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Molecular Modeling Studies of the Reactions of Phenoxy Radical Dimers: Pathways To Dibenzofurans

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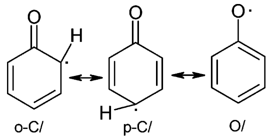
The B3LYP hybrid density functional computational technique was applied to describe the sequence of phenoxy radicals coupling reactions leading to the formation of dibenzofurans. Reaction kinetic parameters were estimated for key reactions. Aromatization of bis-keto dimers of phenoxy radicals followed by intermediate dehydration or dehydroxylation was demonstrated to be a strongly stereoselective process. While the *S*,*S*-diastereomer of the ortho-C//ortho-C keto dimer forms (*o*,*o*′)-dihydroxybiphenyl, a known dibenzofuran intermediate, via inter-ring hydrogen transfer reaction, the less stable *R*,*S*-stereoisomer can easily be transformed into another 5-hydroxyl-4,5-cyclohexadiene-2,3-benzofuran intermediate that provides an energetically more favorable pathway for formation of dibenzofuran. The possible channels of radical-chain processes that convert these intermediates to dibenzofuran and polychlorinated dibenzofurans are discussed.

1. Introduction

The most direct route to formation of polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) in combustion and thermal processes is the gas-phase reaction of chemical precursors such as chlorinated phenols. Dimerization of chlorinated phenoxy radicals has been commonly considered the dominant pathway of formation of PCDFs as well as PCDDs.[1−6]

Several groups have conducted theoretical studies of the coupling mechanisms of chlorinated phenoxy radicals and their derivatives in the context of formation of a stable dimer structures.[7−12] However the mechanism of coupling has not been completely elucidated. Detailed insight into the recombination of nonsubstituted phenoxy radicals and interconversion mechanisms of resulting dimers are a prerequisite for understanding the behavior of their toxic chlorinated and brominated analogues.



Phenoxy radicals can be drawn in an "en−ol" resonance structure (mesomer) in which the unpaired electron is located on an ortho-carbon, denoted as *o*-C/ (or ortho-C/); or para-carbon, denoted as *p*-C/ (or para-C/); or a "keto" resonance structure in which the unpaired electron is associated with the oxygen, denoted as O/. Under valence bond theory, the electronic structure of phenoxy radical can be presented as a superposition of the three above-mentioned principle resonance structures. Limited data are currently available on stabilities, reactions, and interconversions of corresponding keto and enol derivatives. There is insufficient high level computational (or experimental) data concerning the reactivity of these centers that is necessary to predict their gas phase behavior and heterogeneous formation and decomposition mechanisms.

Hitherto, an intermediate π-complex on the dimerization potential energy surface has been found for coupling of unsubstituted phenoxy systems,[11] as well as in the case of more complex tyrosyl radicals[8] within the methods of density functional theory. In both studies, the formation of dimers was the focus of analysis. The Gibbs free energy of activation was determined for phenoxy self-reaction[11] leading to the generation of the (*S*,*S*) diastereomer of the bis-keto *o*-C//*o*-C dimer. A "//" notation is used to denote dimers formed from the *o*-C/, *p*-C, and O/ mesomers illustrated above.

The radical−radical annihilation gives off a large amount of energy due to the low-lying recombination barriers and energized dimer adducts can undergo further transformations. The novel mechanism of interconversions (IC) between dimerized structures has been suggested previously.[4,9,12] The mechanism is generalized and developed in this work. The variety of dimerization and interconversion channels can directly impact the formation of PCDF and distribution of other toxic and nontoxic byproducts. The diversity of substitution patterns can be expected especially for polychlorinated and polybrominated reactants.

In this manuscript, we report the results of density functional theory calculations for pathways of dibenzofuran formation from unsubstituted phenoxy radicals. We have examined the mechanism of typical interconversions and transformations of bis-keto dimers. We have especially focused our efforts on the final stage of dibenzofuran (DF) formation for which two general pathways from reaction intermediates are manifested.

2. Computational Details

Electronic calculations were performed using the Gaussian 98 suite of programs.[13] Stationary points on corresponding

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potential energy surfaces (PES) were studied by hybrid-density functional theory (DFT) using B3LYP functional[14−16] and the split-valence 6-31G(d) basis set.[17] All structures and vibrational frequencies were calculated using analytical energy gradients and second derivatives. The normal vibrational mode analyses of imaginary frequencies as well as intrinsic reaction coordinate (IRC) calculations were performed to identify transition state structures.[18] All thermochemical parameters were estimated using the computed data at 298.15 K and 1 atm.

Potential energy surfaces computed with the B3LYP formalism are very reliable for the types of systems of interest.[19] This formalism combines the three-parameter exchange of Becke with the nonlocal correlation functional of Lee, Yang, and Parr.[14,15] Calculation of structures and frequencies using this level is a good compromise between cost and accuracy of most reliable computational methods.

To verify the stability of hydrogen bonded intermolecular complexes, basis set superposition errors (BSSE) were evaluated by computation of the counterpoise corrections.[17−19]

3. Results and Discussions

3.1. Self-Condensation of Phenoxy Radicals. It is known that the unpaired electron in a phenoxy radical is delocalized and radical character is present at the phenolic oxygen as well as the para and ortho carbons. The relative occupancy of each of the mesomers (*o*-C/, *p*-C/, and O/) has previously been determined using the corresponding spin densities.[9,20,21] Assuming that dimerization occurs at these radical centers, self-reaction of phenoxy radicals can produce one peroxide through O//O coupling, two couplings between O/ and *o*-C/ (or *p*-C/) mesomers, and three couplings between carbon centered mesomers with formation of bis-keto dimers,[3] i.e., a total of 3! = 6 possible structures (Figure 1).

In Figure 1, we also present Newman projections of two diastereomers (*S*,*S*) and (*R*,*S*) of a coupled (*o*-C//*o*-C) system using the *R*,*S* system of nomenclature.[11,22] Stereoisomers were found to have orthogonal ring systems and significant rotational energy barriers.

