

Short Communication

The Polarity of Cu₃Si and the Rochow Reaction

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The so called direct process, or Rochow reaction, is seemingly a very simple process. Catalyzed by copper it converts silicon and methyl chloride into methylchlorosilanes, preferably to (CH₃)₂SiCl₂. The detailed mechanism of the reaction is, however, still in some dispute. It has been suggested¹ that an intermetallic phase of Cu₃Si is the major active catalytic phase. Possibly, additions such as Zn and Sn are of importance in determining the selectivity of the reaction.²

The suggested models imply^{1,2} that the polarity of Cu₃Si, or any other Cu–Si solid phase, could be of importance for guiding the reactant–catalyst interaction towards a high specificity of the reaction.

So far this polarity has been discussed^{2,3} in terms of the Sanderson electronegativity scale.⁴ This treatment results in charges on copper and silicon that are very close to zero. However, the results on more polar substances, e.g. CuO, calculated in the same way,⁴ viz., $q_{\text{Cu}} = +0.31$ $q_{\text{O}} = -0.31$, are in conflict with theoretical calculations,⁵ $q_{\text{O}} = -0.60$, as well as with our analysis of XPS data⁶ giving $q_{\text{O}} = -1.0 \pm 0.1$. This analysis⁶ was based on a series of XPS investigations on the charge distribution in molecules that was begun with the outspoken ambition⁷ that such information might be useful in understanding catalytic reactions.

The reason for this note is that two independent XPS investigations on Cu₃Si and similar intermetallic compounds have recently been presented.^{3,8} One would like to test if our method of assigning effective charges⁹ can be useful in characterizing the polarity of the Cu–Si bond and thus in understanding the interaction of Cu₃Si and CH₃Cl.

The method is based on the use of an internal standard⁷ for all XPS data. This standard is a phenyl group incorporated in the molecule under investigation the chemical status of which could be ascertained by measuring the integrated IR absorption intensity of the C–H stretching vibration.^{7,10} Following the systematic use of

such well calibrated measurements, we succeeded in establishing simple relations between charge and binding energies, a collation of which is given in Ref. 11.

For the present purpose it is sufficient to quote those obtained for copper¹² and for silicon¹³

$$Eb(\text{Cu}2p_{3/2}) = 1.52 q_{\text{Cu}} + 932.2 \quad (1)$$

$$Eb(\text{Si}2p_{3/2}) = 1.53 q_{\text{Si}} + 100.6 \quad (2)$$

It is a coincidence that the charge coefficients are almost identical in these two relations: for chlorine, e.g., we reported¹⁴

$$Eb(\text{Cl}2p_{3/2}) = 4.25 q_{\text{Cl}} + 201.2 \quad (3)$$

The data reported for Cu₃Si and related compounds^{3,8} are given in Table 1.

The charges in Table 1 have been calculated from the relations with the addition of an extra term *a* that corrects for any charging effects in the samples as well as any divergence of calibration procedures in the investigations under present discussion and the measurements that were the basis of relations (1) and (2). Thus

$$Eb(\text{Cu}2p_{3/2}) = 1.52 q_{\text{Cu}} + 932.2 + a \quad (4)$$

$$Eb(\text{Si}2p_{3/2}) = 1.53 q_{\text{Si}} + 100.6 + a \quad (5)$$

An additional requirement, the electroneutrality condition, adds a third equation, e.g. in the case of Cu₃Si

$$3 q_{\text{Cu}} + q_{\text{Si}} = 0 \quad (6)$$

Solving eqns. (4)–(6) gives the charges and also the correction term *a*. This technique has been used previously, e.g. Refs. 11 and 15, and has given good results.

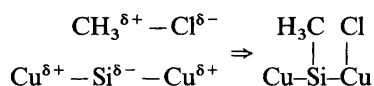
No obvious trend can be seen in the charges of copper in the compounds studied, thus a mean value is $q_{\text{Cu}} = +0.20 \pm 0.07$. Contrary to the suggestion of Lewis *et al.*,^{2,3} these charges do not merit the term zero-valent for the constituents of these compounds, at least if one means the formal oxidation states of the atoms concerned. The use of formal oxidation numbers is not very

Table 1. Literature data on XPS of Cu₃Si and related compounds and charges obtained from eqns. (4)–(6).

| Substance | Ref. | <i>E</i> _b (Cu2 <i>p</i> _{3/2})/eV | <i>E</i> _b (Si2 <i>p</i> _{3/2})/eV | <i>q</i> _{Cu} | <i>q</i> _{Si} | <i>a</i> /eV |
|----------------------------------|------|---|---|------------------------|------------------------|--------------|
| Cu ₃ Si | 8 | 932.7 | 99.4 | +0.28 | −0.83 | 0.07 |
| Si | 8 | | 99.4 | | | |
| Cu | 8 | 932.7 | | | | |
| Cu ₃ Si | 3 | 932.0 | 99.3 | +0.18 | −0.54 | −0.54 |
| Cu ₅ Si | 3 | 931.5 | 99.0 | +0.10 | −0.49 | −0.49 |
| Cu ₁₅ Si ₄ | 3 | 932.4 | 99.2 | +0.22 | −0.83 | −0.13 |
| Cu | 3 | 931.8 | | | | |

productive for discussing the possible influence of charge distribution on reactivity; what matters is the actual polarity of the chemical bond.

Our results indicate a relatively high polarity of the Cu–Si bond. If one adheres to the idea that the positive part of the catalyst is attracting the negative part of the reactant and vice versa; this result supports the proposal¹ of a heterolytic splitting of the CH₃–Cl bond as one important (probably not the rate-determining) step in the Rochow reaction:



Our results might act to dampen the dispute in this matter between two other schools.^{16,17}

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