shift of the SiH₂ wag is predicted to be only 2 cm⁻¹ for H₂SiO and 1 cm⁻¹ for D₂SiO, whereas the ¹⁸O shift of the SiH₂ rock is predicted to be 4 cm⁻¹ for both H₂SiO and D₂SiO. Thus the observed ¹⁸O shift of 3 cm⁻¹ for both H₂SiO and D₂SiO is in slightly better agreement with the predicted ¹⁸O shifts of the rock. In addition, a predicted frequency of 699 cm⁻¹ for the rock is in better agreement with the observed frequency of 697 cm⁻¹ than the predicted frequency of 721 cm⁻¹ for the wag. Therefore the assignment of the band at 697 cm⁻¹ to the SiH₂ rock of H₂Si=O is preferred.

Absorptions which have been identified as belonging to species S in Table I occur at 359, 453, 1023, 1270, and 3677 cm⁻¹. The associated bands at 3682, 1276, and 1027 cm⁻¹ are assigned to S with different chemical environments in the matrix cage. The 38-cm⁻¹ shift of the band at 1270 to 1232 cm⁻¹ on ¹⁸O substitution indicates that this is due to a Si=O stretch, even though it is a little less than the 45-cm⁻¹ shift which would result from an isolated double bond of pure silicon-oxygen stretching character in this frequency region. Furthermore, since the band at 1270 cm⁻¹ gives rise to a doublet of triplets with scrambled ${}^{16,18}O_3$ (see Figure 3), species S contains two further O atoms, which are equivalent. A blue shift of 48 cm⁻¹ of the ν (Si=O) stretch of this species in relation to the ν (Si=O) stretch of diatomic SiO, which was centered on 1222 cm⁻¹ in this work, is consistent with two equivalent hydroxyl groups bonded to the central silicon atom. The shift of the ν (Si=O) stretch would then be accounted for by the inductive effect of the hydroxyl groups in the same way that the electronegative halogen atoms in O=SiCl₂ and O=SiF₂ blue-shift the ν (Si=O) stretch to 1240 and 1309 cm⁻¹, respectively.15,16

The strong intensity of the 453-cm⁻¹ band favors its assignment to an out-of-plane vibration of a planar molecule. It has a small ¹⁸O shift of 2 cm⁻¹ but a large deuterium shift down to 376 cm⁻¹, which bears a ratio of 1.20 with the protonated counterpart, suggesting that the mode has a high percentage of hydrogen character. For the above reasons the 453-cm⁻¹ band is assigned to an OH torsion. The absorption at 359 cm⁻¹, which gave rise to an unresolved multiplet with scrambled ^{16,18}O₃ and showed an ¹⁸O shift of 6 cm⁻¹ and a deuterium shift of 10 cm⁻¹, is tentatively assigned to either the O—Si=O rock or symmetric bend. However, since both of these modes should have a slightly higher ¹⁸O shift, of the order of 10 cm⁻¹, this is probably mixed with another mode such as the SiOH bend.

With SiD₄, a triplet of absorptions appeared at 994, 998, and 1004 cm⁻¹, the first two of which were shifted to 969 and 972 cm⁻¹, respectively, on ¹⁸O substitution, the third one presumably being shifted underneath the ν_3 absorption of ¹⁸O₃. These ¹⁸O shifts are very reasonable for the antisymmetric (O–Si–O) stretch in (HO)₂Si=O, taking an OSiO bond angle of 106° (see below). The protonated counterparts of the aforementioned triplet of absorptions at 994, 998, and 1004 cm⁻¹ absorb at 1023 and 1027 cm⁻¹, with the third component probably masked by the ν_3 absorption of ¹⁶O₃. However, the observed deuterium shift of 29 cm⁻¹ is much higher than the shift of 19 cm⁻¹ which is predicted for the (O–Si–O) antisymmetric stretch of (HO)₂Si=O by treating the hydroxyl groups as point masses; this suggests that an SiOH deformation participates in this mode. The doublet of

SCHEME I

O |1.503 Å H 131.2* Si 1.595 Å H 106.0* O 0.946

weaker absorptions, occurring at 919 and 926 cm⁻¹ in the SiD₄ experiments which are shifted to 896 and 902 cm⁻¹ on ¹⁸O substitution, are readily assigned to the (O–Si–O) symmetric stretch. The counterparts in the protonated samples were not observed because they were probably masked by the strong absorption of parent SiH₄ in this region.

