

A Theoretical Study of Oxidation of Phenoxy and Benzyl Radicals by HO₂

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We present a quantum chemical study of oxidation of phenoxy and benzyl radicals by HO₂. All calculations were carried out using the modified Perdew-Wang (MPW1K) density functional method. We found that adsorption of HO₂ in the ortho and para positions of the aromatic ring leads to stable phenyl-OOH and benzyl-OOH adducts with dissociation energies from 16 to 27 kcal/mol. Calculations indicate that the barriers for various decomposition pathways for phenoxy-OOH and benzyl-OOH complexes are at least 10 kcal/mol above the dissociation thresholds, thus precluding the possibility of chemically activated decomposition. The main products from the decomposition of phenoxy-OOH adduct are found to be phenol, 1,4-benzoquinone, and 1,2-benzoquinone. Similarly, the decomposition of benzyl-OOH leads to toluene and methylene-cyclohexadienone. 1,2-benzoquinone is the least stable specie among these compounds. We found that subsequent thermal decomposition of 1,2-benzoquinone into carbon monoxide and cyclopentadienone proceeds via a 48 kcal/mol barrier.

I. Introduction

An accurate modeling of toluene combustion is currently hindered by the absence of credible chemical kinetic mechanisms for oxidation of benzyl and phenoxy radicals. Benzyl radicals are formed at the initial stages of toluene combustion via abstraction of H by O₂ from the side chain of toluene.¹ Phenoxy radicals are believed to be formed further down the reaction chain via benzaldehyde, benzoyl radical, and phenyl radicals. The main consumption channel for phenoxy radicals is the thermal decomposition into cyclopentadienyl radical and carbon monoxide. However, this reaction has a high activation energy, about 50 kcal/mol,² and will be slow in low temperature combustion systems. Consumption of benzyl radicals is modeled via barrierless decomposition of the benzylhydroperoxide complex.³ While this proposition has received some prior theoretical support,⁴ most of the details remain unknown.

The purpose of the present study was to investigate the reaction mechanism for decomposition of benzyl and phenoxy radicals under low temperature combustion conditions. Therefore, we focused on the recombination of benzyl and phenoxy radicals with HO₂, rather than on the unimolecular decomposition of these radicals, or their reactions with highly energetic radicals such as H, O, or OH.

II. Computational methods

All quantum chemical calculations were carried out using Gaussian98 code.⁵ Geometries were optimized using modified Perdew-Wang 1-parameter for kinetics, MPW1K/6-31G+(d,p), method proposed by Linch and Truhlar.⁶ This method was shown to be superior to other popular hybrid density functional methods in calculation of transition state geometries and energy barriers. At the MPW1K/6-31+G(d,p) level of theory, the mean unsigned error in barriers heights for the set of 22 reactions was reported to be only 1.6 kcal/mol.^{6,7} Vibrational frequency calculations for gas phase species were performed for all ground and transition states at the same MPW1K/6-31+G(d,p) levels of theory and rescaled by the factor, 0.9515.⁶ Intrinsic reaction coordinate⁸ (IRC) calculations were performed for all transition states to verify that they connect correct reactants and products.

Reaction rate constants were computed using Variflex computer code.⁹ Reactions with tight transition states were treated using a canonical non-variational transition state theory. Reactions with loose transition states were treated using a canonical variable reaction coordinate-transition state theory (VRC-TST) formalism.¹⁰ In the VRC-TST calculations a potential energy along reaction coordinate (assumed to be distance between bonding atoms) was represented by Varshni potential¹¹

$$V(r) = D_e \left[1 - \frac{r_e}{r} e^{-\alpha(r^2 - r_e^2)} \right]^2 - D_e \quad (1)$$

Here D_e is the electronic dissociation energy, r_e is the equilibrium bond distance, and α is the parameter controlling tightness of the potential well. To facilitate the use of the reaction rate constants for chemical kinetics modeling, we fitted all rate constants in the temperature range from 300 to 1000 K to the Arrhenius type expression:

$$k = AT^n \exp\left(-\frac{E_b}{k_B T}\right) \quad (2)$$

Here A is the pre exponential factor, n is the fitting parameter, k_B is the Boltzmann constant, E_b is the energy barrier, and T is the temperature.

III. Results and discussion

The recombination of phenoxy and benzyl radicals with HO_2 leads to stable phenoxy-OOH and benzyl-OOH adducts as shown in Figure 1. These adducts, denoted as A1 and A2 in Figure 1, are formed via barrierless adsorption of HO_2 in ortho and para position, respectively.

