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Quantum Chemical Study of Low Temperature Oxidation Mechanism of Dibenzofuran

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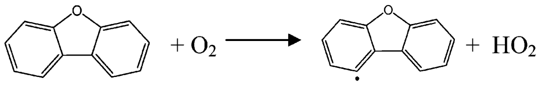
A density functional theory (DFT) study of the reaction of dibenzofuranyl radical with oxygen molecule has been made. The geometries, energies, and vibrational frequencies of the reactant, transition states, intermediates, and products have been calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level of theory. The initial reaction of dibenzofuran (DBF) with molecular oxygen results in the formation of the 1-dibenzofuranylperoxy radical. The stability of this adduct toward decomposition at low to intermediate temperatures results in it undergoing several possible rearrangements. The lowest energy pathway with a barrier of 24.2 kcal/mol involves a rearrangement to the 1,1-dioxadibenzofuran radical. The next lowest energy pathway involves fission of the O−O linkage whose reaction energy was found to be 37.6 kcal/mol. Transition state theory (TST) calculations indicate that the lowest energy pathway should predominate at temperatures up to about 1200 K. Two other unimolecular reaction pathways with barriers of 45.5 and 91.1 kcal/mol have also been discovered. The latter pathway leads to the formation of a *para*-quinone (dibenzofuran quinone) which has been detected experimentally in the low-temperature oxidation of DBF [Marquaire, P. M.; Worner, R.; Rambaud, P.; Baronnet, F. *Organohalogen Compd.* **1999**, *40*, 519]. Our quantum calculations, however, do not support this latter pathway to quinone formation. Instead, the quinone is most probably formed as a consequence of recombination of the 1-dibenzofuranyloxy radical (produced by peroxy fission) with an O atom in the para position. Each of the unimolecular reaction pathways have been subjected to detailed quantum chemical investigation and transition states and intermediates leading to the final products (principally CO, CO_2, and C_2H_2 with traces of benzofuran and benzene) have been identified. For certain stable intermediates, their possible reactions with molecular oxygen have been further investigated quantum chemically. The present work therefore presents a detailed quantum chemical investigation of the reaction pathways in the low-temperature oxidation mechanism of DBF. Since the dibenzofuran moiety is present in the polychlorinated DBFs, our conclusions should be generally applicable to this family of compounds.

I. Introduction

Incineration and thermal decomposition of waste material frequently lead to the production of significant quantities of the pollutants polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF). It is important to develop combustion techniques which minimize the emission of these pollutants. Fundamental to this aim is an understanding of the detailed mechanisms of formation and destruction of PCDD/F. Model development of the oxidation of the dioxin-like compounds under the conditions encountered in the combustion environment requires detailed knowledge of the mechanism governing the oxidation process where thermochemistry and kinetics aspects play a major role toward a correct understanding of the chemical and physical criteria that are needed to design better systems to mitigate their adverse effects. So far, little is known about kinetics governing the gas-phase oxidation of dioxin-like compounds; the study by Marquaire et al.[1] of the oxidation of dibenzofuran at temperatures between 800 and 950 °C may represent the only experimental study on the oxidation of these compounds. The major products observed in the fuel rich conditions were CO and CO_2 and trace amounts of benzene (and its substituted derivatives) together with benzofuran and its substituted derivatives. Based on their results, Marquaire et al.[1] claimed that an optimization of the combustion environment (temperature, oxygen concentration, and residence time) leads to complete destruction of dibenzofuran.

Marquaire et al.,[2,3] using kinetics data estimated from analogous reactions of small molecules, have suggested a mechanism for low and high-temperature regimes. Their high temperature (≥1200 K) mechanism was based on the following steps:

(i) The formation of dibenzofuranyl radical isomers ($DBF'^{\bullet}$) at four sites (1−4) of the benzene ring (reaction at site 1 is shown through reactions 1−5).



(1)

(DBF) (DBF′·)

$$DBF + R^{\bullet} \rightarrow DBF'^{\bullet} + R{-}H \qquad (2)$$

where $R^{\bullet}$ is a radical such as HO_2, HO, O, or H.

(ii) Subsequent reactions of $DBF'^{\bullet}$ in two competing parallel channels. At high temperatures, $DBF'^{\bullet}$ can react with O_2 ($^3\Sigma_g$) to form dibenzofuranylperoxy ($DBF'{-}OO^{\bullet}$) at one of the four radical sites. Bond scission of the peroxy bond (O−O) would

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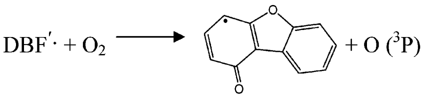
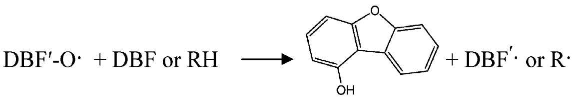
lead to the formation of dibenzofuranyloxy (DBF′−O•) at the four sites and O (^{3}P). The phenolic oxygen atom in dibenzofuranyloxy can then abstract an H atom from the parent DBF to form the four isomers of dibenzofuranol (DBF′−OH) which are expected to be primary products. This high-temperature route is predicted to account for the formation of the phenylacetylene, naphthalene, indene, and benzaldehyde observed experimentally

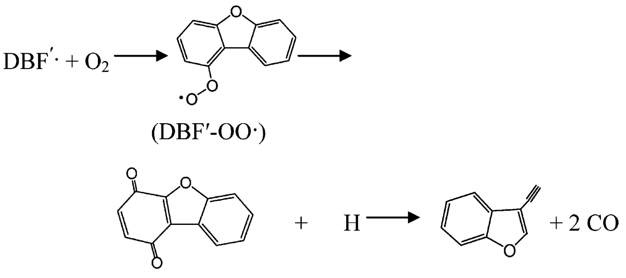


(DBF′-O·) (3)



