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p_π–d_π BONDING IN TRIMETHYLSILYL COMPOUNDS

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Attention has recently been drawn[1] to a linear relationship between the ionization potential of the element X and Δ, the difference between the bond dissociation energies $D(\text{Me}_3\text{Si–X})$ and $D(\text{Me–X})$. It is claimed that this linear relationship is in keeping with the suggestion that the trend in the value of Δ is due to contributions from p_π–d_π bonding in the trimethylsilyl halides.

The availability[2] of heats of formation of a number of trimethylsilyl compounds makes possible a more far reaching consideration of the above relationship. Appropriate data are given in Table 1. The value $\Delta H^0{}_f(\text{Me}_3\text{Si})_g = -25.6$ kcal·mole^{-1} given by Davidson[3] is used throughout and D values are given to the nearest kcal·mole^{-1}.

It is expected that bonds from Si to Group V, VI and VII elements will possess some p_π–d_π bonding and that Si–C, Si–Si and Si–H bonds will not show this effect.

Figure 1 extends the figure given by Band, Davidson and Lambert and shows that, if their relationship holds, it holds only for the three halogens. It is assumed that the ionization potential of methylamino is the mean of those for amino[7] and dimethylamino[8] (this relationship holds for the isoelectronic comparison of methyl, ethyl and isopropyl) and that the ionization potential of n-butylthio is a little lower than that for methylthio[9]. The ionization potentials are given in references 3, 7, 8. It should be noted that the Δ value for X = bromine is approximately the arithmetic mean of those for chlorine and iodine and that as a result a plot of Δ against any physical property for the three halogens which exhibits the same feature of arithmetic progression will also be linear. Inspection of Table 2 shows that Δ as given will vary linearly with electron affinity[10], electronegativity[11], covalent radius[12] and ionic radius[12]. This suggests that the assumption that support for p_π–d_π bonding is afforded from ionization potential data is ambiguous. It is surprising that p_π–d_π bonding appears to be greater in bonding to iodine than to chlorine although the bond length is greater and that negative Δ values are obtained for Si–N bonds where p_π–d_π bonding is expected to be important[13]. It is possible that ionic contributions to the Si–X bonds are responsible for these anomalies. The suggestion[1] that this cannot be so is based upon a misunderstanding; the considerations of Pauling[14] are based not upon bond dissociation energies but upon bond energies. Attention was first drawn to the the effect of variation of ionic contributions to bond dissociation energy variations in the series Me–X → tert-Bu–X by Baughan, Evans

TABLE 1

BOND DISSOCIATION ENERGIES AND HEATS OF FORMATION

X	ΔH^0_f Me_3SiX_g (kcal·mole^{-1})	ΔH^0_f X_g (kcal·mole^{-1})	$D(Me_3Si-X)$ (kcal·mole^{-1})	$D(Me-X)$ (kcal·mole^{-1})	Δ (kcal·mole^{-1})
Cl	−84.6[2]	28.9[4]	88	84[4]	4
Br	−70.1[2], −77[3]	26.7[4]	71, 78	70[4]	1, 8
I	−69[3]	25.5[4]	69	56[4]	13
OH	−119.4[2]	9.3[4]	103	91[4]	12
NHMe	−53.9[2]	34.4[4]	63	73[4]	−10
NMe_2	−59.0[2]	29.3[4]	63	67[4]	−6
S-n-Bu	−81.3[2]	15[5]	71	73[6]	−2
CH_3	−68[3]	34[4]	76	88[4]	−12
$SiMe_3$	−118[3]	−25.6[3]	67	76[3]	−9
H	−55[3]	52.1[4]	81	104[4]	−23

TABLE 2

COMPARISON OF Δ WITH OTHER PARAMETERS

X	Δ[1]	*I.P.* (eV)[7]	*E.A.* (kcal·mole^{-1})[10]	Electronegativity[11]	Covalent radius (Å)[12]	Ionic radius (Å)[12]
Cl	4	13.01	88.2	2.98	0.99	1.81
Br	8.5	11.84	81.6	2.73	1.14	1.95
I	13	10.45	74.6	2.50	1.33	2.16

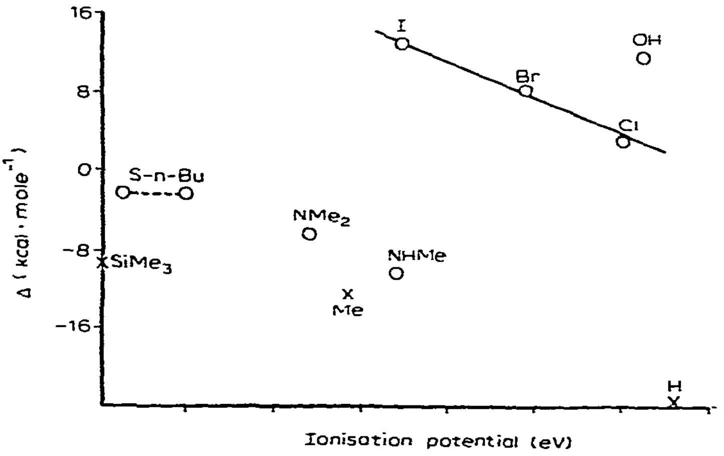

Fig.1. Plot of Δ against ionisation potential for Me_3Si-X. O, where X has p electrons available for $p_\pi-d_\pi$ bonding; X, where X has no p electrons. The line drawn is that given in reference 1.

and Polanyi[15] and the difficulties inherent in assessing the effects was emphasised by Warhurst[16]. Electronegativity considerations would imply that C–I is virtually non-polar but that Si–I bonds have a considerable ionic component. This will have some effect on Δ.

We conclude that it is difficult to separate $p_\pi-d_\pi$ bonding effects from ionic contributions and that the correlation suggested by Band, Davidson and Lambert is ambiguous.

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