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Quantum Chemical Molecular Dynamics

Simulations of 1,3-Dichloropropene Combustion

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Abstract

Oxidative decomposition of 1,3-dichloropropene was investigated using quantum chemical molecular dynamics (QM/MD) at 1,500 and 3,000 K. Thermal oxidation of 1,3-dichloropropene was initiated by (1) abstraction of allylic hydrogen by O₂ and (2) intra-annular C-Cl bond scission and elimination of allylic Cl. A kinetic analysis shows that (2) is the more dominant initiation pathway, in agreement with QM/MD results. These QM/MD simulations reveal new routes to the formation of major products (H₂O, CO, HCl, CO₂), which are propagated primarily by the chloroperoxy (ClO₂), OH and 1,3-dichloropropene derived radicals. In particular, intra-annular C-C/C-H bond dissociation reactions of intermediate aldehydes/ketones are shown to play a dominant role in the formation of CO and CO₂. Our simulations demonstrate that both combustion temperature and radical concentration can influence the product yield, however not the combustion mechanism.

Introduction

1,3-dichloropropene (1,3-D) is a pre-plant fumigant and nematicide that was first applied in agriculture in the 1950s, and is still used to the present day. The oxidative decomposition of chlorinated pesticides such as 1,3-D leads to highly toxic species, such as dioxins and analogous compounds.¹⁻¹² Pesticides such as 1,3-D are widely used in agriculture, and so are extremely susceptible to natural and anthropogenic combustion.^{4, 13-15} It is therefore critical to understand the chemical pathways that give rise to these toxic chemical products.

The oxidative decomposition of halogenated hydrocarbons been investigated on a number of occasions.^{1-5, 16-39} Recent studies suggest that the thermal decomposition of chlorinated straight-chain hydrocarbons proceeds *via* a unimolecular C-Cl bond scission at the allylic carbon, due to this C-Cl bond being weaker compared to other C-H bonds.^{2, 4} The primary chemical products (~90%) of 1,3-D thermolysis are CO, CO₂, H₂O and HCl.⁴ HCl formation can occur *via* H abstraction by Cl from the parent compound and its derived radicals,⁴⁰⁻⁴³ or *via* an intra-annular HCl elimination.^{1, 3, 30, 44-52} However, combustion of non-chlorinated analogous species show that O₂ abstraction of an allylic H, forming the HO₂ radical, is also an important initiation step.⁵³⁻⁵⁵ This HO₂ radical is converted to the relatively more stable OH radical by reactions with 1,3-D and allylic radicals, additionally forming aldehydes/ketones and aldehydic/ketonic radicals.⁵³⁻⁵⁵ The latter can undergo unimolecular or bimolecular C-C bond scissions to form CO or react with O₂ to form an alkylperoxy radical, which can readily react with alkenes to form alkoxides and CO₂.⁵³⁻⁵⁵ H₂O is formed mainly by abstraction or combination reactions of H with OH.^{20, 33, 56-58} Previously, molecular dynamics (MD) has proved to be an invaluable tool in revealing reaction initiation pathways in the combustion as methane⁵⁹⁻⁶⁰, n-dodecane⁶¹, phenol⁶²⁻⁶³ and benzene.⁶⁴ However, there have been no reactive MD simulations for chlorinated hydrocarbon combustion

reported to date, and so details of the initial stages of combustion of species such as 1,3-D remain largely unexplored.

Herein we report quantum chemical MD (QM/MD) simulations of 1,3-D oxidative thermal decomposition. These simulations show that thermolysis of 1,3-D is initiated *via* a number of key pathways, including allylic H/Cl abstraction from 1,3-D by O₂ and unimolecular C-Cl bond scission and/or elimination of allylic Cl from 1,3-D. QM/MD simulations, as well as quantum chemical kinetic parameters demonstrate that unimolecular C-Cl bond scission is the dominant initiation pathway. Our simulations also reveal new routes to the formation of major products (H₂O, CO, HCl, CO₂), with intra-annular C-C/C-H bond dissociation reactions of intermediate aldehydes/ketones playing an important role for CO and CO₂ formation. Our simulations demonstrate that both combustion temperature and radical concentration can influence the product yield, however not the combustion mechanism.