Further keto−enol tautomerization (double enolization/rearomatization) of these structures leads to the formation of several primary products:

$$
2C_6H_5O \rightarrow
\begin{array}{lcll}
(o\text{-C}//o\text{-C}) & \rightarrow & o,o'\text{-HOC}_6H_4-C_6H_4OH & \text{(D1)} \\
(\text{O}//o\text{-C}) & \rightarrow & o\text{-C}_6H_5OC_6H_4OH & \text{(D2)} \\
(\text{O}//p\text{-C}) & \rightarrow & p\text{-C}_6H_5OC_6H_4OH & \text{(D3)} \\
(o\text{-C}//p\text{-C}) & \rightarrow & o,p'\text{-HOC}_6H_4-C_6H_4OH & \text{(D4)} \\
(p\text{-C}//p\text{-C}) & \rightarrow & p,p'\text{-HOC}_6H_4-C_6H_4OH & \text{(D5)} \\
(\text{O}//\text{O}) & \equiv & C_6H_5O-OC_6H_5 & \text{(D6)}
\end{array}
$$

The B3LYP/6-31G(d) computed results are summarized in Table 1. Heats of coupling reactions D1−D5 are estimated in kcal/mol as −13.79, −20.58, −21.32, −10.50, −11.80, respectively. Each of these reactions is exothermic with the exception of the reaction D6 that forms the peroxide which is endothermic by 9.2 kcal/mol.

All possible dimerization reactions and interconversion pathways[23] are summarized in Scheme 1, where some commonly accepted abbreviations for bis-keto dimers have been used. (*R*,*S*) and (*S*,*S*) denote diastereomers of coupled phenoxy radicals at *ortho* carbon sites (*o*-C//*o*-C). The main processes are: dimerization channels (D1−D5), interconversion of dimers (IC1−IC4), hydrogen transfer (HT-1, HT-2), and dehydration (DH-1, DH-2) reactions (The D6, interconversion of (O//O) to (*o*-C//*o*-C), reaction IC-5, as well as the dioxin supporting reaction IC-4 channel are not addressed in this article because they are not principal pathways of the formation of dibenzofuran or intermediates (see also section 3.3).

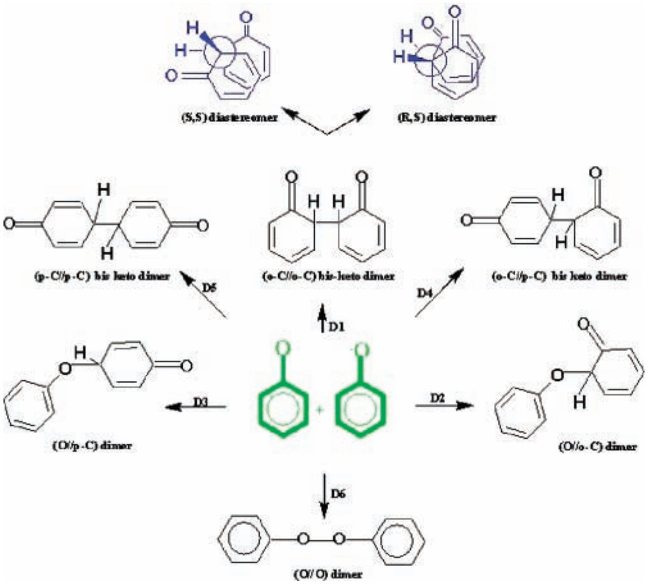


Figure 1. Most stable structures of phenoxy radical dimers (D1−D6).

TABLE 1: Selected Characteristic Data for Phenoxy Radical Dimers and Related Structures Calculated by the B3LYP/6-31G(d) Method

systems	energy,[a] au	entropy, cal/mol·K	dipole, D
phenoxy radical	−306.735854	75.21	3.67
dibenzofuran[b]	−537.164369	90.74	0.71
H_2O[b]	−76.3878020	46.52	2.01
(H-,HO−)DF[c]	−613.509969	100.32	1.80
o,o'-$HOC_6H_4-C_6H_4OH$	−613.551359	103.27	0.67
o-$C_6H_5OC_6H_4OH$	−613.534927	106.36	2.39
bis-keto(O//*o*-C) dimer	−613.504241	106.98	3.69
p-$C_6H_5OC_6H_4OH$	−613.537786	100.98	1.89
bis-keto(O//*p*-C) dimer	−613.505309	105.92	2.62
(O//O) dimer	−613.456798	110.75	1.04
bis-keto(*o*-C//*o*-C) dimers			
(*S*,*S*) diastereomer	−613.493646	107.73	4.35
(*R*,*S*) diastereomer	−613.486381	107.45	0.00
o,p'- $HOC_6H_4-C_6H_4OH$	−613.545582	104.21	1.42
bis-keto(*o*-C//*p*-C) dimer	−613.488339	106.87	6.68
p,p'- $HOC_6H_4-C_6H_4OH$	−613.537016	104.49	0.85
bis-keto(*p*-C//*p*-C) dimer	−613.490381	106.79	4.85

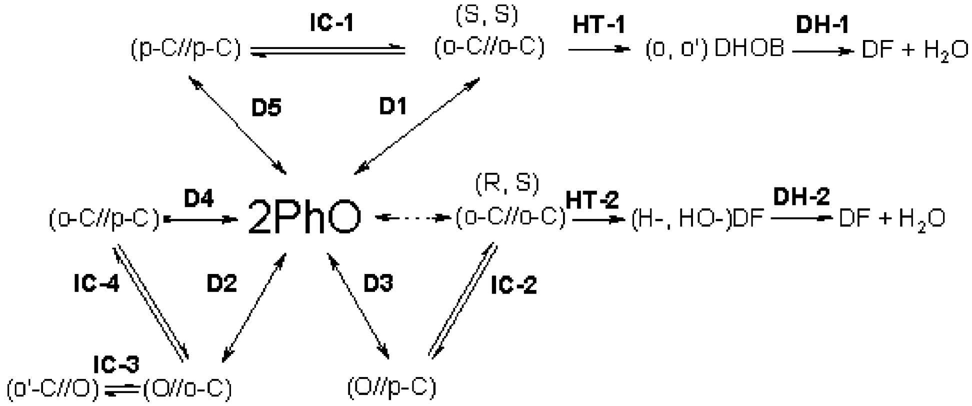
[a] Zero point corrected internal energies. [b] Without basis set superposition error corrections included in further estimations, [c] 5-Hydroxyl-4,5-cyclohexadiene-2,3-benzofuran intermediate, see text.

