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Formation of Chlorobenzenes by Thermal Decomposition of 1,3-Dichloropropene

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Abstract

We combine combustion experiments and density functional theory (DFT) calculations to investigate the formation of chlorobenzenes from the thermal decomposition of 1,3-dichloropropene. Mono- to hexa-chlorobenzenes are observed between 800 – 1150 K, and the extent of chlorination was proportional to the combustion temperature. Heavily chlorinated benzenes (tetra-, penta-, hexa-chlorobenzene) are only observed in trace amounts between 950 – 1050 K. DFT calculations indicate that cyclization of chlorinated hexatrienes proceeds via open-shell, radical pathways and are a key component in the combustion mechanism of halohydrocarbons.

Keywords: 1,3-dichloropropene, chlorobenzene, cyclisation, density functional theory, combustion

Introduction

1,3-dichloropropene (1,3-D) is used extensively in agriculture as a pre-plant soil-fumigant primarily for the control of parasites and soil-borne bacteria and viruses. 1,3-D was first introduced in 1956 and is now widely used in many countries, including the USA, Canada, Australia and the European Union (where it is currently being phased out). The extensive use of pesticides has stimulated research aimed at understanding the chemical mechanism and products of their combustion [1-3]. These products can include highly toxic species, such as dioxins and their precursors. While a number of investigations have focused on toxicity of 1,3-D[4-6], the mechanism(s) and products of its combustion have not yet been reported.

Thermal decomposition of chlorinated alkanes and alkenes typically results in chlorinated aromatic pollutants. Precursors of polychlorinated dibenzodioxin and furan (PCDD/F) have been observed during the heterogenous oxidative/pyrolytic decomposition of chloroaliphatic hydrocarbons.[7] Similarly, chloroaromatic compounds and their precursors have been detected during the decomposition of chlorinated short-chain aliphatic hydrocarbons [7-23]. The latter investigations show that formation of PCDD/F precursors proceeds *via* molecular growth reactions triggered by alkyl and chlorinated vinyl radicals [16, 21, 22] *via* rearrangement and radical recombination between unsaturated intermediates [9].

Benzene and chlorobenzenes have also been identified and quantified in the combustion of chlorinated short-chain hydrocarbons [15, 23]. The formation of these chloroaromatic compounds has been attributed to *de novo* processes enabled by soot particles in the flame in addition to coupling of gas phase precursors. High yields of hexachlorobenzene were observed during fly ash-catalyzed combustion of trichloroethylene [12]. This supports the theory that chloroaromatic compounds can be formed in the high-temperature, post combustion zone, which

provides the precursors necessary for PCDD/F formation in lower temperature zones. Similarly, hexachlorobenzene was observed during the pyrolysis of hexachloropropene above 773 K, *via* self-recombination of C_3Cl_5 and C_3Cl_3 radicals [19]. These radicals are produced during the initial decomposition of hexachloropropene (C_3Cl_6). It is also possible for chlorine atoms to recombine with propene or any available radical to form the trichloropropargyl radical, which can self-recombine to produce chlorinated benzenes. Pyrolysis of trichloroethene above 1000 K has also been observed to yield hexachlorobenzene [21].

In this work, we investigate the formation of PCDD/F and polychlorinated biphenyls (PCBs) precursors, specifically chlorobenzenes, *via* high-temperature combustion of 1,3-D using a combined experimental and quantum chemical approach. Chlorobenzenes have been categorized by International Agency for Research on cancer (IARC) as a Group 2B animal carcinogen and a potential human carcinogen, and in addition they are precursors of PCDD/Fs [8, 17, 18]. Experiments show that between 650 – 1050 K, combustion products of 1,3-D are dominated by mono- to hexa-chlorinated benzenes. Quantum chemical calculations of reaction pathways reveal that these products can form via a number of alternate cyclisation pathways. The most thermodynamically and kinetically favorable pathways are observed to be propagated by perchlorohexatriene-derived radicals. Kinetic and thermodynamic parameters presented here will be useful for future kinetic models of halohydrocarbon combustion. Formation of the first chlorinated aromatic ring typically initiates the formation of chlorinated poly aromatic hydrocarbons (PAHs). It follows that results from this study will also contribute toward a better understanding of the formation of soot during combustion of chlorinated short-chain hydrocarbons.

Methods

Experimental

The experimental apparatus deployed in the thermal decomposition of 1,3-D is illustrated in Figure 1.

