Computational Study of the Oxygen Initiated Decomposition of 2-Oxepinoxy Radical

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Introduction

Benzene is the archetypal aromatic hydrocarbon. Benzene and its derivatives are common fuel constituents in addition to a suitable model from which its oxidative pathways can be used to infer similar oxidation processes for larger polycyclic aromatic compounds. Benzene oxidation has therefore been the subject of numerous studies. Experimental studies using mass spectrometric detection at high and intermediate temperatures indicate that the most common products of benzene oxidation are CO$_2$, CO, C$_2$H$_2$ (acetylene), cyclopentadienyl radical, and various unsaturated C$_x$O$_y$ and C$_x$H$_y$O species. The commonly accepted mechanism based on intermediate to high temperature experiments for the initiation of benzene oxidation with molecular oxygen is the generation of phenyl radical via reaction (Eqn. 1), followed by the addition of molecular oxygen and concomitant lose of oxygen atom (O) (Eqn. 2).

$$\text{C}_6\text{H}_6 + \text{O} \rightarrow \text{C}_6\text{H}_5 + \text{HO}_2 \quad (1)$$

$$\text{C}_6\text{H}_5 + \text{O}_2 \rightarrow \text{C}_6\text{H}_5\text{O} + \text{O}(\text{O}) \quad (2)$$

Yu and Lin, however, performed kinetic studies to determine the rate of reaction of phenyl radical with O$_2$ using cavity-ring down (CRD) spectroscopy and detected phenyl peroxy radical up to 473 K. Norrish and Taylor via identification of ortho and para dihydroxybenzenes, in experiments using a flow system to analyze the reaction of benzene with O$_2$ in a nitrogen diluent at 685 K, predicted the inclusion of phenyl peroxy radical as a probable intermediate.

Computational studies have also been undertaken in order to determine the most thermodynamically and kinetically viable mechanistic pathways involved in benzene oxidation. Theoretical studies, based on B3LYP/6-311+G**/B3LYP/6-31G* free energies, by this group, predict that the phenyl peroxy radical is the more thermodynamically favored intermediate, verses phenoxy radical at T $\leq$ 450 K, while at T $>$ 450 K, entropy dominates thereby making phenoxy radical the prominent intermediate. This implies that under low temperature combustion and atmospheric conditions the phenyl peroxy radical is likely to play an important role in the decomposition of phenyl radical.

Carpenter utilized PM3/UHF semiempirical calculations to elucidate possible decomposition pathways for phenyloxy radical to form cyclopentadienyl radical and CO$_2$. He considered a pathway in which phenyloxy radical proceeds through formation of a spirodioxiranyl radical, with an enthalpic barrier of 26.1 kcal/mol, to form thermodynamically stable seven-membered ring radical, 2-oxepinoyl (1) shown in Figure 1. Barckholtz et.al. and Fadden et. al. have refined the same energy surface using density functional theory and high-level ab initio calculations to study this decomposition process as well as the formation of a dioxygenyl radical intermediate leading to the 2-oxepinoyl radical (1). Decomposition through the spirodioxiranyl radical was shown to be the most viable reaction path leading to 2-oxepinoyl radical, with a free energy barrier of ~41.6 kcal/mol at 298 K, due to the inclusion of an additional high energy triradical intermediate (Figure 1). Despite the inclusion of the high energy triradical species, this pathway exhibited a lower barrier than that for the formation of phenoxy radical and oxygen atom at ~51.0 kcal/mol. These barriers are rough estimates, however, because of spin contamination in the wavefunctions of the key intermediates. At the B3LYP/6-311+G**/B3LYP/6-31G* level, 2-oxepinoyl radical was calculated to have a $\Delta G$(298 K) energy which is 79.9 kcal/mol lower than separated phenyl radical and O$_2$(2) reactants. Consistent values were obtained with UMP4(SDQ)/6-31G** and UCCSD(T)/6-31G** energy calculations in the same study. Mebel and Lin in a theoretical study of C$_6$H$_7$O$_2$ geometrical isomers estimated 2-oxepinoyl radical (1) to have a $\Delta H$(0 K) of ~91.8 kcal/mol based on PUMP3/6-31G**/UHF/6-31G* energies. The stability of 2-oxepinoyl radical indicates that it should be relatively long-lived upon formation and therefore susceptible to further oxidation by reactive species contained in a typical radical pool.

In this study, we will utilize the B3LYP hybrid density functional theory functional to analyze the potential energy surface for the decomposition of 2-oxepinoyl radical after further peroxy radical formation via addition of O$_2$(2). The energies of minima and activation barriers for decomposition following the initial formation of 1,2-dioxetanyl, 1,3-peroxy, 1,4-peroxy, scission of the O-O peroxy bond, and abstraction of an H-atom by the geminal peroxy moiety. The energies for these surfaces will be evaluated from T = 298-1250 K, the range in which phenyloxy radical has been shown to be a viable combustion component.

**Figure 1.** Reaction scheme for the generation of 2-oxepinoyl radical

(1). Energies are B3LYP/6-311+G**/B3LYP/6-31G* $\Delta G$(298 K) relative to phenyloxy radical.