(DBF-OH) (4)

At low temperatures, addition of molecular oxygen to the dibenzofuranyl radical (DBF′•) results in the formation of dibenzofuranylperoxy (DBF′−OO•) which can then react further to give 3-ethynylbenzofuran +2 CO:



(DBF-quinone) (BF-C$_2$H) (5)

Since there is a lack of knowledge of the thermochemistry of many of the intermediates and no experimental rate data for reaction steps, this postulated mechanism at low temperatures has not been established. In the present study, we present detailed quantum chemical calculations to understand the mechanism of reaction of O$_2$ ($^3\Sigma_g$) with dibenzofuranyl (DBF′•). We investigate two regimes: one where the resultant DBF′−OO• is relatively stable and one where scission of the O−O peroxy bond can initiate the high-temperature oxidation of the aromatic compounds. Potential energy surfaces for reactants, intermediates, and products for several possible pathways have been identified, and quantum chemical calculations of their thermochemical and chemical kinetic parameters have been made. Since the dibenzofuran moiety is an important functional group in PCDFs, these studies can provide useful information on the oxidation reactions of these compounds.

II. Computational Details

All calculations were performed with the Gaussian 03 suite of programs.[4] Optimized geometries and harmonic vibrational frequencies of all species and transition states on the reaction potential energy surface have been calculated using the hybrid density functional theory (DFT) of B3LYP which employs the three parameter Becke exchange functional,[5] B3, with the Lee−Yang−Parr nonlocal correctional functional LYP[6] along with the polarized basis set of 6-31G(d).[7] As we are concerned with relatively large molecular species, high accuracy methods such as G3 are not appropriate to obtain reliable relative energies; hence, single-point calculations with the largest practical basis set of 6-311+G(3df, 2p) have been performed on the geometry obtained with the 6-31G(d) basis set. Following the conventional notation in computational chemistry, this approach is denoted as B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d)+ZPVE(B3LYP/6-31G(d)). The stationary points located were either minima or transition states (TS) determined by analysis of the vibrational frequency where first-order saddle points contain one and only one imaginary frequency along the reaction coordinate. Where appropriate, IRC calculations have been used to link reactants and products with their transition states.

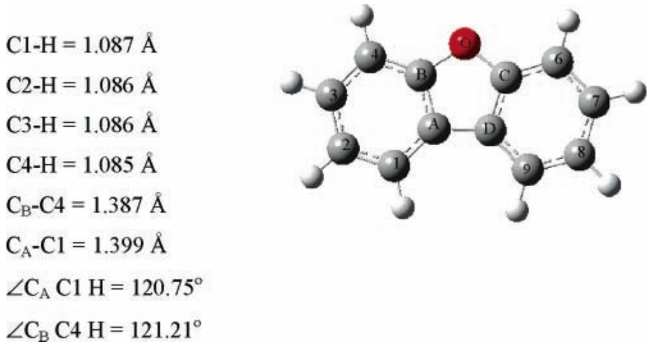


Figure 1. Optimized geometry of dibenzofuran at the B3LYP/6-31G (d) level of theory.

The reliability of our adopted computational approach for dioxin-like compounds has been addressed by Farajian et al.[8] and Okamoto and Tomonari,[9] who tested the available experimental data with their computational results. Agreement is generally regarded as satisfactory. Kinetic parameters have been calculated from the thermochemical parameters for transition states and reactants using transition state theory (TST). Heats of formation of key species involved have been calculated using isogyric and isodesmic reaction schemes to improve the accuracy. Molecular parameters and computed energies for all equilibrium structures and transition states are provided in Supporting Information.

III. Results and Discussion

Structure and Thermochemistry of DBF. The optimized geometry of dibenzofuran is displayed in Figure 1. The heat of formation for dibenzofuran at 298 K has been calculated using isogyric and isodesmic reaction schemes based on enthalpy values obtained at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G-(d) level of theory and experimental heats of formation of reactants and products in these schemes as given in the NIST compilation.[10] The experimental heat of formation of DBF has not been well established. Three experimental values for DBF heat of formation have been found in the literature: viz., 19.9 (ref 11), 11.3 (ref 12), and 13.2 (ref 13) kcal/mol. These values are compared in Table 1 with three values obtained using isogyric reaction schemes where good relative agreement in calculating the DBF heat of formation (15.2−15.4 kcal/mol) has been found. Isodesmic reaction schemes which conserve similar bonds give values ranging from 13.9 to 14.7 kcal/mol. We consider the isodesmic schemes to give the more reliable values and hence adopt their mean value of 14.2 ± 1.5 kcal/mol for the heat of formation of DBF at 298 K.

The C1−H bond in DBF is slightly longer than the other C−H bonds suggesting that an H atom abstraction from site 1 might be favorable compared with abstraction from other sites. Single-point energy calculations at the level of theory of B3LYP/6-311+G(3df, 2p)//6-31G(d) have been carried out to determine the relative stability of the four dibenzofuranyl radical isomers. At this level of theory, the 1-dibenzofuranyl radical is slightly

TABLE 1: Results of Isogyric (1−3) and Isodesmic (4−6) Reaction Schemes for Heat of Formation of DBF at 298 K

reaction scheme	$\Delta_f H^o_{298}$(DBF) theory (kcal/mol)	$\Delta_f H^o_{298}$(DBF) experiment (kcal/mol)
		19.9,[a] 11.3,[b] 13.2[c]
1 DBF + 3 H_2 = 2 C_6H_6 + H_2O	15.2	
2 DBF + 2 H_2 = C_6H_5OH + C_6H_6	15.3	
3 DBF + H_2O + H_2 = 2 C_6H_5OH	15.4	
4 DBF + C_2H_4 = 2 C_6H_6 + C_4H_4O	14.7	
5 DBF + CH_3CH_3 = C_8H_8O + C_6H_6	13.9	
6 DBF + C_2H_4 = C_6H_6 + C_4H_4O	13.9	
mean value (1−6) kcal/mol		14.7
mean value (3−6) kcal/mol		14.2
mean value (exp) kcal/mol		14.8

[a] Reference 11. [b] Reference 12. [c] Reference 13.

