Interpretation of ESCA Chemical Shifts for o-Arylenedioxy Chelates of Silicon*

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ESCA, (o-Arylenedioxy)siliconates

ESCA data on the o-arylenedioxy chelates of silicon have been correlated with data on other organosilicon compounds using Pauling electronegativities. The data do not support p-π → d-π back bonding in the anionic chelates.

Meyer and Nagorsen have studied a series of anionic and cationic o-arylenedioxy chelates of hexacoordinate and pentacoordinate silicon. A simple Pauling charge analysis gave a linear correlation for hexacoordinate cationic species and several tetravalent silicon compounds studied earlier by Nordberg et al. They found that the tetravalent oxysilanes and the anionic species of their study deviated from the correlation line. This deviation was attributed to (d ← n)π backbonding of the oxygenligands to silicon. The data reported in that study are shown in Table I along with data from Nordberg et al.

ESCA chemical shifts are usually interpreted in terms of the electrostatic potential model:

\[ ΔE_B = kΔq + ΔV + ΔR \]  

where ΔE_B is the measured chemical shift, q the partial atomic charge, V the molecular potential and R atomic and molecular relaxation; Δ's refer to differences between compounds compared. Although one can obtain valid correlations between ΔE and Δq, these usually are limited to homologous series where ΔV is linear with Δq and ΔR is negligible. We have shown recently that ΔV must be included to obtain a valid correlation between chemical shifts for organosilicon compounds and charges calculated from Pauling electronegativities.

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In Meyer and Nagorsen’s analysis of ESCA shifts for the o-arylenedioxy chelates of silicon, molecular potential effects were not included. Also, they considered all formal charges to be localized on silicon, a situation which may not be realistic, particularly in the case of the anionic species (silicon is quite electropositive). The low charge calculated by Meyer and Nagorsen for the cationic species (ca. 1.0) is not consistent with the usual method for calculating Pauling charges. Included in their correlation is the species SiF_6^− which also should be subject to (d ← n)π backbonding and thus should deviate from the correlation. Also, it seems unlikely that only the tetravalent oxy and anionic species of silicon would be subject to backbonding.

We have re-evaluated the data presented by M and N and cannot confirm that (d ← n)π backbonding is indicated by the data.

We have considered two approaches to calculating charges for the cationic and anionic silicon complexes. First, the simple Pauling procedure was tried. The results are shown in Table I under the column labeled q_p. These agree with the values calculated by M and N for compounds 2, 3, 4 and 6 of Table I. Attempts to correlate these values with data obtained for other organosilicon compounds were not successful. Similarly, the Δq values of M and N did not correlate.

Second, we made the following assumptions. For the cationic species, we calculated the Pauling charges using Si^+, with the formal charge delocalized over the molecular system. This is reasonable since silicon is the most electropositive element in the system, but it is unlikely the formal charge is...
that our treatment of charge calculations for the anionic and cationic complexes of silicon is valid.

It has been pointed out previously\(^5\) that p\(\pi\)–d\(\pi\) backbonding may be important in the valence band spectra of organosilicon compounds, but no evidence has been found that this type of bonding has a significant effect on core-electron spectra, even though a large number of organosilicon compounds have been measured\(^3\). Calculations of charge based on Pauling electronegativities are a gross approximation and neglect relaxation effects which may be significant. However, it is unlikely that relaxation effects will precisely offset effects of p\(\pi\)–d\(\pi\) backbonding. Thus it is likely that our calculations of \(q_p(\text{dist.})\) accurately reflect the charge distributions in the molecules studied. Because all compounds fall on the correlation line within experimental error (including the cationic and anionic compounds), the ESCA data for these compounds do not support significant (d \(\rightarrow\) n)\(\pi\) backbonding in the anionic complexes as suggested by Meyer and Nagorsen.

\(^3\) R. C. Gray, J. C. Carver, and D. M. Hercules, J. Electron Spectrosc. 8, 343 [1976].