Figure 1. Schematic of the experimental set-up

1,3-D (98 %, Dow Agrosience, Australia), a faint yellow liquid at room temperature, was introduced into the system using a syringe pump operated at a constant rate to keep the reactant concentration at 8,580 ppm, in a dilute stream of air in nitrogen (6 % O₂). We used a heating tape (set at 403 K) to ensure proper vaporization of the reactant prior to entering the reactor and also minimise temperature gradients inside the reactor. The resulting vapour/nitrogen mixture entrained a controlled amount of oxygen, with oxygen concentration monitored on the molecular sieve channel 1 of a 490 micro gas chromatograph (Agilent, USA). We used the molecular sieve

and poraplot Q columns of the same micro GC to measure the CO and CO₂ produced during the experiment with the micro GC calibrated with a gas standard.

The jet stirred reactor (JSR) used here consists of a sphere (54 mm i.d., 82.25 cm³ in volume), made of quartz (99.99 % purity to minimise wall catalytic reactions). The spherical part of the reactor is equipped with four nozzles each of 3 mm i.d. for the injection of the feed gas and reactant vapour thereby obtaining the stirring. The reactor is aligned along the centreline of an electrically heated single-zone furnace (Brother furnace China) calibrated from 623 K to 1123 K with a thermocouple placed along the tube to define a uniform temperature zone. The tail end of the reactor was connected to different product collection systems.

Once the temperature and reactor conditions are stabilized, reactants are introduced into the reactor via the syringe pump at a steady state and product sampling from the reactor commences immediately. The experiments were carried out over a wide temperature range of 673-1073 K with an equivalence ratio of 0.5. For all experiments, the pressure was 1 atm and the residence time was 10 s. Sampling of reactants, stable intermediates and products from the reactor lasted for three hours in each run. The poly tetrafluoroethylene connection tubes are normally rinsed with dichloromethane and/or hexane solution to recover adsorbed products and to avoid contamination of succeeding runs. We used a glass tube loaded with 200 mg of XAD-2 resin (Supelpak-2, Sigma-Aldrich, Australia) and connected it at the reactor outlet as our VOC trap. Hexane and dichloromethane (DCM) solvent trap was chilled in a cold glycol bath (273 K) to collect any condensable products.

Products were analysed with GC-MS. We adapted the general procedures of the National Institute for Occupational Safety and Health (NIOSH) method 1003. We used XAD-2 resin (in place of activated charcoal) as the adsorbent and *n*-hexane (instead of CS₂) as the solvent. After

each experiment, the used XAD-2 resin is collected and sonicated with 40 mL hexane for 2 hours. The XAD-2 extract was filtered and injected (split ratio 10:1) into the Agilent 7890 GC and 7200 Accurate-mass Q-TOF GC/MS with a 30 m Agilent HP-5MS column (i.d. of 250 μ m and film thickness of 0.25 μ m). In addition, we combined the solvent from washing the reactor tube together with solution from the solvent trap and then injected at a split ratio of 10:1 into the same GC-MS with the same operating conditions. The GC-MS carrier gas (helium) flowed at a constant rate of 1.2 mL/min and 9.8 psi. The injector temperature was maintained at 513 K in 1 μ L injection volume. The GC oven temperature commenced at 323 K, and then held for 1 min and then ramped at 283 K per minute to 573 K and held for 1 min. We maintained the transfer line temperature at 513 K. The MS electron impact energy was set at 70 eV and the emission current was maintained at 2.8 μ A with an ion source of 503 K. We identified the product species on the basis of NIST library searches, examination of mass spectra (the ratio of Cl element, loss of characteristic fragments and molecular ions), authentic standard injection and standard elution order. The quantitation of the VOCs relied on the preparation of external standard calibration curves.

Computational Methods

Reaction pathways were investigated using density functional theory (DFT) with Truhlar's (U)M06-2X functional, [24, 25] in conjunction with a 6-311+G(d,p) basis set. Mardirossian and Head-Gordon [26] have recently shown that M06-2X provides good overall performance for reaction thermochemistry. Nevertheless, to ensure this is the case in the current context, we compare M06-2X-calculated kinetic and thermodynamic parameters with G3MP2B3 [27] and experimental values (see tables S1 and S2 in the supporting information). G3MP2B3 has

previously been shown to provide accurate reaction thermochemistry for combustion pathways [28]. The structures of all reaction intermediates and transition states (TSs) were optimised using Gaussian 09[29]; all local minima and TSs were verified by having zero and one harmonic vibrational frequencies, respectively. The intrinsic reaction coordinate (IRC) method [30] was used to ensure that each TS corresponded to the correct reactive pathway. Computed reaction and activation enthalpies were used to generate kinetic parameters using Chemrate [31]. Zero-point energy and enthalpic contributions were computed within the harmonic approximation. Unless stated otherwise, enthalpic contributions were calculated at 298 K.