TABLE 2: Relative Stability of Dibenzofuranyl Isomers

radical site	E_0 (hartree/particle) B3LYP/6-311+G(3df,2p)//6-31G(d)	relative energy
1	−536.660537	0.0
2	−536.660121	0.3
3	−536.660291	0.2
4	−536.657670	1.8

more stable than the 2-, 3-, and 4-dibenzofuranyl radicals. Results are shown in Table 2.

As there is little difference in stability of these four isomers (DBF′•), we would expect all four radicals to be formed on initial reaction of DBF with O_2. This has been confirmed experimentally[1,2] and explains the experimental observation of all four dibenzofuranol isomers as intermediates in DBF oxidation. In our subsequent discussion, oxidation through formation of 1-dibenzofuranyl radical as the starting point in the DBF oxidation is studied as the most stable form of dibenzofuranyl isomer, but reaction channels through other dibenzofuranyl radicals are to be expected.

Initial Reaction of DBF. At low temperature, initiation of oxidation of DBF will take place in the absence of propagating radicals such as OH, O, HO_2, or H. Initial reaction will be between DBF and ground state O_2 ($^3\Sigma_g$). Although we were able to locate several adducts for the reaction of the oxygen molecule and DBF on the singlet surface (i.e., with O_2 ($^1\Delta$) as oxidant), these adducts could not be located on the triplet surface. No triplet adducts could be located on the analogous C_6H_6/O_2 surface, either. Initiation of oxidation must therefore arise by the removal of an H atom from any of the ring positions (1 through 4) giving one of the four dibenzofuranyl radical isomers (DBF′•). In the case of alkanes and O_2, their interaction with the oxygen molecule has been studied theoretically.[14−18] Transition states have been found for abstraction of an H atom to form $R^\bullet + HO_2$ and for displacement to form $RO_2^\bullet$ + H. However, the transition state for the first process is a variational transition state (VTS), its existence[19,20] is sensitive to the basis set employed and its energy is lower than the products $R^\bullet + HO_2$. The transition state for the second process is discrete. For alkanes, the barrier to formation of $R^\bullet + HO_2$ is approximately 50 kcal/mol, whereas for direct formation of RO_2 + H, it is about 70 kcal/mol.

For alkanes, the reactions of $RH + O_2 \rightarrow R^\bullet + HO_2$ have been extensively studied experimentally. For aromatics, however, there is much less information. For $C_6H_6 + O_2 \rightarrow C_6H_5 + HO_2$, the only literature value comes from a complex mechanism postulated for benzene oxidation in a shock tube.[21] Using benzene as a model for the aromatic ring in DBF, we have searched for transition states for both $C_6H_6 + O_2 \rightarrow C_6H_5^\bullet + HO_2$ and $C_6H_6 + O_2 \rightarrow C_6H_5OO^\bullet$ + H. We were unsuccessful in locating a TS for the former but found a discrete TS for the latter. At the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level of theory, the barrier for the latter reaction was found to be 72.1 kcal/mol. This barrier is higher by approximately 11 kcal/mol than the energy required to form $C_6H_5 + HO_2$. Hence, at least in the case of C_6H_6/O_2, we would expect initial reaction to form $C_6H_5 + HO_2$ rather than direct formation of the peroxy. A subsequent reaction between C_6H_5 and O_2 would produce $C_6H_5OO^\bullet$.

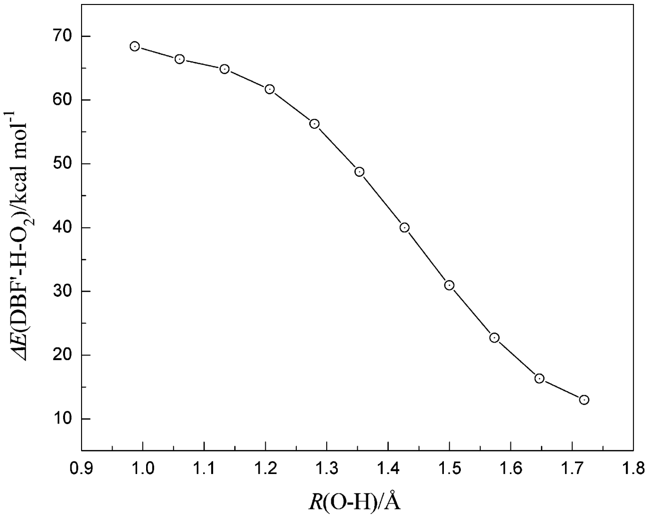


Figure 2. Potential energy profile for H abstraction from DBF (site 1) by O_2 calculated at B3LYP/6-31G(d) level of theory. ΔE is relative to the energy of the reactants (i.e., DBF and O_2).

