Journal of Organometallic Chemistry, 166 (1979) 17—19

BOND DISSOCIATION ENERGIES OF GROUP IVB ORGANOMETALLIC COMPOUNDS

RICHARD A. JACKSON

School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)

(Received August 1st 1978)

Summary

Literature values of heats of formation are combined with kinetic and appearance potential data to give self-consistent values for bond dissociation energies $D(\mathrm{Me_3M{-}X})$ where M is Si, Ge, Sn or Pb, and X is H, CH_3, MMe_3, OEt, Cl or Br.

Values of bond dissociation energies of the organometallic compounds of Group IVB are of considerable value in understanding the chemistry of these compounds. Problems encountered in obtaining such data include the unreliability of older combustion data [1], and the difficulty of establishing key values for heats of formation of metal centred radicals, from which bond dissociation energy data can be derived.

Compilations of heats of formation of Group IVB compounds are now available [1,2]: the values are probably reliable for the most part though some inconsistencies between different compounds remain, and a number will probably eventually be found to be in error.

Data relating to the strengths of bonds in these molecules comes from three sources: appearance potentials in mass spectrometry, kinetics of pyrolysis reactions, and shock tube experiments. In view of uncertainties of interpretation, shock tube results have not been used in the present analysis.

The most comprehensive appearance potential data are those of Lappert, Pedley, Simpson and Spalding [3], who studied 14 compounds of type Me_4M and $Me_3MM'Me_3$ (M = Si, Ge, Sn, Pb). These data are internally reasonably self-consistent and form the start of this discussion. These appearance potential measurements *, combined with current values of heats of formation of organometallic compounds [2], of methane and 2-methylpropane [4], bond dissociation energies for methane [5] and 2-methylpropane [6], and the ionization potential of the t-butyl radical [7], give an overdetermined system of equations

---

* Including Me_3PbBu-t needed since no ΔH_f^0 value is avaiable for hexamethyldilead.

TABLE 1

KEY BOND DISSOCIATION ENERGIES OF GROUP IVB COMPOUNDS [a]

	(1) A.P. Only	(2) Kinetic	(3) A.P. + Kinetic	(4) Kinetic (+A.P.)
$D(\mathrm{Me_3Si{-}SiMe_3})$	81.3	80.5	79.3	80.5
$D(\mathrm{Me_3Si{-}CH_3})$	90.8		89.8	90.4
$D(\mathrm{Me_3Ge{-}CH_3})$	82.4		78.7	75.5
$D(\mathrm{Me_3Sn{-}CH_3})$	73.3	64.5	69.3	64.5
$D(\mathrm{Me_3Pb{-}CH_3})$	49.1	49.4	49.3	49.4

[a] All values in kcal mol^{-1}. For details of assumptions, see text.

(16 equations, 14 unknowns), solution of which gives the heats of formation of $\mathrm{Me_3M^{\bullet}}$ (M = Si, Ge, Sn, Pb) and thus the derived bond dissociation energy data shown in the first column of Table 1.

Kinetic data relating to these compounds are rather sparse, but the thermal decompositions of hexamethyldisilane [8], tetramethyltin [9] and tetramethyllead [10] have been carried out under conditions in which the homolysis of the Si—Si, Sn—C and Pb—C bonds appears to be the rate-determining step and thus the activation energy can be equated with the bond dissociation energy of the bond broken: the results are listed in column 2 of Table 1. It will be seen that there is excellent agreement between the appearance potential (A.P.) and the kinetic results for Si—Si and Pb—C, but there is a considerable discrepancy for Sn—C. The two sets of data have been combined in two ways. In column 3 of Table 1, each of the kinetic results has been given an equal weighting with each A.P. measurement in a least squares procedure, and in column 4 the three

TABLE 2

BOND DISSOCIATION ENERGIES, $D(\mathrm{Me_3M{-}X})$, (in kcal mol^{-1}) OF COMPOUNDS $\mathrm{Me_3MX}$

All thermochemical data in this paper refer to 25°C and the gas phase. Heats of formation of $\mathrm{H^{\bullet}}$, $\mathrm{{}^{\bullet}OH}$, $\mathrm{Cl^{\bullet}}$ and $\mathrm{Br^{\bullet}}$ from ref. 12, $\mathrm{{}^{\bullet}OEt}$ from ref. 13. Other heats of formation as mentioned in the text with additional data from ref. 14. $\Delta H_f^0(\mathrm{Me_6Ge_2})$ −26.0 and $\Delta H_f^0(\mathrm{Me_6Pb_2})$ +39.0 kcal mol^{-1} from the A.P. data and kinetic results used in the last column of Table 1. There is a greater difference than expected between $\Delta H_f^0(\mathrm{Me_6Ge_2})$ and the literature value [2] for $\Delta H_f^0(\mathrm{Et_6Ge_2})$. $\Delta H_f^0(\mathrm{Me_3SnH}) - \Delta H_f^0(\mathrm{Me_3SnCl})$ assumed to be the same as $\Delta H_f^0(\mathrm{Bu_3SnH}) - \Delta H_f^0(\mathrm{Bu_3SnCl})$ [15]. $D(\mathrm{Me_3Pb{-}H})$ estimated by assuming that $D(\mathrm{Me_3M{-}X})$ is greater than the average bond energy in $\mathrm{MX_4}$ by a constant amount: this is approximately true for $\mathrm{Me_3M{-}CH_3}$ (M = Sn, Pb). ΔH_f^0 for $\mathrm{MH_4}$ from refs. 12 and 16. $D(\mathrm{Me_3Si{-}H})$ and $D(\mathrm{Me_3Ge{-}H})$ are direct determinations [17].