The interconversion mechanisms are denoted as IC-***1*** − transformation of (*o*-C//*o*-C) to (*p*-C//*p*-C), IC-2 − (*o*-C//*o*-C) to (O//*p*-C), IC-3 − isomerization of “pre-dioxin” structure (O//*o*-C) to (*o*′-C//O), IC-4 − conversion of (O//*o*-C) into (*o*-C//*p*-C),

Stereoisomerization between (*S*,*S*) and thermodynamically less stable (*R*,*S*) diastereomers may also play a role in the kinetics of product distributions.

The only dimerization channel that has been thoroughly analyzed is the coupling reaction pathway leading to (*o*-C//*o*-

SCHEME 1: Possible Formation and Conversion Mechanisms for Phenoxy Radical Dimers as Revealed by B3LYP/6-31G(d) Calculations[a]



[a] Solid, double-headed arrows represent D1−D5 dimerizations. Solid, double arrows represent IC-1 through IC-4 dimer interconversions. HT-1 and HT-2 are hydrogen transfer (tautomerization) reactions, while DH-1 and DH-2 are dehydration channels.

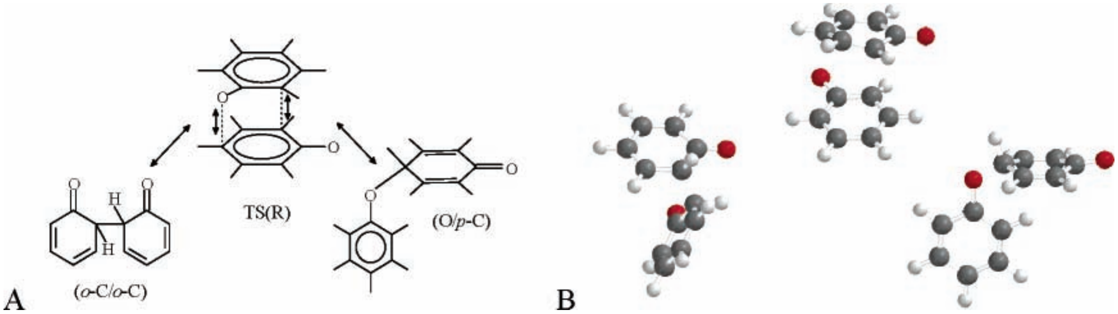


Figure 2. Typical profile for interconversion of bis-keto dimers of phenoxy radicals (IC-2 pathway in Scheme 1): (A) structural view;[9] (B) stereoview of stationary point structures. Gray, red, and white spheres designate carbon, oxygen, and hydrogen atoms, respectively.

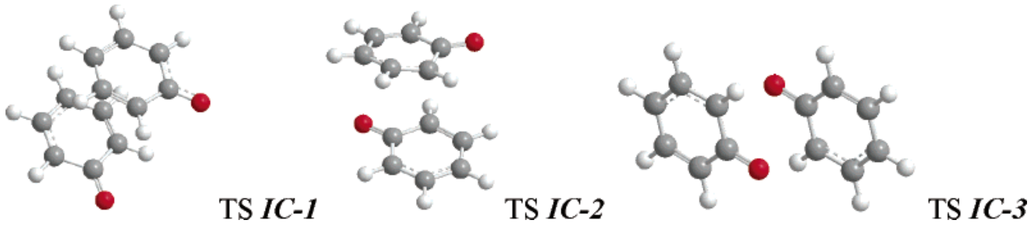


Figure 3. B3LYP/6-31G(d) transition state structures for interconversion processes IC-1, IC-2, and IC-3.

C) formation through π-complex formation (D1 in Scheme 1).[11] Estimated activation parameters for D1 using the same DFT B3LYP/6-31G* method were: $\Delta H^{\#} = 0.024$ kcal/mol, $\Delta S^{\#} = -48.2$ cal/(mol K).

It should be noted that D1 is most reliable channel of DF formation (vide infra). A more detailed discussion of this topic, even though of great total importance to kinetic studies, is beyond of the scope of this article. Concerning the formation of other byproducts based on the thermodynamic parameters of dimerization reactions D2 and D3 can be concluded that the oxygen−carbon cross coupling at the para-carbon D3 is slightly more exothermic than reaction at the ortho-carbon D2. Furthermore, the main product of the phenoxy radical self-reaction in smog chamber experiments is reported to be 4-phenoxy phenol, the O//*p*-C coupling product through pathway D3.[7] These 4-phenoxy phenols are not involved in pathways of dibenzofuran or dibenzo-*p*-dioxin formation but can be intermediates in the formation of polyphenoxy ethers and related macromolecular species.[24]

3.2. Interconversion (IC) Mechanisms. Rearrangements of the phenoxy dimers have been partially addressed in the literature[23,25] including transformations into dibenzofuran.[3] The principal interconversion mechanisms between dimers have been discussed in our previous works.[9,12] Curvature analysis of potential energy surface of radical dimers resulted in the elucidation of a transition state TS(R) for interconversion of bis-keto adduct pairs, viz. (*o*-C//*o*-C) into (O//*p*-C) transformations. Figure 2 illustrates the pathway of this conversion for unsubstituted dimers of phenoxy radicals. The (*R*,*S*) diastereomer of (*o*-C//*o*-C) dimer undergoes selective interconversion into *p*-phenoxyphenyl dimer via a “stair-step” type transition state. The transition state, TS (R), consists of almost parallel rings at inter-ring distances of ca. 2.2 and 2.5 Å.

All interconversions transition structures (TS IC-1, TS IC-2, and TS IC-3, Figure 3) can be categorized as “tight”[26] including TS(R) for IC-2 process. Note that TS IC-2 is comparatively “loose” with no significant overlap of aromatic ring systems (see, Figure 3). Isosteric interconversions through IC-3, which is the isomerization of (O//*o*-C) dimer (Scheme 1), have greater vibrational freedom in the transition state.

