THERMOCHEMISTRY OF THE REACTIONS HO_2 (OR CH_3O_2) + $C_6H_5CH_2C_6H_4OH = H_2O_2$ (OR CH_3O_2H) + $C_{13}H_{11}O$

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Abstract: According to the results of quantum mechanical calculations, it is shown that the reactions of hydro- and methyl peroxide radicals with one of the components of bio-oil — p-benzylphenol — are thermochemically favorable. As a result, the addition of p-benzylphenol to the fuel can lead to its low-temperature chain oxidation and, hence, to a decrease of the time of ignition delays and temperature of ignition.

Keywords: p-benzylphenol; peroxy radical; enthalpy; H atom transfer

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Figure Captions

Figure 1 M06-2X/6-31G(d,p) optimized geometries of the most thermochemically stable structures of p-benzylphenol (1A and 2A) and radicals (1B-4B) formed by the abstraction of H atom from them. Bonds lengths are in nanometers

Figure 2 Correction dependence between the tabulated values of enthalpies of atomization of compounds (X) considered in [9, 10] and their values calculated using the B3LYP/6-31G(d,p) (*a*) and M06-2X/6-31G(d,p) (*b*) approaches

Table Captions

Table 1 Values of $H^0_{298.15}(Y)$ and $G^0_{298.15}(Y)$ determined using the B3LYP/6-31G(d,p) and M06-2X/6-31G(d,p) approaches

Table 2 Parameters of the linear correection dependencies presented in Fig. 2 as well as their values of the root mean squared errors (RMSE) and standard errors (SE)

Table 3 The calculated ($\Delta_r H^0_{298.15}(Y, \mathrm{CALC})_a$) and corrected ($\Delta_r H^0_{298.15}(Y, \mathrm{CORR})_a$) values of standard enthalpies of the atomization of the considered compounds (Y) determined using the B3LYP and M06-2X approaches

Table 4 The calculated ($\Delta_f H^0_{298.15}(Y, \mathrm{CALC})_a$ ($\pm$3RMSE)) and corrected ($\Delta_f H^0_{298.15}(Y, \mathrm{CORR})_a$ ($\pm$3SE)) values of standard enthalpies of formation of the considered compounds (Y) determined using the B3LYP/6-31G(d,p) and M06-2X/6-31G(d,p) values of $\Delta_r H^0_{298.15}(Y, \mathrm{CALC})_a$ and $\Delta_r H^0_{298.15}(Y, \mathrm{CORR})_a$ approaches

Table 5 The homodesmotic reactions and their values of $\Delta_r H^0_{298.15}(\mathrm{Rx}_i)_{\mathrm{REAC}}$ calculated in this study using the B3LYP/6-31G(d,p) and M06-2X/6-31G(d,p) approaches as well as their values determined on the basis of the tabulated values [13]

Table 6 The values of $\delta_f H^0_{298.15}(Y, \mathrm{CALC})_{\mathrm{REAC}}$ determined using their calculated values of $\Delta_r H^0_{298.15}(\mathrm{Rx}_i)_{\mathrm{REAC}}$ as well as the consistent values of $\Delta_f H^0_{298.15}(Y, \mathrm{CALC})_{\mathrm{REACMEAN}}$

Table 7 The considered reactions of H atom transfer to the peroxy radicals, the B3LYP values of $\Delta_r S^0_{298.15}(\mathrm{Rx}_j)$ and $\Delta_r H^0_{298.15}(\mathrm{Rx}_j)$ determined using the results of the B3LYP, M06-2X calculations as well as the values of $\Delta_f H^0_{298.15}(1\mathrm{A})$ and $\Delta_f H^0_{298.15}(1\mathrm{B})$ determined (see Table 6) and used for calculations of the values of $\Delta_r G^0_{298.15}(\mathrm{Rx}_j)$

Table 8 The values of $S^0_{298.15}(Y, \mathrm{CALC})$ determined in the present study using the B3LYP and M06-2X approaches

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