Hence, by analogy, at low temperatures, we expect that DBF will react with O_2 in a two-step process to form dibenzofuranylperoxy (DBF′−OO•)

$$\mathrm{DBF} + O_2 \rightarrow HO_2 + \mathrm{DBF}'^{\bullet} \xrightarrow{O_2} \mathrm{DBF}'{-}\mathrm{OO}^{\bullet} \tag{6}$$

To investigate more carefully whether H abstraction from DBF by an oxygen molecule does or does not incur a barrier, PES calculations have been performed for the system of (DBF′•−H−O_2). As shown in Figure 2, the energy monotonically and smoothly increases as H departs DBF and approaches O_2 to make HO_2. This confirms that no discrete transition state could be obtained for the abstraction process; that is, there exists a variational transition state. Thus, a two-step process producing DBF′−OO• rather than a one step H-expulsion process would appear to be more probable. At low temperature, where the peroxy linkage is stable, DBF′−OO• could undergo isomerization reactions. Once reaction proceeds, the radical pool of O/H would lead to rapid formation of DBF′•. At sufficiently high temperature, we would expect O−O fission to take place (the high-temperature route of Marquaire et al.[1−3]). These reactions are discussed later.

Dibenzofuranyloxy (DBF′−OO•) Reactions. It has been well-established that the initial step in the oxidation reaction of the aromatic and polyaromatic hydrocarbons (PAH) in combustion and in the atmospheric environment involves radical formation followed by reaction with molecular oxygen. The fate of the adduct formed after molecular oxygen addition has been investigated extensively during the last two decades for the simplest aromatic compound (C_6H_6). Many experimental[22−27]and theoretical studies[27−32] have been undertaken to elucidate mechanisms that reconcile with the experimental observations which indicate that CO, CO_2, and C_2H_2 together with H_2O are

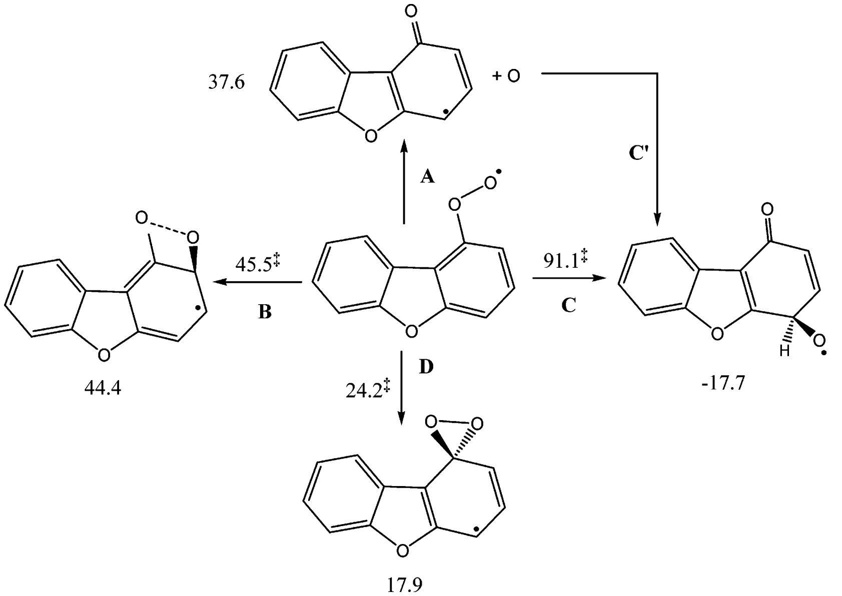


Figure 3. Unimolecular rearrangement pathways for 1-dibenzofuranylperoxy radical. Values are the relative reaction energies and activation energies (‡) at 0 K in kcal/mol, at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level of theory.

major products, in addition to trace amounts of cyclopentadienone (C_5H_4O). The commonly accepted high-temperature channel results in the generation of phenoxy radical (C_6H_5O) and O (^{3}P)

$$C_6H_6 + O_2 \rightarrow C_6H_5O + O\ (^3P) \tag{7}$$

However, experimental data[33−35] have revealed that a pathway through the formation of *para*-benzoquinone (*p*-OC_6H_4O) is an important secondary channel (8) especially at low-temperature based on the experimental finding of *o*- and *p*-dihydroxybenzenes at temperatures as high as 686 K

$$C_6H_5 + O_2 \rightarrow p\text{-}OC_6H_4O + H \tag{8}$$

These reactions have been supported theoretically in many studies.[31,36,37] Including these and their subsequent steps in the overall mechanism of benzene oxidation has been of vital importance to satisfactorily model experimental product distributions.[16,17] Intensive theoretical studies have been undertaken to describe different transformations of the peroxy radical. Here we extend the recent findings for benzene oxidation to the oxidation system of dibenzofuran. The similarities between the dibenzofuranyl radical + O_2 system and phenyl + O_2 have been adequately addressed by Sebber et al.[37] They have shown that the vinyl + O_2 system of Mebel et al.[38] and the phenyl + O_2 system of Fadden et al.[31] can be used as models for dibenzofuranyl/O_2 in the view of the thermochemical similarities between these three systems.

As shown in Figure 3, we have found from quantum chemical calculation that 1-dibenzofuranylperoxy (DBF′−OO$^•$) can rearrange through four reaction pathways A−D. Pathway A is the high-temperature O−O scission route. Pathways B−D involve intramolecular rearrangements, and discrete transition states for each process have been located. The pathways leading to the formation of 1,2-dioxadibenzofuran (path B) and 1,1-dioxadibenzofuran (path D) are the most accessible paths for DBF′−OO$^•$ rearrangements. Path C which leads to the formation of 4-hydroquinone-dibenzofuran is a possible route to the experimentally observed 1,4-dibenzofurandione; however, it has an improbably high-energy barrier of 91.1 kcal/mol. The most likely route to 1,4-dibenzofurandione must therefore involve recombination of an O atom with DBF′−O$^•$ at the 4 position (path C′). The calculated reaction and activation energies (0 K) are presented in Figure 3.

Both the computed activation energies and the reaction energies for these entrance channels are within 2.0 kcal/mol of their phenylperoxy analogues. This supports the hypothesis of Sebbar et al.[37] who took advantage of the similarities between phenylperoxy $C_6H_5OO^•$ and DBF′−OO$^•$ to construct the early stages of the dibenzofuran oxidation potential energy diagram based on the activation energies of the phenylperoxy system.

