The Relative Lewis Base Strengths of Dimethyl Sulphide and Digermyl Sulphide

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IT has been reported that $(SiH_3)_2O$ and $MeOSiH_3$ act as weaker Lewis bases than Me_2O and that $(SiH_3)_2S$ and $MeSSiH_3$ act as weaker bases than Me_2S when B_2H_6 is employed as reference Lewis acid.[1,2] In addition, from a hydrogen-bonding study, it is known that the basicity of $MeOSiH_3$ is intermediate between that of Me_2O and $(SiH_3)_2O$.[3] These relative basicities are not those expected on the basis of simple electronegativity effects and have been explained by considering the presence of $(p \rightarrow d)$ π-bonding in the silicon–oxygen and silicon–sulphur linkages. In the related germanium series of compounds, the ether derivatives act as *stronger* Lewis bases than their carbon and silicon analogues, and, since germanium has about the same electronegativity value as silicon, it has been concluded that $(p \rightarrow d)$ π-bonding in the germanium–oxygen linkage is not as extensive as it is in the silicon–oxygen linkage.[4] We have investigated the hydrogen bonding properties of Me_2S, $MeSGeH_3$, and $(GeH_3)_2S$ in order to determine the relative basicities of simple organic sulphides and germanium sulphides and thus see if evidence could be obtained for the presence of $(p \rightarrow d)$ π-bonding in the germanium–sulphur linkage. Steric factors were avoided in the present work by using the simple hydride derivatives of germanium and employing phenol as reference Lewis acid. For comparative purposes, $(SiH_3)_2S$ and $MeSSiH_3$ were included in the study.

All silyl and germyl sulphides were prepared and purified by reported literature procedures.[2,5,6] Commercial Me_2S was purified by low-temperature fractionation. Hydrogen-bonding studies were carried out in the manner previously described.[7] Carbon tetrachloride was employed as solvent; all sulphide concentrations were 0·12 M; phenol concentration was 0·005 M. The magnitude of the shift $\Delta\nu(OH)$ of the OH stretching vibration at 3610 cm.$^{-1}$ on complexation with the sulphides was taken as a measure of the hydrogen bonding between the proton-donor and acceptor. It is assumed that the sulphide which is the stronger base will give rise to the larger OH frequency shift.[8] The nature of the results prevented more quantitative data from being obtained. Spectral measurements were obtained on a Beckman IR-9 spectrophotometer with the samples contained in 10 mm. glass cells.

Of all the compounds studied, only Me_2S showed any base properties [$\Delta\nu(OH) = 243 \pm 4$ cm.$^{-1}$]. For all other systems, the intensities of the free OH absorptions remained the same as for pure phenol at the same concentration and no hydrogen-bonded OH absorption was observed. The 2·5—15 μ infrared spectra (in 0·08 mm. NaCl cell) of the germanium and silicon sulphides in the carbon tetrachloride–phenol solutions were checked after each base-strength measurement in order to check the purity of the sample under study.

The results confirm the earlier reports that $MeSSiH_3$ and $(SiH_3)_2S$ are weaker bases than Me_2S, and indicate for the first time that simple sulphur derivatives of germane are also weaker bases than Me_2S. It appears that π-bonding is present in the germanium–sulphur linkage and that it is important enough to lower the Lewis basicities of compounds of this type below the basicities of analogous of organic sulphides.

Knowing that $(SiH_3)_2S$ and $(GeH_3)_2S$ do not exhibit any base character with phenol, it is not too surprising to find that $MeSSiH_3$ and $MeSGeH_3$ also do not exhibit any base character. In all of these derivatives, if it can be assumed that the two orbitals of sulphur involved in covalent bonds have considerable *p*-character associated with them,[2] one of the remaining orbitals is occupied by a lone pair of electrons high in *p*-character and the other is nearly a pure *s*-orbital. With the lone pair of electrons in the *p*-character oribtal involved in π-bonding with two *or one* germanium or silicon atoms, the remaining lone pair of electrons in the orbital rich in *s*-character would not give the molecule much base character.

The relative basicities of the simple sulphur derivatives of silane and germane could not be distinguished by using this technique. Additional base-strength measurements employing other reference Lewis acids are now in progress.

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