The sharp, strong 3677-cm⁻¹ absorption in SiH₄/O₃ photolysis experiments increased with the other S absorptions on irradiation of SiH₄/oxygen discharge samples. The ¹⁸O and D isotopic data are consistent with this being due to the strongest O–H stretching fundamental of species S.

The foregoing is in keeping with species S being identified as silicic acid, H_2SiO_3 . O'Keeffe and Gibbs¹⁷ have carried out SCF-MO calculations on H_2SiO_3 in order to optimize its geometry. It was found to be planar with the configuration shown in Scheme I. The fact that only one intense absorption is observed which can be assigned to an out-of-plane torsion is consistent with this structure.

The absorption belonging to species A which occurred at 1249 cm⁻¹ is also assigned to a ν (Si=O) stretch, since it shows a 38-cm⁻¹ shift to 1211 cm⁻¹ on ¹⁸O substitution (see Table I). With scrambled ^{16,18}O₃ it gave rise to a doublet at 1211 and 1249 cm⁻¹ corresponding to the pure ¹⁸O and pure ¹⁶O components, respectively, and furthermore the latter component had a shoulder at 1247 cm⁻¹ which was not present in the pure ¹⁶O spectrum (see Figure 3). This suggests that species A contains a further O atom, although a similar shoulder, which would be expected on the high frequency side of the pure ¹⁸O component, was not seen, probably due to insufficient resolution. In the SiD₄ experiments species A had an absorption at 891 cm⁻¹ and this shifted to 866 cm⁻¹ on ¹⁸O substitution which is very reasonable for a ν (Si–O) stretch. Unfortunately, the protonated counterparts were not seen, probably due to masking by SiH₄ absorptions in this region.

The above is consistent with A being identified as silanoic acid, HSiO₂H. The fact that it has a ν (Si=O) stretch coming, as it does, between that of H₂SiO and (HO)₂SiO fits in well with the trend of increasing ν (Si=O) frequency with electronegative substituents bonded to the >Si=O group. Although HSiO₂H might be expected to have cis and trans isomers, there was no evidence for the existence of more than one isomer in these experiments. It is more likely that the trans isomer was produced since it would be more stable than the cis form as with its carbon-containing analogue, formic acid.

The band at 837 cm⁻¹ in the discharge experiments and those at 839 and 834 cm⁻¹ in the ozone photolysis experiments are due to Si₂H₆, based on a comparison with matrix spectra.¹⁹ Presumably it is present as a doublet in the O₃ photolysis experiments on account of perturbation by a molecule of H₂O which is formed with Si₂H₆ and may take up two distinct orientations with respect to Si₂H₆. On deuteration, this absorption shifted to 620 cm⁻¹.

The intense absorption at 874 cm^{-1} , which appeared on photolysis of Ar matrices containing ${}^{16}O_3$ and SiD₄, exhibited an ${}^{18}O$ shift of 24 cm⁻¹, to 850 cm⁻¹, and so it is assigned to the stretch of a silicon-oxygen single bond. This 874-cm^{-1} band was weak in the discharge experiments where species are usually created with more internal energy than O₃ photolysis experiments. Furthermore, the protonated counterpart of the 874-cm^{-1} band is identified as the band at 859 cm^{-1} , which likewise was observed in the O₃ photolysis experiments but not in the discharge experiments. These bands at $859 \text{ and } 874 \text{ cm}^{-1}$ are tentatively assigned to $\nu(\text{Si-O})$ of SiH₃OH and SiD₃OD, respectively. There

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Phys. 1971, 20, 541. (19) Milligan, D. E.; Jacox, M. E. J. Chem. Phys. 1970, 52, 2594.