The O−O bond energy in DBF′−OO$^•$ is calculated to be 37.6 kcal/mol. This may be compared with the value of 36.4 kcal/mol found for O−O in the phenylperoxy radical.[36] The TS for O−O scission in the latter is actually found[36] to be 0.9 kcal/mol below the energy of C_6H_5O + O. This might also be the case for DBF′−OO$^•$. We have been unable to locate a discrete TS for O−O scission in DBF′−OO$^•$ and expect that this scission takes place via a VTS. For a molecule as large as DBF′−OO$^•$, this decomposition would be expected to occur at or close to the high-pressure limit. Its activation energy should therefore be close to the computed reaction energy, viz., 38 kcal/mol. From TST, we calculate its *A*-factor to be 4.3×10^{15} s^{-1}. However, path D of Figure 3 would be expected to be an important channel at low temperature. Its calculated barrier is only 24.2 kcal/mol and its TST *A*-factor is 1.0×10^{14} s^{-1}. Hence path D would be expected to predominate up to a temperature of about 1200 K.

Secondary Decomposition Paths. Each of the species initially produced from DBF′−OO$^•$ can undergo further reactions. Reaction potential energy surfaces for the various pathways have been computed by DFT. Only unimolecular reaction pathways are depicted for each channel; however, it must be appreciated that, as reaction proceeds, the radical pool will build up, and competition between the unimolecular pathways and bimolecular reactions with radicals and/or O_2 will no doubt occur.

Reaction Path A. The DFT unimolecular decomposition potential energy surface is illustrated in Figure 4. As shown in this figure, A1 (the 1-dibenzofuranyloxy radical) decomposition to CO and A3 has been found to occur through two transition states and the intermediate A2. This behavior differs from the

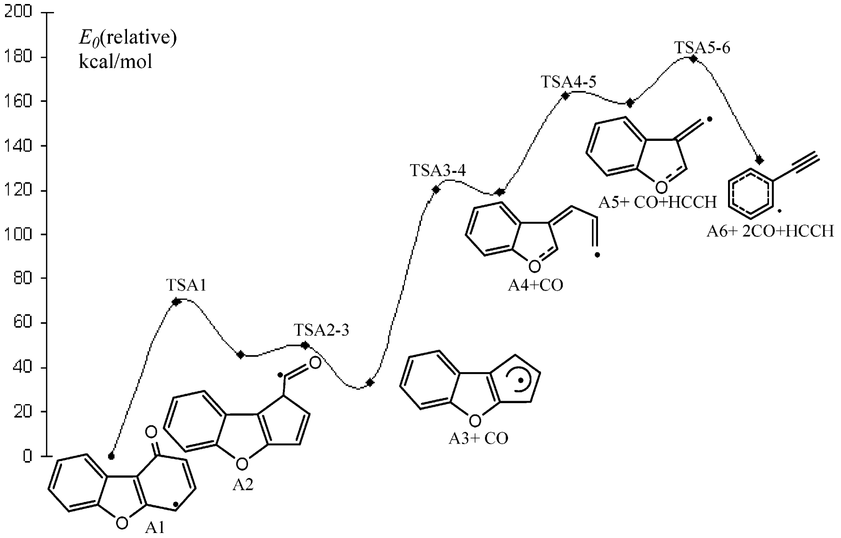


Figure 4. Relative (to A1 at 0 K) potential energy surface for the thermal decomposition of A1 in kcal/mol. Products, intermediates, and transition state energies are calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level of theory.

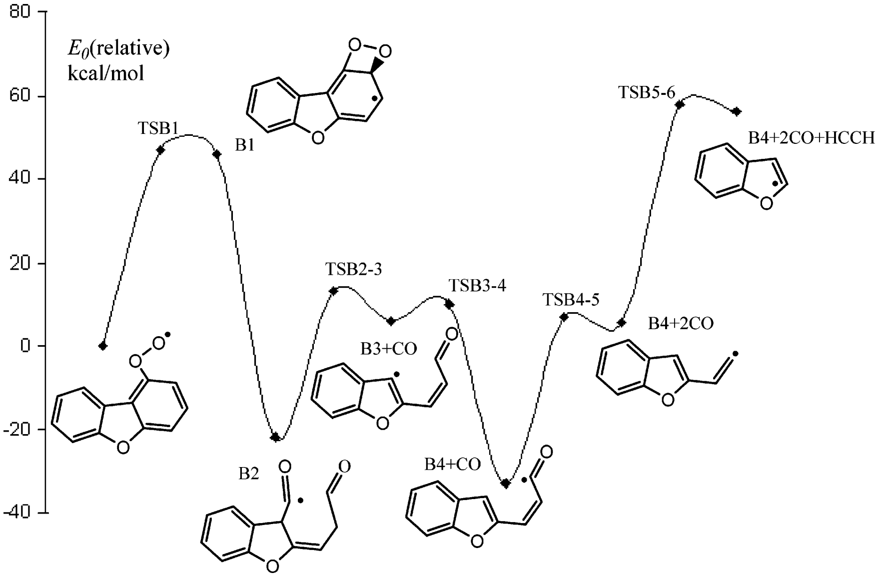


Figure 5. Relative (to DBF′−OO$^•$) potential energy surface for the thermal decomposition of DBF′−OO$^•$ via path B in kcal/mol. Products, intermediates, and transition states energies are calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level of theory.

case of phenoxy[28,31,36] in its loss of CO. The conjunction of the benzene ring with the furan ring in the 1-dibenzofuranyloxy radical inhibits the formation of the oxobicyclo-like structure which has been found to be the first intermediate in the CO expulsion from phenoxy. The rate determining step has an activation energy of 72.0 kcal/mol, and the reaction passes through the tight transition state TSA1. The CO moiety can then leave A2 via the loose transition state (TSA2−3) with an activation energy of only 4 kcal/mol. The resulting cyclopenta[b]benzofuran radical (A3) is a stable structure due to its π delocalized bonds.

