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Formation of Benzofuran and Chlorobenzofuran from 1,3-Dichloropropene: A Quantum Chemical Investigation

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ABSTRACT

We present a quantum chemical investigation of benzofuran and chlorobenzofuran formation mechanisms during the combustion of 1,3-D. Density functional theory and Gaussian-*n* thermochemical methods are used to propose detailed mechanistic reaction pathways. These calculations indicate that oxidation of phenylvinyl radical intermediates and subsequent ring closure are key mechanistic pathways in the formation of benzofuran and chlorobenzofuran. Thermochemical and kinetic parameters presented herein will assist in further elucidation of dioxin formation mechanisms from thermolyses of hydrocarbon moieties.

Introduction

Benzofuran and chlorobenzofuran belong to the family of dioxins and furans. They are classified as possible Class 2B human carcinogens and have also been confirmed to be toxic to rodents by the International Agency for Research on Cancer.¹ Benzofuran is a byproduct of a number of chemical processes, such as the coking of bituminous coal and combustion of common organic chemicals, such as unsaturated hydrocarbon fuels. The combustion of many halogenated straight chain compounds, such as 1,3-dichloropropene (1,3-D), also result in the formation of dioxins/furans²⁻⁴ and dioxin precursors such as benzenes,⁵ chlorobenzenes,⁶⁻⁸ phenols,^{9, 10} chlorophenols^{10, 11} and biphenyls.¹² More complex insecticides such as permethrin have also been found to be a direct precursor of dioxins and furans.^{13, 14} Dioxins/furans constitute only a small fraction of the total product yield from chlorinated hydrocarbon combustion, *ca.* < 1% (major products include H₂O, CO, CO₂ and HCl). However, they pose the highest risk to human health due to their carcinogenic potential.¹⁵⁻¹⁷

This is compounded by the extensive use of compounds such as 1,3-D in combustion-prone contexts, such as agriculture (where it is widely used as a pesticide for the control of soil-borne parasites, bacteria and viruses). Mitigation and control of dioxins/furan formation is therefore fundamentally important, and requires detailed understanding of how these compounds form.

The formation of benzofurans via the combustion of chlorobenzenes and chlorophenols – direct precursors - has been discussed extensively in literature. Dyke et al.¹⁸ demonstrated that intermolecular condensation of polychlorinated phenols, and associated smiles rearrangements yield polychlorinated dibenzodioxins (PCDDs) via HCl elimination. Polychlorinated dibenzofurans (PCDFs) can be formed from dibenzodioxins (DDs) by Cl substituted reactions¹⁸. Buser⁶ observed the formation of chlorophenol following the pyrolysis of chlorobenzene in air, proposing that chlorophenol can either react with unreacted chlorine to form polychlorinated diphenyl ether (PCDPE), which subsequently forms PCDF or dimerizes to form PCDDs. Similarly, in the oxychlorination of chlorobenzene at 613 K, Sommeling et al.⁸ observed chlorinated dibenzofurans, proposing

a mechanism mediated by the formation of a $\text{ClC}_6\text{H}_4\text{O}^\bullet$ chlorophenoxy radical intermediate that undergoes radical dimerization. Born et al.^{9, 11} proposed a similar mechanism following studies of gas phase reactions between phenol and chlorophenols. In this case, dibenzofuran was postulated to arise from a *o,o*-dihydroxybiphenyl intermediate, which forms from reverse coupling of hydroxybiphenyl radicals. PCDDs and PCDFs have also been shown to form via consecutive addition of C_3 units on fly-ash at relatively high temperature.^{4, 19} Thermochemical parameters of PCDD/F formation have also been discussed extensively in the literature.^{13, 20, 21} Benzofuran formation pathways from thermolyses of dibenzofuran have also been investigated with experimental^{22, 23} and theoretical²⁴ methods.

While PCDD/F formation mechanisms from direct precursors have been extensively investigated, there is limited mechanistic information on how PCDD/Fs form from indirect precursors, such as alkenes and their chlorinated analogues. Most notably, Mulder et al.^{4, 19} observed benzofuran and dibenzofuran during oxychlorination and combustion of propene on fly-ash. Nevertheless, indirect precursors such as 1,3-D are used abundantly in situations prone to combustion, such as agriculture.

