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BONDING STUDIES OF COMPOUNDS OF THE GROUP IV ELEMENTS: IONISATION POTENTIALS OF THE Me_3M RADICALS

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As a continuation of our studies on the nature of bonding of the Group III and Group IV elements[1,2], we have measured the ionisation potentials (*IP*) of the radicals $Me_3M^{\bullet}$ (M = Si, Ge, Sn) in order to obtain the M–X bond dissociation energies of compounds of the type Me_3M–X. Previously, values of the ionisation potentials for $Me_3Si^{\bullet} = 7.1 \pm 0.1$ eV[3] and $Me_3Sn^{\bullet} = 7.10 \pm 0.05$ eV[4] or 6.8 ± 0.3 eV[5] have been obtained by two different methods. In our work all the ionisation potentials and appearance potentials (*AP*) of ions of the type Me_3M^+ from the compounds shown in Tables 1 and 2 were determined mass-spectrometrically using an AEI MS 9 instrument. The ionisation efficiency curves were interpreted by the Lossing semi-log plot method[6] and the errors quoted are twice the standard deviation from a series of at least seven determinations.

The ionisation potential of $Me_3Si^{\bullet}$ was calculated using the recently determined value of the silicon–silicon bond dissociation energy[7] $D(Me_3Si\text{–}SiMe_3)$ of 2.91 ± 0.13 eV (67 ± 3 kcal · mole^{-1}), in the expression:

$$AP(Me_3Si) = IP(Me_3Si) + D(Me_3Si\text{–}SiMe_3)$$

TABLE 1

Compound Me_3M–$M'Me_3$	*IP* (eV)	Appearance potentials (*AP*)		$D(Me_3M\text{–}M'Me_3)$ (eV)
		Me_3M	Me_3M'	
Me_3Si–$SiMe_3$	8.35 ± 0.12	10.22 ± 0.18	–	2.91 ± 0.18
Me_3Si–$GeMe_3$	8.31 ± 0.10	10.19 ± 0.12	9.99 ± 0.14	2.88 ± 0.14
Me_3Si–$SnMe_3$	8.18 ± 0.14	10.18 ± 0.26	9.80 ± 0.24	2.87 ± 0.26
Me_3Ge–$SnMe_3$	8.20 ± 0.10	10.01 ± 0.18	9.85 ± 0.22	2.91 ± 0.22
Me_3Sn–CMe_3	8.34 ± 0.11	9.32 ± 0.16	10.03 ± 0.23	2.61 ± 0.23

TABLE 2

Compound Me_4M	*IP* (eV)	*AP* of Me_3M	$D(Me_3M\text{–}Me)$ (eV)
Me_4Si	9.85 ± 0.16	10.53 ± 0.20	3.22 ± 0.20
Me_4Ge	9.29 ± 0.14	10.05 ± 0.14	2.94 ± 0.14
Me_4Sn	8.76 ± 0.12	9.58 ± 0.19	2.65 ± 0.19

This value was subsequently used to obtain the ionisation potentials of $Me_3Ge^{\bullet}$ and $Me_3Sn^{\bullet}$ by substitution in the equation:

$$AP(Me_3Si) - AP(Me_3M) = IP(Me_3Si) - IP(Me_3M) \qquad (M = Ge, Sn)$$

The values obtained were: $IP(Me_3Si) = 7.31 \pm 0.18$ eV, $IP(Me_3Ge) = 7.11 \pm 0.18$ eV, $IP(Me_3Sn) = 6.93 \pm 0.26$ eV. The internal consistency of our results was checked using data obtained from the compounds $Me_3GeSnMe_3$ and Me_3CSnMe_3. In the latter case, the ionisation potential of $Me_3C^{\bullet}$ was taken as 7.42 ± 0.05 eV[8], giving a value for $IP(Me_3Sn)$ of 6.71 ± 0.23 eV. Work is now in progress to extend these studies to a wide range of $Me_3M{-}X$ compounds.

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