

## Studies of the Reactions of SiO and Silver Atoms in Hydrocarbon Matrices at 77 K†

J. H. Bernard Chenier,<sup>a</sup> James A. Howard,<sup>a</sup> Helen A. Joly,<sup>a</sup> Brynmor Mile,<sup>a</sup> and Peter L. Timms<sup>b</sup>

<sup>a</sup> Division of Chemistry, National Research Council of Canada, Ottawa, Ontario K1A 0R9, Canada

<sup>b</sup> School of Chemistry, University of Bristol, Cantock's Close, Bristol B58 1TS, U.K.

Electron paramagnetic resonance (EPR) spectroscopic studies indicate that reaction of Ag atoms with SiO in an adamantane matrix at 77 K yields Ag(SiO), Ag(Si<sub>2</sub>O<sub>2</sub>), Ag(Si<sub>3</sub>O<sub>3</sub>), and Ag(Si<sub>n</sub>O<sub>n</sub>); the bonding in these species is discussed.

Under matrix isolation conditions silver atoms react with carbon monoxide to form a series of carbonyls whose structures have been assigned from their electronic, IR, and electron paramagnetic resonance (EPR) spectra.<sup>1–4</sup> Linear mono- and bis-carbonyls, Ag(CO) and Ag(CO)<sub>2</sub>, are formed together with two tris conformers, Ag(CO)<sub>3</sub>, one of which is planar with a <sup>2</sup>A<sub>2</sub>' ground state and the other pyramidal with a <sup>2</sup>A<sub>1</sub>' ground state. It is of interest to examine the interactions of silver atoms with the CO analogue, SiO, especially since such interactions are important in understanding the nature of the conduction processes in silicon wafers coated with Au and Ag.<sup>5</sup> Mehner, Schnöckel, Almond, and Downs have recently used FTIR spectroscopy to show that Ag(SiO) and Ag<sub>2</sub>(SiO) and possibly Ag(SiO)<sub>2</sub> are formed by reacting SiO with Ag atoms in an argon matrix at 10 K.<sup>6</sup> Here we report an EPR and FTIR study of the reaction in an adamantane matrix at 77 K in a rotating cryostat.

The rotating cryostat technique has been described in detail elsewhere.<sup>7,8</sup> SiO vapour was deposited from solid SiO held in a resistively heated molybdenum furnace on to the freshly frozen surface of the adamantane matrix and then bombarded with <sup>107</sup>Ag atoms from another furnace located in the next port of the outer housing of the cryostat. Reactants and products were immobilized in the interleaving spiral structure

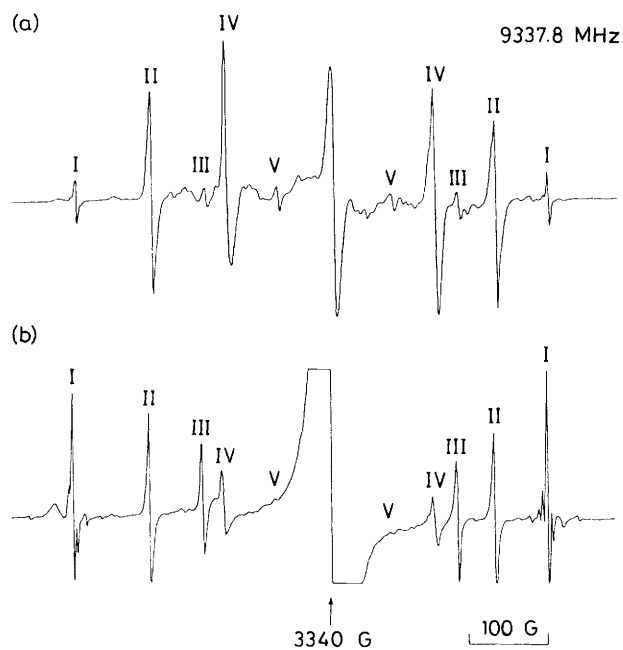
and were examined by *in situ* FTIR and by EPR after transfer from the cryostat still at 77 K and under high vacuum.

