THERMODYNAMIC PROPERTIES OF TRIETHYLALUMINIUM MONOMER AND DIMER

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Abstract: Using molecular modeling, the enthalpies of formation of the monomers and dimers of triethylaluminum (TEA) and triemethylaluminum (TMA) were calculated: $\Delta_f H^\circ(\mathrm{Al(C_2H_5)_3}) = -65.1 \pm 14$ kJ/mol, $\Delta_f H^\circ(\mathrm{Al_2(C_2H_5)_6}) = -211 \pm 18$ kJ/mol, $\Delta_f H^\circ(\mathrm{Al(CH_3)_3}) = -58.5 \pm 14$ kJ/mol, and $\Delta_f H^\circ(\mathrm{Al_2(CH_3)_6}) = -196.7 \pm 18$ kJ/mol. It is demonstrated that, according to thermodynamics, the formation of TEA dimer (DTEA) within existing uncertainties can be expected at $T \leq 400$ K. It is also found that the heat of combustion of TEA ($\Delta_{r1} H^\circ = -9894.5$ kJ/mol), calculated using the derived value of $\Delta_f H^\circ(\mathrm{Al(C_2H_5)_3})$, is consistent with values reported previously. The temperature dependences of the thermodynamic properties of the TEA monomer and dimer were calculated in the temperature range from 0 to 4000 K.

Keywords: pyrophoric fuel; triethylaluminum; trimethylaluminum; monomer; dimer; standard enthalpy of formation; M062X; CBSQB3; G3B3

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Figure Captions

Figure 1 The M062X/6-311++G(d,p) optimized structures of considered TEA conformers S1 (*a*) – S5 (*e*)

Figure 2 The M062X optimized structures of two considered dimers: (*a*) $\mathrm{Al_2(CH_3)_6}$; and (*b*) $\mathrm{Al_2(C_2H_5)_6}$

Figure 3 The temperature dependencies of $\Delta_{r2} G^\circ$ calculated for different TEA conformers (S1–S5)

Table Captions

Table 1 The values of $H_0^\circ(X)_i$, $H^\circ(X)_i$, and $G^\circ(X)_i$ calculated for the five considered structures of TEA (S1–S5)

Table 2 The calculated values of $H_0^\circ(\mathrm{atom})$, $H^\circ(\mathrm{atom})$, and $G^\circ(\mathrm{atom})$ (in Hartree) as well as the literature values of $\Delta_f H^\circ(\mathrm{atom})_{\mathrm{lit}}$ from [12]

Table 3 The calculated values of $\Delta_{\mathrm{ra}} H^\circ(X)_i$, $\Delta_f H^\circ(X)_i$, and $\Delta_f H^\circ(X, \mathrm{HR1})_3$

Table 4 The calculated values of $H^\circ(\mathrm{Al(CH_3)_3})_i$, $H^\circ(\mathrm{C_3H_8})_i$, and $H^\circ(\mathrm{C_2H_6})_i$

Table 5 The calculated values of $\Delta_{\mathrm{HR}m} H^\circ$ and $\Delta_f H^\circ(X, \mathrm{HR}m)$ ($m = 1$ and 2 (see below))

Table 6 The calculated values of $\Delta_{\mathrm{ra}} H^\circ(\mathrm{Al(CH_3)_3})_i$, $\Delta_f H^\circ(\mathrm{Al(CH_3)3})_i$, $\Delta_{\mathrm{ra}} H^\circ(\mathrm{Al_2(CH_3)_6})_i$, and $\Delta_f H^\circ(\mathrm{Al_2(CH_3)_6})_i$

Table 7 Temperature 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 TEA structure S1

Table 8 Temperature 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 DTEA ($\mathrm{Al_2(C_2H_5)_6}$)

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