The Thermochemistry of *o*- and *p*-Tolyldichloroboranes and the Boron-to-Carbon Bond Strength

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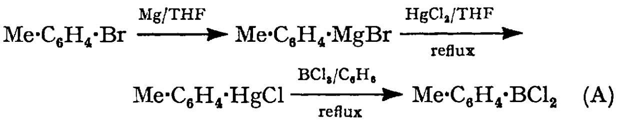
The standard enthalpies of formation of *o*- and *p*-tolyldichloroboranes have been determined from a thermochemical study of their oxidative hydrolyses in an isoperibol reaction calorimeter. Combination of these results with enthalpies of vaporization give the standard enthalpies of formation of these compounds in the gas phase ($-253{\cdot}8 \pm 2{\cdot}7$ and $-294{\cdot}1 \pm 3{\cdot}8$ kJ mol^{-1} respectively) from which the boron–carbon bond energy is derived. Structural implications of these results are discussed.

PREVIOUS thermochemical studies[1,2] of $PhBX_2$ (I), Ph_2BX (II), Ph_3B (III), and (cyclo-$C_6H_{11})_3B$ (IV) where X = Cl and Br showed the order of boron–carbon bond strength (E) in these molecules to be $E(I) > E(II) > E(III) \gg E(IV)$. The marked enhancement of the boron–aromatic-carbon bond energy compared with the boron–aliphatic-carbon bond energy was discussed in terms of $p\pi$–$p\pi$ bonding. The successive decrease in E on replacement of halogen by phenyl in the series $Ph_{3-n}BX_n$ (n = 0, 1, and 2) was rationalized by suggesting increasing steric interaction causing the phenyl groups to be twisted out of plane with concomitant reduction in resonance stabilization. By inference, *ortho*-substitution in $PhBCl_2$ should cause a decrease in E and *para*-substitution should have no steric effect. Accordingly, calorimetric measurements on *o*- and *p*-$Me{\cdot}C_6H_4{\cdot}BCl_2$ were made.

EXPERIMENTAL

Materials.—The aryldichloroboranes were synthesized by established procedures[3-5] according to the reaction scheme



$$Me{\cdot}C_6H_4{\cdot}Br \xrightarrow{Mg/THF} Me{\cdot}C_6H_4{\cdot}MgBr \xrightarrow[\text{reflux}]{HgCl_2/THF} Me{\cdot}C_6H_4{\cdot}HgCl \xrightarrow[\text{reflux}]{BCl_3/C_6H_6} Me{\cdot}C_6H_4{\cdot}BCl_2 \quad (A)$$

(A) (THF = tetrahydrofuran). The b.p.s were 362 K/12 mmHg † for *o*-$Me{\cdot}C_6H_4{\cdot}BCl_2$ (lit.,[5] 361—365 K/12 mmHg) and 363 K/10 mmHg for *p*-$Me{\cdot}C_6H_4{\cdot}BCl_2$ (lit.,[5] 365 K/10 mmHg). Analyses for chloride on hydrolysis and for boron were by conventional titrimetric procedures (Found for *ortho*-isomer: B, 6·25; Cl^-, 41·1. Found for *para*-isomer: B, 6·26; Cl^-, 40·6. Calc. for $C_7H_7BCl_2$: B, 6·25; Cl, 41·02%). This synthesis occasionally results in the contamination[6] of the *ortho*-isomer by *meta*-isomer from isomerization. Hence the isomeric purities of the samples were checked by ^1H n.m.r. spectroscopy. Comparison of the intensity of the signal from the *meta*-isomer methyl protons (δ = 2·15 p.p.m.) with the intensities of the signals from the ^{13}C satellites from the *ortho*-isomer methyl protons (δ = 2·44 p.p.m., J_{C-H} = 127 Hz) showed the concentration of *meta*-isomer in the *ortho*-isomer sample to be less than 0·5 mass % (δ values relative to tetramethylsilane). No isomeric contamination could be detected in the sample of the *para*-isomer. The isomeric purity of the *ortho*-isomer was checked after calorimetry and no significant increase in impurity was found.