Motivated by these findings, we present here thermochemical and kinetic aspects of benzofuran and chlorobenzofuran formation during combustion of 1,3-D, based on oxidation reactions of chlorinated phenylvinyl radicals. Kinetic and thermodynamic parameters presented herein will be invaluable for building a robust kinetic model for formation of dioxins and furans during the combustion of chlorinated hydrocarbons.

Methods

Initial reactive pathways were constructed with density functional theory (DFT), using Truhlar's M06-2X exchange correlation functional^{25, 26} in conjunction with Pople's 6-311+G(d,p) split

valence basis set.²⁷ Transition state structures were obtained via the QST3 algorithm,^{28, 29} and verified via harmonic vibrational frequency analysis. Intrinsic reaction coordinate³⁰ pathways were constructed to ensure all transition states corresponded to the correct reactive pathway. A number of investigations have demonstrated the accuracy of the M06-2X functional in the context of combustion and related thermochemistry.^{25, 26, 31-36} All reaction and activation enthalpies were then re-calculated using the G3MP2B3 composite method.³⁷ This composite method has been shown to be reliable for a wide range of combustion reaction pathways,^{32, 38} including those pertaining to 1,3-D.³² Unless stated otherwise, free energy contributions were calculated at 298 K. All quantum chemical calculations were performed using Gaussian 09.³⁹ The Chemrate code,⁴⁰ employing G3MP2B3 reaction and activation enthalpies, was used to calculate kinetic parameters for key chemical reactions on the basis of conventional transition state theory.

Results and Discussion

Thermochemical Parameters for Benzofuran Formation

It has been previously proposed that ethenyl benzene is an important intermediate during benzofuran formation from oxychlorination of propene at high temperatures.^{4, 19} The mechanistic pathway proposed (which pertains to fly ash - catalyzed experiments between 573 - 853 K) is shown in Figure 1. More recent research has shown that catalytic assisted precursor coupling during dioxin formation is optimal at lower temperatures,^{2, 4, 19, 21, 41-43} whereas homogeneous gas-phase reactions become prominent at higher temperatures (≥ 873 K).^{13, 20, 21, 32, 44-54} The Figure 1 mechanism is therefore likely to be relevant to high-temperature benzofuran formation (i.e. in the absence of a fly-ash catalyst), and also chlorobenzofuran formation, since chlorinated analogues of the styrene precursor (0, Figure 1)

most likely form easily at high temperatures during the oxidative decomposition of 1,3-D (as we discuss below). To the best of our knowledge however, the thermochemical parameters of the Figure 1 reaction pathway have not been reported, either with or without a fly-ash catalyst. We therefore begin our discussion of these parameters, and assess the scheme for homogenous gas phase reactions at higher temperatures.

Our calculations demonstrate that, at high temperatures, the Figure 1 mechanism is thermodynamically and kinetically feasible as a homogeneous gas-phase reaction. However, we do not discount the presence of other reactive pathways during benzofuran formation. The first step of this pathway, hydrogen abstraction via radical Cl from the ethenyl site of styrene (0), forms the 2-phenylethenyl radical (0a). This reaction is barrierless and modestly endothermic ($\Delta G = 41.0$ kJ/mol). Compound 0a can undergo radical addition to ambient O_2 to form [2-phenylethenyl]peroxy radical (0b), and this process corresponds to a reaction free energy of -180.8 kJ/mol using G3MP2B3. The latter result is in reasonable agreement with the B3LYP/6-31+G(d) enthalpic value of -189.1 kJ/mol.⁵⁵ The third step in Figure 1, in which HO_2 abstracts 0b, produces 2-phenylethenyl oxidanyl radical (0c), OH and O_2 via a concerted process. The transition state corresponding to these concerted O-O and O-H bond scissions could not be found on the M06-2X/6-31+G(d,p) potential energy surface. Instead, we propose that this concerted process is unfavourable on thermodynamic grounds, and that the hydrotrioxy radical (HO_3) acts as a metastable intermediate. While the dissociation free energy of this radical ($trans-O_3H \rightarrow OH + O_2$) is 0.3 kJ/mol, the dissociation enthalpy is 11.4 kJ/mol using G3MP2B3, which is in agreement with the experimental value of 11.7 kJ/mol.⁵⁶⁻⁵⁹ Using G3MP2B3 the activation free energy for dissociation is 20.2 kJ/mol. Ultimately the formation of 0c and HO_3 from 0b is exothermic ($\Delta G = -101.2$ kJ/mol) and barrierless. However, we note that at higher temperatures O-O bond