The *in-situ* FTIR reflectance spectra of the deposits with only SiO deposited showed that the most abundant SiO species were polymeric Si<sub>n</sub>O<sub>n</sub> with a broad absorption centred at 980 cm<sup>-1</sup>, Si<sub>3</sub>O<sub>3</sub> with an intense band at 633 cm<sup>-1</sup> and Si<sub>2</sub>O<sub>2</sub> with an intense band at 785.<sup>9–12</sup> Other bands associated with these species were obscured by adamantane absorptions. No new FTIR bands were observed when Ag atoms were deposited with SiO but the concentrations of Ag/SiO species were probably too low to be detected in our system. Thus there was considerable scattering of the IR beam by the powdery deposits and the possibility of overlap of product bands with adamantane bands.

The EPR spectra of Ag/SiO/adamantane deposits at 77 K were sensitive to small changes in the conditions of deposition. Figures 1(a) and 1(b) show spectra from two different experiments. The latter shows a high degree of SiO polymerisation even though the intensities of the mononuclear silver species are more intense. This probably arose because the flux of SiO decreased during deposition. The central isotropic line with *g* 2.0012 was observed in the absence of Ag and is assigned to paramagnetic polymeric (SiO)<sub>n</sub> whose structure still remains obscure.<sup>13,14</sup> The remaining transitions are almost isotropic sets of five doublets arising from interaction of the unpaired electron with a single <sup>107</sup>Ag nucleus (*I* 1/2). On annealing to 252 K lines I and II decayed most rapidly followed by lines III with lines IV and V decreasing much less rapidly. Only the major features or those that persisted to higher temperatures are considered here. A Breit Rabi<sup>15</sup> analysis of transitions I to V gave the EPR parameters listed in Table 1.

The <sup>107</sup>Ag hyperfine coupling for species I is close to that for Ag atoms trapped in site II in adamantane (1681 MHz).<sup>8</sup> Additional lines from Ag atoms in site I in adamantane (1771 MHz) and <sup>109</sup>Ag impurity are also visible in Figure 1(b). The lines from site I showed enhanced proton spin flip satellites separated from the main line by 15 MHz at high power (20 mW) that are characteristics of isolated Ag atoms in hydrocarbon matrices.

Doublets II showed a marked reduction in intensity on annealing. We tentatively assign these lines to the monoligand complex Ag(SiO) on the basis of the known thermal lability of Ag(CO) and the increasing intensity of all the species with higher Ag hyperfine interactions in Figure 1(b). However, the hyperfine coupling to the <sup>107</sup>Ag nucleus is well below that in



**Figure 1.** (a) EPR spectrum of <sup>107</sup>Ag + SiO + adamantane at 77 K; (b) EPR spectrum of <sup>107</sup>Ag + SiO + adamantane at 77 K with a higher degree of SiO polymerisation (*G* = 10<sup>-4</sup> T).

**Table 1.** EPR parameters of the products from reacting <sup>107</sup>Ag atoms with SiO in adamantane at 77 K.

Species	I	II	III	IV	V
<i>g</i> value	2.0016	2.0001	1.9968	1.9999	1.9985
<i>A</i> /MHz	1683	1226	902	750	207
<i>ρ</i> <sub>ss</sub>	1.004	0.73	0.54	0.45	0.12
Assignment	Ag atoms	Ag(SiO)	Ag(Si <sub>2</sub> O <sub>2</sub> )	Ag(Si <sub>3</sub> O <sub>3</sub> )	Ag(Si <sub>n</sub> O <sub>n</sub> )

† Issued as NRC 31251.

Ag(CO), 1226 compared with 1682 MHz.<sup>4</sup> Unfortunately we were not able to observe the <sup>29</sup>Si satellites at their natural abundance that would give unequivocal proof of stoichiometry. The IR absorption at 1163 cm<sup>-1</sup> assigned to Ag(SiO) by Downs and co-workers was not observed but its IR absorption might be difficult to detect above the adamantane and (SiO)<sub>n</sub> polymer background.