Calorimeters.—The glass calorimeter was operated in the isoperibol mode at 298·15 ± 0·01 K or 303·15 ± 0·01 K, and is fully described elsewhere.[7,8] The performance was checked periodically by measuring the enthalpy of neutralization of tris(hydroxymethyl)aminomethane (THAM) in excess of 0·1 mol dm^{-3} HCl. The mean of ten determinations was $\Delta H(298{\cdot}15\text{ K}, 1200 < N < 1364) = -29{\cdot}79 \pm 0{\cdot}08$ kJ mol^{-1}. Hill *et al.*[9] report $\Delta H(298{\cdot}15\text{ K}, 1182 < N < 1569) = -29{\cdot}744 \pm 0{\cdot}006$ kJ mol^{-1} for the same reaction. N is the mole ratio of water to THAM. Samples for calorimetry were handled in dry nitrogen and contained[8] in glass ampoules with two fracture bulbs.

Differential Scanning Calorimetry.—The enthalpy of fusion of *p*-tolyldichloroborane was determined by use of the Perkin-Elmer D.S.C. 1B instrument. 'Volatile Sample' pans (part no. 219–0062) were filled in an atmosphere of dry nitrogen and then sealed. The instrument was calibrated with pure indium metal (99·999 mol %, Halewood Chemicals Ltd.). The heat of fusion of *p*-tolyldichloroborane was calculated from the average area of three replicate scans of the same sample, this process being repeated for two further samples. No attack of the aluminium sample pan and lid was evident from the observed constancy of the scan area for several repeated meltings and freezings of the same sample. Exothermic peaks were not observed on any of the scans; this was taken as additional evidence of no chemical reaction taking place.

Enthalpies of Vaporization.—These were determined from vapour pressures obtained over a range of temperature (360—440 K) by use of semimicro ebulliometer based on the design[10] of Hoover *et al.* and tested as described.[1] These enthalpies were converted from the mean of the experimental temperature interval to 298·15 K by use of Watson's equation.[11]

Errors.—Uncertainties are quoted throughout as $\pm 2\bar{s}$

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† Throughout this paper, mmHg = (101·325/760) kPa.

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($\bar{s}$ being the standard deviation of the mean) except in the case of the d.s.c. result (see Table 3).

RESULTS

The calorimeter contained 200 cm^3 of an aqueous solution, 0·1 mol dm^{-3} with respect to H_2O_2 and 1·00 mol dm^{-3} with respect to NaOH (this mixture designated aqueous excess of base, a.e.b.). Quantities of arylhalogenoborane were chosen so that both peroxide and base were in excess. The *para*-isomer was studied at 303·15 K where the sample is liquid and the correction of the results to 298·15 K was ignored as were the enthalpies of mixing of the products. The enthalpies of solution of H_2O_2, NaCl, and NaOH in (a.e.b.) were assumed equal to the corresponding values in water. The thermal effect of the catalysis of the decomposition of H_2O_2 by base was found to be negligible. Therefore for reaction (1) where Ar = *o*- or *p*-Me·C_6H_4· we have relation (B). Enthalpies of neutralization of the phenols (ArOH) were determined in the same calorimeter. The corresponding figure for boric acid is available.[12]

TABLE 1

Enthalpies of reaction for equation (1) at 298·15 K: *n* is the mole ratio of water to arylhalogenoborane

n	$-\Delta H_1$/kJ mol^{-1} for *ortho*-isomer	*n*	$-\Delta H_1{}^a$/kJ mol^{-1} for *para*-isomer
28 812	720·9	25 431	686·2
23 760	723·4	20 269	677·8
35 540	724·2	32 499	679·9
23 269	720·0	24 028	687·0
42 414	715·5	28 115	685·3
28 182	715·0	26 159	686·2
25 671	722·2	28 878	678·2
30 727	716·7	20 508	675·7
30 341	716·3	30 054	674·9
29 230	718·4	Mean ($\pm 2\bar{s}$)	681·2 ± 3·3
32 387	720·9		
Mean ($\pm 2\bar{s}$)	719·4 ± 1·9		

