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Electronegativity equilibration and organometallic thermochemistry: the strengths of carbon–carbon bonds in metal alkyls☆

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Abstract

Atomic fractional charges in a number of metal alkyls have been estimated by electronegativity equilibration. Assuming that the bond energy terms *E*(M–C) and *E*(C–H) are constant, but that *E*(C–C) depends on the fractional charges on the carbon atoms, the methylene increments in the enthalpies of formation of the alkyls MR_2 (M = Zn, Cd and Hg) can be rationalised, allowing reasonable estimates of the heats of formation in the absence of experimental data. The treatment has been extended to HgRX and to ER_n (E = Group 13 or 14 element); the results provide clear evidence for the electronegativity sequence $C > Si < Ge > Sn \sim Pb$. Ab initio MO calculations at the MP2/6-311G** level support the proposition that the carbon–carbon bond is significantly weakened when one carbon is bonded to an atom of much lower electronegativity; this may contribute to the instability of complexes L_nMEt with respect to $L_nM(H)(\eta^2\text{-}C_2H_4)$. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The strength of a chemical bond can be measured by the amount of energy required to break it. However, bond dissociation energies/enthalpies thus defined may lead to misleading inferences concerning the nature of the bonds within molecules. From experimental measurements of enthalpies of formation $\Delta_f H°$ of gaseous substances we can obtain molecular atomisation enthalpies $\Delta_{atom}H°$ which can be expressed approximately as the sums of additive bond enthalpy terms *E*(X–Y) [1]. Tabulated bond enthalpy terms perhaps convey better than bond dissociation enthalpies the relative strengths of bonds in molecules, and are useful for the estimation of thermochemical data in the absence of experimental measurements. Serious discrepancies between experimental and calculated results may provide evidence for steric effects, resonance stabilisation or other factors which may cause bond enthalpy terms to vary from one molecule to another.

Some bond dissociation enthalpies for zinc dialkyls are collected in Table 1, obtained from experimental enthalpies of formation of ZnR_2(g) [1], Zn(g) [2] and R(g) [3]. The inference could be drawn that the Zn–C bonds in ZnR_2 (R = Et, Pr, Bu) are significantly weaker than those in $ZnMe_2$, and are hence different in character. Alternatively, it could be that the C–C and/or C–H bonds in ZnR_2 are weaker than those in the radical R. I have previously shown [4] that the thermochemistry of alkanes RH and some of their derivatives RX can be rationalised semi-quantitatively on the basis that C–H and C–X bonds can be assigned constant bond enthalpy terms *E*(C–H) and *E*(C–X), but the

Table 1
Bond dissociation enthalpies $\Delta H°$ at 298 K for zinc dialkyls, obtained from experimental data in Refs. [1–3]

Reaction	$\Delta H°$ (kJ mol^{-1})
$ZnMe_2(g) \rightarrow Zn(g) + 2Me(g)$	374 ± 4
$ZnEt_2(g) \rightarrow Zn(g) + 2Et(g)$	312 ± 10
$ZnPr_2(g) \rightarrow Zn(g) + 2Pr(g)$	337 ± 24
$ZnBu_2(g) \rightarrow Zn(g) + 2Bu(g)$	334 ± 25

☆ Dedicated to Professor Warren R. Roper FRS on the occasion of his 60th birthday.

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term $E(C_i–C_j)$ for the bond formed between carbon atoms i and j depends on the fractional charges q_i and q_j according to Eq. (1):

$$E(C_i–C_j) = E°(C–C) - aq_iq_j \quad (1)$$

where $E°(C–C)$ and a are constants, and the fractional charges q_i and q_j are estimated by electronegativity equilibration [5]. The magnitude of a found empirically indicated that the second term on the right hand side of Eq. (1) is not wholly electrostatic; it was suggested that the rationale for Eq. (1) can be found in the argument that the stabilisation of the C–C bond by resonance structures C^+C^- is diminished if the fractional charges are large and of the same sign. It follows that where an alkyl group is attached to an atom of lower electronegativity than hydrogen, thus increasing the fractional negative charges q on the carbon atoms, the bond energy terms for the C–C bonds therein should be smaller than for ethane and the alkanes, which would account qualitatively for the results in Table 1. The purpose of this paper is examine whether the thermochemistry of metal alkyls can be rationalised quantitatively along these lines. Such an approach could be of great value in view of the difficulty involved in making accurate experimental measurements in many cases. We look in detail at the homoleptic alkyls MR_2 (M = Zn, Cd, Hg), and then enquire into whether the parameters in Eq. (1) obtained for these are transferable to HgRX and ER_n (E = Group 13 or Group 14 element).

