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Reactions and Structures of Matrix-Isolated SiO Species at Low Temperatures from Infrared Spectra

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The condensation-polymerization of essentially monomeric SiO has been followed in rare gas matrices using infrared detection over the range 33-4000 cm^{-1}. The species $(SiO)_2$ with a cyclic V_h structure, $(SiO)_3$ with a cyclic D_{3h} structure, and higher polymers have been observed. All possible infrared active frequencies were observed for $(SiO)_2$, e.g., 809.5 (B_{2u}), 766.7 (B_{3u}) and 79 (B_{1u}) cm^{-1} and the structure verified from the observed Si-isotope shifts for the B_{2u} and B_{3u} modes. For $(SiO)_3$ the E′-mode frequencies of 978, 628 and 311 cm^{-1} were observed. In more concentrated matrices many new frequencies appeared which may be attributed to higher polymers of SiO and most likely $(SiO)_5$. From these data the entropy of the dimer has been calculated as $S_{298}^{\circ} = 70.29$ eu and bond energy relationships for the polymers indicated. Co-condensation of SiO with BF_3, SiF_4 and SiF_2 in dilute rare gas matrices produced new frequencies in the latter two cases although the self polymerization of SiO was a stronger competing reaction.

Introduction

The reaction chemistry of divalent silicon species, the analogue to carbene chemistry, has been considerably extended by the availability of SiF_2 as a relatively stable reactant.[1] Little is known however of the reaction chemistry of SiO which can be readily produced as an essentially monomeric gas at temperatures of approximately 1100°C.[2] Also the nature of solid SiO at room temperatures is in considerable doubt.[3]

Both from entropy and pyrolysis considerations the reaction chemistry of high temperature species is best achieved at cryogenic temperatures using the co-condensation of reactants procedure, as demonstrated by SiF_2 and BF, for example.[1] Depending on the relative concentration of reactants, the chemistry of SiF_2 has been influenced by the ready formation of the dimer which from ESR studies[4] is apparently a diradical under cryogenic conditions. The dimer has even been observed in very dilute (10^{-3} molar) rare gas matrices.[5] Similarly BF has shown a strong tendency to polymerize in these dilute matrices.[6]

The present study is therefore directed to testing the suitability of SiO as a « carbene-type » reactant using co-condensation techniques at cryogenic temperatures. The species SiF_4, SiF_2 and BF_3 were used as co-reactants. Also some indication of the formation-mechanism and nature of solid SiO can be obtained from diffusion studies in an inert diluent such as a rare gas solid.

A report on the infrared spectra of $(SiO)_2$, in the region of 200-2000 cm^{-1}, isolated in nitrogen and argon matrices has recently appeared[7] and the results are in good agreement with this work.

Experimental Section

The matrix isolation apparatus used for these experiments has been described elsewhere.[8] Beckman IR–9 and IR–11 spectrometers were used. Commercially available SiO, which was shown[2] mass spectrometrically to vaporize under Knudsen conditions as monomeric SiO with approximately 0.1% dimer, was used in a Pt Knudsen cell. Temperatures of approximately 1100-1170°C were used for production of a molecular beam of SiO. Matrices were formed on a polished Cu surface which was found to be inert to the reactants used. Absorption spectra were obtained by reflection off this surface. Experiments were carried out using neon or argon matrices and various concentrations of solute. Spectra were recorded at approximate matrix temperatures of 5°K and 15°K for neon and argon matrices respectively.

Results

The infrared spectra obtained for these matrices, of differing concentrations, were found to vary considerably but were reproducible under fixed condi-

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(1) J. B. Ezell, J. C. Thompson, J. L. Margrave, and P. L. Timms, « Chemical Reactions of High Temperature Species », p. 219 in *Advances in High Temperature Chemistry*, Ed. LeRoy Eyring. Vol. 1, Academic Press, New York (1967).

(2) K. F. Zmbov and J. L. Margrave, *High Temp. Science*, in publication (1969).

(3) L. Brewer and R. K. Edwards, *J. Phys. Chem.* *56*, 351 (1954).