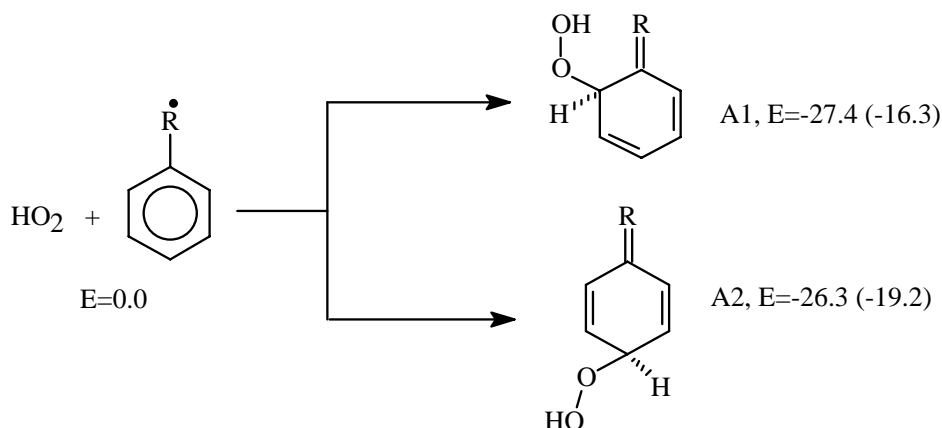


Figure 1. Recombination of benzyl ($\text{R} = \text{CH}_2$) and phenoxy ($\text{R} = \text{O}$) radicals with HO_2 radical. Numbers are relative energies in kcal/mol, including ZPE, at the MPW1K/6-31+G(d,p) level of theory for phenoxy + HO_2 reaction. Numbers in parentheses are for benzyl + HO_2 reaction.

Both reactions are exothermic with reaction energies in the case of the phenoxy-OOH adduct computed to be 27.4 and 26.3 kcal/mol for A1 and A2, respectively. In the case of the benzyl-OOH adduct, reaction energies were computed to be 16.3 and 19.2 kcal/mol for A1 and A2, respectively. Relatively modest reaction energies are due to destabilization of the aromatic ring in A1 and A2 adducts. For comparison, the exothermicity of the addition of HO_2 to the side chain of benzyl radical was computed to be 49.8 kcal/mol. Note that our value falls between the previously reported⁴ values of 39 and 78 kcal/mol computed at the B3LYP and MP2 levels of theory, respectively. We defer further discussion of this compound to future studies; here we consider only the chemical reactivity of A1 and A2 complexes.

The mechanisms for subsequent decomposition of phenoxy-OOH and benzyl-OOH adducts with -OOH in ortho position (A1) are shown in Figure 2. Both mechanisms are very similar, and we discuss in detail only the case of the phenoxy-OOH adduct. The lowest energy pathway is for transformation of A1 into 1,2 benzoquinone via TS8, intermediate compound F1, and TS9. Visual inspection of TS8 geometry suggests that this reaction is due to simultaneous shift of two hydrogen atoms. One hydrogen atom moves from the -OOH group to the =O group while another moves from a backbone carbon atom to the -OOH group. Double hydrogen shift is also apparent from the analysis of the lowest vibrational eigenstate. Indeed, we found that the imaginary frequency is quite large, 1576 cm^{-1} . Reduced mass association with motion along this mode is close to the hydrogen mass, 1.1 a.m.u., and largest contributions to this eigenstate are from two hydrogen atoms. On the next step, TS9, H atom from the -OH group and OH fragment from the -OOH group form a product water molecule. Calculations indicate that a dominant contribution to the reaction coordinate is from the motion of H atom with an imaginary frequency equal to 2200 cm^{-1} . An alternative pathway for the formation of 1,2-benzoquinone is the direct elimination of water via TS10 with an energy barrier of 51.6 kcal/mol.

