

UNIMOLECULAR DECOMPOSITION OF C_3Cl_6 : PATHWAYS FOR FORMATION OF CYLIC CHLORINATED COMPOUNDS

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1. Introduction

Great deal of research has shown that catalytic and non-catalytic thermal decomposition (pyrolysis and oxidation) of chlorinated alkanes and alkenes results in the formation of heavier cyclic chlorinated pollutants. Central to these processes is the Diels-Alder addition/cyclisation of small chlorinated carbon chains and the successive replacement of hydrogen atoms in cyclic compounds by chlorine atoms at high temperatures. Polychlorinated benzenes, dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) are formed during the heterogeneous reactions of propene on fly-ash in the presence of air and HCl between 623-673 K¹. Formation of PCDD/F from thermal oxidation of polychlorinated phenol has been demonstrated to proceed at a rate 100 times faster than the competing de novo pathway². High temperature pyrolysis of 1,3-hexachlorobutadiene concludes in the production of hexachlorobenzene (C_6Cl_6) and other highly chlorinated cyclic hydrocarbons³. Along the same line of enquiry, experimental results have explained that unsaturated aliphatic hydrocarbons such as acetylene are readily converted to hexachlorobenzene, hexachlorobutadiene and other heavier perchlorinated species in the presence of cupric oxide and HCl under post combustion conditions⁴.

Taylor et al. observed the pyrolysis of hexachloropropene to occur readily, even at temperatures as low as 700 K to yield CCl_4 , C_2Cl_4 , C_2Cl_6 and C_3Cl_4 (tetrachloroallene). At higher temperatures (up to 1223 K), distinct molecular growth was observed with reaction products including C_4Cl_6 (1,3-hexachlorobutadiene), C_6Cl_6 (hexachlorobenzene), C_6Cl_8 (1,3,5-octachlorohexatriene), C_8Cl_8 (octachlorostyrene), possible other isomers of C_6Cl_8 , C_8Cl_8 and four isomers of $C_{12}Cl_8$. Cl displacement of CCl_3 radicals was observed to be the overriding origination pathway for conversion of C_3Cl_6 into C_2Cl_4 , CCl_4 and C_2Cl_6 . At higher temperatures, C_3Cl_3 recombination accounted for about 80 % of experimental yields with C_3Cl_5 recombination responsible for formation of the remainder⁵. In the present study, we report the reaction and activation enthalpies for reactions involved in the pyrolytic decomposition of C_3Cl_6 to synthesise C_6Cl_6 . Our results will help in providing an insightful understanding of one of the major routes to the formation of chlorinated cyclic persistent organic pollutant (POP) species from the combustion of hydrocarbon precursors. Thermochemical and kinetic parameters presented herein will be useful in building a robust kinetic model that could satisfactorily describe formation of cyclic chlorinated compounds from the degradation of small aliphatic moieties.

2. Methods

All structural and energy calculations are performed using the Gaussian suite of programs⁶. Calculations are carried out at the second Møller–Plesset perturbation theory (MP2)⁷ with the basis set of 6-31+G(d,p) and the composite chemistry model of G3MP2B3⁸. The intrinsic reaction coordinate (IRC) calculations serve to link all transition structures with their related reactants and products. Reaction rate parameters of key reactions are obtained with the aid of the ChemRate code⁹.

3. Results and discussion

3.1 Initial decomposition of C_3Cl_6

The potential energy surface (PES) mapped out in Fig. 1 indicates that the initial decomposition of C_3Cl_6 produces three distinct C_3Cl_5 radicals. C-Cl fission from the two vinylic sites is found to be endoergic by 92.8 kcal/mol and 91.8 kcal/mol and results in the formation of radicals CCl_2CCCl_3 (M1) and $CCICCCl_3$ (M2), respectively. Fission of one of the three allylic C-Cl bonds and the formation of allylic radical of $Cl_2CCCICCl_2$ (M3) represents the most favourable pathway in the unimolecular decomposition of C_3Cl_6 with an endothermicity amounting to 61.4 kcal/mol. In view of the noticeable difference in reaction endothermicity for the formation of M3 radical in reference to M1 and M2 radicals, we conclude that fission of allylic C-Cl bond dominates the initial decomposition of C_3Cl_6 . As shown in Fig. 1, the fate of M3 radical is either to produce

