Transition Metal Derivatives of SiO: Interaction of Molecular SiO with Silver Atoms in an Argon Matrix

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Co-condensation of silver atoms with monomeric SiO and an excess of argon yields Ag(SiO) and probably $Ag_2(SiO)$, identifiable by their i.r. spectra; $^{28,29,30}Si$ and $^{16,18}O$ isotopic shifts imply not a linear but a triangular structure for Ag(SiO) with $\angle$ AgSiO $\leqslant 90°$

The chemistry of lower silicon oxides excites considerable interest because of its relevance to surface reactions of silicon wafers which are exploited in the semiconductor industry.[1] Furthermore, since silicon wafers can be made conducting by coating with gold, studies of the systems Si/O/Au and Si/O/Ag are potentially important as regards the nature of these semiconductors. Although the 'high temperature' molecule SiO has been shown to have a relatively rich matrix chemistry,[2] there has not hitherto been any indication of whether, like CO and another 'high temperature' molecule PN,[3] it is able to co-ordinate to transition-metal atoms.† Here we describe the interaction of SiO molecules with silver atoms in an argon matrix at *ca.* 10 K, and present i.r. spectroscopic evidence for the formation of two products Ag(SiO) and $Ag_2(SiO)$.

Silver atoms and SiO molecules, produced either by passing a stream of oxygen over silicon and silver or a silver–gold alloy,‡ or by heating a mixture of silicon, silica, and silver at 1250—1350 °C, were co-condensed with an excess of argon on a copper mirror cooled to *ca.* 10 K. The condensate was estimated, typically, to have the composition Ar : SiO : Ag *ca.* 1000 : 5 : 1. Its i.r. spectrum, measured with a Bruker IFS 113 v FTIR spectrometer, showed bands due to CO_2,[4a] CO,[4b] OCS,[4c] and $Ag(CO)_2$[4d] originating in carbon and sulphur impurities in the materials used.[4e] In addition to these and to primary absorptions due to SiO, $[SiO]_2$, and $[SiO]_3$,[5] we observed some very weak features near 770 cm^{-1} probably resulting from the interaction of silver atoms or clusters with the cyclic $[SiO]_2$ molecule co-ordinated, it appears, in a symmetrical η^4-fashion.§ Most conspicuous, however, is the appearance of two stronger absorptions at 1163.0 and 1173.4 cm^{-1} (see Figure 1), the growth and decay patterns of which imply that they originate in two distinct absorbers (A) and (B). For the purposes of this communication, we are concerned with the natures of the species (A) and (B).

The presence of CO as an impurity raises the possibility that (A) and (B) contain carbonyl groups. Scrutiny of the ν_{CO} region failed, irrespective of the concentrations of (A) and (B), to disclose any absorption whose intensity paralleled that at either 1163.0 (I_{1163}) or 1173.4 cm^{-1} (I_{1173}). The possibility that (A) or (B) contains co-ordinated oxygen [*cf.* $(OC)AgO_2$ produced by co-condensing Ag atoms with mixtures of CO and O_2][6] we discount on two grounds: (i) the absorptions

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† U.v.-visible photolysis of $Mo(CO)_6$ isolated in an Ar matrix in the presence of SiO does not afford detectable amounts of species like $Mo(SiO)(CO)_5$, regeneration of $Mo(CO)_6$ and aggregation reactions such as $SiO + Si_2O_2 \rightarrow Si_3O_3$ providing efficient alternative reaction channels. M. J. Almond, A. J. Downs, T. Mehner, and H. Schnöckel, unpublished results.

‡ The vapour pressure of silver at these temperatures (0.2—2 torr) is rather high for matrix experiments, so silver–gold alloys were used to reduce the vapour pressure of the silver and facilitate changes in the flux, and hence the matrix concentration, of silver atoms.

§ This conclusion is based on the i.r. absorption patterns exhibited by matrices containing ^{18}O-enriched $(SiO)_2$.