Computational Methods

Model Systems. We consider two different model systems in this work. The first consists of $11 \times$ 1,3-D and $76 \times$ O₂ molecules, while the second consists of $6 \times$ 1,3-D, $5 \times$ C₃H₄Cl (dechlorinated 1,3-D) radicals, $5 \times$ Cl radicals and $76 \times$ O₂ molecules (Figure 1). These two systems will be referred to as “oxidative” and “radical”, respectively. The “radical” system represents ~50% dechlorination of 1,3-D, and mimics radical initiation of the combustion process. This enables us to elucidate the effects of radical initiation on both the kinetics and reaction mechanism of 1,3-D oxidative decomposition. In both cases, a cubic supercell of dimension $48 \times 48 \times 48 \text{ \AA}^3$ was employed, yielding a density of 0.02 kg/dm^3 . All initial coordinates were generated using the PACKMOL program.⁶⁵

Figure 1. Oxidative and radical simulations following 20 ps equilibration at 298 K, and 100 ps simulation at 3,000 K. (a, b) oxidative system; (c, d) radical system. Cyan, green, red and white spheres represent C, Cl, O and H atoms, respectively.

QM/MD Simulations. Combustion of 1,3-D is investigated using classical MD, with inter-atomic potentials evaluated at each step “on-the-fly” using the 2nd order (self-consistent charge) density functional tight-binding (SCC-DFTB) method,⁶⁶ in conjunction with the halorg-0-1 parameter set.⁶⁷ For both oxidative and radical simulations, all initial structures were equilibrated at 298.15 K for 20 ps. QM/MD simulations were then performed at 1,500 and 3,000 K for a further 100 ps (this timescale is sufficient for complete consumption of 1,3-D in our most reactive simulation conditions). These two temperatures enable us to elucidate the effects of reaction temperature on the combustion mechanism. All MD simulations employed a time step of 1 fs, and were performed with *NVT* ensembles, where temperature was enforced via a Nosé-

Hoover chain thermostat⁶⁸⁻⁶⁹ (chain length = 3) coupled to the degrees of freedom of the system. All QM/MD simulations were performed using the DFTB+ code.⁷⁰

Reaction Enthalpy Calculations. In order to ensure our QM/MD simulations predict a reliable reaction mechanism for 1,3-D oxidative decomposition, SCC-DFTB/halorg-0-1 reaction enthalpies for key QM/MD reaction steps are compared against G3MP2B3⁷¹ results. This approach has been shown to provide accurate reaction and activation enthalpies for the combustion of chlorinated hydrocarbons.^{4, 34, 72} Such a comparison is necessary since the halorg parameters themselves were not explicitly designed for use in the present context. Kinetic parameters of key initiation reactions have also been calculated using G3MP2B3 reaction/activation enthalpies with the CHEMRATE program.⁷³ These parameters have been calculated over a temperature range of 300 – 3,000 K, and so are relevant to the simulations that we present in this work, and recent experimental investigations.⁴ Thermochemical corrections were obtained via the harmonic approximation at 298.15 K. All G3MPB3 calculations were performed using Gaussian09.⁷⁴

Results and Discussion

QM/MD Simulations of 1,3-Dichloropropene Combustion at 1,500 K. Chemical reactivity is minimal for the oxidative system at the lowest temperature considered here (1,500 K). Indeed, it a timescale of 100 ps is insufficient to model the entire combustion process under these conditions. Interestingly however, a single reaction was initiated in trajectory 4 within this timescale, the mechanism for which is shown in Figure 2.

Figure 2. Initiation of 1,3-D thermolysis in the oxidative QM/MD simulation at 1,500 K (trajectory 4), resulting in the formation of H₂O, CO, HCl and chloroethyne.

This reaction began with the abstraction of allylic H from 1,3-D by O₂, forming the 1,3-D derived radical intermediate and HO₂. Although this reaction is endothermic ($\Delta H(\text{G3MP2B3}) = 30.3 \text{ kJ/mol}$), the same initiation reaction mechanism has been observed for non-chlorinated analogues.^{54-55, 59} Kinetic parameters for this process for a temperature range of 300-3,000 K, provided in Table 1, are also consistent with experimental and theoretical results for the analogous H abstraction in propene ($A = 3.2 \times 10^{-12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; $E_a = 164 \text{ kJ/mol}$), between 600-1000 K^{58, 75}. 1,3-dichloropropene-1-peroxol is formed *via* radical recombination of the derived radical intermediate and HO₂. We note that unimolecular C-Cl bond scission at the allylic carbon atom is more kinetically favourable compared with allylic H abstraction, and this is consistent with observations made for many QM/MD trajectories calculated in this work. Analogous reactions with O, ClO or ClO₂ were never observed in our simulations, most likely due to their vanishingly low concentrations (particularly for ClO). Reaction between the 1,3-D derived radical and OH/O₂ was frequently observed however, and is discussed in greater detail below. Following the initial H abstraction, 3-chloro-2-propenal was then formed at 3.8 ps *via* the