Scission of the β bond connecting the cyclopentadienyl ring and the furan ring has a significant barrier where the product (A4) and the transition state lie about 75.2 and 80.3 kcal/mol above the entrance channel of A3, respectively. Loss of C_2H_2 from A4 to give A5 and C_2H_2 has an activation energy of 44.1 kcal/mol. CO elimination from A5 with an activation energy of 20.2 kcal/mol would yield 1-ethylphenyl (A6). Formation of A6 facilitates the formation of PAH such as naphthalene and indene which have been observed experimentally in trace quantities in DBF oxidation.

Steps after A3 formation are unlikely to occur by this unimolecular scheme because of the large energy barriers associated with scission of the cyclopentadienyl ring in A3. Hence, it is much more probable that A3 will decompose via bimolecular reaction. An alternative decomposition scheme involving addition of molecular oxygen to A3 is presented in the last section prior to Conclusions.

Reaction Path B. Intermolecular addition of the oxygen atom in the peroxy moiety of 1-dibenzofuranylperoxy to the neighboring carbon atom in the benzene ring should pass through the tight transition state (TSB1 in Figure 5) which lies 45.5 kcal/mol above the 1-dibenzofuranylperoxy radical.

Elongation of the β bond between carbon atoms connecting with the O atoms in B2 from 1.475 to 1.634 Å yields the chemically energetic adduct B2 in a well −67.5 kcal/mol below B1. Reaction of B1 to B2 is essentially barrierless. A tight transition state (TSB2−3), 31.3 kcal/mol above B2, marks the expulsion of the carbonyl moiety from B2 to result in B3. Intramolecular hydrogen transfer from the carbonyl moiety in B3 to the adjacent carbon atom in the furan ring via the loose transition state (TSB3−4) with activation energy of only 0.6

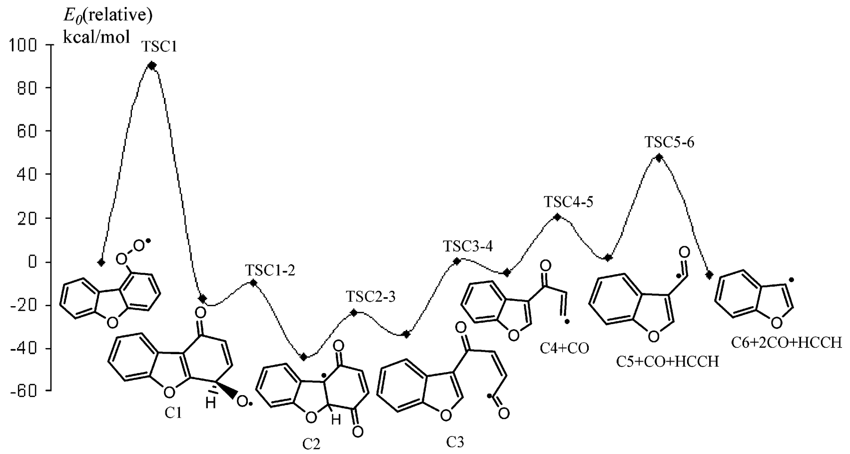


Figure 6. Relative (to DBF′−OO$^•$ at 0 K) potential energy surface for the thermal decomposition of DBF′−OO$^•$ in kcal/mol. Products, intermediates, and transition states energies are calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level of theory.

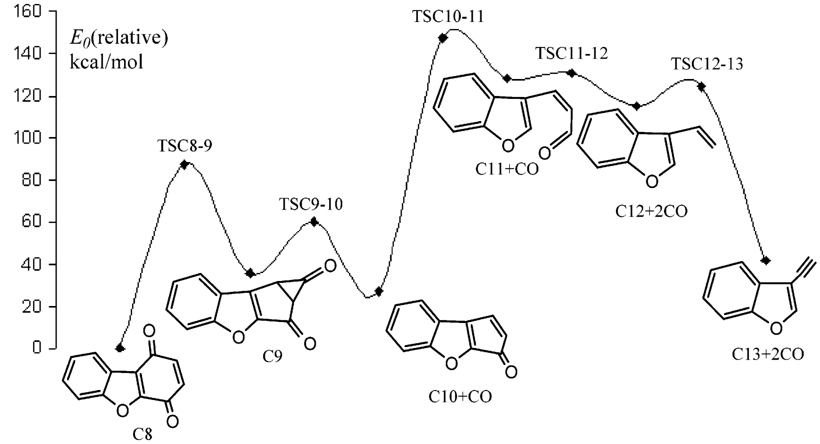


Figure 7. Potential energy surface (kcal/mol) (relative to *p*-DBF quinone at 0 K) for the thermal decomposition of C8. Calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G (d) level of theory.

