

Theoretical study of the thermal decomposition mechanism of phenylperoxy radical.

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Abstract

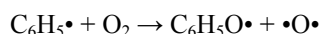
The low temperature decomposition mechanism of the phenylperoxy radical, a key reaction in the oxidation of benzene, has been studied using Density Functional Theory. The B3LYP density functional method was used for geometry optimisation of 30 reaction intermediates and transition structures over the potential energy surface and computation of their harmonic vibrational frequencies. Energy calculations using coupled cluster theory, CCSD(T) were also carried out on the optimized species characterised as minima on the potential energy surface (PES). Several pathways were explored including the initial formation of the dioxiranyl and 1,2-dioxetanyl radical to go to various products that have been experimentally observed. The energetically most favoured pathway has found to be the ring-opening reaction occurring through an oxirane ring.

Introduction

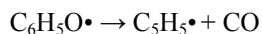
In fuel combustion, aromatic compounds are involved in the formation of particles which are harmful for health. These compounds play a key role in the formation of polyaromatic hydrocarbons (PAHs), which are believed to be soot precursors in hydrocarbon combustion. Since benzene is the simplest aromatic molecule, a large number of studies have been carried out to build a kinetic model fitting the available experimental data. However, mechanistic details of the thermal decomposition of benzene remain unclear and many rate constants, as well as associated thermochemical constants, are poorly estimated.

The initial step in benzene oxidation is the formation of the phenyl (C₆H₅) radical which in turn can react with molecular oxygen.

At high temperatures (T>1000K) the phenyl + O₂ reaction leads to the formation of the phenoxy radical

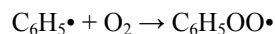


as suggested by Westbrook and Dryer [1]. This reaction is a chain propagation step as it leads to the formation of two radicals. The phenoxy radical can then thermally decompose to yield the C₅H₅ radical and CO:



This high temperature decomposition mechanism has been extensively explored by high level ab initio methods [2,3].

The most often proposed low temperature mechanism is the addition reaction between phenyl radical and O₂ to form the phenylperoxy radical.



An experimental study [4] carried out directly on the phenyl + O₂ reaction by cavity-ring down spectroscopy at low temperatures (297≤T≤437K) shows that phenylperoxy radical was still detected at temperatures as high as 473K while the phenoxy radical (C₆H₅O•) was not detected.

It appears that the phenylperoxy radical thermal decomposition mechanism is important for the understanding of the reaction of phenyl radical with oxygen at low temperatures. So, a large number of computational studies have been carried out on phenylperoxy radical decomposition pathways.

Carpenter [5] has investigated the phenyl + O₂ reaction using the semi-empirical PM3 method. He has proposed a decomposition pathway that proceeds through a rearrangement via key intermediates as phenyldioxiranyl and oxirane ring to yield C₅H₅ radical and CO₂.

Mebel and Lin [6] studied C₆H₅OO isomers at the Hartree-Fock level, as well as different decomposition pathways like phenyldioxiranyl rearrangement followed by O-atom migration or O-O bond scission to form C₆H₅O• and •O• that could further give *o*-benzoquinone.

Barckholtz et al. [7] have intensively explored the potential energy surface of the phenyl + O₂ reaction at low temperatures using the B3LYP method. A low free energy pathway was first established leading to phenyldioxiranyl. In following papers [8,9], they described five possible routes of the unimolecular decomposition of the phenylperoxy radical at various temperatures. The most favored pathways were 1) the formation of cyclopentadienyl radical C₅H₅• and CO₂

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2) the formation of pyranyl radical and CO, 3) the formation of an acyclic C₆H₅OO• radical structure.

Although several ab initio studies have been carried out to determine pathways for the thermal decomposition of the phenylperoxy radical, a complete scheme for the process is not yet available. Thus, for instance, no theoretical studies have been devoted to the formation of benzoquinone, although it is detected in benzene oxidation experience and often overestimated in kinetic models. Moreover, other pathways have been envisaged for the formation of cyclopentadienone and •CHO radical [10]. In this work, we have carried out a theoretical study which focus on the reaction mechanisms leading to these products.