(4) H. Hopkins, J. C. Thompson, and J. L. Margrave, *J. Am. Chem. Soc.*, *90*, 901 (1968).

(5) J. W. Hastie, R. H. Hauge, and J. L. Margrave, *J. Am. Chem. Soc.*, *91*, 2536 (1969).

(6) J. W. Hastie, R. H. Hauge, and J. L. Margrave, unpublished work (1969).

(7) J. S. Anderson, J. S. Ogden, and M. J. Ricks, *Chem. Comm.*, 1585 (1968); also given in more detail by J. S. Anderson, and J. S. Ogden, to be published (1969).

(8) J. W. Haste, R. H. Hauge, and J. L. Margrave, *High Temp. Sci.*, *1*, 76 (1969); *J. Inorg. Nucl. Chem.*, *31*, 281 (1969).

tions. Even under optimum isolation conditions, *e.g.* less than 0.01 mole % SiO calculated concentration, seven distinct absorption frequency regions were observed over a wide spectral range (79-1229 cm^{-1}). From previous experiments with the same apparatus and with similar matrix concentrations, matrix temperature and molecular beam temperature, using SO_2[8] or PbF_2,[6] one would have expected complete isolation of SiO and hence only one infrared absorption feature around 1229 cm^{-1}. It is of particular note that of the many molecules that have been matrix isolated only the electronically similar species CO[9] and BF[6] were difficult to isolate. By carrying out numerous depositions in neon and argon matrices at various concentrations, which were achieved both by controlling the relative rates of deposition of rare gas and SiO and by subsequent diffusion experiments in the matrix, one could classify at least four sets of infrared absorptions.

the gas phase value for the monomer, showed the correct ^{28}Si—^{29}Si—^{30}Si isotope shift, and decreased in intensity on warming and recooling the matrix. Similarly the features at 810, 767 and 79 cm^{-1} decreased but those at 978, 628 and 311 cm^{-1} increased, thereby indicating the matrix reaction of SiO monomer with a second species to form a higher polymer. A more drastic warmup, but without destroying the matrix, resulted in the eventual decrease of all of these peaks with the concomitant formation of new features indicated as p or z in Figure 1.

Matrix Effects. As is often the case, the spectra of the isolated species show distinct, reproducible matrix effects, *e.g.* splitting of frequencies when observed with optimum resolution and also a shift of frequencies from the gas phase values. In this case the shift effect appears to be minimal as $\nu(SiO)_{gas} = 1229.9$ cm^{-1} as compared with the matrix values of 1228.5 and 1226.0 cm^{-1} in neon and argon respectively as given in Table I. Also, from accurate measurement of the Si-isotopic structure for ν(SiO), one obtains a value of $\omega_e x_e = 7.6 \pm 2$ cm^{-1} indicating essentially the same anharmonic behaviour for matrix isolated SiO as for the gaseous species where $\omega_e x_e = 6.0$ cm^{-1}. The H_2O spectrum was used as an internal calibrant to accurately obtain these measurements.