C_3Cl_4 (M4, tetrachloroallene) molecule through a barrierless reaction with a sizable endothermicity of 71.3 kcal/mol or to dissociate into C_2Cl_2 and CCl_3 radical via the transition structure TS1 through an activation enthalpy of 54.6 kcal/mol. In view of the energetics for the PES shown in Fig. 1, unimolecular decomposition of C_3Cl_6 is predicted to proceed mainly to form C_2Cl_2 and CCl_3 species, consistently with the results of experiments of Taylor et al.⁵ who observed the formation of C_2Cl_6 , CCl_4 and tetrachloroallene (M4). In particular, in the experiments, C_3Cl_4 mass spectrum indicated tetrachloroallene, as the isomer formed rather than tetrachloropropyne; the latter would involve the loss of a CCl_3 fragment. Dichloroacetylene was only detected in experiments conducted at high temperature above 1100 K. As we demonstrate in subsequent discussion, M3 and C_2Cl_2 represent major building blocks for the formation of cyclic chlorinated compounds, including C_6Cl_6 , in an analogy to the well-established Diels-Alder mechanism for the growth of polyaromatic hydrocarbons. In support of our scheme, Tsang et al.¹⁰ found the initial pyrolysis of propene (C_3H_6) to proceed in an analogous mechanism; i.e., decomposition into C_3H_5 and H radical as is also evident from the results of a kinetic sensitivity analysis of Davis and Law¹¹.

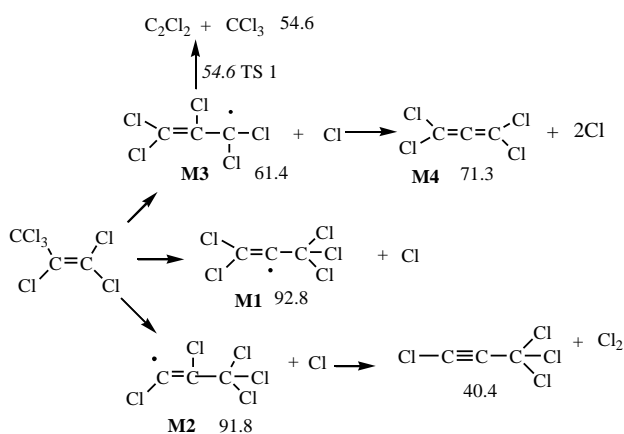


Fig. 1. Potential energy surface for the initial decomposition of C_3Cl_6 . Values (in kcal/mol) are calculated at 298.15 K at the G3MP2B3 level of theory.

3.2. Reaction of Cl atoms with C_3Cl_6

Reaction of Cl atom with the parent C_3Cl_6 molecule proceeds via addition and abstraction pathways. Figure 2 shows that Cl atom preferentially adds at the $=ClC-$ group to form M6 moiety (C_3Cl_7) through a barrierless reaction that is exothermic by 17.2 kcal/mol. Addition at the terminal $Cl_2C=$ group is predicted to be exothermic by 8.0 kcal/mol and results in the formation of M5 adduct. M6 dissociates to CCl_3 and C_2Cl_2 through an activation enthalpy that amounts to 32.1 kcal/mol (TS3). Alternatively, Cl radical abstracts Cl atom from the $Cl_2C=$ group through a modest reaction barrier of 11.7 kcal/mol (TS2). Comparatively, it has been shown in literature studies that Cl atom abstracts Cl atom from Cl_3C- group through an activation energy of 17.9 kcal/mol¹². Similarly, in the pyrolysis of CCl_4 and C_2Cl_6 , Cl radical was also shown to abstract Cl atom from Cl_3C- group through an activation energy of 17.3 kcal/mol¹³. Accordingly, abstraction channel is predicted to be of less importance and the overall reaction of Cl atom is found to provide a facile route for the formation of CCl_3 and C_2Cl_2 moieties; i.e., major intermediates in the growth of chlorinated cyclic compounds.

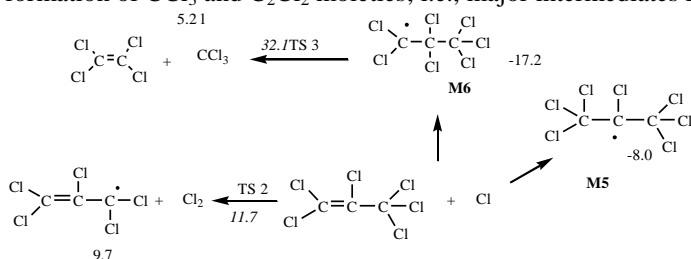


Fig. 2. PES for C_3Cl_6 reaction with Cl atoms. Values (in kcal/mol) are calculated at 298.15 K at the G3MP2B3 level of theory.