Computational Methods

All geometry optimizations and vibrational frequency calculations have been performed with Gaussian 98 [11] on an IBM/RS6000 workstation. The geometries of reactants, transition states, intermediates and products have been pre-optimized at the semi-empirical PM3 level followed by optimization at the B3LYP/6-311++G** hybrid density functional theory level. It has been shown [12,13] that density functional theory methods, and the B3LYP functional in particular, can be accurately applied to aromatic radicals studies at a relatively low cost. In addition, in the B3LYP method, spin-contamination is not in general a significant problem. The limitations of the computational method will be briefly discussed at the end of the paper. Within this aim, we have carried out a series of coupled cluster calculation.

Harmonic vibrational frequencies have been calculated for each chemical species to assess that reactants, products intermediates and transition states have the correct number of real or imaginary vibrational frequencies. Transition states have been identified by the existence of only one imaginary frequency, while reactants, products and intermediates have only real vibrational frequencies. Zero-point vibrational energy (ZPE) provided by frequency calculations have been scaled by 0.9806 as recommended by Scott and Radom [12]. Intrinsic reaction coordinate (IRC) calculations have been performed on transition states to ensure that they are correctly connected to the desired reactants and products.

Thermal contributions to Gibbs free energies have been computed using standard statistical mechanics expressions for an ideal gas. In this case, we have used unscaled vibrational frequencies, without any special treatment for low frequency modes.

The Gibbs free energy has been calculated by adding the B3LYP energy, E, the scaled ZPE and the thermal contributions to the free energy:

$$G=E + ZPE + G_{\text{thermo}}$$

Our results have been obtained at 298K so that they can be compare to other values available in the literature.

In the following, all energy values correspond to free energies computed at the B3LYP/6-311++G** level, unless noted otherwise. We present some calculations obtained in the so-called "dual level" approximation. These calculations are usually noted Level A//Level B and correspond to single point energy calculations at Level A for optimised geometries at Level B. This approximation is suitable when the optimised geometries do not depend much on the computational levels A and B.

Results and discussion

As noted above, our interest in this work was focused on the description of the lowest energy pathways leading to products that have been detected in experiments or involved in the modelling of aromatic species. Specifically, we have considered the formation of *o*-benzoquinone and cyclopentadienone.

Our final scheme is presented in Figure 1 in which we summarize the computed structures and the corresponding relative free energies. A number of species in this scheme were already described in the paper reported by Fadden et al.[8]. Note however that their free energy values were obtained at the B3LYP/6-311+G**//B3LYP/6-31G* computational level whereas our values are obtained at the B3LYP/6-311++G** level. Comparison of the two schemes shows that both computational levels lead to similar free energies. In other words, geometries optimized at the B3LYP/6-31G* and B3LYP/6-311++G** levels are close so that the dual level approach employed by Fadden et al. [8] appears to be a good approximation for the study of the thermal decomposition of the phenylperoxy radical.

It can be seen in Figure 1 that several possible pathways have been identified leading to the products. Before discussing them in detail, we analyse the nature of structure **5** in Figure 1 since our calculations show that this species plays an important role in the process. It is worth noting that this intermediate was absent in the mechanistic scheme proposed by Fadden et al. [8].