Table 1. Observed and calculated isotopic shifts for ν_{SiO} and ν_{CO} of the molecules Ag(SiO), Ni(CO), and Rh(CO)

Molecule	$\nu(^{28}Si^{16}O)$ $\nu(^{12}C^{16}O)$ /cm^{-1}	Isotopes	Calculated $\Delta\nu$/cm^{-1} [a] ∠OXM = 180°	∠OXM = 135°	∠OXM = 90°	∠OXM = ∠XOM = 72.5°	∠XOM = 90°	∠XOM = 135°	∠XOM = 180°	$\Delta\nu$/cm^{-1} obs.	corr.[b]
Ag(SiO)	1163.0	^{16}O—^{18}O	40.94[c]	41.59	42.06	42.35[d]	42.11	44.68	51.57	41.7[e]	42.1[e]
		^{28}Si—^{29}Si	7.65	7.45	7.33	7.23[d]	7.31	6.49	4.23	7.1[e]	7.2[e]
		^{28}Si—^{30}Si	14.80	14.42	14.19	14.00[d]	14.16	12.55	8.15	14.0[e]	14.1[e]
Ni(CO)	1996	^{16}O—^{18}O	43.8[f]	45.9[f]	48.3[f]	—	—	—	—	43.0[g]	43.5[e]
Rh(CO)	2013	^{12}C—^{13}C	47.8[h]	46.3[h]	44.7[h]	—	—	—	—	47.2[i]	47.8[e]

[a] X = Si or C. [b] Corrected for anharmonicity; see ref. 11. [c] Where not otherwise specified, the following distances and frequencies have been assumed: AgSiO, Ag–Si 250, Si–O 150 pm, ν(Ag–Si) 200, δ(Ag–Si–O) 60 cm^{-1}; AgOSi, Ag–O 200, Si–O 150 pm, ν(Ag–O) 400, δ(Ag–O–Si) 70 cm^{-1}. The frequencies have been estimated with the aid of the tables given in ref. 12. The calculated frequency shifts are influenced but little by the precise values assigned to either the distances or the frequencies of the unobserved fundamentals. [d] The following parameters have been assumed: Ag–Si 250, Ag–O 250, Si–O 150 pm, ν(Ag–O) 400, ν(Ag–Si) 200 cm^{-1}. [e] This work. [f] The following parameters have been assumed: Ni–C 180, C–O 112 pm, f(Ni–C) 215 N m^{-1}, f_δ(NiCO) 9 N m. [g] Ref. 9a. [h] The following parameters have been assumed: Rh–C 200, C–O 112 pm, f(Rh–C) 215 N m^{-1}, f_δ(RhCO) 9 N m. [i] Ref. 9b.

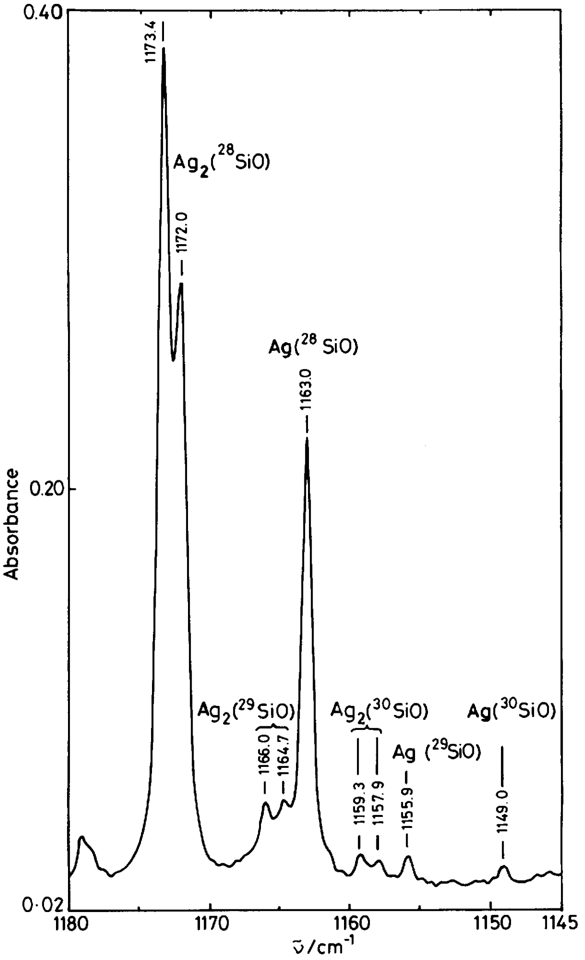

Figure 1. The i.r. absorption spectrum (1145—1180 cm^{-1}) of an Ar matrix containing Ag atoms and SiO molecules, showing the ν_{SiO} features of the species believed to be Ag(SiO) and Ag_2(SiO). The splitting of the band at 1173.4 cm^{-1} (and each of its satellites) into two components separated by 1.4 cm^{-1} is attributable to matrix site effects.