scission *via* interaction with OH is perhaps more likely, since this species is more stable than HO_2 ⁶⁰⁻⁶². Subsequent ring closure of 0c, *via* cyclization of the ethenyl moiety is the rate-limiting step of this reaction sequence, with an activation free energy of 137.7 kJ/mol, and is also endothermic ($\Delta G = 95.0$ kJ/mol). By comparison, the abstraction of the benzofuranylic hydrogen from 0d by ambient O_2 is labile (a free energy barrier of only 21.3 kJ/mol) and strongly exothermic ($\Delta G = -187.5$ kJ/mol).

Formation of Chlorobenzofuran Precursors

The Figure 1 mechanism is based on the styrene radical precursor. This precursor is known to result from combination of phenyl and ethenyl radicals during combustion of acetylene and ethylene in laminar flames.⁶³ The rate expression for this process is k [cm³/s molecule] = $1.2 \times 10^{27} T^{-4.22} e^{(-\Delta G^\ddagger/RT)}$ ($\Delta G^\ddagger = 30.1$ kJ/mol) between 600-1600 K,⁶³ which demonstrates that these radical recombination processes are kinetically labile. Equivalently, the radical recombination of chloroethenyl and chlorophenyl radicals, both of which are known to form during the combustion of 1,3-D (at temperatures above 873 K),³² is a plausible pathway to the formation of chlorinated analogues of styrene.

This reaction between chloroethenyl and chlorophenyl radicals is considered in Scheme 1. Radical recombination (Scheme 1(a)) is barrierless, and the reaction free energy ($\Delta G = -446.4$ kJ/mol) is independent of whether Cl is present at the *para* (isomer 1) *meta* (isomer 2) or *ortho* (isomer 3) positions on the benzene ring. The rate expression for this reaction (k [cm³/s molecule] = $2.3 \times 10^{27} e^{(-\Delta G^\ddagger/RT)}$ ($\Delta G^\ddagger = 27.3$ kJ/mol) agrees with the rate for the non-chlorinated analogue. The alternative possibility, Scheme 1(b), is addition of the chlorophenyl radical to the chlorinated carbon atom in chloroethenyl radical. This reaction results in a relatively unfavourable diradical product ($\Delta G = -136.7$ kJ/mol, $\Delta G^\ddagger = 32.5$ kJ/mol). In

the discussion that follows, we focus on the formation of benzofuran *via* isomers 1, 2 and 3.

Figure 1. Mechanism of formation of monobenzofuran from ethenyl benzene ^{4, 19}. All values calculated (in this work) using G3MP2B3 are given in kJ/mol, and include zero-point energy and thermal contributions at 298.15 K.

Benzofuran Formation Mechanisms

For isomer 1 (1-chloro-4-[2-chloroethenyl benzene]) the C-Cl bond at the vinylic site is weaker than all other C-H bonds (bond dissociation free energy $\Delta G^\ddagger = 356.3$ kJ/mol), suggesting that vinyl Cl elimination is favourable compared to Cl/H elimination from other sites. Hence, we expect initial reactions to be dominated by Cl elimination from the vinylic site of isomer 1. Figure 2 depicts a suggested radical mechanism of formation of chlorobenzofuran from isomer 1. Abstraction of vinylic Cl from isomer 1 to form a radical 1a exhibits a modest barrier of 77.0 kJ/mol (TS4), and is exothermic ($\Delta G^\ddagger = -50.0$ kJ/mol). Our calculated rate expression for this reaction (k [cm³/molecule s] = $5.70 \times 10^{-11} e^{-\Delta G^\ddagger/RT}$, $\Delta G^\ddagger = 40.8$ kJ/mol) agrees with previously reported values for the hydrogen abstraction of vinyl Cl from chloroethene (k [cm³/molecule s] = $6.61 \times 10^{-11} e^{-\Delta G^\ddagger/RT}$, $\Delta G^\ddagger = 38.91$ kJ/mol) for $T = 872$ -1080 K.⁶⁴ A direct addition of (³P)O to the chlorophenylvinyl radical leading to the formation of chlorophenyl ethenyl oxidanyl (1c) is very likely given its high exothermicity ($\Delta G^\ddagger = -511.4$ kJ/mol) and lack of a free energy barrier. Hydroxylation of radical 1a, forming 4-chlorophenylethenol (1b), is also likely because of the abundance of OH in our reaction conditions. The rate expression for the latter reaction is (k [cm³/molecule s] = $5.58 \times 10^9 e^{-\Delta G^\ddagger/RT}$, $\Delta G^\ddagger = 10.0$ kJ/mol). We do not consider