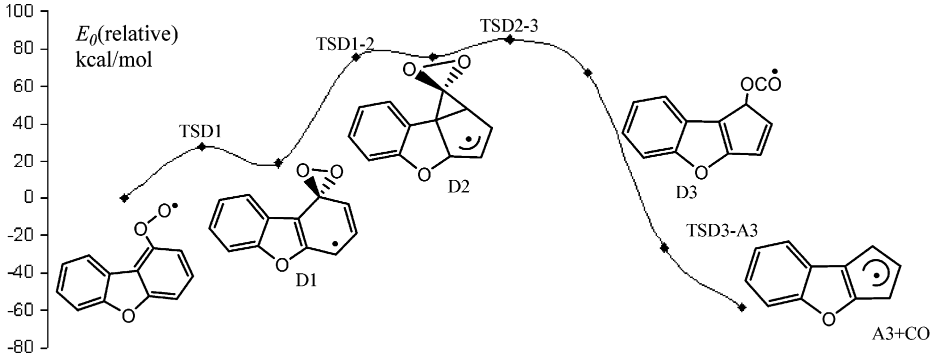


Figure 8. Relative potential energy surface (kcal/mol) for decomposition of DBF′−OO$^•$ via path D, as calculated at the B3LYP/6-311+G(3df,-2p)//B3LYP/6-31G(d) level of theory.

kcal/mol results in B4 which is more stable than B3 by about 43 kcal/mol. It is most likely that reaction from B1 to B4 would be chemically activated. Further unimolecular decomposition of B4 is likely to encounter a significant barrier as shown in Figure 5, with B4 unlikely to undergo further unimolecular decomposition. Instead, it should undergo bimolecular reaction. However, on account of the relatively high initial barrier of 45.5 kcal/mol, pathway B is unlikely to be competitive with either pathway A or D.

Reaction Path C. The intramolecular addition of the free end of the peroxy group in DBF′−OO$^•$ to form the *p*-4-hydroquinone-dibenzofuran structure (C1 in Figure 6) incurs a significant energy barrier of 91.1 kcal/mol (TSC1). However C1 is more stable by 17.7 kcal/mol than the DBF′−OO$^•$ reactant. Thus, it is unlikely that C1 would be formed through intramolecular rearrangement of DBF′−OO$^•$ but through path C′ of Figure 3 where an oxygen atom produced in fission of DBF′−OO$^•$ to yield 1-dibenzofuranyloxy could undergo a facile addition to the 4-carbon of this intermediate to produce C1. (Note that one of the possible resonance structures of 1-dibenzofuranyloxy has a radical site on the 4-carbon.)

Hydrogen atom transfer from the ipso (H−C−O$^•$) to the neighboring carbon atom on the furan ring stabilizes C1 by an additional 26.5 kcal/mol through the formation of C2 which can undergo ring opening to the less stable intermediate C3. As illustrated in Figure 6, C3 can further decompose eventually producing 2 CO, HCCH, and the 1-benzofuranyl radical (C6) which is a precursor of benzofuran and its substituted derivatives

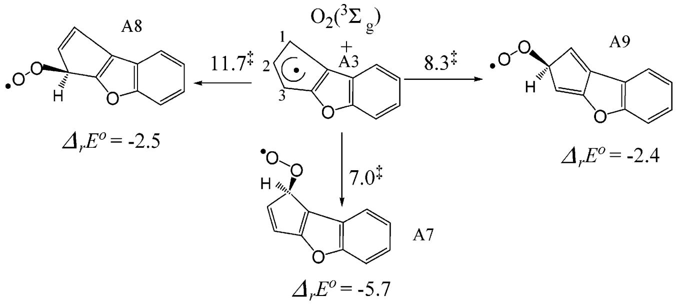


Figure 9. Energetics of triplet oxygen addition to A3. Energies are in kcal/mol Activation energies are denoted by ‡, and the reaction energies are at 0 K.

that have been detected experimentally. CO extrusion from C5 is found to have the highest energy barrier, assuming reaction proceeds through path C′ (and not through TSC1), along this pathway with an activation energy of 45.5 kcal/mol (TSCB5−6). The overall path (from C1 to C6 + 2CO + HCCH) is found to be slightly exothermic by about 7 kcal/mol.

In order to explain their observed products, Marquaire et al.[1−3] suggested an alternative mechanism for decomposition of C1. According to their postulate, the H atom on the 4-carbon of C1 undergoes a migration to the oxygen atom, also attached to the 4-carbon, to produce an intermediate, *p*-DBF-semiquinone, C7. Subsequent loss of this hydrogen atom produces 1,4-dibenzofurandione, C8, traces of which they detected in their products. Marquaire et al.[1−3] then suggested the sequence of reaction steps shown in Figure 7. Also shown in Figure 7 is our reaction potential energy surface, computed at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level of theory. Although the rearrangements depicted in Figure 7 were an important aspect of the mechanism proposed by Marquaire et al. for the low-temperature oxidation of DBF, our DFT calculations indicate that the barrier to this route would be too large.

We consider that the most probable route to the quinone, C8, is by bimolecular reaction of C1 with radicals or O_2. Once formed by hydrogen loss from the 4-carbon in C1, C8 can persist at low temperatures on account of its resonance stabilization. Our calculations suggest, however, that the quinone is not a key intermediate through which most reaction flux passes on the way to final products. Instead, we predict that most reaction flux will pass through C2 and C3 of Figure 6.

Reaction Path D. Formation of D1 (Figure 8) from DBF′−OO$^\bullet$ has the lowest activation energy (24.2 kcal/mol) of any of the reaction pathways we have discovered. Further unimolecular decomposition of D1 involves the extrusion of CO_2 via intermediates D2 and D3 (see Figure 8), producing the A3 species which can also be formed by path A. However, the overall barrier to this unimolecular pathway from D1 to A3 + CO_2 is expected to be too high, at least at low temperatures. Hence, the most probable fate of D1 is its further reaction with radicals and/or O_2 at the 4-position. Addition of O_2, for example, will lower the total energy, effectively reducing significantly the overall barrier to forming precursors such as A3 or C10 of final products.

Molecular Oxygen Addition to Cyclopenta[b]benzofuran (A3). A3 is expected to play a role in the dibenzofuran oxidation both at high temperature through path A and possibly at lower temperatures through path D owing to its resonance stabilization. It is probably sufficiently long-lived to react with O_2. Transition states for addition of molecular oxygen to the three positions in the five-membered ring of A3 have been located, and energy calculations for these processes are shown in Figure 9.