It seems reasonable to associate the *three* remaining major doublets III to V with the *three* major silicon monoxide species observable by FTIR, Si<sub>2</sub>O<sub>2</sub>, Si<sub>3</sub>O<sub>3</sub>, and Si<sub>n</sub>O<sub>n</sub>. We assign the doublets as follows: III, Ag(Si<sub>2</sub>O<sub>2</sub>); IV, Ag(Si<sub>3</sub>O<sub>3</sub>); V, Ag(Si<sub>n</sub>O<sub>n</sub>). Only the use of <sup>29</sup>SiO will allow the stoichiometries of the carriers of these transitions to be confirmed with certainty.

For Ag(SiO), dividing *a*<sub>107</sub> by the atomic parameter *A* 1676 MHz for an electron in a silver 5s orbital<sup>16</sup> yields a value of 0.73 for the 5s contribution to the SOMO which is much lower than that of 1.003 in Ag(CO). Like Ag(CO) the bonding could result from donation of lone pair electrons on the silicon to an empty sp hybrid orbital of Ag with π-type back donation of Ag 4d electrons into empty antibonding π\* orbitals and empty 3d orbitals on the silicon. The decrease in unpaired spin density (ρ<sub>5s</sub>) could arise from higher p orbital contributions to the SOMO together with back donation of unpaired electron density into empty SiO orbitals. Although the anisotropic electron parameter for <sup>107</sup>Ag(5p) is small a 25% occupation of the 5p orbital should show anisotropic hyperfine structure which is not observed experimentally. The lower energy of the Si lone pair orbital together with its less diffuse character mitigate against such σ-donation and disfavour a linear AgSiO structure. The other extreme linear structure is that with the Ag bonded to the oxygen, SiOAg. *Ab initio* calculations<sup>17</sup> indicate that the hydrogen analogue, HOSi, is more stable than HSiO by 45 kJ mol<sup>-1</sup>, similar to earlier theoretical predictions about the relative stabilities of HNSi/HSiN,<sup>18</sup> HSiOH/H<sub>2</sub>SiO,<sup>19</sup> and HOSi/HSiO cations.<sup>20</sup> However such an oxygen bonded structure is unlikely for II since the unpaired spin density at the Ag nucleus should be small. In the corresponding isocarbonyl(carbonyl) gold (C=O)Au(C≡O) there is no observable Au hyperfine interaction.<sup>21</sup> Mehner *et al.* have suggested a triangular, side-bonded structure for AgSiO.<sup>6</sup> This is consistent with the isotropic EPR spectrum if there is merely a 25% loss of 5s spin density at the <sup>107</sup>Ag by electron transfer to the SiO. Preliminary *ab initio* calculation also suggest that this is the most stable geometry.<sup>22</sup>

The EPR parameters for Ag(Si<sub>2</sub>O<sub>2</sub>) and Ag(Si<sub>3</sub>O<sub>3</sub>) show large 5s orbital contributions to the SOMO, 0.53 and 0.44, respectively, in contrast to linear Ag(CO)<sub>2</sub> and planar Ag(CO)<sub>3</sub> in which the SOMO at the silver nucleus has mainly 5p character.<sup>2-4</sup> The difference arises because SiO can form stable Si<sub>2</sub>O<sub>2</sub>, Si<sub>3</sub>O<sub>3</sub>, and Si<sub>n</sub>O<sub>n</sub> polymeric structures whereas CO does not form such stable oligomers and polymers and each CO is bonded to the metal atom individually.

There is now general agreement<sup>9,10,12</sup> that both Si<sub>2</sub>O<sub>2</sub> and Si<sub>3</sub>O<sub>3</sub> are cyclic planar molecules in *D*<sub>2h</sub> and *D*<sub>3h</sub> symmetry, respectively, although Kharma *et al.*<sup>11</sup> suggested that the dimer may have open structures. Si<sub>3</sub>O<sub>3</sub> is isoelectronic with benzene with alternating single and double SiO bonds and delocalisation of the oxygen lone pairs and could form a well bound complex with a Ag atom located symmetrically below the ring. In Ag(Si<sub>2</sub>O<sub>2</sub>) and Ag(Si<sub>3</sub>O<sub>3</sub>) the silver atom could be

η<sub>4</sub>- and η<sub>6</sub>-co-ordinated beneath the silicon oxygen framework. The EPR transitions of these complexes are isotropic indicating that the reduction in ρ<sub>5s</sub> is not due to hybridisation of Ag 5s and 5p orbitals but arises by spin transfer from Ag to Si<sub>2</sub>O<sub>2</sub> and Si<sub>3</sub>O<sub>3</sub> accompanied by π-electron back donation into empty Ag 5p orbitals. The other possibility of a direct insertion of Ag atoms into SiO bonds to give electron deficient cyclic complexes is unlikely since they will involve hybridisation of the silver atom with spin population of Ag 5p orbitals.