The second lowest energy pathway in Figure 2 is the transformation of A1 into phenol via TS5 with an energy barrier of 42 kcal/mol. This reaction involves H transfer from the -OOH group to the =O group with simultaneous elimination of an oxygen molecule. An analysis of bond distances in TS5 indicates that this reaction path is associated with concerted motion of all atoms of the -OOH group. Indeed, C-O bond is stretched from 1.396 \AA in A1 to 1.922 \AA in TS5, OH bond is stretched from 0.967 to 1.463 \AA while O-O bond is reduced from 1.407 to 1.271 \AA . An additional indication of concerted motion is a low imaginary frequency mode, 445 cm^{-1} , and high reduced mass, 6.1 a.m.u., associated with a motion along the reaction coordinate. An alternative pathway via TS1-B1-TS4 has a much higher energy barrier, and therefore is of little importance.

The ring opening reactions, TS3 and TS6, proceed via attack of a neighboring carbon atom by O atom of the -OOH group. Both reactions have high energy barriers, 60.9 and 65.6 kcal/mol for TS3 and TS6, respectively. The alternative pathway for the ring opening via TS1, 46 kcal/mol, and TS2, 31.8 kcal/mol, is more viable.

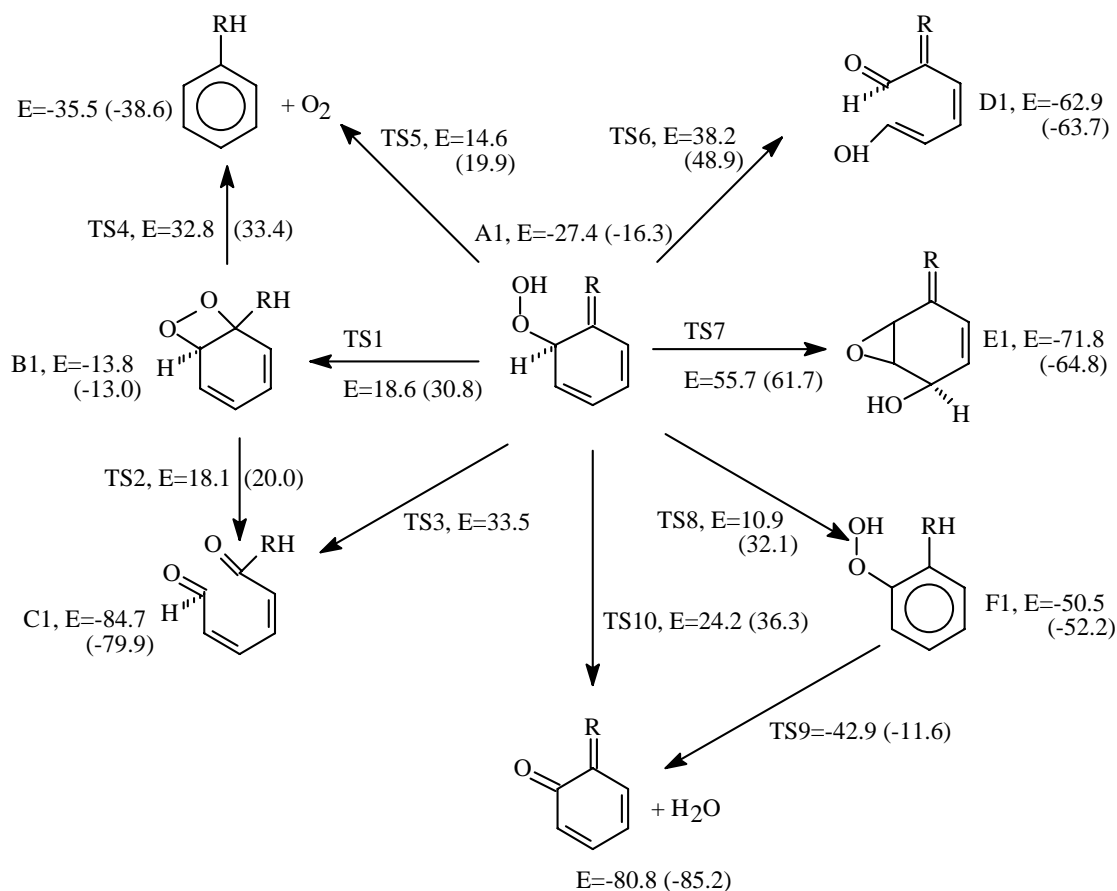


Figure 2. Reaction mechanism for decomposition of A1 intermediate of benzyl ($R = \text{CH}_2$) and phenoxy ($R = \text{O}$) radicals. Numbers are relative energies in kcal/mol, including ZPE, at the MPW1K/6-31+G(d,p) level of theory for phenoxy- HO_2 adduct. Numbers in parentheses are for benzyl- HO_2 adduct.