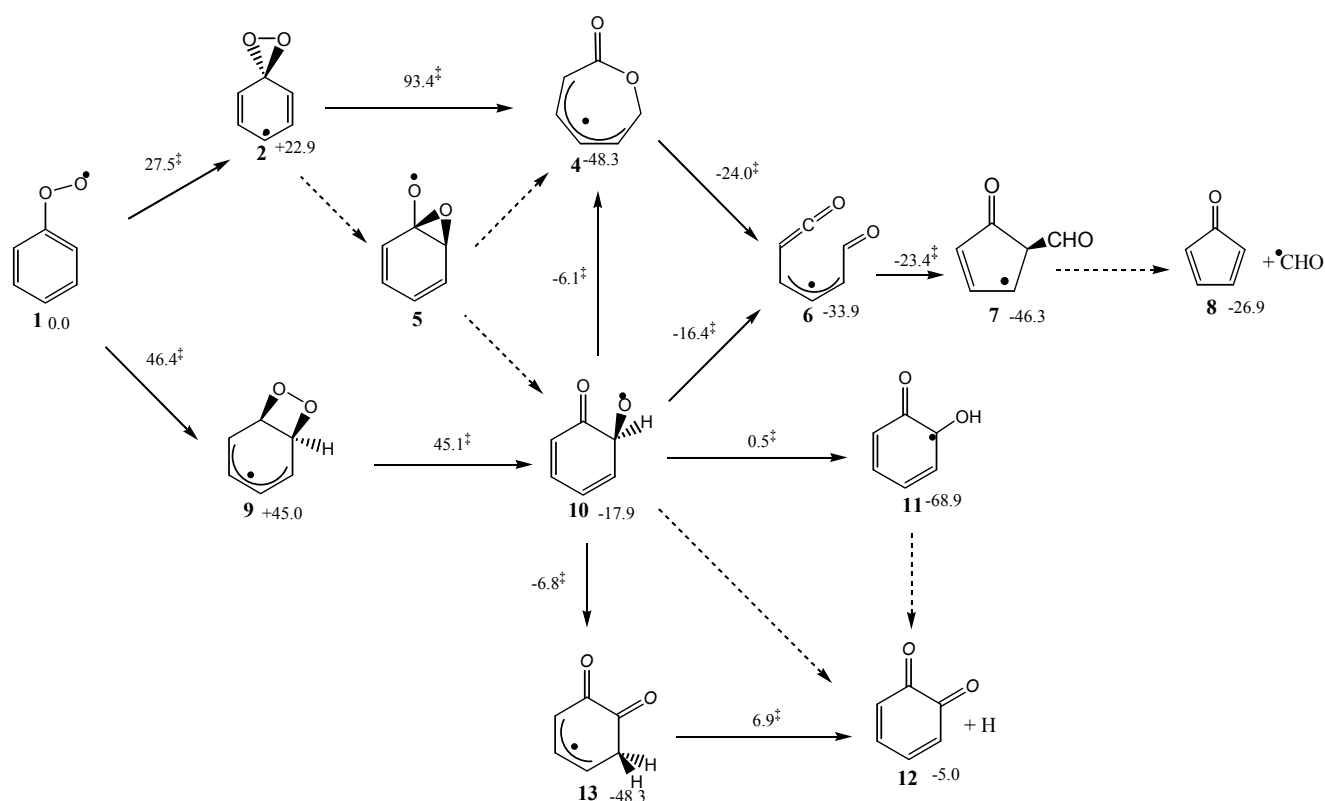


Figure 1 : Thermal decomposition pathways of phenylperoxy radical (1). The relative free energies (298K, kcal/mol) are obtained at the B3LYP/6-311++G** level. Values for reaction intermediates, transition states and products are given relative to the reactant 1. Formally, structure 5 has not been located at this computational level but it appears to play a fundamental role in the isomerisation process $2 \rightarrow 4$. For further details, see the text.

Structure of intermediate 5

Formation of this radical was first envisaged by Carpenter [5] and by Barckholtz *et al.* [7] in their studies of the reaction of phenyl radicals with molecular oxygen. Carpenter [5] carried out geometry optimisations at the PM3 level and was not able to locate an energy minimum on the PES. Barckholtz *et al.* [7] located the structure at the UHF level but not at the B3LYP level.