Results and Discussion

Thermal decomposition of 1,3-Dichloropropene

The primary products of the thermolysis of 1,3-dichloropropene (1,3-D) include CO, CO₂, H₂O and HCl. The chloride ion obtained from NaOH trap was analysed using Dionex DX-100 ion chromatograph and the total yield of product species are included the supporting information. For example, at 823 K, the primary products include 53.7 % of 1,3D, 23.15 % of HCl, 4.86 % of CO and 8.57 % of CO₂. Water vapour was observed but was not quantified. We used drierite to remove the water vapour prior to product analyses in order to avoid damaging our analytic instruments. Mono to hexachlorobenzenes are the minor products of the experiment. Other minor products obtained included hexachlorobutadiene, hexachloroethane, 2-chloronaphthalene, dibenzofuran, ethenylbenzofuran, chlorinadanon and chloronaphthalenol (see Supporting Information, Tables S3, S4, Figures S8, S9). In this study, we concentrate on the mechanism of formation of chlorinated micropollutants (mono to hexachlorobenzenes) which are observed in incineration and are important indicator and precursors of polychlorinated dibenzodioxins and

furans (PCDD/Fs). Figures 2 and 3 show the yields of mono- to hexa-chlorobenzenes obtained from thermal decomposition of 1,3-D between 650 – 1050 K. 1,3-D exhibited only minimal degradation at temperatures < 673 K, with combustion initiating at *ca.* 673 K (Figure 2). At 823 K, approximately half of the 1,3-D is consumed, and this increases dramatically to > 90% by 873 K. At higher temperatures, effectively all 1,3-D is consumed by the combustion process.

Figure 2. Percentage yields of 1,3-D (1,3-D) and mono- and di-chlorinated benzenes from thermal decomposition of 1,3-D, as a function of temperature. Yields of all chlorinated species are scaled by a factor of 1000. Quantified results are provided in Table S3.

Production of chlorobenzenes is observed at 773 K and above, with the highest yield occurring at 823 K for chlorobenzene and 923 K for dichlorobenzene. We note here there is little to no selectivity between 1,3- and 1,4-dichlorobenzene, while the yield of 1,2-dichlorobenzene is *ca.* 10% higher by comparison. Trichlorobenzenes were produced at 923 K and above (Figure 3). The maximum yield of 1,3,5-trichlorobenzene, *ca.* 65% (obtained at 923 K), was far greater than

either 1,2,3-trichlorobenzene and 1,2,4-trichlorobenzene, which peaked at *ca.* 10% (between 923-1023 K). This can be understood in terms of steric/electrostatic repulsion between individual Cl atoms on the benzene ring, and is consistent with the relative thermodynamic stabilities of these three isomers (not shown). At temperatures higher than 1023 K, di- and tri-chlorobenzenes were not observed. Figure 3 shows that higher temperatures favoured the production of tetra- to hexa-chlorobenzenes. Of these, pentachlorobenzene was produced with the greatest yield (40% at 973 K), followed by 1,2,3,4-tetrachlorobenzene (20% at 973 K). This suggests that 1,2,3,4-tetrachlorobenzene plays a more active role as a reactive intermediate during combustion, compared to pentachlorobenzene (which is more of a reactive “sink”). The alternative tetrachlorobenzene isomer was not observed here. Hexachlorobenzene was also observed in this temperature range, however at relatively low levels (maximum yield was < 10% at 973 K).

Figure 3. Percent yield of 1,3-D and tri-, tetra-, penta- and hexa-chlorinated benzenes from thermal decomposition of 1,3-D, as a function of temperature. Yields of all chlorinated species are scaled by a factor of 1000.