Remarkably, the formation of the (O//*p*-C) dimer occurs only through the energetically less favorable (*R*,*S*) stereoisomer of the (*o*-C//*o*-C) dimer (IC-2 process indicated in Scheme 1). The enthalpy and entropy of activation are estimated as $\Delta H^{\#} = 17.59$ kcal/mol and $\Delta S^{\#} = -2.29$ cal/(mol K) (for the reverse reaction $\Delta H^{\#} = 29.63$ kcal/mol, $\Delta S^{\#} = -0.76$ cal/(mol K)).

Interconversion of the more stable (*S*,*S*) diastereomer, IC-1, leads to the formation of (*p*-C//*p*-C) dimer through a rather compact classical "tight" TS with $\Delta H^{\#} = 23.00$ kcal/mol, $\Delta S^{\#} = -3.28$ cal/(mol K) (for the reverse reaction: $\Delta H^{\#} = 19.93$ kcal/mol, $\Delta S^{\#} = -2.34$ cal/(mol K)). Intriguingly, the formation of the (*p*-C//*p*-C) bis keto-dimer instead of the predioxin structure, (O//*o*-C), could explain the absence of PCDDs in experimental studies in which the main dimerization channel was implicitly assumed to be through the (*o*-C//*o*-C) bis-keto dimer.[2] Depending on the dimer structure, activation energies for interconversion processes can vary in the range of 17−30 kcal/mol. As radical−radical recombination occurs, sufficient energy is released to support interconversion to the thermodynamically most stable dimer. The thermochemical properties of IC, HT, and DH processes are collected in Table 2.

It should be emphasized based on our stereochemical analysis (Scheme 1), that interconversions can only occur between limited, structurally favored pairs of keto dimers. The interconversion of phenoxy radical coupling isomers will directly effect the formation of different products. It can be expected that interconversion will also affect reactions in the liquid phase. Greater diversity of products can be expected in the case of halogenated precursors even in the case of (IC-3)-type interconversions. The stationary points of nonsubstituted, isostructural IC-3 process have also been studied and activation parameters are calculated as $\Delta H^{\#} = 24.46$ kcal/mol and $\Delta S^{\#} = -3.42$ cal/(mol K).

Hydrogen transfer (HT) reaction channels leading to the formation of dibenzofuran via different intermediates (Scheme 1) are systematized as HT-1—the single inter-ring H-transfer process from the (*S*,*S*) diastereomer directly generating the bis-enol form of the (*o*,*o*′)-dihydroxybiphenyl−DHOB dimer—and HT-2 which is a single inter-ring H-transfer, from the (*R*,*S*) stereoisomer of the bis-keto dimer leading to the formation of the 5-hydroxyl-4,5-cyclohexadiene-2,3-benzofuran intermediate, (H−,HO−)DF, which has a single benzene conventionally fused to furan and two tetravalent out of plane C−H and C−OH bonds belonging to cyclohexadiene ring. Dehydration of the this intermediate (reaction DH-2) as well as the bis-enol dimer (*o*,*o*′)-dihydroxybiphenyl (DHOB) via reaction DH-1 leads to the final formation of DF. According to current DFT calculations the latter pathway by-passes the formation of an intermediate keto−enol structure (vide infra) in contrast to the results of previous HF/3-21G** calculations.[4]

Vibrational frequencies for transition state structures are presented in Table 3. Imaginary frequencies indicate that a transition state has been found. These imaginary frequencies involve the motion of monomer atoms being transferred along the reaction coordinate. Aromatic rings in IC reactions undergo two center motions as is clearly demonstrated in Figure 2-A

In contrast to H-transfer (HT-1, HT-2 in Scheme 1) and dehydration (DH-1, DH-2) reactions, small frequencies (minimal curvature) were found along the reaction coordinates of the interconversion processes. Small imaginary frequencies (86*i*, 179*i*, and 107*i* cm^{-1} for IC-1, IC-2, and IC-3 processes, respectively, Table 3) are indicative of the broad nature of the interconversion barriers. IRC calculations were used to verify these pathways. Accordingly, the quantum-mechanical tunneling effect can be expected to be significant only in hydrogen transfer reactions due to the existence of moderately high-frequency vibrations (1491 and 1443 cm^{-1}) along the reaction coordinate in the transition state pathways.

3.3. Pathways of Formation of Dibenzofuran. Molecular pathways leading to the formation of the product of main interest are presented in Figure 4.

TABLE 2: Calculated by B3LYP/6-31G(d) Characteristics of Interconversion (IC), Hydrogen Transfer (HT) and Dehydration (DH) Reactions

process	E_{TS},[a] au	S_{TS},[b] cal/mol·K	$\Delta H^{\#}$, kcal/mol	$\Delta S^{\#}$, cal/mol.K	μ(TS), D
IC-1	−613.456769	104.45	23.00 (19.93)	−3.28 (−2.34)	6.71
IC-2	−613.458216	105.16	17.59 (29.63)	−2.29 (−0.76)	2.46
IC-3	−613.464968	103.56	24.46 (24.46)	−3.42 (−3.42)	0.00
HT-1	−613.463573	101.42	18.32 (54.79)	−6.31 (−1.85)	5.31
DH-1	−613.447772	99.68	64.68 (65.19)	−3.58 (−37.58)	2.54
HT-2	−613.461663	101.85	15.06 (30.43)	−5.60 (1.54)	4.54
DH-2	−613.443451	98.45	41.68 (67.02)	−1.87 (−38.91)	1.29

[a] Zero point corrected energies, [b] Transition state entropy. Activation parameters for reverse reactions are given in parentheses.