Indeed, the description of this structure is somewhat problematic. In the present work, the analysis of the Intrinsic Reaction Coordinate (IRC) calculations from the transition structure TS 2-5 shows that, initially, the reaction proceeds through a structure resembling 5. Nevertheless, 5 cannot be located as a formal energy minimum in the B3LYP/6-311++G** PES. We have made several attempts to optimize its geometry starting from different guess geometries but, systematically, energy minimisation led to structure 4. Further computations shows that this structure, if it exists, should lie on a very flat region of the PES, where identifying local minima represents a quite difficult task.

Though structure 5 could not be located at the B3LYP level, we have succeeded to describe it at the

UHF/6-31G* level, as already made by Barckholtz *et al.* [7]. Moreover, we have been able to locate a transition state between 5 and 10 at the same level. Some geometrical parameters are summarized in Figure 2 for 5. Note that the optimized structure 5 does not suffer from large spin contamination. The computed $\langle S^2 \rangle$ value is 0.79, very close to the expected value for a pure doublet (0.75). Moreover, spin densities and bond lengths are consistent with an electronic structure as the one schematized in Figure 2. As shown, the unpaired electron is basically localized on the oxygen atom and two C-C double bonds are well characterized. Single-point energy calculations at the B3LYP/6-311++G** level lead to relative free energies of 0.2 kcal/mol for 5 and -2.9 kcal/mol for the transition state (ZPE and thermal contributions in this case are obtained at the UHF level, a scaling factor of 0.8953 [12] has been used for the ZPE calculation). Unexpectedly, the transition state is predicted to lie below the reaction intermediate. This can be due to the use of a dual level approach, on one hand, and to the flatness of the PES, on the other hand.

Though the interpretation of these results is not straightforward, one may derive some trends. First, our calculations suggest that intermediate 2 could evolve to either 4 or 10 through a transition structure that is only 2.9 kcal/mol below 2. It is not yet clear whether both

reactions may result from a bifurcation in the reaction path after reaching the transition state but this hypothesis seems quite plausible. As a consequence, the previous scheme proposed by Fadden *et al.* [8] must be revised. In their scheme, three different pathways were proposed to obtain the reaction intermediate **4** (though one pathway involved structures exhibiting very large spin contamination and was considered as doubtful). The possibility to reach **4** via the **TS 2-5**, as suggested in this preliminary work, would be however much more favoured.

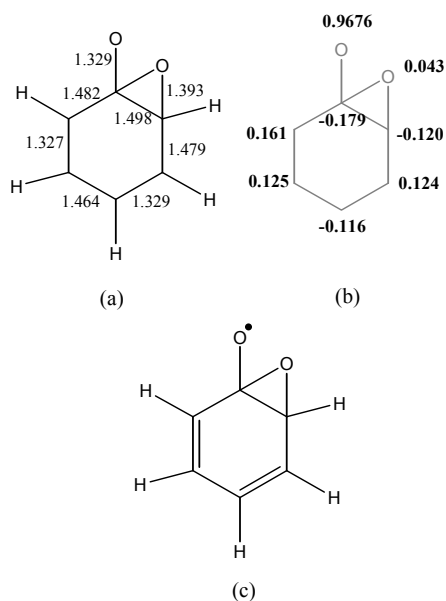


Figure 2: Computed properties for structure **5** at the UHF/6-31G* level. (a) Bond lengths in Angstroms, (b) spin densities, (c) schematic electronic structure suggested by analysis of the geometrical parameters and spin densities.

Obtaining definitive conclusions on this point will require the use of higher computational levels. In fact, one must keep in mind that the B3LYP approach is a monoconfigurational method and one may wonder whether a method including several Slater determinants would be necessary to get a correct description of the problem. For example Ghigo *et al.* [14] succeeded in exploring the mechanisms of the reaction between dioxygen and a set of radicals with CASSCF methods and showed that B3LYP method fails in some cases. CASSCF calculations for **5** are being carried out and will be reported in due course.