The addition of O_2 is preferred both thermodynamically and kinetically on the 1-carbon of the cyclopentadienyl ring to produce A7. At temperatures high enough to fission off the terminal oxygen atom from the peroxy group of A7 and A8, A10 and A18 (Figure 10) are formed respectively.

Three decomposition channels for A10 have been located. Shift of the H atom from the (C)(H)(O) group in A10 to the

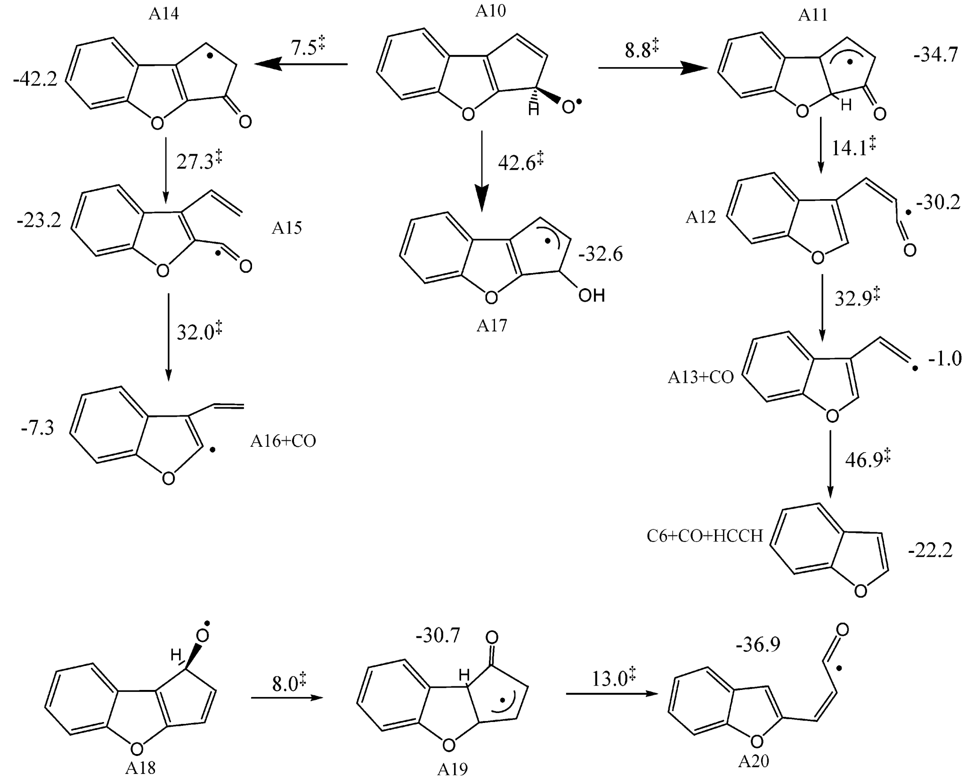


Figure 10. Unimolecular decomposition pathways for A3 after reaction with O_2 and loss of the terminal O atom from the peroxy group. Activation energy (‡) is relative to the reactant of each step, and the reaction enthalpy is relative to A10 in the upper scheme and to A18 in the lower scheme.

neighboring outer carbon atom on the cyclopentadienyl ring to form a CH_2 group is slightly preferred over its transformation to the adjacent carbon atom on the furan ring. Both these shifts have significantly lower barriers than OH group formation in A17. These first two H-shifts in A10 precede relatively low barrier processes to the precursors of final products such as benzofuran, viz., C6 and A16. A17, upon the breakage of its O−H bond, transforms into the closed shell structure of C10.

IV. Conclusions

Oxidation of dibenzofuran commences with formation of the dibenzofuranyl radical ($DBF'^{\bullet}$) which forms the dibenzofuranyl peroxy radical ($DBF'{-}OO^{\bullet}$) on reaction with molecular oxygen. Quantum chemical calculations have located four distinct reaction channels for decomposition of $DBF'{-}OO^{\bullet}$. Two of these channels, paths D and A, have low barriers. The former path involves an initial rearrangement of the peroxy group to form D1, a structure containing a three-membered OCO ring (see Figure 8). The latter path involves fission of the terminal O atom of the peroxy group. TST evaluations indicate that the former channel will predominate at temperatures up to about 1200 K. Initial barriers to paths B and C (Figure 3) are large and significant reaction directly through these two channels is unlikely. However, the initial product of path C, the 4-hydroquinone-dibenzofuran structure, C1, can be readily formed from the initial product of path A, viz., 1-dibenzofuranyloxy (A1), by O atom addition at the 4-carbon. Further decomposition of C1 via path C to form benzofuran precursors can take place with relatively low-energy barriers. Although the initial barrier to form D1 is the lowest of the four pathways, further unimolecular decomposition of D1 encounters a significant barrier. It is most likely, then, that D1 undergoes bimolecular decomposition reacting with O_2 and/or the developing radical pool. The experimentally observed[1−3] trace product of *p*-dibenzofuran quinone does not appear to be a key reaction intermediate, and the reaction scheme proposed by Marquaire et al.[1−3] has been found to have a large energy barrier. Reaction schemes involving addition of molecular oxygen to key intermediates have been found to lead with modest barriers and reaction energies to precursors of observed end products.

Since the dibenzofuran moiety is present in polychlorinated dibenzofurans, our present studies should enable oxidative mechanisms of destruction of PCDFs to be developed.

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Supporting Information Available: Calculated total energies, zero-point energies, Cartesian coordinates, rotational constants, and vibrational frequencies of all equilibrium and transition states structures are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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