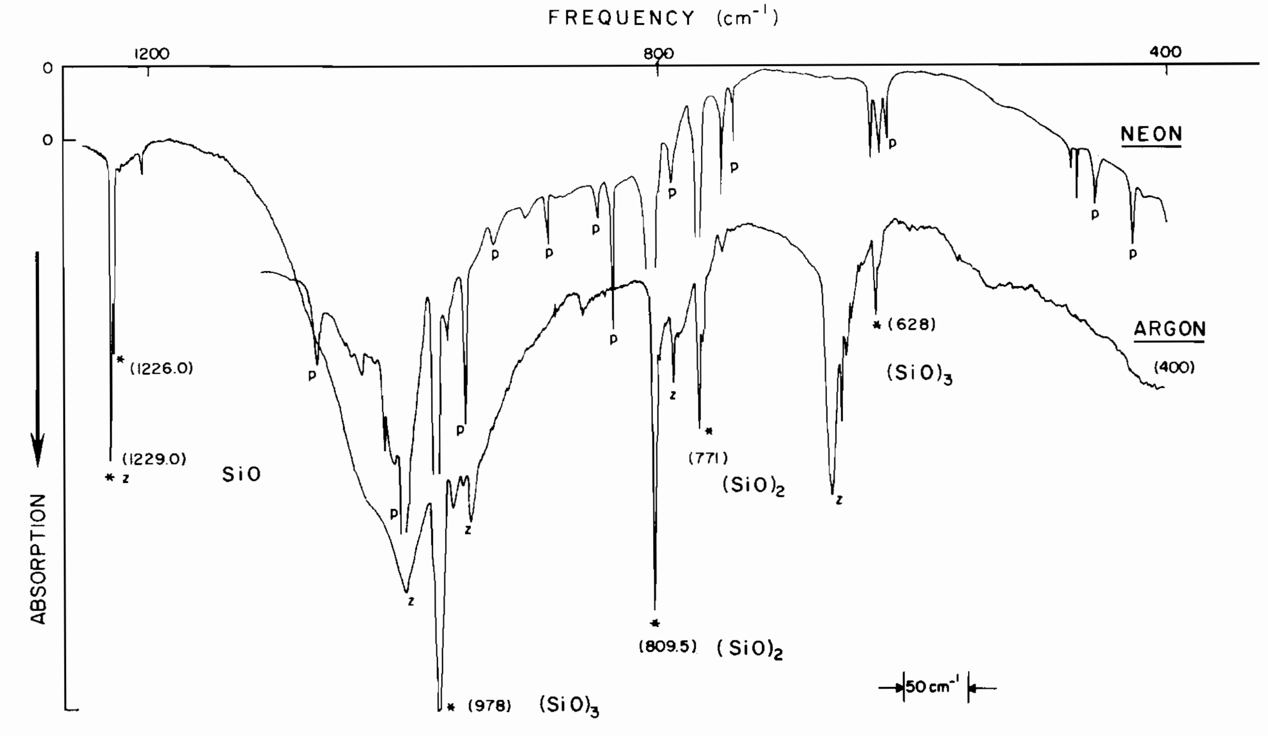

Figure 1. Infrared absorption spectra of matrix isolated SiO in neon (top curve) and argon (lower curve) matrices. * Indicates those features that disappear when considerable diffusion is allowed to occur due to warming of the matrix to 25-30°K for the case of an argon matrix. Z and p indicate features that are not present under optimum isolation conditions.

Typical spectra are shown in Figures 1 and 2 for the infrared and far-infrared regions respectively. Separate experiments were required for both these regions and hence there is no absolute relation between the intensities of Figures 1 and 2. With the best possible isolation conditions the following seven frequencies only were observed at approximately 1229, 978, 810, 767, 628, 311 and 79 cm^{-1}. Small frequency differences of a few wave numbers were noted for neon and argon matrices. The 1229 cm^{-1} absorption, which is in very close agreement with

Matrix splitting, of the order of a few wave numbers, was often seen in the initial matrices. For example, the argon spectrum of Figure 1 shows a splitting of the ν(SiO) absorption and in Figure 3 the 771.7 cm^{-1} absorption can be interpreted as a matrix splitting of the 766.7 cm^{-1} feature. This split-

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(9) G. E. Leroi, G. E. Ewing, and G. C. Pimentel, *J. Chem. Phys.*, *40*, 2298 (1964).

ting could often be removed by a mild warmup, *i.e.*, annealing of the matrix after deposition as indicated, for example, in Figure 3. However, it also appears that some of the new features arising from matrix warmup experiments are due to new trapping sites. For example, in argon matrices the higher dimer frequency decreased while an adjacent feature grew in at 788 cm^{-1}.

