

Dioxetane Formation in the Phenol-Inhibited Oxidation of Hydrocarbons

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Abstract—The structures and energies of possible products of the reaction between the phenoxy radical OAr^{\bullet} and dioxygen are calculated using the PM6 semiempirical method. The possible adducts are the peroxy radical OArOO^{\bullet} and dioxetane radicals. The latter are the cyclization products resulting from the addition of the terminal atom of OArOO^{\bullet} to a carbon atom of the Ar ring. This reaction is nearly thermoneutral and is, therefore, likely.

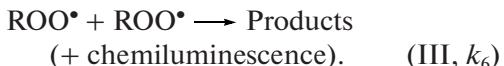
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The oxidation of organic materials (RH) is often a detrimental, undesirable process. This process can be hampered by introducing an inhibiting antioxidant to intercept chain carriers, which are peroxide radicals ROO^{\bullet} (in the presence of O_2 , the C-centered R^{\bullet} radicals turn rapidly into ROO^{\bullet}) [1, 2]. The antioxidants important to practice are substituted phenols and polyphenols (ArOH) [3]. The reaction of ROO^{\bullet} with phenol yields the hydroperoxide ROOH and the phenoxy radical, which is capable of intercepting another ROO^{\bullet} radical. Thus, the stoichiometric inhibition coefficient f is 2 and the effect of the antioxidant can be presented as follows:



where Pr are the addition and/or hydrogen abstraction products.

Processes (I) and (II) compete with the quadratic-law chain termination reaction



The unpaired electron in the phenoxy radical is distributed over the π system of the ring and is localized, to a considerable extent, on the C atom that is *para* or *ortho* to the $\text{C}=\text{O}$ group [4]. This specific feature of the phenoxy structure is taken into account above by using the designation OAr^{\bullet} instead of ArO^{\bullet} .

In practice, the effect of an antioxidant can disobey the simple scheme consisting of reactions (I) and (II) and f may differ from 2. There can be side or secondary reactions in which the inhibitor is consumed uselessly or the antioxidant effect is weakened (for comparison, see the study of polyphenolic plant flavonoids [5]).

In the present work, we focus on the possibility of the reaction between the phenoxy radical and dioxy-

gen and discuss the likely structure and the role of the product of the reaction

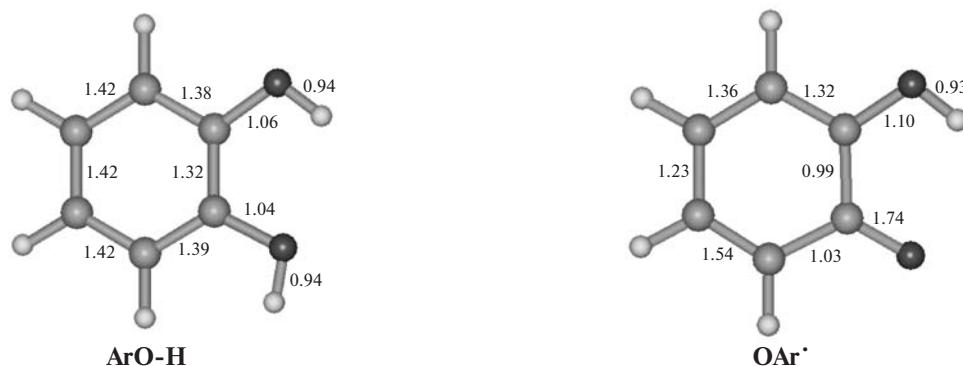


Reaction (IV) competes with reaction (II). Both are reactions between two radical centers because the ground state of O_2 is triplet and can be viewed as biradical. Therefore, comparable preexponential factors should be expected for these two reactions.

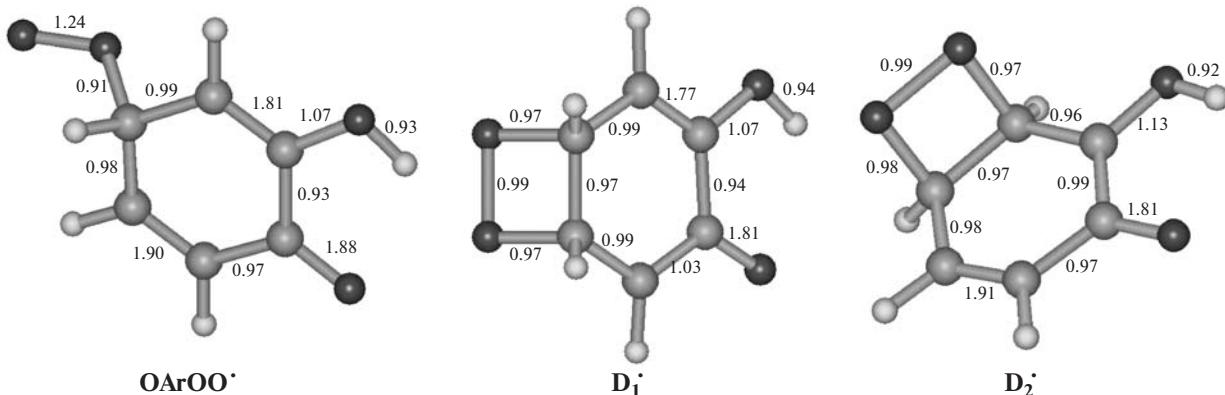
The liquid-phase oxidation of a substrate in contact with air occurs at a concentration of dissolved oxygen between 10^{-4} and 10^{-3} mol/l. The ROO^{\bullet} concentration depends on the initiation rate w_i and on the rate constant $2k_6$: $[\text{ROO}^{\bullet}] = (w_i/2k_6)^{1/2}$. At $w_i = 10^{-8}$ mol $\text{l}^{-1} \text{s}^{-1}$ and $2k_6 \approx 10^6$ (RH = ethylbenzene) and 10^8 1 mol $\text{l}^{-1} \text{s}^{-1}$ (RH = diphenylmethane), $[\text{ROO}^{\bullet}]$ is 10^{-8} and 10^{-7} mol/l [1, 2], respectively, which is 4–5 orders of magnitude lower than the above estimate of $[\text{O}_2]$. The *probabilities of encounter* of ROO^{\bullet} and O_2 with phenoxy radicals differ by the same factor. Anyway, the reaction between OAr^{\bullet} and O_2 seems quite probable, although its actual contribution depends on the relative rates (activation energies) of the competing processes.