Reaction Initiation

Thermal decomposition of hexachloropropene [19] and propene [32, 33] can be initiated by unimolecular processes (bond scission) and bimolecular processes involving O₂. It is likely that similar processes and kinetics are present during the initial stages of 1,3-D thermal decomposition studied here. For propene, the kinetic data for O₂ abstraction of allylic hydrogen atom, forming HO₂ and a propene-derived radical have been estimated previously [32, 33]. Hexachloropropene has been shown to undergo unimolecular C-Cl bond scission at elevated temperatures, comparable to those used in this work. Kinetic parameters for the latter process are more favourable; C-Cl bond scission corresponds to an Arrhenius prefactor (A) and activation energy (E_a) of $5.0 \times 10^{16} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and 236.6 kJ/mol, respectively for a temperature range of (573-773 K)[19]. On the other hand, for H-abstraction from the allylic site of propene by O₂, $A = 1 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $E_a = 199.1 \text{ kJ/mol}$ between 300-2500 K [33]. The rate for H-abstraction by O₂ can therefore be considered to be negligible in comparison to the rate of C-Cl bond scission. C-Cl bond scission of 1,3-D forming 1,3-D-derived radical species is therefore a plausible activation step in 1,3-D thermal decomposition. DFT and G3MP2B3 calculations corroborate this assumption (see supporting information).

A number of previous investigations have shown that small aromatic molecules can form via cyclisation of unsaturated hydrocarbons (e.g. 1,3,5-hexatriene [28], hexachloropropene [19, 34]). Here we investigate if this is also potentially the case for chlorobenzenes. Chlorobenzene can conceivably form via cyclisation of the 1,6-dichlorohexatriene precursor (IM4), which is observed in appreciable amounts in our combustion experiments (see supporting information). During combustion, there are undoubtedly many chemical reactions including many chemical

pathways to IM4 and subsequently chlorobenzene. We postulate that radical recombination reactions, beginning with 1,3-D-derived radical (IM1), are prominent amongst these. Recombination of IM1 (Scheme 1(a)) produces 1,6-dichlorohexadiene (IM2) and is exothermic ($\Delta H = -210.5$ kJ/mol). Subsequent dehydrogenation of IM2 at either allylic carbon via $\bullet\text{Cl}$ is also exothermic ($\Delta H = -67.2$ kJ/mol) and results in the 1,6-dichlorohexadiene radical IM3. Abstraction of hydrogen from the remaining allylic carbon by $\bullet\text{Cl}$ ($\Delta H = -232.3$ kJ/mol) results in the formation of the cyclisation precursor IM4. M06-2X/6-311+G(d,p) calculations show that both of these latter abstractions are barrierless, as anticipated.

Scheme 1. ΔH (kJ/mol) for recombination of allylic radicals to form IM9 (a) and hydrogen abstraction by Cl radicals to form IM10 (b) and IM11 (c). G3MP2B3 results (top), M06-2X results (bottom).

Chlorobenzene Formation

Closed-shell cyclization of 1,6-dichlorohexatriene (forming chlorobenzene) and octachlorohexatriene (forming hexachlorobenzene) are unlikely on a kinetic basis (see supporting information). Under our reaction conditions, it is far more likely that radical cyclisation is responsible for chlorobenzene formation, as proposed by Hudson et al. [35] In the case of chlorobenzenes, radical cyclization would necessitate the scission of either a C-Cl or C-H bond in 1,2-dichlorohexatriene, and as noted above, the former is the more likely pathway (based on the results for 1,3-D, see supporting information). As for 1,3-D, an alternative to bond scission here is Cl/H abstraction by ambient $\bullet\text{Cl}$. ΔH and $\Delta H^\ddagger$ for this process in 1,6-dichlorohexatriene are similar to those for 1,3-D (Scheme 2(a)). However, abstraction of H by $\bullet\text{Cl}$ at the C(3) carbon (Scheme 2(b)) is substantially more favourable, with $\Delta H^\ddagger = 104$ kJ/mol and $\Delta H = 96.3$ kJ/mol. H/Cl abstraction by $\bullet\text{H}$ atoms is also possible, (Scheme 2(c),(d)), and follow the same kinetic trend as abstraction with $\bullet\text{Cl}$. For instance, H abstraction at the terminal position has an activation enthalpy of 121.9 kJ/mol, whereas abstraction at C(3) is only 45.8 kJ/mol. The thermodynamics of Cl abstraction by $\bullet\text{H}$, or H abstraction by $\bullet\text{Cl}$, are consistent with the higher bond enthalpy in HCl as opposed to Cl_2 .