[a] At 303·15 K.

$$ArBCl_2(liq) + [H_2O_2 + 2NaOH](a.e.b.) = [ArOH + H_3BO_3 + 2NaCl](a.e.b.) \quad (1)$$

$$\Delta H_f{}^0[ArBCl_2,liq] = \Delta H_f{}^0[ArOH,a.e.b.] + \Delta H_f{}^0[H_3BO_3,a.e.b.] + 2\Delta H_f{}^0[NaCl,a.e.b.] - 2\Delta H_f{}^0[NaOH,a.e.b.] - \Delta H_f{}^0[H_2O_2,a.e.b.] - \Delta H_1 \quad (B)$$

TABLE 3

Enthalpies of formation and transition for *o*- and *p*-tolyldichloroboranes at 298·15 K in kJ mol^{-1}

	$\Delta H_f{}^0$(c)	ΔH(c $\longrightarrow$ liq)	$\Delta H_f{}^0$(liq)	ΔH(liq $\longrightarrow$ g)	$\Delta H_f{}^0$(g)
o-Me·C_6H_4·BCl_2	—	—	−300·7 ± 2·5	46·9 ± 0·9	−253·8 ± 2·7
p-Me·C_6H_4·BCl_2 [a]	−339·2 ± 3·6	4·39 ± 0·13 [b]	−334·8 ± 3·6	40·7 ± 1·3	−294·1 ± 3·8

[a] M.p. 300·1 K. [b] The uncertainty interval is the range of three determinations and includes a calibration error.

Experimental results are in Tables 1 and 2. With the above approximations the term ($\Delta H_f{}^0$[NaCl,a.e.b.] − $\Delta H_f{}^0$[NaOH,a.e.b.]) reduces to ($\Delta H_f{}^0$[Cl^-,aq] − $\Delta H_f{}^0$[OH^-,aq]) and this and the value for H_2O_2(aq) were taken from ref. 13. Using heats of formation for the cresols from ref. 11, $\Delta H_f{}^0[H_3BO_3,c] = -1094{\cdot}5 \pm 1{\cdot}2$ kJ mol^{-1} (mean of two [14,15] reliable determinations) and the enthalpies of fusion and vaporization, we obtain the derived enthalpies of formation collected in Table 3.

TABLE 2

Enthalpies of neutralization for ArOH(cryst.) + a.e.b. = [ArOH,a.e.b.] at 298·15 K: *n* is the mole ratio of water to phenol

n	$-\Delta H$/kJ mol^{-1} for *ortho*-isomer	*n*	$-\Delta H$/kJ mol^{-1} for *para*-isomer
979	15·5	738	17·3
860	15·5	656	17·4
884	15·9	737	16·7
925	16·3	776	16·9
855	16·3	Mean ($\pm 2\bar{s}$)	17·1 ± 0·3
Mean ($\pm 2\bar{s}$)	15·9 ± 0·4		

DISCUSSION

The boron–carbon bond energy in the arylhalogenoboranes is defined by equations (2) and (3). Hence the difference in the bond energies for the isomers is given by equations (4)—(7). Equating the term in parentheses in equation (5) to zero is equivalent to equating the carbon to *ortho*-hydrogen bond dissociation energy to the carbon to *para*-hydrogen bond dissociation energy in toluene. There is no direct evidence [16,17] to support this assumption but it is likely that the steric effect of a methyl group on an *ortho*-hydrogen is small and that the difference in

$$MeC_6H_4{\cdot}BCl_2(g) = Me{\cdot}C_6H_4{\cdot}(g) + B(g) + 2Cl(g) \quad \Delta H_2 \quad (2)$$

