THERMODYNAMIC PROPERTIES OF $B(CH_3)_3$, $B(C_2H_5)_3$, $B_2(CH_3)_6$, AND $B_2(C_2H_5)_6$

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Abstract: The values of standard enthalpies of atomization ($\Delta_{\rm ra}H^\circ$) and formation ($\Delta_f H^\circ$) of pyrophoric $B(CH_3)_3$ (trimethylborate, TMB) and $B(C_2H_5)_3$ (triethylborate, TEB) as well as their dimers $B_2(CH_3)_6$ (dimer of TMB, DTMB) and $B_2(C_2H_5)_6$ (dimer of TEB, DTEB), are determined using the DFT (M062X/6-311++G(d,p)) and the composite (CBS–QB3, G3B3) quantum chemical approaches. The calculated values of TMB and TEB are $\Delta_f H^\circ(B(CH_3)_3)_3 = -111.3$ kJ/mol and $\Delta_f H^\circ(B(C_2H_5)_3)_3 = -145.4$ kJ/mol. The best consistency with the literature values is observed in the case of G3B3 calculations. Thus, in these acses, their differences for both monomers are equal to 15 kJ/mol. The values of $\Delta_f H^\circ(B_2(CH_3)_6) = -180 \pm 30$ kJ/mol and $\Delta_f H^\circ(B_2(C_2H_5)_6) = -219 \pm 30$ kJ/mol are determined and reported for the first time. The temperature dependencies of $\Delta_{\rm r1}G^\circ$ and $\Delta_{\rm r2}G^\circ$, determined for the reactions of dissociation of DTMB and DTEB, respectively, demonstrate their nearly complete dissociation even at $T < 300$ K. Therefore, it can be concluded that the contribution of dimers to the heat of combustion of TMB and TEB is insignificant.

Keywords: trimethylborate; triethylborate; dimer; standard enthalpy of formation; CBSQB3; G3B3; M062X

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Figure Captions

Figure 1 The M062X optimized structures of considered conformers of trimethyl borate (S1)

Figure 2 The M062X optimized structures of considered conformers of triethyl borate: (*a*) S2; (*b*) S3; (*c*) S4; and (*d*) S5

Figure 3 The M062X optimized structures of considered dimer of trimethyl borate: (*a*) S6; and (*b*) S7

Figure 4 The M062X optimized structures of considered dimer of triethyl borat: (*a*) S8; and (*b*) S9

Figure 5 Temperature dependencies of $\Delta_{\rm r1}G^\circ$ (*1*) and $\Delta_{\rm r2}G^\circ$ (*2*)

Table Captions

Table 1 The values of $H_0^\circ(X)$, $H^\circ(X)$, and $G^\circ(X)$ of the considered structures of triethyl borate (S1–S4), trimethyl borate (S5), dimers of trimethyl borate (S6 and S7) and triethyl borate (S8 and S9) calculated using the different quantum chemical approaches ($i = 1, 2, 3$)

Table 2 The values of $H_0^\circ(\text{atom})_i$, $H^\circ(\text{atom})_i$, and $G^\circ(\text{atom})_i$ as well as their literature values $\Delta_f H^\circ(\text{atom})_{\rm lit}$ [12]

Table 3 The calculated values of $\Delta_{\rm ra}H^\circ(X)_i$, $\Delta_f H^\circ(X)_i$, and $\Delta_f H^\circ(X)^{\rm rec}$ (the values in brackets correspond to the difference between the thermodynamically most stable and the other conformers)

Table 4 The calculated values of $\Delta_f H^\circ(\text{S1})_i$ ($i = 2, 3$) and $\Delta_f H^\circ(\text{S5})_i$ ($i = 2, 3$) as well as the literature values of $\Delta_f H^\circ(\text{S1})_{\rm lit}$ and $\Delta_f H^\circ(\text{S2})_{\rm lit}$ and the derived values of $\Delta_{\text{S2–S1}} = \Delta_f H^\circ(\text{S2})_i - \Delta_f H^\circ(\text{S1})_i$

Table 5 The values of $H^\circ(C_3H_8)_i$, $H^\circ(C_2H_6)_i$, $H^\circ(BH_3)$, and $H^\circ(B_2H_6)$

Table 6 The calculated values of $\Delta_{{\rm HR}m}H^\circ(i)$ and $\Delta_f H^\circ(X, {\rm HR}m)_i$ ($m = 1, 2$)

Table 7 Temperatures dependencies of $(C_p)_T$, S_T°, $H_T^\circ - H^\circ$, $\Delta_f H_T^\circ$, and $\Delta_f G_T^\circ$ calculated for the conformer S2

Table 8 Temperatures dependencies of $(C_p)_T$, S_T°, $H_T^\circ - H^\circ$, $\Delta_f H_T^\circ$, and $\Delta_f G_T^\circ$ calculated for the conformer S1

Table 9 Temperatures dependencies of $(C_p)_T$, S_T°, $H_T^\circ - H^\circ$, $\Delta_f H_T^\circ$, and $\Delta_f G_T^\circ$ calculated for the conformer S6

Table 10 Temperatures dependencies of $(C_p)_T$, S_T°, $H_T^\circ - H^\circ$, $\Delta_f H_T^\circ$, and $\Delta_f G_T^\circ$ calculated for the conformer S9

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