# TEMPERATURE DEPENDENCE OF THE RATE CONSTANT OF FORMATION OF $p$-PhCH$_2$PhO$^\bullet$ IN THE REACTION OF $p$-PhC(O$_1^\bullet$)HPhOH WITH $p$-PhCH)$_2$PhOH AND ITS CONTRIBUTION TO THE CHAIN OXIDATION OF $p$-PhCH$_2$PhOH

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**Abstract:** In the present work, the values $\Delta_f H^\circ(\mathrm{TS, MEAN}) = 45.9 \pm 3$ kJ/mol and $S^\circ(\mathrm{TS, CORR})_{\mathrm{IRot}} = 797.6$ J/(mol·K) of the transition state (TS), formed in the reaction $p$-PhC(O$_2^\bullet$)HPhOH + $p$-PhCH$_2$PhOH = $p$-PhC(O$_2$H)HPhOH + $p$-PhCH2PhO$^\bullet$, are determined using the DFT calculations. The temperature dependence of the rate constant of this reaction is calculated and described by extended Arrhenius equation ($k_T = 8.2 \cdot 10^{-19}(T/298.15)^{3.49} e^{-6189/(RT)}$ cm$^3$/(molec.·s)). In addition, the values of $\Delta_f H^\circ(\mathrm{TS, MEAN}) = 65.8 \pm 9$ kJ/mol and $k_T = 2.14 \cdot 10^{-23}(T/298.15)^{4.24} e^{-23\,640/(RT)}$ for the reaction of formation PhC$^\bullet$HPhOH, competing with the formation of PhCH$_2$PhO$^\bullet$ are evaluated. The simplified mechanism of formation of $p$-PhC(O$_2$H)HPhOH and bimolecular tautomerization of PhCH$_2$PhO$^\bullet$ to PhC$^\bullet$HPhOH are proposed. The optimal conditions for the formation of $p$-PhC(O$_2$H)HPhOH are estimated using the determined values of $k_T$.

**Keywords:** $p$-benzylphenol; chain oxidation; heat (enthalpy) of formation; hydroperoxide, C$_{13}$H$_{12}$O$_3$

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## Figure Captions

**Figure 1** The B3LYP/6-311++G(d,p) optimized structure of TS(R6)

**Figure 2** The B3LYP/6-311++G(d,p) optimized structure of TS(R5)

**Figure 3** Temperature dependencies of $k_T$ calculated for the reactions (R5) and (R6) and reported for the reactions (R1), (R2), and (R10)–(R14)

**Figure 4** The considered mechanism of low-temperature radical oxidation of p-PhCH$_2$PhOH and the formation of its hydroperoxide

## Table Captions

**Table 1** The values of bond length of geometry-optimized structures

**Table 2** The parameters for the calibration dependencies determined for the peroxides [10] using the M062X/6-31G(d,p) ($i = 1$), B3LYP/6-31G(d,p) ($i = 2$), and B3LYP/6-311++G(d,p) ($i = 3$) approaches as well as the values of root mean squared errors (RMSEP$_{Pi}$) and standard deviations ($\sigma_{Pi}$)

**Table 3** The values of $E_a^\ddagger(X_i)$, $\Delta_{\mathrm{r}a} H^\circ(X_i, \mathrm{CORR})$, $\Delta_f H_0^\circ(X_i, \mathrm{CORR})$, and LL$_i$–UL$_i$ as well as the values of $\Delta_f H^\circ(X, \mathrm{MEAN})$, $\Delta_f H_0^\circ(X, \mathrm{MEAN})$, $E_a$(R6, MEAN), $E_a$(R5, MEAN), $E_a^\ddagger$(R6, MEAN), and $E_a^\ddagger$(R5, MEAN) calculated at $T = 298.15$ and 0 K

**Table 4** The values of $H^\circ$($^3$C, $^3$O, and H) calculated using the M062X/6-31G(d,p) ($i = 1$) and B3LYP/6-31G(d,p) ($i = 2$) approaches as well as the literature values of $\Delta_f H^\circ(X, \mathrm{TAB})$ [13]

**Table 5** The values of $\Delta_{\mathrm{R}x} H^\circ$ calculated using the literature values of $\Delta_f H^\circ(X, \mathrm{TAB})$

**Table 6** The literature values of $\Delta_f H^\circ(X, \mathrm{TAB})$ used for the determination of the thermochemistry of reactions (R1), (R2), (R5), (R6), and (R10)–(R13)

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