2. Electronegativity equilibration and atomic fractional charges

The principle of electronegativity equilibration has been expounded in Refs. [4,5]. A more elegant method of determining atomic fractional charges has been described in detail [6]; only an outline is given here. The electronegativity χ_A of an atom A in a molecule is given by Eq. (2), and its fractional charge q by Eq. (3), where χ°_A represents the 'prebonded' electronegativity of A:

$$\chi_A = \chi^\circ_A(1 + q_A) \quad (2)$$

$$q_A = (\chi^\circ_A - \chi_A)/\chi^\circ_A \quad (3)$$

The reciprocal electronegativity $\xi_A = \chi_A^{-1}$ is a weighted arithmetic mean of the reciprocal electronegativities ξ°_i of all the atoms in the molecule; the weighting is reduced by a factor of 0.5 for each step along the chain of bonded atoms from the atom A under scrutiny. This scheme allows non-equivalent atoms of the same element to have different electronegativities, unlike the electronegativity equalisation schemes of Sanderson [7] and Bratsch [8]. It also very nearly ensures charge conservation; the sum of all calculated fractional charges for a neutral atom differs from zero by a small number for which corrections can easily be made. Traditional Pauling values [9] are used for prebonded electronegativities χ°. Some might view Pauling's scale as of little more than historical interest, but for the zinc Group (Group 12) elements there is little alternative. The popular Allred–Rochow scale [10] ascribes quite unrealistic electronegativities to the heavier transition elements, presumably as a consequence of its inadequacies in the estimation of shielding parameters for such elements as gold and mercury. Mulliken electronegativities cannot be assigned to the Group 12 elements since their electron affinities are indeterminate [11], and Allen's spectroscopic electronegativities are difficult to determine for d-block elements [12]. Since Pauling's scale is based on thermochemical data, it may seem to be the most appropriate one to use for thermochemical purposes. Pauling's classical values [9], quoted to one decimal place, have been revised [13] to two decimal places in the light of modern experimental data; this paper relies primarily the traditional values, as used in Refs. [4–6], but the results will be compared with those obtained using the revised values. The revised values may be more appropriate for the heavier Main Group elements, since they portray the alternation in elecronegativities down a Group which is consistent with much experimental evidence and which is such an attractive feature of the Allred–Rochow scale.

3. The methylene increment

In a homologous series of alkane derivatives the methylene increment (MI) is defined as the difference between the enthalpies of formation of homologues differing by one methylene group, i.e.:

$$\mathrm{MI}(n, n+1) = [\Delta_f H°(C_nH_{2n+1}X, g) - \Delta_f H°(C_{n+1}H_{2n+3}X, g)] \quad (4)$$

Except for small values of n, or sometimes in branched-chain species, the MI is approximately constant at about 20.8 kJ mol^{-1} [14]. This is useful in estimating enthalpies of formation for relatively large values of n. For $n = 1$, there is a correlation with the electronegativity of X; MI(1,2) ranges from 9.4 ± 0.5 kJ mol^{-1} for X = H [15] to about 40 kJ mol^{-1} for X = F [16,17]. Luo and Benson [18] adopted a new scale of electronegativity (or covalent potential) in order to rationalise quantitatively this dependence. It can also be explained in terms of the variation of the

