Journal of Organometallic Chemistry, 55 (1973) C65–C67

Preliminary communication

The use of mass spectrometry to obtain thermochemical data from series of organometallic compounds

T.R. SPALDING

Department of Chemistry, The City University, London, ECIV 4PB (Great Britain)

(Received May 15th, 1973)

SUMMARY

A general procedure is described for deriving, from mass spectrometric measurements, thermochemical data for ions, radicals, and molecules from series of R_nML_x compounds (R = organic group, M = metal, L = ligand).

Mass spectrometry has been used to obtain thermochemical data for organometallic compounds with varying degrees of success[1]. In continuation of our studies[2], a general procedure has been devised for obtaining data for ions, radicals and molecules from series of compounds, R_nML_x (R = organic entity, M = metal, L = ligand). The procedure requires the knowledge of the gas phase heat of formation of at least one member of the series and the appearance potentials of selected ions. It is best illustrated by an example, the series of compounds $Me_nSnCl_{(4-n)}$ (n = 0–4). In this series the gas phase heats of formation of both Me_4Sn and $SnCl_4$ were known[3]. The appearance potentials (AP) of the tricoordinate ions $Me_nSnCl_{(3-n)}^+$ and $Me_{(n-1)}SnCl_{(4-n)}^+$, formed by the loss of a chlorine atom or methyl radical respectively from the corresponding parent molecular ions, were calculated using the semi-logarithmic plot method[2]. Assuming the reaction sequence (1)–(5), the gas phase heats of formation of all molecules and ions may be calculated starting from either Me_4Sn or $SnCl_4$ and the known data for $\Delta_fH(Me\cdot)$ and $\Delta_fH(Cl\cdot)$[3].

$$Me_4Sn \longrightarrow Me_3Sn^+ + Me\cdot$$

$$AP(Me_3Sn^+) = \Delta_fH(Me_3Sn^+) + \Delta_fH(Me\cdot) - \Delta_fH(Me_4Sn) \qquad (1)$$

$$Me_3SnCl \begin{cases} \longrightarrow Me_3Sn^+ + Cl\cdot \\ AP(Me_3Sn^+) = \Delta_fH(Me_2Sn^+) + \Delta_fH(Cl\cdot) - \Delta_fH(Me_3SnCl) \quad (2) \\ \longrightarrow Me_2SnCl^+ + Me\cdot \end{cases}$$

$$AP(Me_2SnCl^+) = \Delta_fH(Me_2SnCl^+) + \Delta_fH(Me\cdot) - \Delta_fH(Me_3SnCl) \quad (3)$$

$$Me_2SnCl_2 \begin{cases} \longrightarrow Me_2SnCl^+ + Cl\cdot \\ AP(Me_2SnCl^+) = \Delta_fH(Me_2SnCl^+) + \Delta_fH(Cl\cdot) - \Delta_fH(Me_2SnCl_2) \quad (4) \\ \longrightarrow MeSnCl_2^+ + Me\cdot \end{cases}$$

etc. to

$$SnCl_4 \longrightarrow SnCl_3^+ + Cl\cdot$$

$$AP(SnCl_3^+) = \Delta_fH(SnCl_3^+) + \Delta_fH(Cl\cdot) - \Delta_fH(SnCl_4) \quad (5)$$

The results are shown in Table 1. The difference between the calculations was 1.7 kcal·mol^{-1}. The averaged values may be compared in this example with values of gas phase heats of formation estimated from the published values of the liquid heats of formation of Me_3SnCl, Me_2SnCl_2 and $MeSnCl_3$ by the addition of an estimated heat of evaporation of 10 kcal·mol^{-1} (Table 1). Agreement was within the experimental errors quoted.

TABLE 1

THERMOCHEMICAL DATA FOR $Me_nSnCl_{(4-n)}$ (n = 0–4) COMPOUNDS[a]

Compound	Δ_fH *(g) (kcal·mol)*$^{-1}$ *calculated from*		*Estimated values from literature (kcal·mol*$^{-1}$*)*
	Me_4Sn	*$SnCl_4$*	
Me_4Sn	(−4.8)[b]	−6.5	–
Me_3SnCl	−40.5	−42.2	−39.9
Me_2SnCl_2	−72.2	−73.9	−67.8
$MeSnCl_3$	−94.8	−96.5	−95.2
$SnCl_4$	−111.0	(−112.7)[b]	–

[a]Gas phase heats of formation for the ions observed were Me_3Sn^+ (183.0), Me_2SnCl^+ (148.3), $MeSnCl_2^+$ (139.3) and $^+SnCl_3$ (139.4) kcal·mol^{-1}. [b]Ref. 3.

The method has been extended to the series $Me_nSiCl_{(4-n)}$ and $Ph_nSnCl_{(4-n)}$. Where comparison is possible, the results are in agreement within experimental error with published data obtained by other means[3].

Several points may be noted with regard to the method described. Firstly, Stevenson's Rule[4] will be obeyed since *IP* of the organometallic radical will always be less

than *IP* of radical (X) or (R). Secondly, any number of elements may be present in the compounds studied in contrast to some other methods *e.g.* bomb calorimetry, where problems often arise due to the complexity of the reaction products. Thirdly, if the heats of formation of the compounds at the beginning and end of the series are known, then the self-consistency of the results may be checked. Fourthly, ion fragmentation pathways may be confirmed. Fifthly, the method is much more rapid than other methods. Work to extend the application of the method to other main group and transition metal compounds is in progress.

I thank the University of Sussex for the use of the AEI MS 9 mass spectrometer and Dr. J.B. Pedley for discussions.

REFERENCES

1 M.R. Litzow and T.R. Spalding, *Mass Spectrometry of Inorganic and Organometallic Compounds*, Elsevier, London 1973, p. 217, 220, 583, 588.
2 M.F. Lappert, J. Simpson and T.R. Spalding, *J. Organometal Chem.*, 29 (1971) 195; D.J. Cardin, S.A. Keppie, M.F. Lappert, M.R. Litzow and T.R. Spalding, *J. Chem. Soc. (A)*, (1971) 2262.
3 J.D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London, 1970; D.D. Wagman, W.H. Evans, V.B. Parker, I. Harlow, S.M. Bailey and R.H. Schrumm, *Selected Values of the Chemical Thermodynamic Properties*, Nat. Bur. Stand., Tech Note 270–3, U.S. Government Printing Office, Washington D.C., (1968); W.A. Chupka, *J. Chem. Phys.*, 48 (1968) 2337.
4 D.P. Stevenson, *Discuss. Faraday Soc.*, (1951) 35.