Oxygen Addition to 2-oxepinoyl Radical

The addition of O$_2$ to 2-oxepinoyl radical (1) is most likely to occur at three different positions on the 2-oxepinoyl radical ring, forming three distinctive peroxyxepinone radicals (1a, 1b, or 1c, Figure 2), due to delocalization of the lone electron within the aromatic ring of the ring carbons. Addition can occur at the 2, 4 and 6 ring positions, numbered relative to the carbonyl carbon, as position 1, moving counterclockwise. Figure 2 shows the structure of 2-oxepinoyl radical (1) and the peroxy radical structures formed after the addition of molecular oxygen. Also shown in Figure 2 are the 298 K free energies ($\Delta G$(298 K)) for each intermediate and transition state relative to reactants at infinite separation. Each free energy of activation barrier is relative to the reactant for that individual step.

**Figure 2.** Three unique transition state (TS) structures for the formation of 2-peroxyxepinone radical (1a) were found. In each transition state, the oxygen molecule approaches perpendicular to the ring plane and differs in the relation of the O-O bond rotation about the forming C=O bond. All three TS wavefunctions have considerable spin contamination, giving (S$^2$) values of ~1.0, rendering the transition state barriers to be suspect. Regardless, the 298 K free energy barrier ($\Delta G$(298 K)) for the lowest energy TS structure, with the O-O oxygen bond setting above the C$_1$-C$_2$ ring bond, is 17.7 kcal/mol with (S$^2$) value of 0.96, the least spin contaminated of the

three wavefunctions. The 298 K reaction is endoergic by 10.4 kcal/mol with a reverse $\Delta G^\circ$ (298 K) of only 7.3 kcal/mol.

4-Addition. Two TS structures were found for addition of oxygen to the 6 ring carbon to form 6-peroxy-oxepinone radical (1b). In both transition structures, the oxygen molecule enters from above the ring plane. In the lower energy TS, the O-O bond adds anti to the C-H bond and over the inside of the ring while the higher energy structure has the O-O bond almost eclipsing the C-H bond. Spin contamination for both transition states was also significant, (S^2) ~ 1.0. The $\Delta G^\circ$ (298 K) for the lowest energy transition structure was 17.0 kcal/mol. This barrier is also the lowest for molecular oxygen addition to the three carbon positions. A simple Hückel analysis for the 5-carbon ring $\pi$ system for 1 indicates that most of the electron density should be localized on the 4 carbon. Examination of the C-C bond lengths on the ring are consistent with Hückel theory, with the two C-C bonds containing the 4 carbon at 1.40 and 1.42 Å, with bond lengths intermediate between typical C–C single and double bond character. The C-C bonds adjacent have lengths of 1.38 and 1.36 Å exhibiting more pure C–C double bond character. Formation of 1b, however, is endoergic by 13.2 kcal/mol. It is the most unstable addition product likely due to disruption of resonance in the carbon ring $\pi$ system caused by its formation. Recrossing back to reactants costs a mere 3.8 kcal/mol.

6-Addition. Three transition state structures for the formation of 6-peroxy-oxepinone radical (1c) were also found. Each TS structure has the oxygen molecule approaching from above the ring plane and differs only by a rotation of the O-O bond about the forming C-O bond. All three wavefunctions again have considerable spin contamination, (S^2) values of ~ 1.0, making the TS energies suspect. The $\Delta G^\circ$ (298 K) for the lowest energy TS, with the O-O oxygen bond setting above the C-O ring bond, is 17.5 kcal/mol and an (S^2) value of 1.1. The reaction is endoergic by 9.0 kcal/mol making it the most stable of the peroxyoxepinone radical species. Return to reactants has a $\Delta G^\circ$ (298 K) of 8.5 kcal/mol, the largest of the return barriers.

![Figure 2](image_url)

Figure 2. Reaction scheme for the addition of oxygen molecule ($^1P$) to 2-peroxy radical (1). Energies are B3LYP/6-311+G**//B3LYP/6-31G* $\Delta G$(298 K) relative to O3 and 2-Oxepinoxy at infinite separation.

Conclusions

Subsequent unimolecular fragmentations emanating from 1a, 1b, and 1c have also been calculated at the same level of theory. Several possible pathways for the decomposition of 2, 4, and 6-peroxyoxepinone radical have been examined at 298, 500, 750, 1000, and 1250 K. Pathways initiated via the formation of a dioxetane, 1,3-peroxy, 1,4 peroxo or hydrogen abstraction via geminal peroxyyl radical are competitive with the pathways proposed by Fadden for the unimolecular decomposition of 2-oxepinoxy radical (1). The kinetically most favored decomposition pathway at all temperatures involves formation of the 1,4-peroxy intermediate resulting in the formation of furan, CO2 and formyl radical. Thermodynamically, the most favored pathway forms a 1,2-dioxetanyl intermediate and decomposes to form 1-oxo-3-pent-2,3-dienyl radical, CO2 and CO. However, a large entropic penalty is incurred at higher temperatures, thereby making the O2-addition pathways to the 2-oxepinoxy radical less competitive.

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References