Pathways leading to cyclopentadienone

A reaction pathway leading to cyclopentadienone and $\bullet\text{CHO}$ radical was envisaged by Da Costa *et al.* [10] in their oxidation model for benzene. However, the corresponding reaction mechanism has not been investigated yet. In Figure 1, different possible pathways are presented, including the one proposed by Da Costa *et al.* and represented by the sequence **1** \rightarrow **9**

\rightarrow **10** \rightarrow **6** \rightarrow **7** \rightarrow **8**. In this reaction mechanism, a free energy barrier of 46.4 kcal/mol is predicted for the first step transition state **TS 1-9**. This transition state would correspond to the highest point in the reaction path. From **9**, the reaction proceeds to intermediate **10** and then to the cyclopentadienone through a ring-opening reaction displaying a low energy barrier of 1.5 kcal/mol. Finally, the open-ring structure **6** closes to form a five membered ring **7** then the final product cyclopentadienone **8**. Note that in this final step of the reaction, there is formation of the small and highly reactive radical $\bullet\text{CHO}$. Accordingly, one may expect this step to be favoured by bimolecular processes though this possibility will not be examined in the present work. Besides, we have not been able to locate a transition state **TS 7-8** at the B3LYP level. Dual-level calculations B3LYP/6-311++G**//UHF/6-31G* predict a **TS 7-8** energy of 42.5 kcal/mol (relative energy with respect to **7**).

Another possible pathway is defined by the sequence **1** \rightarrow **2** \rightarrow **4** \rightarrow **6** \rightarrow **7** \rightarrow **8**. The activation barrier between **1** and **2** is 27.5 kcal/mol, much lower than that for the initial step **1** \rightarrow **9** in the preceding mechanism but, as shown in Figure 1, reaching **4** directly from **2** through **TS 2-4** is very energy demanding (70.5 kcal/mol above **2**) and the mechanism defined by this sequence is unlikely to occur. As discussed in the previous section, our calculations suggest that the intermediate **4** could be reached through the reaction steps **2** \rightarrow **5** \rightarrow **4** or even **2** \rightarrow **5** \rightarrow **10** \rightarrow **4** thus avoiding **TS 2-4**. Finally cyclopentadienone could also be formed by the following sequence: **1** \rightarrow **2** \rightarrow **5** \rightarrow **10** \rightarrow **6** \rightarrow **7** \rightarrow **8**.

Pathways leading to *o*-benzoquinone

According to our reaction scheme, the decomposition of **1** into *o*-benzoquinone **12**, requires the prior formation of intermediate **10**. We have described some processes leading to this intermediate above, so that in this section we shall focus on the reaction steps allowing to reach **12** from **10**. Three main pathways were envisaged. The first one holds for direct dissociation of **10** into *o*-benzoquinone and a hydrogen atom. Therefore, the reaction coordinate in this case would simply involve the C-H distance. B3LYP calculations predict a barrierless process (dual-level B3LYP/6-311++G**//UHF/6-31G* calculations predict a saddle point **TS 10-12** with relative energy 25.9 kcal/mol). The other two reaction paths envisaged in this work occur via the formation of the very stable intermediates, **11** or **13**. In fact, the radical **11** is the most stable species among all those described in Figure 1. Transitions states for conversion of **10** into **11** and **13**, respectively, **TS 10-11** and **TS 10-13** have been located and the predicted activation energies show that formation of **13** should be preferred. No transition state has been located between **11** and **12** so that the corresponding dissociation process seems to be also barrierless. In contrast, the H-abstraction process from

13 to **12** involves a substantial activation barrier (**TS 13-12**). As in the case of cyclopentadienone, the relative energy of the products is relatively high as compared to that of some reaction intermediates. Here too, there is formation of a very reactive radical (a hydrogen atom) and therefore the final step is expected to be favoured by the presence of other molecular or radical species that could stabilize the transition states and/or react in an exoergic manner with the H-atom. One should finally note that intermediates **11** or **13** might be linked by a transition structure although we have not been able to locate it.

