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PRELIMINARY COMMUNICATION

p_π–d_π BONDING IN TRIMETHYLSILYL HALIDES

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The question of p_π–d_π bonding in silicon compounds is of considerable current interest and the need for non-stereochemical evidence has been stressed[1]. In this context we draw attention to the recently-determined[2] strengths of the silicon–halogen bonds in the trimethylsilyl halides. These bond dissociation energies are given in Table 1, together with those for the tert-butyl and methyl halides[3]. In the last

TABLE 1

BOND DISSOCIATION ENERGIES

X	D(R–X)(kcal·mole^{-1})			D(Me$_3$Si–X)–D(Me–X)
	R=Me$_3$Si	R=Me$_3$C	R=Me	(kcal·mole^{-1})
Cl	88	79	84	4
Br	78.5	63	70	8.5
I	69	50	56	13

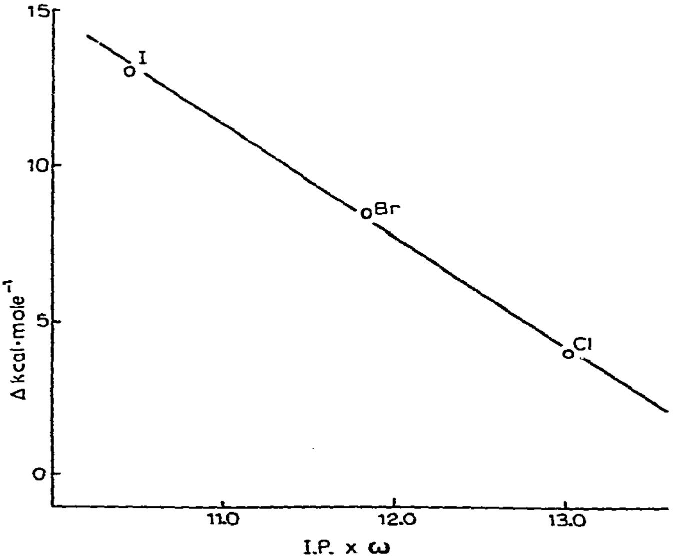

Fig. 1. Graph of Δ against ionization potential of X(D).

column of the Table are the differences, Δ, between the bond dissociation energies of corresponding trimethylsilyl and methyl halides (the methyl series was preferred to the tert-butyl for comparison because of the possibility of steric hindrance in the latter). The value of Δ increases significantly from chloride to iodide. This increase cannot be due solely to the difference in electronegativity between silicon and carbon, since if so, Δ would be constant[4]. Nor can it be due to a bond-length effect, since variations in bond lengths in the trimethylsilyl halides are little different from those in the alkyl halides[5].

We suggest that the trend in the value of Δ is due to contributions from p_π–d_π bonding in the trimethylsilyl halides, the reason for the increase from chloride to iodide being that the appropriate orbital energies, *i.e.* Si (3*d*) and X (*np*), are closest together in the iodide and furthest apart in the chloride. Ionization potentials are an approximate measure of the relative energies of the *p*-orbitals involved, and in keeping with our suggestion, a graph of Δ against the ionization potential of the halogen atom is linear (see Fig. 1)

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