THERMOCHEMICHAL PROPERTIE OF p-$C_6H_5C(O_2H)HC_6H_4OH$ AND CHAIN OXIDATION OF p-BENZYLPHENOL

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Abstract: The values of $\Delta_f H^\circ(\mathbf{1}, \mathrm{CORR})_{\mathrm{HRmean}} = -105.5 \pm 6.9$ kJ/mol and $S^\circ(\mathbf{1}, \mathrm{CORR})_{\mathrm{IRot}} = 517.9$ J/(mol·K) of p-benzylenehydroperoxidephenol ($C_6H_5HC(O_2H)C_6H_4OH$, **1**) are determined using the quantum mechanical calculations. Based on these values, it is concluded that the formation of $C_6H_5C^{\bullet}HC_6H_4OH$ and $C_6H_5CH_2C_6H_4O^{\bullet}$ in reactions of p-benzylenephenolperoxy radical ($C_6H_5HC(O_2^{\bullet})C_6H_4OH$) with p-benzylphenol ($C_6H_5CH_2C_6H_4OH$) are thermochemically favorable. This conclusion supports the assumption that the addition of p-benzylphenol to methane–air mixtures can be capable to decrease their ignition time.

Keywords: p-benzylphenol; chain oxidation; heat (enthalpy) of formation; hydroperoxide; $C_{13}H_{12}O_3$

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Figure Caption

The literature infrared spectrum of p-benzylphenol (*a*, solid line) [10] as well as the spectrum of p-benzylenehydroperoxidephenol (*b*, vertical bars) calculated at a B3LYP/6-31G(d,p) level of theory and corrected using the scaling factor 0.964 [16] for the vibration frequencies

Table Captions

Table 1 The geometries of the most thermochemically stable conformers of p-$PhC(O_2H)HPhOH$ optimized at a B3LYP/6-31G(d,p) level of theory (bond lengths are in Å)

Table 2 The values of $\Delta_r H^\circ(Y_i, \mathrm{CALC})_{\mathrm{atom}}$, $\Delta_r H^\circ(Y_i, \mathrm{CORR})_{\mathrm{atom}}$, $\Delta_f H^\circ(Y_i, \mathrm{CORR})_{\mathrm{atom}}$, and $\Delta_f H^\circ(Y, \mathrm{CORR})_{\mathrm{mean}}$ determined for 6 considered conformers of p-$PhC(O_2H)HPhOH$ (see Table 1) using the thermochemistry of atomization reactions as well as the values of their 99.7 percent confidence intervals ($3\sigma_i$)

Table 3 The coefficients for the linear calibration dependencies ($\Delta_r H^\circ(Y_i, \mathrm{CORR})_{\mathrm{atom}} = (A_1)_i + (B_1)_i \times \Delta_r H^\circ(Y_i, \mathrm{CALC})_{\mathrm{atom}}$)) determined using the literature values of $\Delta_r H^\circ(X_n, \mathrm{TAB})_{\mathrm{atom}}$ as well as their values of the root mean squared (RMSE_i) and standard (SE_i) errors

Table 4 The values of $\Delta_r H^\circ((\mathrm{R}_j)_i, \mathrm{CALC})_{\mathrm{HR}}$, $\Delta_f H^\circ((\mathbf{1}_j)_i, \mathrm{CALC})_{\mathrm{HR}}$, $\Delta_r H^\circ((\mathrm{R}_j)_i, \mathrm{CORR})_{\mathrm{HR}}$, and $\Delta_f H^\circ((\mathbf{1}_j)_i, \mathrm{CORR})_{\mathrm{HR}}$ determined for the considered homodesmotic reactions (R_j, $j = 7$–11), the consistent values of $\Delta_f H^\circ(\mathbf{1}, \mathrm{CALC})_{\mathrm{HRmean}}$, and $\Delta_f H^\circ(\mathbf{1}, \mathrm{CORR})_{\mathrm{HRmean}}$ as well as the values of their root mean squared (RMSE_i) and standard (σ_{REAC_i}) errors

Table 5 The literature values of $\Delta_f H^\circ(X_n, \mathrm{TAB})$ used for the calculations

Table 6 The values of $S^\circ(\mathbf{1}, \mathrm{CALC})$, $S^\circ(\mathbf{1}, \mathrm{CORR})$, and $S^\circ(\mathbf{1}, \mathrm{CORR})_{\mathrm{IRot}}$ (J/(mol·K)) determined, respectively, without and with the correction of vibration frequencies as well as an accounting of the corrected vibration frequencies and the internal rotations

Table 7 Temperature dependence of thermochemical properties ($(C_p(\mathbf{1}))_T$, $S_T^\circ(\mathbf{1})_{\mathrm{IRot}}$, $\Delta_f H_T^\circ(\mathbf{1})$, and $\Delta_f G_T^\circ(\mathbf{1})$) of conformer **1** (see Table 1)

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