Species V with the lowest 5s character probably involves Ag atoms associated with long siloxyl chains.

One of us (H. A. J.) thanks the National Sciences and Engineering Research Council of Canada for the award of a post doctoral fellowship (1987-1988). J. A. H., B. M., and P. L. T. are indebted to NATO for a collaborative grant.‡

Received, 8th January 1990; Com. 0/00135J

## References

- 1 D. McIntosh and G. A. Ozin, *J. Am. Chem. Soc.*, 1976, **98**, 3167.
- 2 P. H. Kasai and P. M. Jones, *J. Phys. Chem.*, 1985, **89**, 1147.
- 3 C. A. Hampson, J. A. Howard, and B. Mile, *J. Chem. Soc., Chem. Commun.*, 1985, 966.
- 4 J. H. B. Chenier, C. A. Hampson, J. A. Howard, and B. Mile, *J. Phys. Chem.*, 1988, **92**, 2745.
- 5 M. Grunder and H. Jacob, *Appl. Phys., A*, 1986, **39**, 73.
- 6 T. Mehner, H. Schnöckel, M. J. Almond, and A. J. Downs, *J. Chem. Soc., Chem. Commun.*, 1988, 117.
- 7 J. E. Bennett, B. Mile, A. Thomas, and B. Ward, *Advan. Phys. Org. Chem.*, 1970, **8**, 1.
- 8 A. J. Buck, B. Mile, and J. A. Howard, *J. Am. Chem. Soc.*, 1983, **105**, 3381.
- 9 J. S. Anderson and J. S. Ogden, *J. Chem. Phys.*, 1969, **51**, 4189.
- 10 J. W. Hastie, R. H. Hauge, and J. L. Margrave, *Inorg. Chim. Acta*, 1969, **3**, 601.
- 11 R. K. Kharma, D. D. Stranz, and B. Donn, *J. Chem. Phys.*, 1981, **74**, 2108.
- 12 H. Schnöckel, T. Mehner, H. S. Plitt, and S. Schunck, *J. Am. Chem. Soc.*, 1989, **111**, 4578.
- 13 T. Mizutani, O. Ozawa, T. Wada, and T. Arizumi, *Jpn. J. Appl. Phys.*, 1970, **9**, 446.
- 14 J. A. Yasaitis and R. Kaplow, *J. Appl. Phys.*, 1972, **43**, 995.
- 15 G. Breit and I. I. Rabi, *Phys. Rev.*, 1931, **38**, 2082.
- 16 J. R. Morton and K. F. Preston, *J. Magn. Reson.*, 1978, **30**, 577.
- 17 G. Frenking and H. F. Schaefer, III, *J. Chem. Phys.*, 1985, **82**, 4585.
- 18 R. Preuss, R. J. Buenker, and S. D. Peyerimhoff, *Chem. Phys. Lett.*, 1979, **62**, 21.
- 19 'The Carnegie-Mellon Quantum Chemistry Archive,' 3rd edn, ed. R. A. Whiteside, M. J. Frisch, and J. A. Pople, Pittsburgh, 1983.
- 20 S. Wilson, *Astrophys. J.*, 1978, **220**, 737.
- 21 J. H. B. Chenier, J. A. Howard, H. A. Joly, B. Mile, and M. Tomietto, *Can. J. Chem.*, 1989, **67**, 655.
- 22 J. S. Tse, personal communication.

‡ Note added in proof. Recent *ab initio* calculations (G. E. Quelch, R. S. Grev, and H. F. Schaefer, III, *J. Chem. Soc., Chem. Commun.*, 1989, 1498) favour a quasi-linear AgSiO structure but Tse has found that the structure determined by geometry optimisation depends critically on the initial configuration and has shown that the bridge structure is in fact stable (J. S. Tse, to be published).