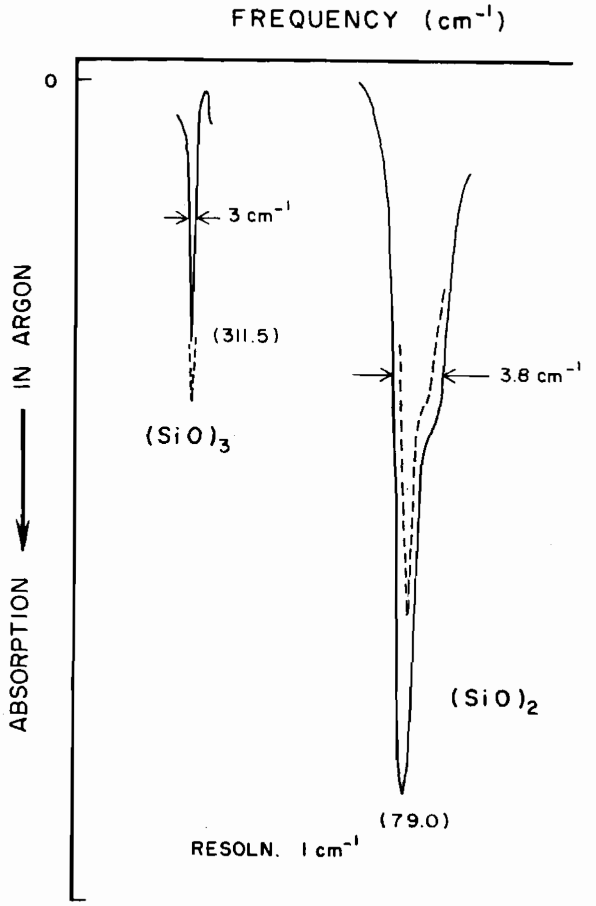

Figure 2. Far-infrared spectra of SiO in an argon matrix using good isolation conditions. The broken curve shows the change in intensity that occurs when diffusion is allowed to take place.

$(SiO)_2$ Dimer. Analysis of the fine structure of the 809.5 cm^{-1} and 771 cm^{-1} absorptions which always appeared with the same relative intensity suggested that these absorptions were due to a species containing two equivalent Si nuclei, namely $(SiO)_2$. This is in agreement with a recent independent observation by Anderson, Ogden and Ricks[7] using the ^{18}O isotope and nitrogen matrices. A normal coordinate analysis, as presented by Anderson *et. al.*[7] for a V_h bridged dimer srtucture, with a valence force field, leads to the following isotopic dependence, where μ is the reciprocal of mass, for the B_{2u} and B_{3u} stretching modes:

$$\frac{\nu_{B2u}}{\nu^{i}_{B2u}} = \frac{\nu_{B3u}}{\nu^{i}_{B3u}} = \left(\frac{\mu_{Si}+\mu_{O}}{\mu^{i}_{Si}+\mu_{O}}\right)^{1/2}$$

A comparison of the expected and observed isotope spacing based on this analysis is shown in Figure 3. The unsymmetrical species such as ($^{28}Si^{29}SiO_2$) are assumed to fall approximately between the symmetrical analogues. The good agreement indicates the frequencies to be associated with the B_{3u} and B_{2u} modes of the V_h $(SiO)_2$ species.

Following the analysis of Berkowitz[10] for the isostructural alkali-halide dimers Anderson and Ogden[7] have calculated as a lower limit to the B_{1u} frequency a value of 33 cm^{-1}. The lowest frequency observed at 79 cm^{-1}, which showed the same diffusion characteristics as the assigned B_{3u} and B_{2u} frequency species, is almost certainly the B_{1u} mode of the dimer. Thus, the adopted procedure for calculating the experimentally difficult to obtain out of plane B_{1u} mode appears to be a reasonable approximation and the method has recently been used to determine the entropy of $(TeO)_2$.[11] All possible infrared active frequencies have therefore been observed for the dimer of SiO.