simultaneous dehydroxylation and dechlorination of 1,3-dichloropropene-1-peroxol ($C_3H_3Cl_2OOH$), which is also endothermic ($\Delta H(G3MP2B3) = 186.4$ kJ/mol). The analogous reaction for propene, leading to the formation of OH and C_3H_6O has been observed previously.⁵⁵ Such reactions are significant for olefins, especially at temperatures < 800 K,⁵⁵ since they convert the relatively unreactive HO_2 radical into the more reactive OH. At 3.88 ps, the exothermic Cl abstraction from 3-chloro-2-propenal, forming the C_3H_2ClO radical and HCl, was observed ($\Delta H(G3MP2B3) = -52.6$ kJ/mol). At 4.25 ps this propenoyl radical underwent unimolecular dehydrogenation forming 3-chloropropa-1,2-dien-1-one, which in turn underwent C=C bond scission at 9.06 ps, forming CO ($\Delta H(G3MP2B3) = 394.8$ kJ/mol) and chloroethyne at 9.22 ps ($\Delta H(G3MP2B3) = -372.0$ kJ/mol) respectively.

Table 1. G3MP2B3 kinetic parameters of key initiation pathways during 1,3-D thermolysis, for temperatures between 300 – 3,000 K.

Reaction	A	n	E_a kJ/mol
2.72×10^{-13} ^a	0.0	127.4
1.05×10^{16} ^b	0.0	238.9
1.12×10^{-14} ^a	0.0	261.0
3.39×10^{-13} ^a	0.7	5.9

^a $cm^3/(s \text{ molecule})$. ^b s^{-1} .

Figure 3. (a) Major products (HCl , H_2O , CO , CO_2) and (b) prominent minor products/reactive intermediates observed during radical QM/MD simulations at 1,500 K. (c) Reaction pathway observed in trajectory 1. Molecular populations in (a) and (b) are averaged over 10 trajectories.

Figure 3 summarizes the molecular composition and initiation reaction schemes of the radical simulation at 1,500 K. Unsurprisingly, increasing the radical concentration at this temperature leads to much richer chemistry (compared to the oxidative simulations discussed above). HCl and CO are the most abundant major products, followed by H₂O and CO₂ (Figure 3(a)). Figure 3(b) shows that while the population of the 1,3-D derived radical (C₃H₄Cl) is depleted by around ~60 ps, other radical species, particularly Cl, OH and ClO₂ remain present throughout the simulation, highlighting their role as reaction initiators/propagators during the combustion process.

An example of 1,3-D derived radical consumption (observed in trajectory 1) is shown in Figure 3(c). At 0.27 ps, the derived radical reacts with ambient O₂ to yield 3-chloroprop-2-en-1-yl peroxy radical. This reaction is highly exothermic ($\Delta H(\text{G3MP2B3}) = -199.0 \text{ kJ/mol}$) and for a temperature range of 300 – 3,000 K G3MP2B3 calculations give A and E_a values of $4.29 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and 16.4 kJ/mol, respectively, showing that this is a kinetically favourable reaction. HCl is formed at 8.2 ps *via* Cl abstraction of allylic H to form the [(3-chloroprop-2-en-1-ylidene)oxo]- λ^1 -oxidanyl radical. The latter subsequently formed 3-chloroprop-2-enal *via* intra-annular O-O scission at 8.42 ps and also *via* O₂ abstraction of O to form O₃ at 33.66 ps. At 14.47 ps, the 3-chloropropenoyl radical was formed *via* abstraction of H from 3-chloroprop-2-enal. Further OH abstraction forms H₂O and 1-chloro-3-oxoprop-1-en-1-yl at 17.31 ps. The latter undergoes unimolecular C-C bond scission at 17.62 ps, forming chloroethyne and CO. The mechanism of chloroethyne formation here therefore varies slightly from that shown in Figure 2. A third route to chloroethyne, *via* C-C bond scission of 3-chloroprop-2-enal (54.380 ps) and H abstraction by Cl (54.41 ps) was also observed, which also resulted in CO formation.