Scheme 1. Potential radical recombination reactions between chlorobenzyl and chloroethenyl radicals forming (a) *p*-, *m*-, *o*- chloro-[2-chloroethenyl benzene] and (b) an unfavourable diradical product. In (a), numbers are G3MP2B3 $\Delta_{at}H_{298K}$ values (kJ/mol).

the reaction analogous to $0b \rightarrow 0c$ (Figure 1), as OH is more stable than HO_2 at relevant experimental temperatures.⁶⁰⁻⁶² Further reaction between 1b and OH results in the abstraction of the hydroxyl hydrogen atom, forming water and chlorophenyl ethenyl oxidanyl radical (1c). This abstraction process is exothermic ($\Delta G = -167.7$ kJ/mol) with a trivial activation free energy $\Delta G^\ddagger = 7.3$ kJ/mol (TS5). The calculated rate parameter for this process (k [cm³/molecule s] = $2.80 \times 10^{-12} e^{-\Delta G^\ddagger/RT}$, $\Delta G^\ddagger = 5.2$ kJ/mol) is in good agreement with literature data concerning the abstraction of OH hydrogen atoms to form water.⁶⁵⁻⁶⁸

Figure 2. Radical mechanism of formation of chlorobenzofuran from isomer 1. Free energies of reaction and activation are G3MP2B3 values (298.15 K) in kJ/mol.

Ring closure of 1c, in either a clockwise or anticlockwise direction, then presents a direct route to the formation of 6-chlorobenzofuran (1e) via the hydrogenated benzofuranyl radical 1d. Such cyclization is highly endothermic ($\Delta G = 96.1$ kJ/mol), and exhibits activation free energies of 137.9 kJ/mol (TS6); there is no difference in the reaction energy profile here between clockwise and anticlockwise ring closure. 6-chlorobenzofuran can then be formed from 1d by two pathways – either by unimolecular hydrogen elimination via TS7 ($\Delta G^\ddagger = 94.4$ kJ/mol), or radical hydrogen abstraction. Under typical experimental conditions, the latter most likely corresponds to abstraction by Cl, OH, HO_2 or H radicals. Each of these abstraction reactions is barrierless, and reaction free energies (Figure 2) reflect the relative stabilities of the hydrogenated radical species, i.e. $\Delta H(H-OH) < \Delta H(H-H) < \Delta H(H-Cl) < \Delta H(H-O_2H)$.

Figure 3. An alternative radical pathway to the formation of chlorophenyl ethenyl oxidanyl radical (1c) from 1a. Free energies of reaction and activation are G3MP2B3 values (298.15 K) in kJ/mol.

An alternative pathway to species 1c, and thus 6-chlorobenzofuran, is via reaction between isomer 1a and O_2 . This reaction, considered in Figure 3, forms the 4-chlorophenyl ethenyl peroxy radical (1f); reaction and activation free energies are -157.5 and 0.0 kJ/mol respectively and the rate expression k [cm³/molecule s] =

Figure 4. Ring closure of 2c forming 2d and 2e. All G3MP2B3 ΔG , $\Delta G^\ddagger$ values (kJ/mol) include zero-point energy and thermal contributions at 298.15 K.