$(SiO)_3$ Trimer. With the elimination of the SiO and $(SiO)_2$ frequencies from the spectra there remain, for the very dilute matrices, three unexplained frequencies, namely 978, 628 and 311 cm^{-1}. These frequencies appear with similar relative magnitudes

Table I. Infrared Frequencies (cm^{-1}) of SiO Species

Monomer [a]			Dimer [b]			Trimer [c]		Higher Polymers [d]	
Ne	Ar	Assign.	Ne	Assign.		Ar	Assign.	Ne	Assign.
1228.5	1226.0	^{28}SiO	809.5	$^{28}Si_2O_2$	B_2u	978	E′	1074(m)	$(SiO)_5$
1220.8	1218.4_3	^{29}SiO	806.8	$^{28}Si^{29}SiO_2$				1004(s)	$(SiO)_5$
1213.6	1211.3_0	^{30}SiO	804.3	$^{28}Si^{30}SiO_2$		628	E′	957(m)	$(SiO)_5$
				$^{29}Si^{29}SiO_2$		311	E′	840(m)	$(SiO)_5$
			801.7	$^{29}Si^{30}SiO_2$				787(m)	$(SiO)_5$
			798.7	$^{30}Si^{30}SiO_2$		74 (?)	A_2''	755(m)	$(SiO)_5$
								625 (m)	$(SiO)_5$
			766.7	$^{28}Si_2O_2$	B_3u			455(m)	$(SiO)_5$
			764.5	$^{28}Si^{29}SiO_2$				425(m)	$(SiO)_5$
			762.0	$^{28}Si^{30}SiO_2$					
				$^{29}Si^{29}SiO_2$					
			79.0 (Ar)	Si_2O_2	B_1u				

[a] Absolute frequency accuracy of ±0.2 cm^{-1}, but relative frequencies are accurate to ±0.05 cm^{-1}. [b] Relative frequencies accurate to ±0.1 cm^{-1}; the absolute values can vary by several wave numbers depending on the concentration of species in the matrix. [c] Frequency accuracy ±1 cm^{-1}; the 74 cm^{-1} assignment is doubtful as it overlaps with a dimer absorption in the same region. [d] Frequency accuracy ±2 cm^{-1}; unlisted weaker bands can be observed in Figure 1. Several of these absorptions could also possibly be attributed to $(SiO)_4$