Scheme 2. ΔH (kJ/mol) for Cl/H abstraction by ambient Cl and H

Figure 4. Cyclisation pathway for conversion of 1,6-dichlorohexatriene radical (IM5) to chlorobenzene (P1). All values are given in kJ/mol and include zero-point energy and thermal contributions at 298 K.

The PES for cyclisation of 1,6-dichlorohexatriene-derived radical IM5 is shown in Figure 4. The most prohibitive step of this pathway is the initial rotation around the C(3)-C(4) bond, which has an activation enthalpy of 159.4 kJ/mol. The rate constant k for this step (IM5 $\rightarrow$ IM7) at 873 K is 445.5 s⁻¹. All subsequent steps in this mechanism are considerably more labile. The rotations around the C(2)-C(3) bond (IM7 $\rightarrow$ IM8) and C(4)-C(5) bond (IM8 $\rightarrow$ IM9) require only 32.5 and 44.1 kJ/mol, respectively. IM9 undergoes ring closure to form the chlorocyclohexadiene-derived radical IM10. The latter step is highly exothermic ($\Delta H = -239.3$ kJ/mol) with a barrier of

33.4 kJ/mol. Formation of chlorobenzene from IM10 can occur *via* H abstraction with $\bullet\text{Cl}$; this process is effectively barrierless and is exothermic by -278.7 kJ/mol.

Figure 5. Cyclisation pathway for 1,6-dichlorohexatriene radical (IM6) to IM14. All values are given in kJ/mol and include zero-point energy and thermal contributions at 298 K.

As opposed to the cyclisation of IM5, the cyclisation of IM6 represents a more favourable reaction pathway (Figure 5). The initial rotation about the C(2)-C(3) bond passes through an isoenergetic TS before forming IM11 ($\Delta H = -33.3$ kJ/mol). The two subsequent bond rotations

that result in IM13 have barriers less than 30 kJ/mol. Ultimately the rate-limiting step in this reaction pathway is ring closure (IM13 $\rightarrow$ IM14), which has a barrier of 140.3 kJ/mol.

IM14 can subsequently undergo H addition at C(3), which is highly exothermic ($\Delta H = -475.3$ kJ/mol) and barrierless (Figure 6(a)). The thus formed dichlorocyclohexadiene (IM15) can lead to chlorobenzene *via* HCl elimination, as described previously with an activation enthalpy of 115.6 kJ/mol and reaction enthalpy of -92.5 kJ/mol (figure 6(b)).

Figure 6. Formation of chlorobenzene from IM14. All values are given in kJ/mol and include zero-point energy and thermal contributions at 298 K.

Generally, the results from M06-2X/6-311+G(d,p) and G3MP2B3 calculations are similar except for the reactions 2IM1→IM2 (Scheme 1(a)), IM10+Cl→P1 (Figure 4), IM13→IM14 (Figure 5) and TS14 (Figure 6). In our M06-2x calculations, we have optimized geometries and calculated vibrational frequencies using M06-2X/6-311+G(d,p). However, our G3MP2B3 method optimized structural geometries, vibrational frequencies and zero point energies using B3LYP/6-31G(d). We found no significant variance in the optimized geometries, frequencies and zero point energies using the two different methods. The deviations between M06-2X and G3MP2B3 results could be attributable to an improved single point energy results of G3MP2B3 using MP2(FC)/G3MP2large.

Conclusions

The formation of chlorobenzenes *via* thermal decomposition of 1,3-D has been investigated with a combined experimental and computational approach. Yields of mono- and dichlorobenzenes are highest between 800 – 950 K, while higher temperatures can lead to tri- to hexa-chlorobenzenes at significantly lower yields. DFT and G3MP2B3 calculations have revealed that radical propagation plays a potentially major role in the formation of mono and dichlorobenzenes. Cyclization of 1,3-D derived molecular precursors is associated with prohibitively high kinetic barriers. On the other hand, H-abstraction at both allylic and vinylic sites in these precursors leads to kinetically more competitive reaction pathways.

Supporting Information

Cyclisation of perchlorohexatrienes to chlorobenzenes, optimised transition structures (TS) for cyclisation reactions, kinetic and thermodynamic benchmarks for computational method,

calculated and experimental reaction rate parameters, yield of volatile organic compounds (VOC) and the m/z ratio, chromatogram of product species at selected temperatures, and cartesian coordinates of the optimised TS. This material is available free of charge via the internet at <http://pubs.acs.org>.

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