3.3. Pathways for the formation of C_6Cl_6

Figure 3 shows the pathways for the formation of C_6Cl_6 from C_2Cl_3 , C_2Cl_2 and C_2Cl_4 . Addition of a C_2Cl_2 molecule to the radical site of C_2Cl_3 requires a trivial barrier of 1.3 kcal/mol (TS4) and results in the formation

of M7 moiety with an exothermicity of -50.4 kcal/mol. Further reaction of C₄Cl₅ with C₂Cl₂, to yield a linear C₆Cl₇ (M8) radical, was found to be exothermic by -49.3 kcal/mol via a transition state structure (TS5) through an activation enthalpy of 2.3 kcal/mol. M8 undergoes cyclisation to form C₆Cl₇ (M9) radical via a reaction enthalpy of 5.4 kcal/mol. Cyclic C₆Cl₇ (M9) is predicted to be more stable than its linear counterpart (M8) by 54.5 kcal/mol. Fission of one of the out-of-plane C-Cl bond affords C₆Cl₆ without encountering a saddle point, resulting in the reaction that is endoergic by 8.1 kcal/mol. This is contrary to the experimental measurement whereby the addition of C₂Cl₂ molecule to the C₂Cl₃ radical to form M7 moiety required a barrier of 7 kcal/mol¹⁴ and the reaction of C₄Cl₅ with C₂Cl₂ to yield linear C₆Cl₇ required a barrier of 0.5 kcal/mol¹⁴. In addition, the decomposition of linear C₆Cl₇ to cyclic C₆Cl₆ was observed to be barrierless in the experiments¹⁴. Figure 3b depicts the initial reaction of C₂Cl₃ with C₂Cl₄. C₂Cl₄ molecule adds at the radical site of C₂Cl₃ through a low activation enthalpy of 3.2 kcal/mol. The product of the latter reaction (M10) resides in a significant well-depth of 38.0 kcal/mol. The fate of M10 is either to undergo further analogous addition/cyclisation or Cl abstraction induced by other species including Cl atoms and the parent C₃Cl₆ molecule.

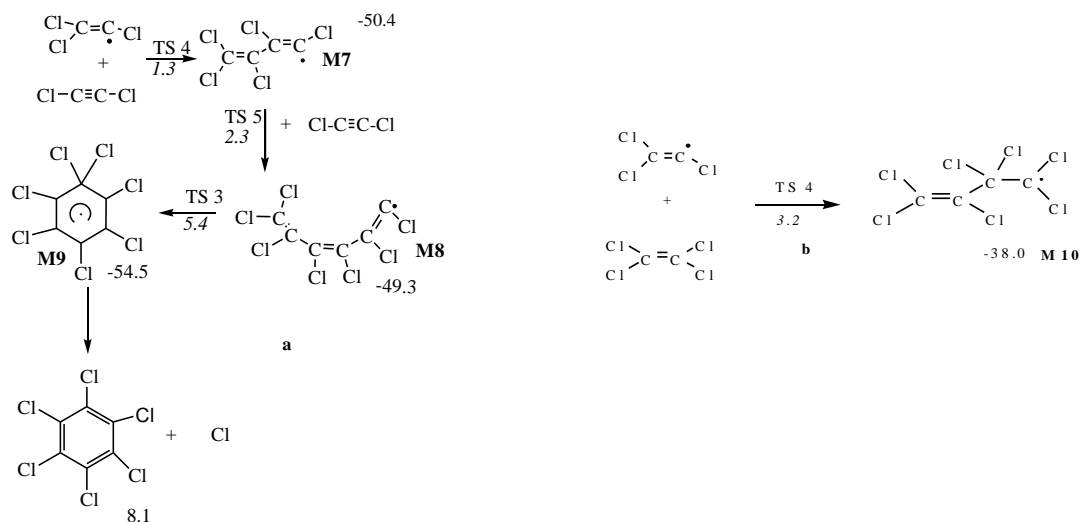


Fig. 3. PES for C₂Cl₃ reactions with (a) C₂Cl₂ and (b) C₂Cl₄. Values (in kcal/mol) are calculated at 298.15 K at the MP2/6-31+G(d,p) level of theory.

In view of the expected formation of C₃Cl₅ in the early stages of the pyrolysis of C₃Cl₆, a potent pathway towards the formation of cyclic chlorinated compounds is expected to proceed through self-reaction of C₃Cl₅ radicals. According to their kinetic model, Dellinger's group⁵ postulated this route to be important at temperatures higher than 837 K. Figure 4 illustrates an enthalpic trend for this process.