QM/MD Simulations of 1,3-Dichloropropene Combustion at 3,000 K. The molecular composition and key reaction pathways observed in the oxidative simulations at 3,000 K are summarized in Figure 4.

The major initiation reactions observed were (1) intra-annular elimination of an allylic Cl from 1,3-D *via* unimolecular C-Cl scission (Figure 4(c)) and (2) abstraction of allylic Cl from 1,3-D by O₂ (Figure 4(d)). The G3MP2B3 kinetic parameters (Table 1) yield a rate constant of $k = 7.3 \times 10^{11} \text{ s}^{-1}$ for unimolecular C-Cl bond scission. For (2), G3MP2B3 shows that this reaction is also endothermic ($\Delta H = 296.8 \text{ kJ/mol}$), and the kinetic parameters in Table 1 give a rate constant $k = 3.2 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 3,000 K. Initiation *via* Cl abstraction by O₂ is therefore kinetically limited, and C-Cl bond scission is the more dominant of these initiation pathways at 3,000 K. This is consistent with QM/MD simulations at 3,000 K, which show C₃H₄Cl populations (which result from unimolecular C-Cl bond scission) increasing at a faster rate than C₃H₃Cl₂ populations (which result from H abstraction by O₂) and chloroperoxy radical, ClO₂ (which result from Cl abstraction by O₂), during the first 50 ps. In any case, populations of these radicals are quickly depleted due to their high chemical reactivity. Temperature is not expected to alter the dominant reaction initiation pathways; at 1,500 K for example, k for unimolecular C-Cl bond scission and Cl abstraction by O₂ are $5.2 \times 10^7 \text{ s}^{-1}$ and $9.2 \times 10^{-24} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively. The abstraction of allylic H from 1,3-D by O₂, forming HO₂, was also observed, but is not shown in Figure 4. G3MP2B3 kinetic parameters for this reaction (Table 1) yield a rate constant $k = 1.7 \times 10^{-14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 3,000 K, far lower than the rate of C-Cl bond scission (Table 1). This initiation reaction was only seldom observed in our QM/MD simulations, and led to no further reactions.

Figure 4. (a) Major products (HCl, H₂O, CO, CO₂) and (b) prominent minor products/reactive intermediates observed during oxidative QM/MD simulations at 3,000 K. (c) Observed reaction pathway following allylic C-Cl bond scission. (d) Observed reaction pathway following allylic Cl abstraction by O₂. Molecular populations in (a) and (b) are averaged over 10 trajectories. Mechanisms (c) and (d) were observed in trajectory 10.

The reaction sequence following unimolecular C-Cl bond scission in 1,3-D is shown in Figure 4(c). Chloroallene (C_3H_3Cl) was initially formed at 38.08 ps *via* Cl abstraction of the vinylic hydrogen. Chloroallenes have also been shown to be important intermediates in the formation of heavier chlorinated cyclic compounds *via* pericyclic self-recombination reactions.¹⁰ At 38.12 ps, chloroallene underwent unimolecular C-Cl bond scission to form the propargyl radical intermediate. Within a further 0.01 ps, this intermediate underwent self-abstraction of H to form HCl and the C_3H_2 diradical. The latter combined with O_2 to form C_3H_2OO at 38.39 ps. O-O bond cleavage in this intermediate leads to the formation of atomic oxygen and the C_3H_3O radical at 39.16 ps. Atomic oxygen combined with 1,3-D at 48.37 ps to form the 1,3-D derived and OH radicals. This process is barrierless and highly exothermic (ΔH (298.15 K) = -270 kJ/mol) due to the high reactivity of oxygen. G3MP2B3 kinetic parameters given in Table 1 yield a reaction rate constant of $k = 7.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 3,000 K. This rate constant indicates that this reaction is most likely diffusion limited. We note also that these kinetics are comparable to analogous reactions for propene⁷⁶ and ethane.^{20, 58} At 48.39 ps, OH substituted vinylic Cl on this 1,3-D derived radical, forming 1-chloro-3-hydroxyprop-2-enyl radical ($HO-C_3H_3Cl$), which then reacted with ambient O_2 to give HO_2 *via* H abstraction and 3-chloroprop-2-enal (49.17 ps). Similar reactions have been observed in oxidation of alkenes *via* O_2 abstractions of hydroxyl H from hydroxyalkenyl radicals to form acrolein.^{33, 53, 56} At 50.04 ps, 3-chloroprop-2-enal underwent intra-annular C-C scission to form the 2-chloroethenyl and formyl radicals. Formyl radicals are important precursors to CO formation in combustion of a number of hydrocarbons.⁵⁵ Indeed, at 50.53 ps, this formyl radical abstracted allylic Cl from 1,3-D, to yield the 1,3-D derived radical, HCl and CO. Further direct oxidation of CO (by atomic oxygen) gave CO_2 at 63.94 ps.