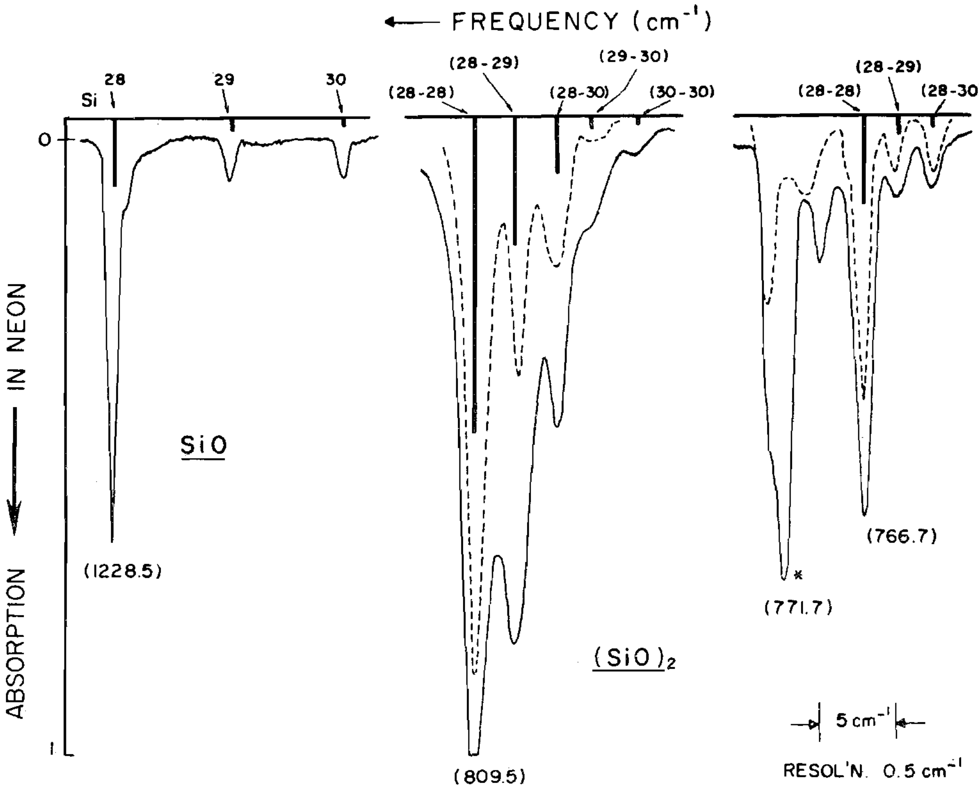

Figure 3. Infrared spectra of SiO species showing the fine structure produced by isotope and matrix splitting. The broken curve indicates the spectra obtained after annealing. The solid vertical lines indicate the predicted positions and approximate relative intensities of the various naturally occurring Si—28, 29 and 30 isotopic species.

and each shows an increase in intensity on initial warmup at the expense of SiO and $(SiO)_2$. Thus, the spectra are very likely due to a trimer $(SiO)_3$. With the assumption of a planar ring (D_{3h}) model one would expect to observe three E′ in-plane modes and one A_2'' out-of-plane mode. A valence force field analysis[7] with the neglect of certain interaction force constants successfully accounts for the three observed frequencies as the E′ modes. From the dimer analogy the A_2'' mode should produce a frequency in the far-infrared region. However, no absorption feature other than the 79 cm^{-1} dimer frequency was seen. One may have expected a reasonably intense absorption, as was found to be the case for the B_{1u} species of the dimer. It is possible that both the A_2'' and B_{1u} frequencies overlap and the broad nature of the 79 cm^{-1} absorption would support this view. It appears unlikely that the symmetry of $(SiO)_3$ is anything other than that indicated, as a greater number of infrared active frequencies would be expected for other geometries.

One notes the existence of analogous structures, for example, hexamethylcyclotrisiloxane and benitoite from the areas of organo-silicon and mineral chemistry respectively.[12]

Higher Polymers: $(SiO)_n$. The formation of higher matrix isolated polymers was also recorded down to 400 cm^{-1} as shown by Figure 1. The sharpness of the spectral features, particularly for the neon matrix, is taken to indicate that these frequencies arise from discrete matrix isolated molecules and not crystallites of SiO. Qualitatively the spectral features, denoted by p in Figure 1, are what one might expect on addition of an $(SiO)_2$ group to the six membered $(SiO)_3$ ring. The reaction of monomeric SiO with either the dimer or trimer to form higher polymers may be excluded from consideration as these higher polymers are observed to grow even when all the SiO has been previously used in the trimer production.

Very little molecular rearrangement would be required to form a double six-membered ring species, $(SiO)_5$, from the reaction of $(SiO)_2$ and $(SiO)_3$. A quantitative analysis of this interpretation of the spectra will require the use of both ^{18}O isotopic substitution, extension to the far infrared and possibly the use of Raman spectroscopy.

Practically all of the frequencies denoted as p in Figure 1 can be accounted for by the proposed double ring pentamer as it would be of C_{2v} point group having the symmetry species $9A_1+9A_2+4B_1+2B_2$ with the A_1, B_1 and B_2 modes being infrared active. That is, the formation of the pentamer from the dimer and trimer would be expected to increase the number of observed frequencies by fifteen. The observation of at least eleven new frequencies, in the

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(10) J. Berkowitz, *J. Chem. Phys.*, *29*, 1386 (1958).
(11) D. W. Muenow, J. R. Hastie, R. Hauge, R. Bautista, and J. L. Margrave, *Trans. Faraday Soc.*, in press (1969).
(12) A. J. Barry and H. N. Beck p. 189, « Inorganic Polymers, » F. G. A. Stone and W. A. Graham (Ed.), Academic Press, New York (1962).

region of 400-1100 cm^{-1} alone, is therefore in accord with the proposed pentamer although the formation of the tetramer from a bi-molecular dimer reaction or the hexamer from a bi-molecular trimer reaction cannot be completely discounted.