$$\Delta H_2 = 2E(B{-}Cl) + E(B{-}C) \quad (3)$$

$$E(B{-}C)_p - E(B{-}C)_o = \Delta H_2(para\text{-isomer}) - \Delta H_2(ortho\text{-isomer}) \quad (4)$$

$$= \Delta H_f{}^0[o\text{-}Me{\cdot}C_6H_4{\cdot}BCl_2,g] - \Delta H_f{}^0[p\text{-}Me{\cdot}C_6H_4{\cdot}BCl_2,g] + (\Delta H_f{}^0[p\text{-}Me{\cdot}C_6H_4{\cdot},g] - \Delta H_f{}^0[o\text{-}Me{\cdot}C_6H_4{\cdot},g]) \quad (5)$$

$$\approx \Delta H_f{}^0[o\text{-}Me{\cdot}C_6H_4{\cdot}BCl_2,g] - \Delta H_f{}^0[p\text{-}Me{\cdot}C_6H_4{\cdot}BCl_2,g] \quad (6)$$

$$= 40{\cdot}3 \pm 4{\cdot}7 \text{ kJ mol}^{-1} \quad (7)$$

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the electronic effect of the methyl group on the *ortho*- and *para*-hydrogens is similarly small. The assumption is probably valid to within ±4 kJ mol^{-1}. In order to derive explicit values for the boron–carbon bond energies rather than their difference it is necessary to estimate $\Delta H_f^0[\mathrm{Me{\cdot}C_6H_4{\cdot},g}]$. If we assume that $D(\mathrm{C_6H_5{-}H}) \approx D(\mathrm{Me{\cdot}C_6H_4{-}H})$ this function is readily obtained from equation (8). In support of this second assumption,

$$\Delta H_f^0[\mathrm{Me{\cdot}C_6H_4,g}] = D(\mathrm{C_6H_5{-}H})^{18} - \Delta H_f^0[\mathrm{H,g}]^{12} + \Delta H_f^0[\mathrm{MePh,g}]^{13} = 192 \pm 8\ \mathrm{kJ\ mol^{-1}} \quad (8)$$

gas-phase kinetic studies [19] indicate $D(\mathrm{CF_3{\cdot}C_6H_4{-}H}) = 456 \pm 10$ kJ mol, a figure close to the accepted value [18] for $D(\mathrm{C_6H_5{-}H}) = 460 \pm 8$ kJ mol^{-1}. It is probable that $-\mathrm{CF_3}$ will have a more marked influence on the ring C–H bond energies than $-\mathrm{CH_3}$ so the assumption is probably valid to within the difference between $D(\mathrm{CF_3{\cdot}C_6H_4{-}H})$ and $D(\mathrm{C_6H_5{-}H})$, *i.e.*, ±4 kJ. Values for the carbon–boron bond energies in the title compounds are compared in Table 4 with corresponding recalculated results for $\mathrm{Ph_{3-n}BX_n}$ ($n = 0$, 1, and 2, X = Cl and Br). The latter results differ from those originally reported [20] because of (*a*) the use of $\Delta H_f^0[\mathrm{C_6H_5{\cdot},g}] = 325 \pm 18$ [18] kJ mol^{-1} instead of 301 ± 18 [1,20] kJ mol^{-1} and (*b*) the conversion [21] of the original [1] enthalpies of vaporization to 298·15 K by use of Watson's equation.[13]

TABLE 4

Values for the boron–carbon bond energy [b] [defined by equations (2) and (3)] in arylhalogenoboranes and triphenylborane at 298·15 K