The reaction mechanism of 1,3-D thermolysis following Cl abstraction by O₂ is shown in Figure 4(d). In trajectory 10 this initiation step was observed at 63.46 ps, and formed the ClO₂ and 3-chloro-prop-2-enyl radicals. Almost immediately, interaction between the latter and ambient O₂ led to O-O bond cleavage and the 3-chloroprop-2-enyl oxidanyl radical (63.47 ps). Subsequent H abstraction from the latter species by atomic oxygen (63.5 ps) lead to the formation of the 2-chloroethenylidene diradical, formaldehyde and OH. Formaldehyde is a notable intermediate in many combustion reactions⁷⁷ and can lead to CO formation via dehydrogenation⁷⁸ (although this reaction was not observed in the QM/MD simulations presented in this work). At 63.61 ps, the 2-chloroethenylidene diradical underwent an internal rearrangement to form chloroethyne. G3MP2B3 calculations show that this reaction is exothermic ($\Delta H = -372.0$ kJ/mol, $\Delta H^\ddagger = 89.0$ kJ/mol), and give A and E_a values of 9.08×10^9 s⁻¹ and 70.6 kJ/mol, respectively, for a temperature range of 300-3,000 K, indicating that this rearrangement is kinetically labile. However, chloroethyne was not observed abundantly in these QM/MD simulations. This is because, despite the fact that rearrangement of 2-chloroethenylidene is labile and exothermic, the formation of the principal precursor (3-chloroprop-2-enyl oxidanyl radical) is highly endothermic ($\Delta H(\text{G3MP2B3}) = 255.8$ kJ/mol).

Figure 5 summarizes the molecular composition and initiation reaction schemes of the radical simulations at 3,000 K. Comparison of Figure 5 with Figures 3 and 4 shows that, somewhat unexpectedly, consumption of 1,3-D and O₂ is accelerated in these simulations, as is the production of HCl, H₂O, CO and CO₂. These simulation conditions are the only ones considered here that result in the 1,3-D feedstock being completely consumed within the first 100 ps of reaction. The 3,000 K radical simulations also result in a quicker depletion of ClO₂ and 1,3-D

derived radical intermediate populations, and a higher population of Cl and OH radicals through the course of the reaction.

Figure 5. (a) Major products (HCl, H₂O, CO, CO₂) and (b) prominent minor products/reactive intermediates observed during radical QM/MD simulations at 3,000 K. (c) Reaction pathway observed in trajectory 1. Molecular populations in (a) and (b) are averaged over 10 trajectories.

In general, the predominant initiation mechanisms and reaction pathways do not differ substantially from those observed in the oxidative QM/MD simulations at 3,000 K. For example, the reaction mechanism shown in Figure 5(c) features activation of 1,3-D *via* allylic Cl abstraction by O₂ to form the chloroperoxy and 3-chloro-prop-2-enyl radical intermediates. The latter species abstracted O from the peroxy group at 53.42 ps, forming 1,3-dichloroprop-2-

enyl oxidanyl radical and atomic oxygen. As observed in Figure 4(d), this species then lead to the formation of 2-chloroethenylidene diradical, formaldehyde and OH. As observed in the oxidative QM/MD simulations 2-chloroethenylidene diradical almost immediately rearranged to give chloroethyne.

The most notable difference between oxidative and radical QM/MD simulations at 3,000 K (true also at 1,500 K) is the higher product yield obtained in the latter. For example, in the radical simulations, CO yield is approximately twice that of the yield in the oxidative simulations, which is a consequence of the higher initial radical concentration in the simulation. This is also the case for CO₂ and H₂O, while the populations of HCl in the 3,000 oxidative and radical QM/MD simulations are approximately the same after 100 ps of simulation. Extended reaction mechanisms observed in these QM/MD simulations are presented in Figures S1 and S2 in Supporting Information.