Limitations of the theoretical approach

The present study have been carried out using density functional theory and the hybrid exchange-correlation functional B3LYP. At this theoretical level, the molecular wavefunction is described by a single determinant and this might be a source of error. We have checked that this approximation is correct by carrying out single-point CCSD(T) calculations for all the species using a relatively small basis set 6-31G*. We then use the so-called T1 diagnostic [15] to check the reliability of the monodeterminantal approach. It is confirmed in all cases.

We shall not present detailed results of the single-point CCSD(T) calculations here since they do not provide further insights on the reaction. We simply stress two results: 1) spin contamination is relatively large in this case and 2) comparison with B3LYP/6-311++G** calculation suggests that basis set effects are quite large.

Conclusions

Previous theoretical studies in the literature have proposed a reaction scheme for the thermal decomposition of the phenylperoxy radical. In the present work, some new features and reaction species have been described that could play a fundamental role on the kinetics of combustion processes at low-temperatures. First, we have taken into account the formation of *o*-benzoquinone and cyclopentadienone, as these molecules have been detected in experiments or involved in the modelling of aromatic species. Besides, we have described possible pathways for the formation of the 7-membered ring **4** and of the radical **10**, which appear to be much more favoured than previous reactions paths reported to date. This is an important result since these reaction intermediates play a key role in the decomposition of the phenylperoxy radical, particularly in the formation of cyclopentadienone and *o*-benzoquinone. In both cases, the process should start by formation of the species **2**. Afterwards, **2** could evolve to either **4** or **10**. We have located a transition state (**TS 2-5** in Figure 1) that seems to be involved in these processes. However, the intermediate structure **5** is not well characterized at the B3LYP level and this part of the PES deserves further theoretical work. Cyclopentadienone is obtained from **4** through the intermediates **6** and **7** whereas benzoquinone can be

obtained directly from **10** through a barrierless reaction step. Finally, some stable intermediates (**11** and **13**) have been included in the phenylperoxy decomposition mechanism for the first time.

References

- [1] Westbook, C. K.; Dryer, F.L. *Prog. Energy Combust. Sci.* **1984**, *10*, 1-57.
- [2] Olivella, S.; Sole, A.; Garcia-Raso, A. *J. Phys. Chem.* **1995**, *99*, 10549.
- [3] Liu, R.; Morokuma, K.; Mebel, A. M.; Lin, M. C. *J. Phys. Chem.* **1996**, *100*, 9314-9322.
- [4] Yu, T.; Lin, M.C. *J. Am. Chem. Soc.* **1994**, *116*, 9571-9576.
- [5] Carpenter, B.K. *J. Am. Chem. Soc.* **1993**, *113*, 9806-9807.
- [6] Mebel, A. M.; Lin, M. C. *J. Am. Chem. Soc.* **1994**, *116*, 9577-9584.
- [7] Barckholtz, C.; Fadden, M. J.; Hadad, C. M. *J. Phys. Chem. A* **1999**, *103*, 8108-8117.
- [8] Fadden, M. J.; Barckholtz, C.; Hadad C.M. *J. Phys. Chem. A* **2000**, *104*, 3004-3011.
- [9] Fadden, M. J.; Hadad C.M. *J. Phys. Chem. A* **2000**, *104*, 8121-8130.
- [10] Da Costa, I.; Fournet, R.; Billaud, F.; Battin-Leclerc, F. *Int. J. Chem. Kin.* **2003**, *35*(10), 503-524.
- [11] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98, Revision A.6*; Gaussian, Inc.: Pittsburgh, PA, 1998.
- [12] Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502-16513.
- [13] Barckholtz, C.; Barckholtz, T.A.; Hadad C.M. *J. Am. Chem. Soc.* **1999**, *121*, 491-500.
- [14] Ghigo, G.; Maranzanna, A.; Tonachini, G. *J. Am. Chem. Soc.* **2000**, *122*, 1414-1423.
- [15] Lee, T.J.; Taylor P.R. *Int. J. Quantum. Chem.Symp.* **1989**, *23*, 199.