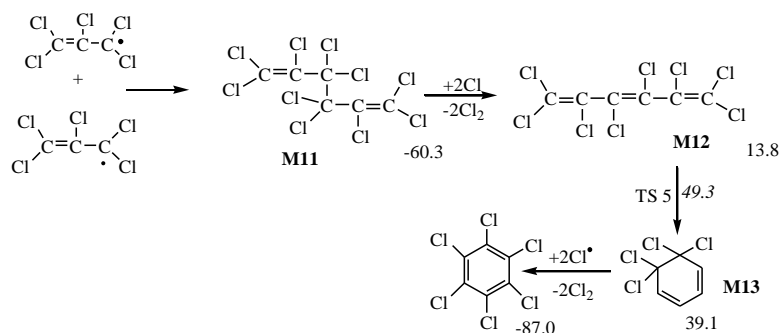


Fig. 4. PES for C₃Cl₅ recombination reactions. Values (in kcal/mol) are calculated at 298.15 K at the MP2/6-31+G(d,p) level of theory.

Self-recombination of C₃Cl₅ radicals affording 1,5-decachlorohexadiene C₆Cl₁₀ (M11) was discovered to be barrierless and exothermic (-60.3 kcal/mol). As shown in Fig. 4, M11 could convert to M12 (C₆Cl₈) moiety through Cl abstraction reactions. Contrary to C₆Cl₇, we identified the cyclisation of C₆Cl₈ to be endothermic by 39.1 kcal/mol, demanding a significant activation enthalpy of 49.3 kcal/mol. Comparing the reaction enthalpies

for the hydrogenated species, the pyrolysis of acetylene-vinylacetylene mixtures between 673-773 K yields benzene as the sole product via an activation energy of 30.0 kcal/mol¹⁵. Likewise, pyrolysis of 1,4-cyclohexadiene at 603-663 K has been observed to yield benzene by H₂ abstraction reactions with an activation energy of 47.7 kcal/mol¹⁶. C₆H₈ decomposition to C₆H₆ has also been studied in another set of experiments, yielding an activation energy of 42.8 kcal/mol¹⁷.

3.4. Reaction rate constants

Table 1 presents a summary of the rate parameters calculated for prominent reactions. At a temperature of 1000 K, the rate constant for the formation reaction of C₄Cl₅ amounts to 1.74×10⁻¹³ s⁻¹. Comparatively, the corresponding value for C₂H₂+C₂H₃→ C₄H₅¹⁸ of 1.45×10⁻⁸ s⁻¹ is much higher at the same temperature. However, we find *k* for the formation reaction of C₆Cl₇ (5.54×10⁻¹⁴ s⁻¹) to be significantly higher than that for C₆H₇ formation¹⁹ (3.33×10⁻¹⁷ s⁻¹).

Table 1: Arrhenius reaction rate parameters; $k = A T^\alpha \exp(-E_a/(R T))$

	Reaction	A ^a	α	E _a (kcal/mol)
1	C ₃ Cl ₅ →C ₂ Cl ₂ +CCl ₃	9.12×10 ¹¹	0.03	58.8
2	C ₃ Cl ₇ →C ₂ Cl ₄ +CCl ₃	1.12×10 ¹³	0.08	32.8
3	Cl+C ₃ Cl ₆ →C ₃ Cl ₅ +Cl ₂	5.45×10 ⁻¹⁴	1.59	12.0
4	C ₂ Cl ₂ +C ₂ Cl ₃ →C ₄ Cl ₅	6.31×10 ⁻²¹	2.55	0.96
5	C ₄ Cl ₅ +C ₂ Cl ₂ →C ₆ Cl ₇	8.31×10 ⁻²²	2.67	0.85
6	C ₆ Cl ₇ →C ₆ Cl ₆ +Cl	1.66×10 ¹¹	0.12	5.9

^a Units are s⁻¹ for first order reactions and cm³/(s molecule) for the second order reaction;

In a nutshell, fission of one of the three allylic C-Cl bonds and the formation of alkylic radical of Cl₂CCCICCl₂ (M3) represents the most favourable pathway in the unimolecular decomposition of C₃Cl₆. In addition, decomposition of linear C₆Cl₇ to cyclic C₆Cl₆ was observed to be barrierless in the experiment but we have found this pathway to proceed via a modest barrier of 5.4 kcal/mol.

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