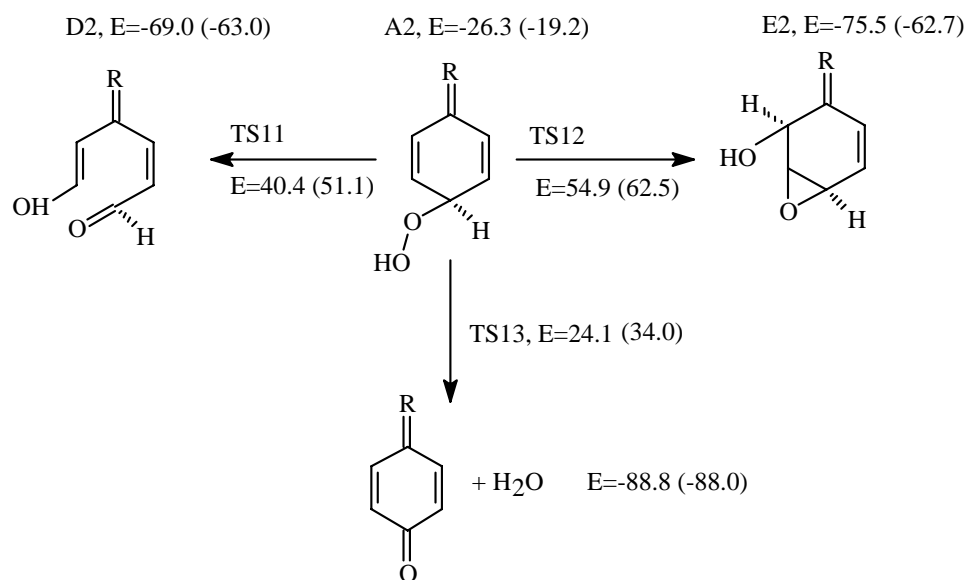


Figure 3. Reaction mechanism for decomposition of A2 intermediate of benzyl ($R = \text{CH}_2$) and phenoxy ($R = \text{O}$) radicals. Numbers are relative energies in kcal/mol, including ZPE, at the MPW1K/6-31+G(d,p) level of theory for phenoxy- HO_2 adduct. Numbers in parentheses are for benzyl- HO_2 adduct.

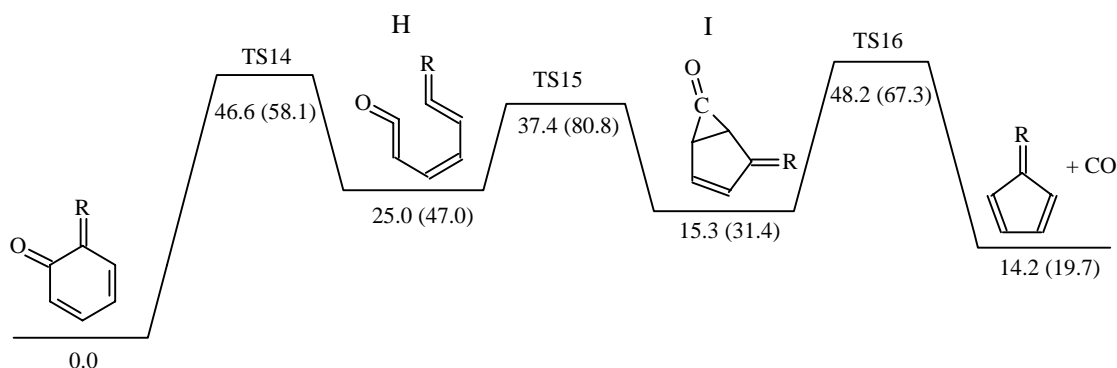


Figure 4. Reaction mechanism for decomposition of 2-methylene-3,5-cyclohexadiene-1-one ($R = \text{CH}_2$) and 1,2-benzoquinone ($R = \text{O}$). Numbers are relative energies in kcal/mol including ZPE at the MPW1K/6-31+G(d,p) level of theory for 1,2-benzoquinone. Numbers in parentheses are 2-methylene-3,5-cyclohexadiene-1-one.

TABLE 1. Rate constants, k_{inf} , for phenoxy + HO_2 ($R = \text{O}$) and benzyl + HO_2 ($R = \text{CH}_2$) reaction mechanisms. Units are s , cm^3 , K , kcal/mol. Species notations are given in Figures 1 - 4.