is a 15-cm⁻¹ blue shift on deuteration, because strong mode mixing occurs in SiH₃OH between the symmetric SiH₃ deformation and the ν (Si–O) stretch. The δ_s (SiH₃) fundamental absorption was not observed but it would come higher than ν (Si–O) in the 900-cm⁻¹ region. The effect of the interaction between these modes of a' symmetry is to separate the fundamentals; thus the band at 874 cm⁻¹, which is virtually a pure Si–O stretch in D₃SiOD, is pushed down to 859 cm⁻¹ in H₃SiOH. This absorption has a high percentage of SiH₃ deformation character since it shows an ¹⁸O shift of only 8 cm⁻¹. The blue shift of 15 cm⁻¹ of the ν (Si–O) stretch of H₃SiOH on deuteration is very similar to the blue shift of 14 cm⁻¹ of ν (Si–F) of SiH₃F on deuteration.¹⁸ This is to be expected because it is known that the properties of Si–OH and Si–F bonds are very much alike.¹⁰

The strong band, at 868 cm⁻¹, in both ozone photolysis and discharge studies with SiD₄, is also due to a ν (Si–O) stretch as it had an ¹⁸O shift of 24 cm⁻¹, to 844 cm⁻¹. The protonated counterpart was not observed. This absorption is tentatively assigned to the ν (Si–O) stretch of either D₂SiOD or SiOD, which could be formed in these experiments.

The bands at 951 and 986 cm⁻¹ show a SiH₄ concentration dependence similar to disilyl ether and they probably belong to species containing two Si atoms. Also, the band at 951 cm⁻¹ shows a 2-cm⁻¹ ¹⁸O shift and the band at 986 cm⁻¹ may have an ¹⁸O shift but it cannot be determined coming, as it does, in the same region as ¹⁸O₃. Thus both bands are attributed to aggregates of the form $H_xSi_yO_z$.

Mechanisms. The mechanisms of the reactions in the microwave discharge experiments are quite different from those in the ozone photolysis experiments as evidenced by the differences in reaction products and their yields, so they will be treated separately.

The microwave discharge experiments produced oxygen atoms for direct reaction with silane during codeposition; further blind discharge experiments showed that the contribution of vacuum-UV light from the argon discharge was unimportant in these studies. The gas-phase reaction of $O({}^{3}P)$ atoms and SiH₄ has been observed to proceed with a low activation energy (1.6 kcal mol⁻¹).²⁰ The primary step might be one of three reactions: (i) insertion of O atoms into a Si-H bond, (ii) H abstraction, and (iii) addition of an O atom to the Si atom to give a five-centered intermediate 1.



Intermediates containing 5-coordinated Si have been proposed before in, for example, the attack of halosilanes by bases via an S_N^2 mechanism.²¹ In view of the large yield of HSiOH, the major primary step is probably the insertion mechanism which would initially give silanol in a vibrationally excited state:

$$SiH_4 + O \rightarrow (SiH_3OH)^{\dagger}$$
(1)

Under the conditions of the microwave discharge experiments it is likely that reaction 1 takes place during deposition. Excited silanol can be quenched by the matrix to its ground state (2),

$$(SiH_3OH)^{\dagger} \rightarrow SiH_3OH$$
 (2)

otherwise it probably decomposes by eliminating hydrogen in one of two pathways 3 and 4. Pathway 4 is less likely than pathway

$$(SiH_3OH)^{\dagger} \rightarrow HSiOH + H_2 \tag{3}$$

$$(SiH_3OH)^{\dagger} \rightarrow H_2SiO + H_2 \tag{4}$$

3 because (i) the O-H bond stronger than the Si-H bond, and

(ii) there appears to be less possibility of eliminating molecular hydrogen from across the Si-O bond than eliminating it from the Si atom via pathway 3.

