Magneto-chemical Studies of Some Organo-Silicon Compounds Containing Si–O Bonds

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The environmental role of the diamagnetic susceptibilities has been recently studied in detail in the case of some aliphatics,[1-5] and it has been established beyond doubt that the environments do affect the magnetic values. A similar phenomenon appears in silicon chemistry, where there is a much controversy over the atomic susceptibility value of silicon; values ranging from 20.7 to −3.01 have been reported.[6-7]

In two different homologous series of organo-silicon compounds, Pascal's law holds good only if different values are assigned to χ_{Si} in each series.[6] This opens a new era in the magneto-chemical studies of organo-silicon compounds. With this in view, the present paper will deal with the magnetic susceptibilities of a few silicon compounds with different numbers of Si–O bonds, and the results will be discussed from the structural point of view.

Experimental

The substances used were of A. R. quality. Before the magnetic measurements were taken, the purity of the samples was checked by standard methods. The diamagnetic susceptibility of the compounds was measured with the help of a very sensitive microbalance devised by Neogy and Lal.[8] This balance has the capacity of correctly measuring the total susceptibility of the order of 0.5×10^{-12} c.g.s. e.m.u.

This balance essentially consists of a quartz fibre stretched between two pins, one attached to a torsion head and the other to the chuck. The ends of the quartz fibre are fused to two thin quartz rods which are fitted to the brass pins. This system ensures a perfect returning to the zero position of the balance beam for every set of readings. A mirror is attached at the centre of the beam, and a small circular coil of thin copper wire is clamped to the beam at the centre, with its horizontal plane. The two leads of the coils are taken out of the box along the quartz fibre to ensure minimum resistance to the rotation of the beam. In order to reduce the oscillations of the beam, a damping vane is also provided. The coil is connected to a voltage source, lead accumulators in series with a number of rheostats, in order to control the current, and with a standard one ohm resistance, the terminals of which are connected to the test terminals of a potentiometer. The balance is mounted on a sturdy wooden bench above the pole pieces. The constant field gradient is secured by attaching the pole shoes on the pole faces, making an angle of 6° with the pole surface.

The organo-silicon compound is placed in a capsule. This capsule is then suspended from one end of the beam. When the field is switched on, the whole capsule experiences a force, which is measured by sending a current through the copper coil and by measuring the potential drop across the standard one ohm resistance with the help of a high-precision portable pye potentiometer capable of measuring 0.05 mV. For determining the susceptibility of silicon compounds, the push on the capsule filled with the sample is compared with that on the same capsule filled with pure benzene, the mass susceptibility[9] of which was taken to be -0.7081×10^{-6} c.g.s. e.m. units. The results are shown in Table I.

Discussion

From Table I we see that the mean value of χ_{Si} in this series of the compounds is 17.0, while in individual members it varies from 14.4 to 19.1. χ_{Si} has been calculated from the molecular susceptibilities of the compounds and by subtracting from χ_M the atomic susceptibilities of hydrogen (2.0)[10,11] and of oxygen (5.3)[10] and the group susceptibilities of methyl (13.45)[12] and of χ_{CH_2} (11.68[12] units). It is interesting to note that as the number of Si–O bonds increases, the value of χ_{Si} decreases. The observed force constants[13] for the Si–O bond in a number of molecules are all higher than the value calculated by using Siebert's formula, while the Si–O bond is shorter than the sum of the relevant atomic radii.[14] All these observations are consistent with a significant contribution by $p\pi$-$d\pi$ interactions to

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TABLE I. MOLECULAR DIAMAGNETIC SUSCEPTIBILITIES OF CERTAIN ORGANO-SILICON COMPOUNDS (-10^6 c.g.s. units)

Compound	χ_M (Observed)	χ_{Si}	χ_{Si} (Mean value)	Previously recorded value of χ_{Si} in these compounds
Trimethyl-silanol	66.3	18.6		
Trimethyl-methoxy-silane	78.2	19.1		
Ethoxytri-methylsilane	89.5	19.1		
Dimethyl-dimethoxy-silane	81.6	17.2		
Dimethyldi-ethoxysilane	104.7	17.0	17.0	12.50[7]
Methyldi-ethoxysilane	92.8	17.3		12.75[7]
Di-*n*-propyldi-ethoxysilane	150.8	16.4		
Dimethyl-silanediol	58.4	16.9		
Diethylsilane diol	81.0	16.1		
Methyl-trimethoxy-silane	85.6	15.9		
Methyltri-ethoxysilane	120.3	16.8		12.03[7]
Tetraethoxy-silane	134.5	14.4		12.06[7]

the Si–O bond in organo-silicon compounds. Such interactions decrease the Pauli's diamagnetic term in the well-known van Vleck's quantum mechanical equation:

$$\chi_M = \frac{-Ne^2}{6mc^2}\sum r^2 + \frac{2}{3}N\sum_{n'\neq n}\frac{|m_0(n,n')|^2}{h\nu(n',n)}$$

The symbols have the usual significance. This decrease lowers the value of χ_{Si} in the compounds containing Si–O bonds. Thus, the magnetic studies add to the evidence that silicon is capable of forming π bonds with ligands by the use of d-type orbitals involving $p\pi$-$d\pi$ transactions. Such transactions have been beautifully discussed in some detail by Eaborn.[15]

In tetraalkyl silanes, $p\pi$-$d\pi$ bonding is not so specious as in alkoxy silanes, so the value of χ_{Si} in tetraalkyl substituted silanes will be conclusively higher than that in the alkoxy silicon derivatives.

Summary

The diamagnetic susceptibilities of a few organo-silicon compounds have been measured with the help of a very sensitive and accurate microbalance, with an accuracy of the order of 0.5×10^{-12} c.g.s. e.m.u. The mean value of χ_{Si} in these compounds containing Si–O bond is 17.0. The environmental role of Si–O liaisons on the value of χ_{Si} has been discussed from the structural point of view.

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