Reaction	TS	Rate constant, $R = \text{O}$			Rate constant, $R = \text{CH}_2$		
		A	n	E_b	A	n	E_b
$\text{C}_6\text{H}_5\text{R} + \text{HO}_2 \rightarrow \text{A1}$	-	3.2e-11	0.17	0.0	2.9e-11	0.13	0.0
$\text{C}_6\text{H}_5\text{R} + \text{HO}_2 \rightarrow \text{A2}$	-	1.5e-11	0.19	0.0	1.3e-11	0.29	0.0
$\text{A1} \rightarrow \text{C}_6\text{H}_5\text{R} + \text{HO}_2$	-	6.9e18	-0.41	28.1	5.0e18	-0.64	15.4
$\text{A2} \rightarrow \text{C}_6\text{H}_5\text{R} + \text{HO}_2$	-	3.6e17	-0.36	24.6	1.0e19	-0.73	18.8
$\text{A1} \rightarrow \text{B1}$	TS1	1.5e11	0.52	45.5	1.7e11	0.31	49.0
$\text{B1} \rightarrow \text{C1}$	TS2	1.6e10	0.83	31.2	2.9e10	0.82	34.4
$\text{A1} \rightarrow \text{C1}$	TS3	1.5e10	0.73	57.0	-	-	-
$\text{B1} \rightarrow \text{C}_6\text{H}_5\text{RH} + \text{O}_2$	TS4	2.5e10	0.90	46.4	2.6e11	0.60	49.0
$\text{A1} \rightarrow \text{C}_6\text{H}_5\text{RH} + \text{O}_2$	TS5	3.2e11	0.58	43.7	2.6e11	0.40	39.8
$\text{A1} \rightarrow \text{D1}$	TS6	1.6e11	0.47	63.7	1.5e11	0.41	66.7
$\text{A1} \rightarrow \text{E1}$	TS7	6.2e10	0.78	80.7	4.4e11	0.48	80.4
$\text{A1} \rightarrow \text{F1}$	TS8	6.3e10	0.47	37.9	1.1e11	0.31	51.7
$\text{F1} \rightarrow \text{A1}$	TS8	7.9e10	0.47	62.2	6.3e10	0.31	87.4
$\text{F1} \rightarrow 1,2\text{-C}_6\text{H}_4\text{OR} + \text{H}_2\text{O}$	TS9	9.2e10	0.51	18.0	2.7e11	0.48	44.8
$\text{A1} \rightarrow 1,2\text{-C}_6\text{H}_4\text{OR} + \text{H}_2\text{O}$	TS10	1.8e11	0.76	52.1	5.0e11	0.64	58.7
$\text{A2} \rightarrow \text{D2}$	TS11	6.1e10	0.43	65.7	1.1e10	0.70	71.7
$\text{A2} \rightarrow \text{E2}$	TS12	9.4e10	0.58	80.8	2.8e11	0.49	84.9
$\text{A2} \rightarrow 1,4\text{-C}_6\text{H}_4\text{OR} + \text{H}_2\text{O}$	TS13	7.8e10	0.57	49.1	4.3e10	0.88	58.7
$1,2\text{-C}_6\text{H}_4\text{OCH}_2 \rightarrow \text{H}$	TS14	7.5e10	1.08	46.6	7.0e11	0.56	59.6
$\text{H} \rightarrow 1,2\text{-C}_6\text{H}_4\text{OR}$	TS14	3.8e9	0.62	20.4	6.9e9	0.44	10.0
$\text{H} \rightarrow \text{I}$	TS15	5.1e9	0.47	11.2	1.2e10	0.53	34.1
$\text{I} \rightarrow \text{H}$	TS15	5.4e10	1.01	22.0	3.0e10	1.20	51.8
$\text{I} \rightarrow \text{C}_5\text{H}_4\text{R} + \text{CO}$	TS16	5.2e10	1.00	32.6	1.6e10	1.08	37.1

Finally, an epoxy-like structure, E1, can be formed via TS7. This reaction proceeds via transfer of the OH group to the para position. Due to the very high energy barrier, 83.1 kcal/mol, this reaction is of little importance for low temperature oxidation.