Comparison of SCC-DFTB and G3MP2B3 Reaction Enthalpies. In order to ensure the reliability of our proposed QM/MD-based reaction mechanisms, we present a comparison of reaction enthalpies calculated using SCC-DFTB/halorg-0-1 and G3MP2B3 for several key reaction steps observed in our QM/MD simulations. This comparison is presented in Table 2.

Table 2 shows that SCC-DFTB and G3MP2B3 reaction enthalpies are in consistent qualitative agreement for key reaction steps in the thermolysis of 1,3-D. This means that the QM/MD simulations of 1,3-D oxidative decomposition presented here follow reliable thermodynamic pathways. The general level of quantitative agreement between SCC-DFTB and G3MP2B3 reaction enthalpies is also as expected.^{67, 79} Reaction enthalpy differences for reactions 2, 5, 6 and 7, for example, are below 50 kJ/mol. In some cases, close quantitative agreement is

Table 2. Comparison of SCC-DFTB/halorg-0-1 and G3MP2B3 reaction enthalpies (kJ/mol) for key reactions observed during QM/MD simulations of 1,3-D oxidative decomposition

Reaction		SCC-DFTB/halorg-0-1	G3MP2B3
1	$\text{OH} + \text{H} \rightarrow \text{H}_2\text{O}$	-661.9	-493.0
2		-100.1	-52.6
3		398.0	394.8
4		-363.4	-372.0
5		462.4	405.6
6		85.9	63.9
7		-61.8	-19.5
8		-358.8	-263.0

obtained; for reactions 3 and 4, the deviation between SCC-DFTB and G3MP2B3 reaction enthalpies is less than 10 kJ/mol. The close agreement here is most likely due to a fortuitous cancellation of errors in the SCC-DFTB results. The most notable quantitative deviations between SCC-DFTB and G3MP2B3 results here are observed for reaction 1 (H_2O formation) and reaction 8 (H abstraction from chloroethenyl radical by Cl (reaction 8), forming chloroethyne and HCl). SCC-DFTB reaction enthalpies for these reactions deviate from

G3MP2B3 values by *ca.* -170 and -100 kJ/mol, respectively. Both of these reactions involve the homolytic cleavage of H-X bonds (X = O, C, respectively). Such bond cleavage poses specific challenges to the SCC-DFTB method, due to delocalization errors arising from the onsite terms in the 2nd order term in the SCC-DFTB formalism (elucidated in detail elsewhere⁸⁰). We note that the difference observed for reaction 1, ~160 kJ/mol, is approximately the same as the overestimation of the bond dissociation energy for the closed shell singlet H₂ molecule.⁸⁰ We therefore do not expect SCC-DFTB to provide quantitative agreement with more reliable approaches, such as G3MP2B3, for reactions of this nature.

Conclusion

The thermal oxidation of 1,3-D has been investigated using QM/MD simulations and Gaussian-*n* thermochemical calculations. The thermal oxidation process was initiated by both abstraction of an allylic hydrogen by O₂, and the intra-annular C-Cl bond scission and elimination of an allylic Cl from 1,3-D. Kinetic analysis indicates that unimolecular C-Cl scission of 1,3-D is the more dominant initiation pathway, and this was consistent with our observations from QM/MD simulations. For the radical QM/MD simulations, an additional initiation reaction involving reaction of allylic radicals with O₂ was also observed. Thermochemical analysis shows that the radical-mediated initiation reactions are kinetically and thermodynamically competitive with other initiation reactions. The major products of 1,3-D combustion – CO, CO₂, H₂O and HCl – were observed in all 3,000 K simulations and the 1,500 K radical simulations. CO was formed mostly *via* the unimolecular C-C or C-H bond scissions of observed aldehydes, ketones and aldehydic/ketonic radicals. CO₂ was formed by direct oxidation

of CO. H₂O was formed mostly by either addition or abstraction reactions of OH with H while HCl was formed by Cl abstraction reactions of hydrogen atom. At 1,500 K, product yield was minimal for all MD simulations, indicating that both temperature and the radical concentration in the combustion environment have a marked effect on the yield of major and minor products. However, no dependence of the combustion reaction mechanism was observed either on reaction temperature, or radical concentration.

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Supporting Information

Extended reaction schemes for radical oxidation simulation at 3,000 K. This material is available free of charge via the Internet at <http://pubs.acs.org>

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