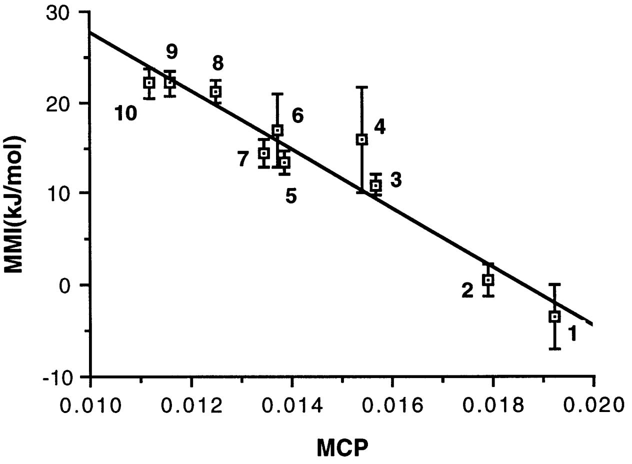

Fig. 1. Plot of mean methylene increment MMI (kJ mol^{-1}) against mean charge product MCP for Group 12 dialkyls: **1** = $ZnEt_2$, **2** = $CdEt_2$, **3** = $HgEt_2$, **4** = $ZnPr_2$, **5** = $HgPr^i_2$, **6** = $ZnBu_2$, **7** = $HgPr_2$, **8** = $HgBu_2$, **9** = $HgBu^i_2$, **10** = Hg(3-methylbutyl)$_2$.

term E(C–C) according to Eq. (1); for X = H, the carbon atoms have negative fractional charges which decrease as hydrogen is replaced by more electronegative substituents [4]. In extending these ideas to the realm of metal alkyls MR_m (R = C_nH_{2n+1}), it is convenient to use the mean methylene increment (MMI) defined as:

$$\mathrm{MMI} = [\Delta_f H^\circ(\mathrm{MMe}_m,\ \mathrm{g}) - \Delta_f H^\circ(\mathrm{MR}_m,\ \mathrm{g})]/m(n-1) \qquad (5)$$

Invoking Eq. (1), and assuming a constant E(C–H) = 415.8 kJ mol^{-1}, the value obtained for the mean bond enthalpy in methane, Eq. (5) can be re-expressed as:

$$\mathrm{MMI} = [E^\circ(\mathrm{C{-}C}) - 321.1\ \mathrm{kJ\ mol^{-1}}] - (a\ \Sigma\ q_i q_j)/m(n-1) \qquad (6)$$

where the term $\Sigma\ q_iq_j/m(n-1)$ (the summation being performed over all pairs of bonded carbon atoms) is the *mean charge product* (MCP) per C–C bond. The figure of 321.1 kJ mol^{-1} arises from:

$$2E(\mathrm{C{-}H}) - 2[\Delta_f H^\circ(\mathrm{H,\ g})] - \Delta_f H^\circ(\mathrm{C,\ g}) = -321.1\ \mathrm{kJ\ mol^{-1}} \qquad (7)$$

4. Calculations for metal alkyls

4.1. MMI values for MR_2

It follows from Eq. (6) that a plot of MMI against the MCP for alkyls MR_m should be linear, with a slope equal to $-a$ in Eq. (1) and an intercept equal to [E°(C–C) − 321.1 kJ mol^{-1}]. Such a plot for MR_2 (M = Zn, Cd, Hg) is indeed linear (R = 0.96), as shown in Fig. 1. The experimental enthalpies of formation were taken from Refs. [1,19]. From Fig. 1 we obtain a = 3198 ± 159 kJ mol^{-1} and E°(C–C) = 380.7(2.5) kJ mol^{-1} (standard deviations in parentheses). From the experimental error bars shown in Fig. 1, it is apparent that these constants can be used to estimate the enthalpies of formation of Group 12 dialkyls with accuracy not far short of that attainable experimentally. This is remarkable, given that we are relying on the traditional Pauling electronegativities of 1.6, 1.7, 1.9, 2.1 and 2.5 for Zn, Cd, Hg, H and C respectively [9]. Using the revised Pauling values [13] (Zn = 1.65, Cd = 1.69, Hg = 2.00, H = 2.20, C = 2.55), we obtain a = 3400 ± 171 kJ mol^{-1} and E°(C–C) = 372.2 ± 2.7 kJ mol^{-1}; the correlation is slightly worse (R = 0.94). Can these results be extended to other Group 12 organometallics, and to homoleptic alkyls of other Groups?