$4.40 \times 10^{12} e^{-\Delta G^\ddagger/RT}$, $\Delta G^\ddagger = 9.7$ kJ/mol) agrees with the experimental value for the oxidation of phenylvinyl radicals to phenylvinyl peroxy radicals $k = 3.71 \times 10^{12}$ at 298 K.⁵⁵ Thus, despite the favourable kinetic parameters shown in Figure 2, it is likely that O_2 association with 1a (i.e. $1a \rightarrow 1c$, Figure 3) is a dominant chemical pathway because of the relative abundance of O_2 versus those of radical species such as H, OH and HO_2 . This pathway occurs via the intermediate species 1f, which can either undergo a barrierless, intra-annular O-O bond scission ($\Delta G = 96.2$ kJ/mol) to form 1c or react with H to form 4-chlorophenyl etheneperoxol (1g) via a barrierless and exothermic pathway ($\Delta G = -326.8$ kJ/mol). Scission of the O-OH bond in 1g forming 1c is also barrierless, and moderately endothermic ($\Delta G = 16.9$ kJ/mol).

Isomer 2 can also undergo the addition and abstraction reactions depicted in Figure 2 and 3 (for Isomer 1), to form 2c (Figure 4). No significant variation of the reaction/activation free energies for the formation of 1c and 2c was found, i.e. on whether the ethenyl moiety is located at the *meta* or *para* positions on the benzene ring. Similarly, there was only ~ 5 kJ/mol difference in the activation free energies for $1c \rightarrow 1d$ cyclization, and the two possible cyclizations of 2c, which yield 7- and 5-chlorobenzofuranyl radicals (2d, 2e), respectively. The benzofuranylic hydrogen atom can be removed via either unimolecular elimination ($\Delta G = 21.2$ kJ/mol, $\Delta H^\ddagger = 94.3$ kJ/mol) or barrierless hydrogen abstraction (Cl, OH, HO_2 or H abstraction of hydrogen ($\Delta G(Cl) = -385.7$, $\Delta G(OH) = -494.2$, $\Delta G(HO_2) = -309.7$, $\Delta G(H) = -$

389.6 kJ/mol), as is the case for species 1d (Figure 2). In all cases, both 2d and 2e exhibit the same reaction and activation free energies.

Similarly, Isomer 3c, in which the ethenyl moiety is located *ortho* to the chlorine, is capable of forming 4-chlorobenzofuran (3e) via clockwise cyclization, which gives the chlorobenzofuranyl radical 3d, as depicted in Figure 5. The free energy barrier preventing this cyclization is only marginally lower than those observed for the *meta* (2c) and *para* (1c) analogues, indicating that the position of the chlorine atom bears no significant influence on the rate-limiting kinetics of chlorobenzofuran formation. Similarly, abstraction of the benzofuranylic hydrogen atom from 3e with Cl, OH, HO_2 and H radicals corresponds to almost identical energetics as observed for isomers 1e and 2e.

Anticlockwise cyclization, in which the chlorinated carbon atom forms the C-O bond, results in Cl elimination via the concerted reaction mechanism, forming benzofuran ($3c \rightarrow 3f$). This reaction is slightly endothermic ($\Delta G = 15.6$ kJ/mol) and has a moderately high barrier ($\Delta G^\ddagger = 113.8$ kJ/mol), but is expected to be more labile than chlorobenzofuran formation. Similarly, formation of benzofuran via $3c \rightarrow 3f$ is kinetically more favourable, compared to the reaction scheme proposed by Mulder et al.^{4, 19}. This is because the latter is a two-step process, with a rate limiting activation free energy of 137.7 kJ/mol (Figure 1).

Table 1. Arrhenius reaction rate parameters at 300-2000 K and 1 atm. k values are calculated at 873 K.

Reaction	A	$E_a^{[a]}$	k	Reaction	A	$E_a^{[a]}$	k
5.70×10^{-11}	40.8	$2.06 \times 10^{-13} [c]$		1.46×10^{11}	131.9	$1.86 \times 10^3 [d]$
2.80×10^{-12}	5.2	$1.36 \times 10^{-12} [c]$		2.41×10^{13}	91.9	$7.60 \times 10^7 [d]$
4.40×10^{12}	9.7	$1.16 \times 10^{12} [c]$		2.31×10^{11}	135.7	$1.76 \times 10^3 [d]$
5.58×10^9	10.0	$1.41 \times 10^9 [c]$		6.03×10^{13}	12.7	$6.02 \times 10^{13} [d]$
1.13×10^{11}	116.3	$1.25 \times 10^4 [d]$		5.56×10^{11}	6.8	$2.19 \times 10^{11} [d]$

[a] kJ/mol. [b] Cl abstraction shown for Isomer 1 only. [c] $\text{cm}^3/(\text{s molecule})$. [d] s^{-1} .