Silanone would more likely be formed by elimination of hydrogen from the 5-centered intermediate, 1:

$$H_4Si-O_{\bullet} \rightarrow H_2Si=O + H_2$$
 (5)

Alternatively rearrangement of 1, by H migration, would lead to silanol:

$$H_4Si-O_2 \rightarrow SiH_3OH$$
 (6)

The abstraction of H by O atoms is also an important primary step as evidenced by the presence of Si_2H_6 , which would be formed by reactions 7–9. The reaction of SiH_4 with OH radicals has

$$H_{3}Si-H + O \rightarrow SiH_{3} + OH$$
(7)

$$SiH_4 + OH \rightarrow SiH_3 + H_2O$$
 (8)

$$SiH_3 + SiH_3 \rightarrow Si_2H_6$$
 (9)

- - -

a rate constant of 1.2×10^{-11} cm³ molecule⁻¹ s⁻¹ at room temperature compared to a value of 4.8×10^{-13} cm³ molecule⁻¹ s⁻¹ for the reaction of SiH₄ with O(³P) atoms.²⁰ Furthermore, reaction 7 has been observed by ESR in the temperature range 288–549 K.²² Failure to detect SiH₃ in these microwave discharge experiments is believed to be indicative of the fast rate of reaction 9 which must take place, largely, before SiH₃ radicals can be trapped in the matrix cage.

In addition, for high concentrations of O atoms, trace amounts of silanoic and silicic acids were produced, probably via the secondary reactions:

$$HSiOH + O \rightarrow HSiO_{2}H$$
(10)

$$HSiO_2H + O \rightarrow H_2SiO_3 \tag{11}$$

The reaction of O atoms with Si_2H_6 gave HSiOH and probably SiH_4 . Unfortunately, identification of SiH_4 as a product of the reaction was made difficult by its presence in the Si_2H_6 sample as a trace impurity in spite of attempts to eliminate it by means of three fractional distillations. It appears from these observations that the weak silicon-silicon bond $(D = 74 \text{ kcal mol}^{-1})^{23}$ is cleaved. The primary step is almost certainly the insertion of the O atom into an Si-H bond.

$$Si_2H_6 + O \rightarrow (SiH_3SiH_2OH)^{\dagger}$$
 (12)

 SiH_4 is eliminated via the concerted rupture of the silicon-silicon and one of the silicon-hydrogen bonds in a reaction analogous to (3):

$$(SiH_3SiH_2OH)^{\dagger} \rightarrow SiH_4 + HSiOH$$
 (13)

The fact that no disilyl ether, $H_3SiOSiH_3$, was observed in the Si_2H_6 experiments is evidence that the O atom did not insert into the silicon-silicon bond of Si_2H_6 .

Ozone matrix photolysis experiments involve photodissociation of O_3 , eq 14, followed by reaction of SiH₄ with O(¹D), which is

$$O_3 + h\nu(220 < \lambda < 310 \text{ nm}) \rightarrow O_2({}^1\Delta_g \text{ or } {}^1\Sigma_g^+) + O({}^1D)$$
(14)

not quenched to $O(^{3}P)$ by the argon matrix.²⁴ The oxygen atom reaction with SiH₄ has already been discussed in the previous section, and reactions 1–9 again provide a plausible scheme. An important difference here is that the reactions take place in the matrix cage unlike the reactions of the microwave discharge experiments which took place during deposition. This accounts for the low yield of HSiOH since trapping of SiH₃OH via reactions

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1 and 2 is more favored under these conditions. This is analogous to the formation of SiCl₃OH as a major reaction product of the UV photolysis of SiHCl₃/O₃ mixtures in solid argon.²⁵ The low yield of HSiOH might also be due to photolysis with the high-pressure mercury arc via reaction 15.¹⁰

$$HSiOH + h\nu \rightarrow SiO + H_2 \tag{15}$$

In contrast to the microwave discharge experiments a large amount of disilyl ether was produced in ozone photolysis experiments. A plausible mechanism for the formation of the ether is via the nucleophilic attack of an oxygen lone pair of silanol on the Si atom of SiH₄ in the same matrix cage.

$$H_3 si$$
 $H_3 si$ $H_3 si$ $H_3 si$ $H_3 si$ H_2 (16)

Although the hydroxysilylene-silane reaction has the correct stoichiometry, only a trace amount of disilyl ether was observed in the discharge experiments with the highest yield of this intermediate species.