Thermodynamic Considerations for $(SiO)_n$. The observation of $(SiO)_n$ species where n varies from two to at least five has certain thermodynamic implications. From the gas phase mass spectrometric study of the monomer-dimer equilibrium the following atomization energies are known: SiO = 186±5 kcal/mole[13] and $(SiO)_2$ = 420±10 kcal/mole. Therefore, the average SiO bond energy in the dimer, which contain four equivalent bonds, is $D_{SiO} = 105 \pm 2$ kcal/mole. A lower limit can also be obtained for the trimer stability as the free energy of formation from monomer and dimer must be negative and the entropy change has a negligible effect at these low matrix temperatures. Hence, a lower limit to the stability is given by the sum of monomer and dimer heats of atomization, *i.e.* ΔH_{atoms} $(SiO)_3 > 606$ kcal/mole, which, for the six-membered ring structure, yields an Si–O bond energy of at least 101 kcal/mole. Similarly, the postulated bi-cyclic pentamer would have a minimum Si–O bond energy of 91 kcal/mole.

Although one expects to have more of the complex polymers in the equilibrium vapor at the high temperatures, only the dimer has been observed mass spectrometrically. The total pressure over SiO increases beyond the limits of conventional mass spectrometric instrumentation before sufficiently high temperatures to produce higher polymers in detectable concentrations are reached. For lower vaporization temperatures– for example with PbO—one does observe $(PbO)_n$ where n varies from one to five.[14] If one invokes use of the same structures for $(PbO)_n$ as for $(SiO)_n$, *i.e.* four M–O bonds for the dimer, six for the trimer, nine for the tetramer and eleven for the pentamer, then from the known atomization energies,[14] the average bond energy for all of these PbO species is in the range of 63±3 kcal/mole. This approximate invariance of bond energy with ring size compares favorably with the $(SiO)_n$ case where the average energy is in the range 90-100 kcal/mole.

The structure of SiO solid has not been resolved, however it is interesting to note that if it is basically one of planes of hexagonal units with weak cross linkage planes, then the vaporization energy of SiO can be satisfactorily predicted as follows. To split-off an SiO group from a two dimensional hexagonal ring system would require rupture of four Si–O bonds and, from the bi-cyclic pentamer example, would require approximately 364 kcal/mole of energy. Two new Si–O bonds would form due to reclosing of the ruptured ring system, with the release of approximately 182 kcal/mole. Also the free SiO group would form a bond of higher order than when contained by the ring system. The energy release accompanied by this process would amount to the difference in the dissociation energy of the monomer and an SiO bond in the dimer, *i.e.* approximately 95 kcal/mole. Thus the total energy-loss, produced by the removal of SiO from the ring system, amounts to 87±10 kcal/mole. This compares very favorably with the measured heat of sublimation for SiO of 83±3 kcal/mole.[2]

Entropy of $(SiO)_2$. From the known geometry, estimated internuclear separations, measured and calculated vibrational frequencies one can accurately determine the entropy of this species. From Anderson et al[7] the Si–O separation is 1.71 Å and the O–Si–O and Si–O–Si angles 87° and 93° respectively. The frequencies (cm^{-1}) used are: 809 (B_{2u}), 775 (B_{1g}), 771 (B_{3u}), 767 (A_g), 216 (A_g), and 79 (B_{1u}). The ground electronic state is most likely that of monomeric SiO, *i.e.* ^1A_g.[15] The entropy of $(SiO)_2$ is then $S_{298}^\circ = 70.29$ eu and at the temperature at which it appears as a vapor species over the solid of the same stoichiometry the value increases to $S_{1463}^\circ = 99.44$ eu. Schick[13] has previously estimated the entropy to be $S_{298}^\circ = 64.1$ eu. Using the reported mass spectrometric partial pressure data and the known entropy of SiO one obtains a revised third law heat for the reaction:

$$2\ SiO\ (g) = (SiO)_2\ (g)$$

of $\Delta H_{298}^\circ = -47.2 \pm 2$ kcal/mole. The error estimate allows for an error by a factor of three in the relative partial pressures of SiO and $(SiO)_2$. This value does not differ very significantly from the reported value of $\Delta H_{298}^\circ = -46 \pm 2$ kcal/mole, based on an estimated dimer entropy.[2]