Figure 5. Ring closure of 3c and formation of benzofuran/4-chlorobenzofuran. All G3MP2B3 ΔG , $\Delta G^\ddagger$ values (kJ/mol) include zero-point energy and thermal contributions at 298.15 K.

Table 1 and Figure 6 present a detailed kinetic analysis of the chemical reactions pertinent to the formation of benzofuran and chlorobenzofuran from 1,3-D. The rate expression for the H abstraction of vinyl Cl from isomers 1-3 (forming 1a-3a) are identical, i.e. k [$\text{cm}^3/\text{molecule s}$] = $5.70 \times 10^{-11} e^{(-\Delta G^\ddagger/RT)}$, $\Delta G^\ddagger = 56.4$ kJ/mol. At 873 K, the lowest temperature at which both chlorobenzene and benzofuran were detected in the homogenous gas phase decomposition of 1,3-D,³² $k = 2.06 \times 10^{-13} \text{ cm}^3/\text{molecule s}$. With a fixed concentration of reacting species, the formation rates of radical 1a-3a as well as the abstraction of a hydroxyl hydrogen atom by OH from species 1b-3b are therefore the respective rate-limiting steps. The kinetic parameters presented in Table 1 and Figure 6 demonstrate further that the counter-clockwise/clockwise electrocyclic ring closure of 3c, yielding benzofuran (3c → 3f) and 4-

chlorobenzofuranyl radical (3c → 3d), are competitive reaction processes with no significant variance in activation enthalpies. However, benzofuran formation is anticipated to be more favourable than the formation of 4-chlorobenzofuranyl radical due to a marginally lower reaction enthalpy (105.0 vs 127.0 kJ/mol, respectively) and slightly higher Arrhenius factor (1.13×10^{11} vs $1.46 \times 10^{11} \text{ s}^{-1}$, respectively). Furthermore, 4-chlorobenzofuranyl radical (3d) requires subsequent hydrogen elimination to form 4-chlorobenzofuran, which is relatively kinetically unfavourable ($k = 7.60 \times 10^7 \text{ s}^{-1}$).

Figure 6. Arrhenius plots for the formation of benzofuran (3f) and 4-chlorobenzofuranyl derived radical (3d) from 4-chlorophenyl ethenyl oxidanyl radical (3c)

Conclusions

We have investigated the formation of benzofuran/chlorobenzofuran during the oxidative thermal decomposition of 1,3-D. Quantum chemical calculations reveal that electrocyclic ring closure and dehydrogenation of 2-(4-chlorophenyl) ethenyl oxidanyl radical (1c) in either clockwise or counter-clockwise directions yield 6-chlorobenzofuran; 2-(3-chlorophenyl) ethenyl oxidanyl radical (2c) in clockwise and counter-clockwise directions yield 5-chlorobenzofuran and 7-

chlorobenzofuran respectively; counter-clockwise ring closure of 2-(2-chlorophenyl) ethenyl oxidanyl radical (3c) yields benzofuran and Cl *via* a concerted process, while clockwise ring closure yields 4-chlorobenzofuranyl radical, which can then form 4-chlorobenzofuran by dehydrogenation. The formation of benzofuran is found to be slightly more favourable on thermodynamic and kinetic grounds, compared to the formation of 4-chlorobenzofuran *via* this process. Thermochemical and kinetic parameters generated in this work will assist in the development of a robust kinetic model for dioxin formation during the combustion of hydrocarbons, and halogenated hydrocarbons.

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Keywords: 1,3-dichloropropene, benzofuran, chlorobenzofuran, dioxin, electrocyclic ring closure

Additional Supporting Information (G3MP2B3 optimised transition state and intermediate structures, cartesian coordinates of optimized transition states and intermediate structures) may be found in the online version of this article.

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