The high concentration of silicic acid in the ozone photolysis reactions compared to only trace amounts in the microwave discharge experiments without photolysis suggests that it is formed by photolysis of a heterodimer.

$$SiH_4 + O_3 \xrightarrow{n\nu} H_2SiO_3 + H_2$$
(17)

This reaction involved two insertions of O atoms into Si-H bonds, so it is very unlikely to proceed in one step. Perhaps the initial step involves photodissociation of an ozone molecule followed by reactions 1 and 3 to produce excited HSiOH which could react with O_2 in the same matrix cage. This mechanism is supported by the observation of silicic acid on irradiation of HSiOH in the presence of O_2 in discharge experiments employing higher oxygen concentrations.

$$HSIOH^* + O_2 \longrightarrow \begin{bmatrix} 0 & \cdots & 0 \\ S_1 & \cdots & H_2 SIO_3 \end{bmatrix} (18)$$

There was a considerable hydrogen-deuterium kinetic isotope effect in the photolysis experiments. The intensity of the SiO diatomic after photolysis of SiD_4-O_3 (see Table II) was less than half of its intensity following the photolysis of SiH_4/O_3 containing matrices (see Table I), provided the experimental conditions were the same. This is due to the higher zero-point vibrational energy

of the Si-H bond compared with that of the Si-D bond, since all four Si-H (or Si-D) bonds are broken in the formation of SiO.

It is perhaps noteworthy that 290–1000-nm irradiation gave only 10–20% of the product absorbance produced by full-arc photolysis. These observations suggest that SiH₄ and O₃ do not interact strongly enough to alter the ozone photochemistry. This stands in marked contrast to PH₃ and O₃, which form a strong complex that photolyzes with red light.²⁶

Conclusion

H₃SiOH, H₂SiO₃, H₂SiO, HSiO₂H, HSiOH, SiO, H₃SiOSiH₃, and Si₂H₆ have been identified as products of the photolysis of O₃ in argon matrices containing SiH₄. Three of these products, H₂SiO₃, H₂SiO, and HSiO₂H, contain a silicon-oxygen double bond and have not been previously observed spectroscopically. H₂SiO and HSiO₂H are not stable at room temperature unlike their C analogues, formaldehyde and formic acid. This reflects a major difference in the chemistry of C and Si, namely that C forms double bonds much more readily than Si, often attributed to the closer s-p orbital energy gap in the C atom than in Si. Instead Si has a greater ability to show divalent character: this trend increases steadily down group 4 as the pair of s electrons in the valence shell becomes more "inert". Thus, *cis*- and *trans*-HSiOH are slightly more stable⁴ than their isomer H₂SiO, but HCOH is unknown whereas H₂CO occurs abundantly.

HSiOH, which has been prepared by insertion of Si atoms into H_2O in solid argon,¹⁰ was formed in high yield in this work by reaction of SiH₄ with O atoms, produced by the discharge of O_2 in excess argon. It was almost certainly formed by insertion of an O atom into an Si-H bond of SiH₄ to give excited silanol, (H₃SiOH)[†], which eliminated H₂. HSiOH and SiH₄ were also produced in the O atom reaction with Si₂H₆.

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Registry No. O₃, 10028-15-6; SiH₄, 7803-62-5; H₃SiOH, 14475-38-8; H₂SiO₃, 7699-41-4; H₂SiO, 22755-01-7; HSiO₂H, 59313-55-2; HSiOH, 83892-34-6; SiO, 10097-28-6; H₃SiOSiH₃, 13597-73-4; Si₂H₆, 1590-87-0; SiD₄, 13537-07-0; ¹⁸O, 14797-71-8; Si₂D₆, 13537-08-1; SiHD₃, 13537-02-5; D₂SiOD, 96444-84-7; SiOD, 96444-85-8; D₃SiOD, 96444-86-9; HSi¹⁸OH, 83892-37-9; DSiOD, 83892-36-8; DSi¹⁸OD, 83892-39-1; O, 17778-80-2.

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