4.2. RHgX (R = Me, Et; X = Cl, Br, I)

We look first at RHgX (R = Me, Et; X = Cl, Br, I) whose enthalpies of formation are tabulated in ref. [19]. From the experimental enthalpy of formation of $HgMe_2$(g) [1], and the constant E(C–H) of 415.8 kJ mol^{-1}, we deduce a value for E(Hg–C) of 107.0 kJ mol^{-1}. From this and the experimental enthalpies of formation of MeHgX(g), we find E(Hg–Cl) = 250.4 kJ mol^{-1}, E(Hg–Br) = 208.0 kJ mol^{-1} and E(Hg–I) = 162.7 kJ mol^{-1}. Hence we can estimate the enthalpies of formation of EtHgX(g) from traditional Pauling electronegativities [9], calculating E(C–C) from Eq. (1) with a = 3198 ± 159 kJ mol^{-1} and E°(C–C) = 380.7 ± 2.5 kJ mol^{-1}. These are found to be −67.8 ± 3.3, −33.3 ± 3.3 and +9.4 ± 3.4 kJ mol^{-1} for X = Cl, Br and I respectively, in reasonably good agreement with the experimental values [19] of −64.9, −31.0 and +13.8 kJ mol^{-1} (all ±4.2 kJ mol^{-1}), respectively.

4.3. Group 13 alkyls

The results here are less impressive, partly on account of experimental uncertainties. For gaseous BEt_3, BPr_3 and BBu_3 the MMI values calculated with E°(C–C) = 380.7 ± 2.5 kJ mol^{-1} and a = 3198 ± 159 kJ mol^{-1} (as obtained from Fig. 1) are respectively 14.2, 19.2 and 21.4 kJ mol^{-1} (all ±3.0 kJ mol^{-1}) compared with the experimental values [19] of 8.7 ± 4.2, 19.0 ± 2.8 and 18.7 ± 1.3 kJ mol^{-1}, respectively; the use of Allred's revised Pauling electronegativities [13] gives calculated values of 14.7, 19.2 and 21.2 kJ mol^{-1} (all ±3.2 kJ mol^{-1}), respectively, not significantly different from those obtained from traditional values [9]. For the aluminium trialkyls, the reported enthalpies of formation of $AlMe_3$(g) and $AlEt_3$(g), −81 ± 11 and −164 ± 4 kJ mol^{-1}, respectively, are clearly inconsistent with our theory; the Pauling electronegativity of aluminium

(1.5) should lead to a negative value for MI(1,2). The experimental MI(1,2) for GaR_3 of 6.3 ± 3.3 kJ mol^{-1} may be compared with calculated values of -2.7 ± 3.9 kJ mol^{-1} using the traditional Pauling electronegativities, and 5.5 ± 3.4 kJ mol^{-1} with the revised values; the latter clearly has the advantage.

4.4. Group 14 alkyls

Pauling assigned the same electronegativity (1.8) to Si, Ge, Sn and Pb, although recognising that Sn(IV) might require the higher value of 1.9 [9]. With a constant $\chi^{o}(M)$ of 1.8, the calculated MMI for MEt_4 is 11.3 ± 3.4 kJ mol^{-1}, compared with experimental values of 8.0 ± 3.9, 22.8 ± 3.2, 6.5 ± 0.9 and 6.5 ± 1.6 kJ mol^{-1} for M = Si, Ge, Sn and Pb, respectively. Using Allred's revised Pauling electronegativities, the calculated values are respectively 13.3 ± 3.1, 15.3 ± 3.0, 11.3 ± 3.2 and 12.7 ± 3.1 kJ mol^{-1}, which do not quite emphasise the 'anomalous' situation of germanium in Group 14.

5. Ab initio MO calculations

The model set out here implies that the C–C bond in any M–C–C moiety where M is an element of relatively low electronegativity will be weaker than in most organic molecules, on account of the large, negative fractional charges on the carbon atoms. In search of more weighty theoretical support for this proposition, ab initio SCF–MO calculations were performed on EtX (X = H, Li, F) at the MP2/6-311G** level using the SPARTAN package [20]. The optimised C–C distances were found to be 1.529, 1.543 and 1.513 Å for EtH, EtLi and EtF, respectively; the value for ethane is in good agreement with that found experimentally, viz. 1.534 Å [21]. It would appear that there is indeed a correlation between the C–C bond strength in the molecule and the electronegativity of the substituent in EtX. The relative weakness of C–C bonds in, e.g. L_nMEt may help to account for the instability of such compounds compared with L_nMMe or $L_nMCH_2SiMe_3$. The well-known reaction:

$$L_nMEt \rightarrow L_nM(H)(\eta^2\text{-}C_2H_4)$$

finds a convenient mechanistic route via β-elimination [3,22] but weakening of the C–C bond in L_nMEt may be a significant thermochemical and kinetic factor.

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