X	M				
	C [a]	Si	Ge	Sn	Pb
H	105	90	82	74	(62)
$\mathrm{CH_3}$	90	90	76	65	49
$\mathrm{MMe_3}$	90 [b]	81	73	56	55
OH	92	126		110	
OEt	82	111	107	84	
Cl	84	111	116	101	
Br	71	94	104	85	

[a] Methyl, not t-butyl. [b] In ethane.

kinetic results have been given a weighting of 1000 compared with the A.P. results to ensure conformity of the computed values with the kinetic results. Columns 3 and 4 differ significantly only in the germanium and tin entries. Column 4 has been preferred, largely because the higher value of $D(\mathrm{Me_3Sn{-}Me})$ is difficult to reconcile with the reversibility of the addition of organotin radicals to alkenes even at low temperatures [11]. The higher value would also lead to $D(\mathrm{Me_3Sn{-}H})$ 78 kcal mol^{-1} which seems rather high.

Heats of formation ΔH_f^0 corresponding to the figures in column 4 of Table 1 are $\mathrm{Me_3Si^{\cdot}}$ −3.1; $\mathrm{Me_3Ge^{\cdot}}$ + 23.7; $\mathrm{Me_3Sn^{\cdot}}$ 25.0; $\mathrm{Me_3Pb^{\cdot}}$ 47.0 kcal mol^{-1}. Use of these figures gives the bond dissociation energies listed in Table 2. For most of the bonds, there is a smooth fall from silicon to lead in accord with the known chemistry of these compounds, though there appears to be a maximum at germanium for the $\mathrm{Me_3M{-}Cl}$ and $\mathrm{Me_3M{-}Br}$ bonds. Also in line with qualitative observations is the fact that all the M—H bond strengths are weaker than $D(\mathrm{CH_3{-}H})$, whereas the bonds to oxygen, chlorine and bromine are stronger for silicon, germanium and tin than for carbon.

Further work will be needed to confirm or modify these values, particularly those relating to germanium and tin, but the data in Table 2 appear to give a basis for rationalization of much of the known organometallic chemistry of Group IVB.

References

1 J.D. Cox and G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, London, 1970.
2 J.B. Pedley and J. Rylance, Sussex — N.P.L. Computer Analysed Thermochemical Data, University of Sussex, Brighton, 1977.
3 M.F. Lappert, J.B. Pedley, J. Simpson and T.R. Spalding, J. Organometal. Chem., 29 (1971) 195.
4 D.A. Pittam and G. Pilcher, J. Chem. Soc. Faraday I, 68 (1972) 2224.
5 W.A. Chupka, J. Chem. Phys., 48 (1968) 2337; H.A. Skinner, Ann. Rep. Chem., Soc. A, 65 (1968) 49.
6 D.M. Golden and S.W. Benson, Chem. Rev., 69 (1969) 125.
7 F.P. Lossing and J.B. DeSousa, J. Amer. Chem. Soc., 81 (1959) 281.
8 I.M.T. Davidson and A.B. Howard, J. Chem. Soc. Chem. Commun., (1973) 323.
9 R.P. Johnson and S.J.W. Price, Canad. J. Chem., 50 (1972) 50.
10 K.M. Gilroy, S.J. Price and N.J. Webster, Canad. J. Chem., 50 (1972) 2639.
11 H.G. Kuivila and R. Sommer, J. Amer. Chem. Soc., 89 (1967) 5616; A.G. Davies, B.P. Roberts and Man-Wing Tse, J. Chem. Soc. Perkin II, (1978) 145.
12 D.D. Wagman, W.H. Evans, I. Halow, V.B. Parker, S.M. Bailey and R.H. Schumm, Technical Notes 270-1 and 270-2, National Bureau of Standards, Washington, D.C., 1965 and 1966.
13 J.A. Kerr, M.J. Parsonage and A.F. Trotman-Dickenson in R.C. Weast (Ed.), Handbook of Chemical Physics, Chemical Rubber Publishing Company, Cleveland, Ohio, 1975, F230.
14 J.C. Baldwin, M.F. Lappert, J.B. Pedley and J.S. Poland, J. Chem. Soc. Dalton, (1972) 1943.
15 W.A. Stack, G.A. Nash and H.A. Skinner, Trans. Faraday Soc., 61 (1965) 2122.
16 F.E. Saalfeld and H.J. Svec, Inorg. Chem., 2 (1963) 46.
17 R. Walsh and R.M. Wells, J. Chem. Soc. Faraday I, 72 (1976) 100; A.M. Doncaster and R. Walsh, J. Chem. Soc. Chem. Commun., (1977) 446.