TEMPERATURE DEPENDENCE OF THE RATE CONSTANT OF FORMATION OF p-PhC(O_2H)HPhOH IN THE REACTION OF p-PhC($O_2^\bullet$)HPhOH WITH p-PhCH_2PhOH AND THE RATE OF CHAIN OXIDATION OF p-PhCH_2PhOH

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Abstract: The values $\Delta_f H^\circ(\mathrm{TS1,MEAN}) = 770.7 \pm 16.8$ kJ/mol and $S^\circ(\mathrm{TS1,CORR})_{\mathrm{IRot}} = 808.9$ J/(mol·K) of the transition state (TS1) formed in the reaction p-PhC($O_2^\bullet$)HPhOH + p-PhCH_2PhOH = p-PhC(O_2H)HPhOH + p-PhC$^\bullet$HPhOH are determined using the density functional theory calculations. The temperature dependence of the rate constant of this reaction has been calculated and described by extended Arrhenius equation ($k_T = 1.8 \cdot 10^{-16}(T/298.15)^{4.17} e^{-35752/(RT)}$ cm^3/(mol·s)). Based on the analysis of the thermochemistry and rate constants of this and similar reactions (avialable in the literature), it was assumed that the reaction of H atom transfer from p-PhCH_2PhOH to peroxide radicals ($RO_2^\bullet$) occurs in two stages: (i) transfer of the H atom followed by (ii) the subsequent barrierless structural reorganization of the PhC$^\bullet$HPhOH radical. The calculated temperature dependence of k_T allowed to estimate the possible chain lengths and reaction rates of formation of PhC(O_2H)HPhOH as well as to outline temperatures range for the production of p-PhC(O_2H)HPhOH (p-benzylenehydroperoxidephenol).

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 structure of TS1 optimized using the B3LYP/6-31G(d,p) approach

Figure 2 The temperature dependences of k_T determined in the present study for the reaction (R5) (*1*) and the literature values of k_T (*2* — (R1); *3* — (R9); *4* — (R10); *5* — (R11); and *6* — (R12)) as well as their values of $\Delta_{\mathrm{Rx}}H^\circ$

Figure 3 The dependence of rate of formation of p-PhC(O_2H)HPhOH (W_T(R5)) upon the rate of formation of radicals ($W(RO_2)$) and temperature

Figure 4 The dependence of chain length (υ_T) upon the rate of formation of radicals ($W(RO_2)$) and temperature

Table Captions

Table 1 The values of O–O and O–H bond lengths determined using the M062X/6-31G(d,p) ($i = 1$), B3LYP/6-31G(d,p) ($i = 2$), M062X/6-311++G(d,p) ($i = 3$), B3LYP/6-311++G(d,p) ($i = 4$), wB97XD/6-311++G(d,p) ($i = 5$), M08HX/6-311++G(d,p) ($i = 6$), and MN15/6-311++G(d,p) ($i = 7$) approaches as well as their measured values

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

Table 3 The values of $E_a^\ddagger(X_i)$, $\Delta_{\mathrm{ra}}H^\circ(X_i,\mathrm{CORR})$, $\Delta_f H^\circ(X_i,\mathrm{CORR})$, LL-UL as well as the values of $\Delta_f H^\circ(\mathrm{TS1,MEAN})$ and E_a(R5) calculated at $T = 298.15$ and 0 K

Table 4 The values of $H^\circ(3\mathrm{C}, {}^3\mathrm{O},$ 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 $\Delta_f H^\circ(X,\mathrm{TAB})$ [11]

Table 5 The literature values of $\Delta_f H^\circ(X,\mathrm{TAB})$ of compounds used for the determination thermochemistry of reactions (R1), (R5), and (R9)–(R12)

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