In the case of the benzyl-OOH adduct A1, the lowest energy pathway with 36.2 kcal/mol barrier leads to the formation of toluene, while formation of 2-methylene-3,5-cyclohexadiene-1-one (analog of 1,2-benzoquinone) proceeds via TS10 with an energy barrier of 52.6 kcal/mol or via TS8 and TS9 with energy barriers of 48.5 and 40.6 kcal/mol, respectively. Overall, decomposition of the benzyl-OOH A1 adduct proceeds via somewhat higher energy barriers as compared to those for the phenoxy-OOH A1 adduct.

The mechanism of decomposition of phenoxy-OOH and benzyl-OOH compounds with -OOH in the para position (A2) is shown in Figure 3. This mechanism is much simpler than decomposition of A1 due to an absence of interaction between the adsorbed OOH group and the side group. The lowest energy pathway leads to 1,4-benzoquinone and 4-methylene-2,5-cyclohexadiene-1-one from the phenoxy-OOH and benzyl-OOH adducts, respectively. This reaction is analogous to decomposition of A1 adduct via TS10 and has a similar reaction barrier of 50.4 kcal/mol for phenoxy-OOH and 53.2 kcal/mol for benzyl-OOH. Ring opening via TS11 is an analog of ring opening for the A1 adduct via TS6, and formation of the epoxy-type compound E2 via TS12 is an analog of formation of E1 compound via TS7.

Simple comparison of barriers heights for different reaction channels indicates that benzoquinones and methylene substituted cyclohexadienones formed via TS13, TS8 and TS19, and TS10 will be the dominant intermediate compounds. Further investigation of the decomposition of these compounds is therefore warranted. The barrier for thermal decomposition of 1,4-benzoquinone into cyclopentadienone and CO was estimated previously by Frank *et. al.*¹² to be 59 kcal/mol. However, no data are available for 1,2-benzoquinone or methylene substituted cyclohexadienones. The mechanism for thermal decomposition of these compounds is shown in Figure 4. The first step in this mechanism is the ring opening via TS14, followed by formation of fused 5 and 3-member ring intermediates (I) via TS15. Finally, compound I ejects a CO molecule and forms cyclopentadienone or 5-methylene-1,3-cyclopentadiene (a.k.a. fulvene) via TS16. For 1,2-benzoquinone decomposition, the highest energy barrier is 48.2 kcal/mol above the reactant and the overall reaction energy is 14.2 kcal/mol. In contrast, 2-methylene-3,5-cyclohexadiene-1-one appears to be more stable with the highest barrier being 80.8 kcal/mol above the reactant and with the overall reaction energy of 19.7 kcal/mol.

IV. Summary

We have conducted a density functional study of oxidation of phenoxy and benzyl radicals by HO₂. It was found that HO₂ can adsorb into the ortho and para positions leading to the formation of benzyl-OOH and phenoxy-OOH adducts. The dissociation energies for benzyl-OOH and phenoxy-OOH adducts are relatively low, between 16 and 27 kcal/mol, as compared to typical values for radical recombination reactions. This is due to destabilization of the aromatic ring in the benzyl-OOH and phenoxy-OOH compounds.

We also studied a number of the decomposition pathways for benzyl-OOH and phenoxy-OOH adducts. Calculations indicate a wide range of possible reactions such as ring openings, elimination of H₂O, and formation of hetero rings. The proximity of side groups in A1 type (OOH in the ortho position) adducts leads to a number of addition reactions such as H transfer between side groups and elimination of H₂O and O₂.

The main products from the decomposition of phenoxy-OOH adducts were found to be phenol and benzoquinone. Similarly, the decomposition of benzyl-OOH adducts leads to toluene and methylene-cyclohexadienone. However, energy barriers for all decomposition pathways identified in the present study are higher than dissociation energies of benzyl-OOH and phenoxy-OOH adducts. This result precludes the possibility of chemically activated decomposition of these adducts.

The rate constants for chemical mechanisms shown in Figures 1-4 are summarized in Table 1. Inspection of these data indicates that the most likely decomposition pathway is the formation of 1,2-benzoquinone and its subsequent decomposition into carbon monoxide and cyclopentadienone. The energy barrier for 1,2-benzoquinone decomposition was computed to be 48 kcal/mol. The effect of these reactions on the chemical kinetics of toluene oxidation is currently under investigation and will be reported in the future.

Finally, we found that adsorption of HO₂ into the side chain of benzyl radical leads to a stable adduct with dissociation energy about 50 kcal/mol. Large adsorption energy opens the possibility for fast chemically activated reactions.⁴ The reactivity of this adduct is currently under investigation and will be reported elsewhere.

Acknowledgements

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