The structures and heats of formation (ΔH_f^0 , kcal/mol) of several phenols, their phenoxy radicals, and reaction products were determined by the semiempirical method PM6 (MOPAC 2007 program package) [6]. The iteration protocol was always analyzed during the calculations. In the case of a non-monotonic decrease in energy (spikes indicating false minima), the result was rejected and the computational experiment was repeated.

The structures and bond orders of the antioxidant catechol and its phenoxy (product of hydrogen abstraction: $\text{ArOH} \longrightarrow \text{OAr}^{\bullet} + \text{H}$) are shown in Scheme 1.



Scheme 1.



Scheme 2.

The heats of formation were calculated to be $\Delta H_f^0(\text{ArOH}) = -65.0 \text{ kcal/mol}$, $\Delta H_f^0(\text{OAr}^\bullet) = -36.2 \text{ kcal/mol}$, and $\Delta H_f^0(\text{H}) = 52.1 \text{ kcal/mol}$. Hence, the dissociation energy of the $\text{ArO}-\text{H}$ bond is $D(\text{ArO}-\text{H}) = \Delta H_f^0(\text{OAr}^\bullet) + \Delta H_f^0(\text{H}) - \Delta H_f^0(\text{ArOH}) = 81.0 \text{ kcal/mol}$. This value is close to the experimental value of 81.6 kcal/mol, indicating that the calculation is reliable.

We expected that the product of O_2 addition to OAr^\bullet would be the peroxide radical $OArOO^\bullet$. The calculations confirmed this hypothesis. As judged from the ΔH_f^0 value (-32.9 kcal/mol), the energy of the $OArOO^\bullet$ radical, which has a well defined quinoid structure, is similar to the energy of the initial phenoxyl (higher by 3.3 kcal/mol).

Unexpectedly, the calculations evidenced the formation of other structures—four-membered cyclic dioxetane radicals D^\bullet (Scheme 2). These radicals are formally the products of addition of the tail O atom of the $OArOO^\bullet$ radical to the adjacent carbon atoms of the ring, with $\Delta H_f^0(D_1^\bullet) = -32.4$ and $\Delta H_f^0(D_2^\bullet) = -40.3$ kcal/mol.

The formation of the second, more stable dioxetane radical is exothermic to the extent of 4 kcal/mol, whereas the formation of the first radical is most likely to be thermoneutral. The difference is determined by the specific features of the electron density distribution over the OAr^\bullet ring (sf. the bond orders).

The remaining O–H bond in the phenoxy (D(O–H) = 66 kcal/mol) is weaker than the same bond in ArOH, so reaction (II) can be not only the addition of dioxygen, but also hydrogen atom abstraction from OAr[•] yielding *ortho*-quinone ($\Delta H_f^0 = -22.3$ kcal/mol) and the radical HO₂ ($\Delta H_f^0 = 5.1$ kcal/mol). However, this reaction is very endothermic ($\Delta H_r = 19$ kcal/mol) and its contribution is insignificant.

The calculations showed that, for the other phenolic antioxidants (guaiacol and caffeic and ferulic acids), the dioxetane formation reaction is almost thermoneutral. The D^\bullet radical can abstract hydrogen from an appropriate substrate and turn into the dioxetane molecule D. In recent decades, dioxetanes have been the subject of numerous studies. These strained-ring peroxides are viewed as a kind of energy storage system [7, 8]. Both the radicals and the molecules are

moderately stable: their typical activation energies are 20–30 kcal/mol. Their thermal decomposition yields two carbonyl fragments, one of which is electronically-excited and luminescent. This “molecular” chemiluminescence differs from the “classical” radical chemiluminescence excited in reaction (III). Both types of chemiluminescence are used in the study of antioxidants and their activity [9].

Dioxetane is bicyclic; i.e., its structure is more ordered than the structure of the initial pair $OAr^{\bullet} + O_2$. Therefore, the expected negative change in entropy and the slight exothermicity cannot provide a strong equilibrium shift toward dioxetane. (A study of the pulsed radiolytic generation of phenoxy radicals in alkali solutions revealed the reaction between OAr^{\bullet} and $O_2^{\bullet-}$ [10]. However, the question of whether the same reaction involving O_2 can take place remained unanswered.) Dioxetane can be revealed due to the high reactivity of its strained four-membered ring and chemiluminescence. The latter can be detected by modern photometers even at extremely low light intensities.

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