Reactions of SiO with SiF_4, SiF_2 and BF_3. The infrared spectra of matrix isolated SiF_4,[5] SiF_2[5] and BF_3,[16,6] have been previously recorded. As was the case for SiO, the species SiF_2 and BF_3 undergo self-polymerization when their concentration is increased in the matrix. Co-condensation of SiO with the reactants was carried out using a large excess of rare gas for matrix production. Effective isolation of unreacted monomeric SiF_4, SiF_2 and BF_3 was obtained but the dimer and trimer of SiO were still present. For SiF_4 and SiF_2 several new frequencies, some of which increased in intensity on matrix warming, appeared with the co-condensation of SiO. BF_3 appeared unreactive in the matrix, forming only $(BF_3)_2$ and $(SiO)_2$ and $(SiO)_3$. The reactivity of SiF_4 with SiO species is most likely related to the low tendency for SiF_4 to self-polymerize in matrices. Thus the lack of reaction of BF_3 is in accord with its known strong tendency to self-polymerize in matrices. The SiF_2 reaction is an intermediate case as it is observed to dimerize, though not as readily as BF_3.

Two products appeared to be formed by the reaction of SiO with SiF_4. The first-one, formed during the matrix co-condensation period, gave rise to a

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(13) This is an average of several reported values, see for example refs. 2, 14; D. L. Hildenbrand, private communication (1969); H. L. Schick, *Chem. Revs.*, *60*, 331 (1960).

(14) J. Drowart and P. Goldfinger, *Angew. Chem. Intl. Ed.*, 6, 581 (1967).

(15) D. R. Stull, Ed., « JANAF Thermochemical Tables. » No. PB-168-370 (1964).

(16) J. M. Bassler, P. L. Timms, and J. L. Margrave, *J. Chem. Phys.*, *45*, 2704 (1966).

new sharp absorption at 1048 cm^{-1} (argon matrix). The second formed during warmup of the matrix and produced two new absorptions at 928 cm^{-1} and 882 cm^{-1}. The high value of the frequency for the former product could be attributed to a Si=O stretch in an adduct species where SiF_4 is bonded to SiO through several silicon-fluorine-silicon bridges. The latter product could be the result of the reaction of either $(SiO)_2$ or $(SiO)_3$ with SiF_4.

The reaction of SiF_2 with SiO likewise resulted in the formation of a least two new products. The first, formed during co-condensation gave rise to a frequency at 958 cm^{-1} which is not sufficiently high to be assigned as an Si=O stretch. Hence, the most likely product is one involving either the dimer or trimer with SiF_2 and where Si–F–Si bridging bonds are formed to one of the Si-groups in the ring. A second product appeared when the matrix was warmed and gave rise to frequencies at 1116 and 1081 cm^{-1}. These are sufficiently high to be associated with silicon-double-bond-oxygen stretching and and indicate the probable reaction of monomeric SiO with SiF_2. A reduction in the value of the Si=O stretch frequency, from 1229 to the 1000-1100 cm^{-1} region, can readily be accounted for in terms of an increased effective mass of Si due to the addition of an SiF_2 group. A useful example of this effect is given by the H_2CO and D_2CO analogy. The CO frequencies are 1744 cm^{-1} and 1700 cm^{-1} respectively[17] whereas from the increase in effective mass on C one would predict a CO frequency of approximately 1685 cm^{-1} for the deuterated formaldehyde. Similarly, treating the addition of SiF_2 to SiO as an increase in the effective Si-mass of from 28 to 94 amu, one would predict an Si=O frequency decrease to approximately 1058 cm^{-1}, in agreement with the above observations. Silicon-fluorine bridging would produce a feasible structure. It is highly probable that not all possible infrared absorptions, associated with the formation of products, were observed owing to overlap with the many reactant peaks present.

It may be concluded from these reactions that most of the SiO is unavailable for reaction due to its strong tendency to self-polymerize and thus only minor yields of product are observed.

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(17) G. Herzberg, « Infrared and Raman Spectra, » p. 300, Van Nostrand, New York (1945).