Compound	E(B–C) [a]/kJ mol^{-1}
o-$\mathrm{Me{\cdot}C_6H_4BCl_2}$	463 ± 10
p-$\mathrm{Me{\cdot}C_6H_4{\cdot}BCl_2}$	504 ± 10
$\mathrm{PhBCl_2}$	508 ± 10
$\mathrm{PhBBr_2}$	489 ± 10
$\mathrm{Ph_2BCl}$	485 ± 10
$\mathrm{Ph_2BBr}$	475 ± 10
$\mathrm{Ph_3B}$	462 ± 10

[a] The major part of the error in these values is from ΔH_f^0[B,g] and ΔH_f^0[aryl radical, g.] The difference between appropriate values will lead to error cancellation. [b] Ancillary heats of formation at 298·15 K required for the calculation of these results were taken from ref. (21) unless indicated otherwise and are as follows: B(g), 555·6 ± 16·7; Cl(g), 121·0 ± 0·1; Br(g), 111·9 ± 0·3; Ph(g), 325 ± 8;[18] $\mathrm{PhBCl_2}$(g), − 265·9 ± 1·7; $\mathrm{PhBBr_2}$(g), − 115·5 ± 1·7; $\mathrm{Ph_2BCl}$(g), − 84·1 ± 3·8; $\mathrm{Ph_2BBr}$(g), 2·5 ± 3·8; $\mathrm{Ph_3B}$(g), 143·1 ± 4·2 kJ mol^{-1}; also required are E(B–Cl) = 440·1 and E(B–Br) = 365·7 kJ mol^{-1} $\mathrm{BX_3}$.

The difference between the boron–carbon bond energy in p-$\mathrm{Me{\cdot}C_6H_4{\cdot}BCl_2}$ and $\mathrm{PhBCl_2}$ is 4 kJ mol^{-1} which is within experimental error and so is not significant. If we accept the validity of the assumptions discussed above and the transferability [1] of the B–Cl bond *energy* from $\mathrm{BCl_3}$ to $\mathrm{ArBCl_2}$, this implies that the electronic effect of a *para*-methyl substituent on the B–C bond energy in the aryldichloroboranes is small. In contrast, the B–C bond energy in p-$\mathrm{Me{\cdot}C_6H_4{\cdot}BCl_2}$ is greater than in the *ortho*-isomer by *ca.* 40 kJ mol^{-1}. This is significant and reflects the steric effect of an *ortho*-methyl substituent. It is known that the atoms in $\mathrm{PhBCl_2}$(g) are coplanar [22] and a vibrational spectroscopic study [23] of the diphenylhalogenoboranes supports the suggestion [1] that the phenyl groups are twisted out of the skeletal plane in these molecules. Similarly, it is probable that in o-$\mathrm{Me{\cdot}C_6H_4{\cdot}BCl_2}$(g) the $-\mathrm{BCl_2}$ group is twisted out of the ring plane to minimize steric interaction resulting in loss of $p\pi$–$p\pi$ character to the B–C bond. A significant $p\pi$ contribution persists in this bond, however, as the boron to aliphatic carbon bond strength [1] (*ca.* 370 kJ mol^{-1}) is much smaller.

A mass spectrometric study [24] of photoionization yields from $\mathrm{B_2Cl_4}$ and $\mathrm{BCl_3}$ gives $\Delta H_f^0[\mathrm{BCl_2{\cdot},g}]298 = -61 \pm 5$ kJ mol^{-1}. Using this result we can calculate bond dissociation energies in the aryldichloroboranes which do not include the implicit assumption of bond-energy transferability as do the bond energy calculations described above. The same trends are observed in the bond dissociation energy results although the absolute magnitudes differ.

TABLE 5

Bond dissociation energies in the aryldihalogenoboranes at 298·15 K

Compound	o-$\mathrm{Me{\cdot}C_6H_4{\cdot}BCl_2}$	p-$\mathrm{Me{\cdot}C_6H_4{\cdot}BCl_2}$	$\mathrm{PhBCl_2}$
$D(\mathrm{Aryl{-}BCl_2})$/kJ mol^{-1}	485 ± 10	525 ± 10	530 ± 10

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