According to DFT calculations, *o*,*o*′-dihydroxybiphenyl, (*o*,*o*′)-DOHB, can be generated only through transformation of the (*S*,*S*) diastereomer of the (*o*-C//*o*-C) keto dimer through the HT-1 reaction (Scheme 1 and Figures 4 and 5).

$$S,S\text{-}(o\text{-C}//o\text{-C}) \rightarrow o,o'\text{-HOC}_6\text{H}_4\text{-C}_6\text{H}_4\text{OH} \quad (\Delta H = -36.47\ \text{kcal/mol}) \quad \text{(HT-1)}$$

$$o,o'\text{-HOC}_6\text{H}_4\text{-C}_6\text{H}_4\text{OH} \rightarrow \text{DF}\cdots\text{H-OH} \quad (\Delta H = -3.85\ \text{kcal/mol}) \quad \text{(DH-1)}$$

$$\text{DF}\cdots\text{H-OH} \rightarrow \text{DF} + \text{H}_2\text{O} \quad (\Delta H = 2.09\ \text{kcal/mol}) \quad \text{(DH-1}'\text{)}$$

Intramolecular H-transfer within the (*R*,*S*) isomer leads to the formation of a different stable intermediate, a 5-hydroxyl-4,5-cyclohexadiene-2,3-benzofuran (reaction HT-2), which can be considered formally as dibenzofuran structure with out-of-plane H and OH moieties (Scheme 1 and Figures 4 and 6).

$$R,S\text{-}(o\text{-C}//o\text{-C}) \rightarrow (\text{H-,HO-})\ \text{DF} \quad (\Delta H = -15.37\ \text{kcal/mol}) \quad \text{(HT-2)}$$

$$(\text{H-,HO-})\ \text{DF} \rightarrow \text{DF}\cdots\text{OH}_2 \quad (\Delta H = -27.96\ \text{kcal/mol}) \quad \text{(DH-2)}$$

$$\text{DF}\cdots\text{OH}_2 \rightarrow \text{DF} + \text{H}_2\text{O} \quad (\Delta H = 0.58\ \text{kcal/mol}) \quad \text{(DH-2}'\text{)}$$

Taking into account geometry considerations to produce the bis-enol molecule via exothermic reaction HT-1 (ΔH = −36.47 kcal/mol), a concerted double H-transfer process is expected, as was found in HF/3-21G(d) calculations.[4] However, according to DFT calculations, even the keto−enol intermediate is not a stationary point on the potential energy surface. For a concerted double H-transfer cross section, a second-order transition state with two imaginary frequencies is detected.

According to current DFT B3LYP/6-31G(d) calculations, reaction HT-1 generates the doubly enolized bis-keto tautomer (bis-enol form) through a single inter-ring H-transfer with $\Delta H^{\#} = 18.32$ kcal/mol, $\Delta S^{\#} = -6.31$ cal/(mol K) (for reverse reaction: $\Delta H^{\#} = 54.79$ kcal/mol, $\Delta S^{\#} = -1.85$ cal/(mol K)). The HT-2 reaction has a lower barrier of activation: $\Delta H^{\#} = 15.06$ kcal/mol, $\Delta S^{\#} = -5.60$ cal/mol. K (for reverse reaction $\Delta H^{\#} = 30.43$ kcal/mol, $\Delta S^{\#} = 1.54$ cal/(mol K)).

It is important to note that the calculated barrier[10] for hydrogen transfer from ortho phenoxy cyclohexadienone

TABLE 3: B3LYP/6-31G(d) Transition State Vibrational Frequencies for Interconversion,Hydrogen Transfer and Dehydration Reactions[a]

reactions	frequencies, cm^{-1}
IC-1	86*i*,[b] 44, 102, 107, 155, 156, 177, 230, 390, 403, 448, 449, 471, 489, 522, 524, 587, 589, 687, 696, 784, 788, 794, 805, 808, 821, 892, 933, 987, 990, 991, 992, 999, 1004, 1009, 1095, 1096, 1177, 1178, 1188, 1190, 1270, 1272, 1391, 1395, 1440, 1442, 1493, 1516, 1550, 1559, 1635, 1653, 1692, 1696, 3181, 3182, 3205, 3207, 3216, 3217, 3220, 3221, 3229, 3230
IC-2	179*i*, 43, 82, 112, 116, 160, 179, 235, 372, 407, 449, 456, 482, 506, 525, 531, 589, 602, 692, 710, 784, 788, 801, 811, 832, 855, 921, 951, 974, 986, 992, 1000, 1001, 1005, 1010, 1016, 1080, 1090, 1182, 1185, 1191,1193, 1265, 1281, 1373, 1386, 1429, 1435, 1477, 1502, 1550, 1561, 1607, 1652, 1710, 3183, 3194, 3198, 3199, 3212, 3216, 3220, 3229, 3235, 3242
IC-3	107*i*, 52, 72, 105, 126, 206, 220, 284, 405, 415, 451, 452, 505, 513, 545, 547, 609, 610, 686, 699, 794, 797, 822, 825, 837, 844, 927, 940, 968, 971, 991, 997, 998, 1000, 1024, 1024, 1097, 1098, 1183, 1186, 1194, 1195, 1300, 1300, 1356, 1382, 1419, 1436, 1479, 1480, 1525, 1559, 1571, 1592, 1644, 1649, 3185, 3196, 3196, 3209, 3209, 3215,3216, 3248, 3249
HT-1	1491*i*, 73, 82, 93, 88, 191, 253, 291, 351, 469, 487, 514, 521, 546, 554, 576, 605, 620, 689, 747, 757, 784, 812, 822, 864, 873, 891, 947, 982, 991, 1000, 1007, 1022, 1023, 1094, 1116, 1141, 1179, 1182, 1193, 1210, 211, 1266, 1279, 1342, 1360, 1423, 1426, 1472, 1495, 1561, 1570, 1595, 1620, 1675, 1676, 1776, 2429, 3170, 3174, 3189, 3203, 3208, 3214, 3219, 3229
DH-1	565*i*, 89, 102, 154, 191, 233, 294, 327, 388, 426, 438, 459, 511, 552, 562, 583, 590, 614, 616, 694, 739, 745, 764, 768, 783, 836, 857, 869, 916, 931, 935, 961, 969, 996, 1032, 1054, 1063, 1129, 1149, 1184, 1188, 1242, 1291, 1329, 1337, 1346, 1357, 1460, 1491, 1497, 1520, 1596, 1610, 1649, 1660, 1676, 2629, 3177, 3185, 3189, 3199, 3206, 3214, 3241, 3729
HT-2	1443*i*, 47, 97, 106, 177, 190, 262, 287, 359, 448, 466, 504, 521, 547, 555, 562, 604, 618, 687, 718, 755, 779, 792, 811, 855, 871, 891, 943, 956, 979, 997, 1004, 1017, 1025, 1067, 1122, 1146, 1175, 1185,1190, 1196, 1212, 1262, 1274, 1331, 1347, 1420, 1427, 1468, 1501, 1564, 1571, 1599, 1628, 1676, 1683, 1799, 2949, 3160, 3170, 3189, 3203, 3206, 3211, 3219, 3232
DH-2	1736*i*, 92, 123, 178, 214, 263, 291, 318, 394, 414, 449, 482, 499, 524, 553, 563, 593, 616, 645, 724, 733, 759, 766, 784, 792, 821, 859, 871, 871, 930, 953, 970, 988, 998, 1008, 1047, 1113, 1135, 1166, 1188, 1206, 1219, 1259, 1295, 1313, 1353, 1374, 1391, 1464, 1489, 1510, 1523, 1559, 1643, 1660, 1670, 1677, 3184, 3188, 3190, 3199, 3210, 3212, 3223, 3226, 3673