characteristic of (A) and (B) were also observed in experiments designed to exclude O_2 from the reaction mixture; and (ii) none of the experiments revealing the presence of (A) and (B) showed any sign of an i.r. band attributable to an AgO_n moiety. Changes in the matrix concentration of SiO showed that I_{1163} and I_{1173} invariably changed in direct proportion to the intensity of the band at 1226 cm^{-1} due to the SiO monomer;[5] experiments carried out under identical conditions but excluding Ag atoms identified monomeric SiO as the principal matrix guest. There is strong circumstantial evidence therefore that both (A) and (B) contain but one SiO group. This inference is supported by the observation of bands due to isotopomers of (A) and (B) containing naturally occurring ^{29}Si and ^{30}Si or generated by deliberate enrichment in ^{18}O. As illustrated in Figure 1, for example, both the bands at 1163.0 and 1173.4 cm^{-1} are accompanied by satellites due to $\nu(^{29}SiO)$ and $\nu(^{30}SiO)$, the intensities and energies of which are consistent with the formulation Ag_n(SiO) for both (A) and (B).

It is less easy to determine the value of n. Increasing the matrix concentration of Ag atoms results in intensification of both the new bands. Significantly, however, I_{1173} increases at slightly more than twice the rate of I_{1163}. The most obvious interpretation is that (A) is Ag(SiO), whereas (B) contains two, or conceivably more, Ag atoms.¶ Species containing more than two Ag atoms have not been detected when silver vapour is co-condensed in a matrix with C_2H_4[7] or CO,[4d] although it appears that the Ag_3 cluster is formed on co-condensation of silver vapour with an excess of noble gas.[8] Control experiments showed that vaporisation of silver under the conditions leading to the formation of (A) and (B) followed by co-condensation with CO rather than SiO, afforded i.r. spectroscopic evidence of no species other than $Ag(CO)_2$,[4d] *i.e.* a molecule containing just a single Ag atom.

Notwithstanding repeated and careful scrutiny of the spectral region down to 150 cm^{-1}, we failed to find any absorption attributable to a vibration involving significant motion of the Ag atoms in either (A) or (B). This is not

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¶ If it is assumed that equilibrium conditions prevail, that the equilibrium $2Ag \rightleftharpoons Ag_2$ provides the only source of Ag_2 species, and that SiO is the sole reagent scavenging Ag and Ag_2 with equal efficiency, the intensity of the absorption due to Ag_2(SiO) should vary as the *square* of the intensity of the absorption due to Ag(SiO). That I_{1173} exhibits a slightly more-than-quadratic relation to I_{1163} finds a ready explanation in the relaxation in practice of one or more of the simplifying assumptions [*e.g.* Ag_2(SiO) may be derived not only from the reaction $Ag_2 + SiO \rightarrow Ag_2(SiO)$, but also from the reaction $Ag + Ag(SiO) \rightarrow Ag_2(SiO)$]. In the circumstances, it would be difficult to reconcile the intensity changes with any pair of products other than Ag(SiO) and Ag_2(SiO).

altogether surprising in view of the problems presented by the location by i.r. spectroscopy of analogous modes of metal carbonyls, *e.g.* Ni(CO) and Rh(CO).[9] However, the degree of perturbation of ν(SiO), which for (A) is red-shifted by 63 cm^{-1} (5.1%) with respect to unco-ordinated SiO, implies relatively strong interaction between SiO and Ag. Weak interaction comparable with that in the loosely bound complex $OSi \cdots Cl_2$[2] is expected to change ν(SiO) by no more than *ca.* 5 cm^{-1} (<0.4%). We note that ν(CO) is red-shifted by 4.2—11% with the transition from free CO to a transition-metal monocarbonyl.[9,10]

To assess the geometry of the molecule Ag(SiO) we have analysed the ^{16}O—^{18}O, ^{28}Si—^{29}Si, and ^{28}Si—^{30}Si isotopic shifts experienced by the ν(SiO) band of (A) at 1163.0 cm^{-1}, after due allowance for anharmonicity.[11] Vibrational frequencies have been calculated for different models, *viz.* Ag–Si–O or Ag–O–Si, on the basis of an SVFF with only diagonal *F*-matrix elements; the assumed interatomic distances and frequencies of unobserved fundamentals are specified in Table 1. Hence it emerges that the isotopic shifts can best be reproduced by a triangular molecule with $\angle AgSiO \leqslant 90°$; whether this implies 'side-on' bonding of the SiO ligand is an open question. On the other hand, neither these nor calculations involving more sophisticated force fields can be reconciled with a linear structure. By contrast, similar calculations for the monocarbonyls Ni(CO) and Rh(CO), characterised by their ν_{CO} modes in matrix experiments,[9] confirm the expected linearity of the MCO framework (M = Ni or Rh).

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