[a] Nonscaled values. [b] Imaginary frequencies for TS structures.

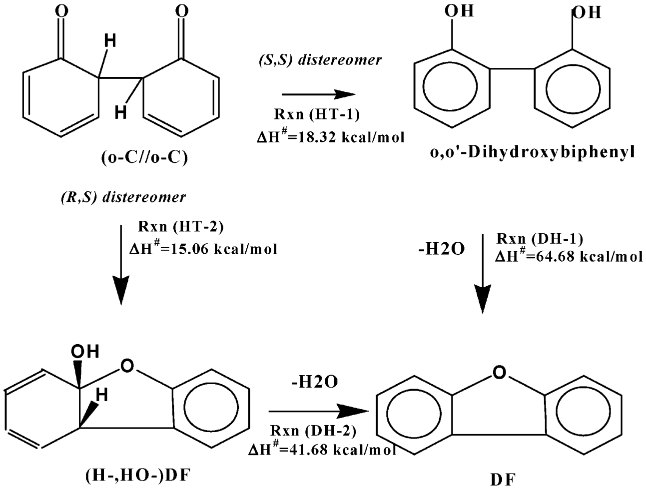


Figure 4. Molecular pathways to generation of dibenzofuran (DF). H-transfer rxns HT-1 and HT-2 occur through the (*S*,*S*) and (*R*,*S*) stereoisomers of (*o*-C//*o*-C) dimer, respectively. Decomposition of both *o*,*o*′-dihydroxybiphenyl and 1-hydroxyl-cyclohexadiene-1,6−benzofuran, (H−,HO−)DF, intermediates lead to the formation of dibenzofurans (DF) via dehydration reactions DH-1 and DH-2.

(O//*o*-C dimer, Figure 1) to "pre-dioxin" structure of 2-phenoxy phenol using CBS-QB3//B3LYP/6-311G(d,p) is much higher (51 kcal/mol) than above-mentioned HT-1 and HT-2 barriers. This result supports the scarcity of the yields of dibenzo-*p*-dioxins in experimental conditions (vide supra).

Direct route to the formation of DF is the monomolecular dehydration of intermediate structures via reactions DH-1 and DH-2**.** Table 2 shows that both reactions have high barriers. The enthalpy and entropy of activation of the latter are estimated as $\Delta H^{\#} = 41.68$ kcal/ mol, $\Delta S^{\#} = -1.87$ cal/(mol K), respectively, (for the reverse reaction: $\Delta H^{\#} = 67.02$ kcal/mol, $\Delta S^{\#} = -38.91$ cal/(mol K)). Reaction DH-1 has higher activation energy ($\Delta H^{\#} = 64.68$ kcal/ mol, $\Delta S^{\#} = -3.57$ cal/(mol K)). These barriers are sufficiently high that lower energy bimolecular reactions may compete with ring closure, especially since the overall energetic for dibenzofuran formation from phenoxy radical is expected to be only ∼9−11 kcal/mol. [2]

It is interesting to note that the final products, DF and H_2O, prefer to be linked by intermolecular complexes. Two types of H-bonded complexes are formed, the stability of which with respect to isolated products, is estimated taking into account BSSE corrections. Association enthalpy ΔH for the complex of DF···H−OH in reaction DH-1, where H-bonding is mediated by the oxygen atom of DF and a hydrogen atom of water molecule (Figure 5 and reaction DH-1′), is estimated as low as 2.09 kcal/mol. Meanwhile the reaction DH-2 resulted in the formation of another type DF···OH_2 complex, where H_2O is bonded to the pair of hydrogen atoms of DF via its own O atom (Figure 6 and reaction DH-2′). This structure is energetically preferable by 0.58 kcal/mol compared to the isolated components.

3.4. Radical—Molecule Reactions. Highly reactive radicals, such as OH, H, and Cl, can be considered as potential chain carriers that abstract/displace H atom and/or OHgroups from the reaction intermediates.[4] In particular, the bis-enol dimer reacts according to the following radical schemes.

$$o,o'\text{-}HOC_6H_4{-}C_6H_4OH + OH \rightarrow o,o'\text{-}HOC_6H_4{-}C_6H_4O + H_2O \quad (\Delta H = -28.78\ \text{kcal/mol}) \quad \text{(R-1)}$$

$$o,o'\text{-}HOC_6H_4{-}C_6H_4O \rightarrow DF + HO \quad (\Delta H = +29.07\ \text{kcal/mol}) \quad \text{(R-1a)}$$

Previous ab initio HF/3-21G** calculations have shown a relatively large barrier (39.65 kcal/mol) for elimination of OH in chlorinated systems via reaction R-1a.[4]

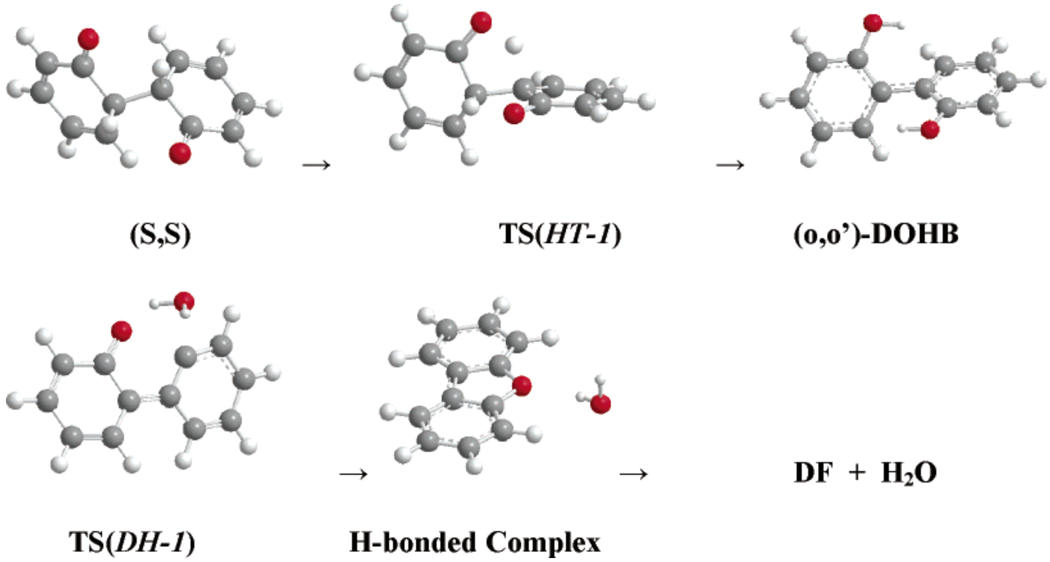


Figure 5. Sequence of (*S*,*S*) diastereomer reactions (cf. Scheme 1) as calculated by the B3LYP/6-31G(d) method. Gray, red, and white spheres designate carbon, oxygen and hydrogen atoms, respectively.

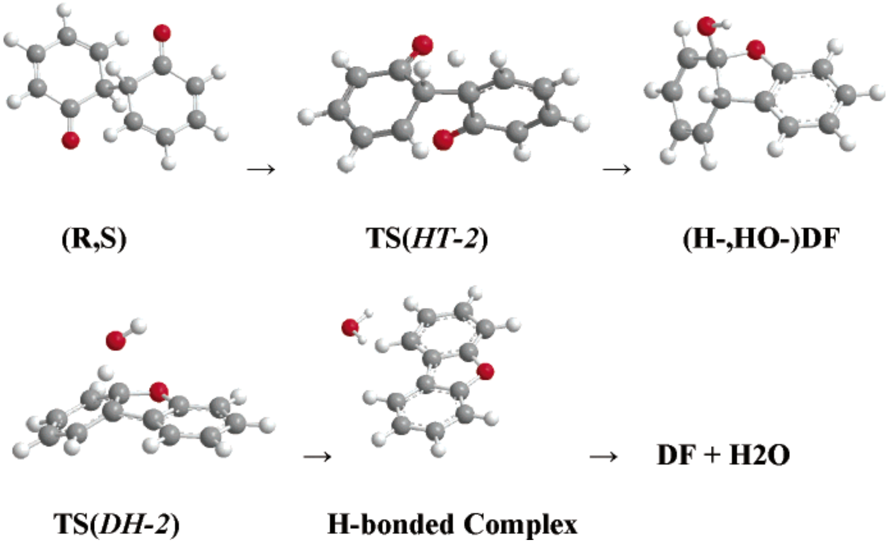


Figure 6. Geometries of (*R*,*S*) transformation pathways (Scheme 1) as calculated by the B3LYP/6-31G(d) method.

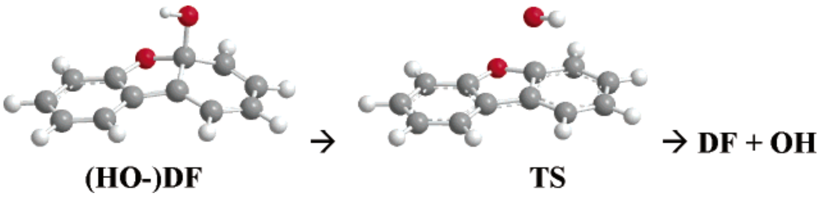


Figure 7. Intermediate hydroxylated dibenzofuran radical (5-hydroxyl-4,5-cyclohexadieneyl-2,3-benzofuran) decomposes into DF and OH radical. Gray, red, and white spheres designate carbon, oxygen and hydrogen atoms, respectively.

An alternative pathway to DF is through a 5-hydroxyl-4,5-cyclohexadiene-2,3-benzofuran intermediate. By analogy to reactions R-1 and R-1a, an H-abstraction by dominant hydroxyl radicals can be considered:

$$\text{(H-,HO}-\text{)DF} + \text{HO} \rightarrow \text{(HO}-\text{)DF} + \text{H}_2\text{O} \quad (\Delta H = -40.35 \text{ kcal/mol}) \quad \text{(R-2)}$$

$$\text{(HO}-\text{)DF} \rightarrow \text{DF} + \text{OH} \quad (\Delta H = +15.02 \text{ kcal/mol}) \quad \text{(R-2a)}$$

Accordingly, the intermediate monohydroxylated DF radical (HO−)DF can eliminate an extra hydroxyl group to form a closed-shell dibenzofuran (reaction R-2a and Figure 7):

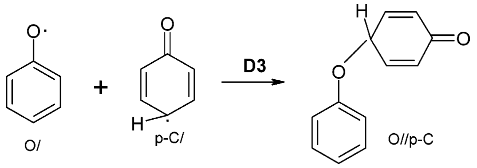
Apparently, intermediate dibenzofuranyl type radicals can react with O_2 (see ref 27), but decomposition and side reactions of such radicals are beyond the scope of this presentation and not addressed. On the other hand the carbon−oxygen bond in the hydroxyl attached DF radical is significantly enlarged ($R_{\text{C}-\text{OH}} = 1.421$ Å) and can be expected to have a low activation barrier toward bond cleavage process. The R-2a reaction is relatively more preferable thermodynamically than the competitive endothermic reaction R-1a; therefore only transition state of the R-2a process has been localized and reaction parameters have been estimated: $R^{\#}(\text{C}\cdots\text{OH}) = 1.992$ Å, $S^{\#} = 101.20$ cal/(mol K), $\Delta H^{\#} = 14.86$ kcal/mol, $\Delta S^{\#} = 1.33$ cal/(mol K), and $\nu^{\#} =$

−385.85 cm^{-1}. The existence a modest energetic barrier supports the possibility of simple unimolecular decomposition reactions to form DF.

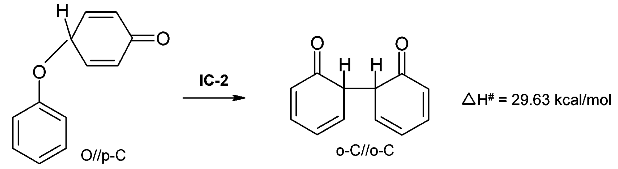
4. Summary and Conclusions

Reaction sequences leading to dibenzofuran formation from recombination reactions of phenoxy radical have been investigated using B3LYP/6-31G* level of theory and led to identification of the following key steps in dibenzofuran formation pathways.

1. Phenoxy radical can exist as ortho-carbon, para-carbon, or oxygen-centered resonance structures that can undergo self-reaction in 6 combinations (D1−D6) to form dimers. Only the initial dimerization reaction, D1, directly forms the *o*-C//*o*-C dimer necessary to form DF. However, the *p*-C//*p*-C, O//*p*-C and O//O dimers formed by D5, D3, and D6, respectively, (D3 shown below) can isomerize to the *o*-C//*o*-C dimer through reactions IC1, IC2, and IC5, respectively.



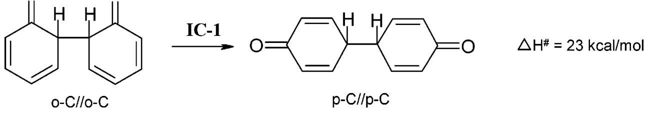
There has been considerable discussion within the literature over which resonance structures react to form PCDFs. The barrier to initial recombination is sufficiently low, that most of the initially formed dimers are chemically activated and will convert to the *o*-C//*o*-C dimer that is a direct precursor of dibenzofuran (e.g., O//*p*-C to *o*-C//*o*-C conversion by IC2 shown below).



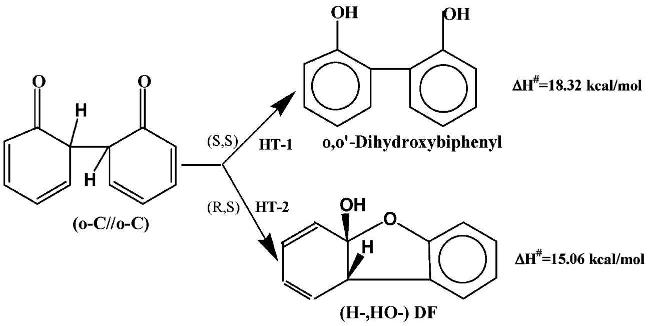
Our results manifested that the *o*-C//*o*-C dimer does not convert to the O//*o*-C predioxin precursor and thus explain the experimental observation that dibenzofuran is the major product of reaction of phenol and phenoxy radical rather than dibenzo-*p*-dioxin.[2]

2. The *o*-C//*o*-C dimer can exist as two diastereomers (*S*,*S*)- and (*R*,*S*) that lead to the formation of dibenzofurans through two different intermediates.

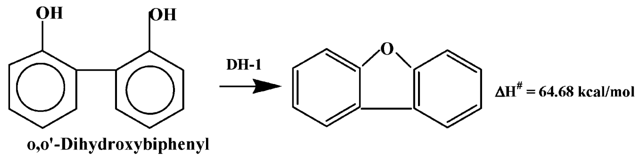
3. Of all the dimer intercoversion processes (IC1−IC5), the IC-1 side reaction may lead to the formation of polybiphenyls and polybiphenyl ethers as the major product of phenoxyl radical reaction and consequently, reduce the yield of formation of dibenzofuran.

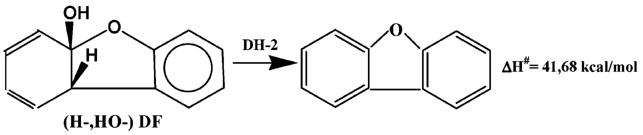


4. The aromatization of the keto-dimers proceeds through low energy **inter**-ring stereoselective H-transfer mechanisms to form two stable intermediates: *o*,*o*′-dihyroxybiphenyl and 5-hydroxyl-4,5-cyclohexadiene-2,3-benzofuran via HT-1 ($\Delta H^{\#} = 18$ kcal/mol) and HT-2 ($\Delta H^{\#} = 15$ kcal/mol), respectively.



The formation of dibenzofuran from these intermediates by dehydration through concerted elimination of water have high activation barriers, viz. $\Delta H^{\#} = 65$ kcal/mol for DH-1 and 42 kcal/mol for DH-2, respectively, which indicates that these commonly accepted channels are energetically infeasible.





5. Alternative ring closure pathways to form dibenzofuran via radical-molecule reactions are much more favorable. While hydrogen abstraction by radical pool species such as the R1 and R2 reactions of hydroxyl radical are fast, the further displacement of attached to DF hydroxyl group to form dibenzofuran is endothermic by 29 kcal/mol for the inter-ring displacement reaction R1a

$$o,o'\text{-HOC}_6\text{H}_4\text{−C}_6\text{H}_4\text{O} \rightarrow \text{DF} + \text{HO} \quad (\Delta H = +\,29.07 \text{ kcal/mol}) \quad \text{(R-1a)}$$

and 15 kcal/mol for the intra-ring elimination R2a.

$$\text{(HO−)DF} \rightarrow \text{DF} + \text{OH} \quad (\Delta H = +15.02 \text{ kcal/mol}) \quad \text{(R-2a)}$$

This is compared to the activation enthalpies of reaction of 42 and 65 kcal/mol for dehydration.

The activation parameters indicate that pathway R2

$$\text{(H-,HO−)DF} + \text{HO} \rightarrow \text{(HO−)DF} + \text{H}_2\text{O} \quad (\Delta H = \text{-}40.35 \text{ kcal/mol}) \quad \text{(R-2)}$$

is the most favorable reaction with an activation enthalpy for R2a of only 15 kcal/mol.

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