

Pyrolysis of dieldrin and formation of toxic products. II. Reaction mechanism.

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Abstract

The mechanism of pyrolysis of dieldrin, a now-banned member of the cyclodiene group of pesticides, has been studied by quantum chemical calculation. The pyrolysis is initiated by retro Diels-Alder dissociation into hexachlorocyclopentadiene and norbornadiene oxide. At low temperatures (623-800 K) intramolecular processes lead to benzene, CO and H₂ as major products. Above ~800 K hexachlorocyclopentadiene undergoes rapid Cl bond fission and Cl atoms abstract H atoms from dieldrin forming HCl and lead to four different types of dieldrin radicals, one of which undergoes a complex series of intramolecular rearrangements and fissions, producing pentachlorostyrene, ketene, acetylene and Cl atom as products. These products accord with results of previous experimental pyrolysis experiments conducted on dieldrin.

1 Introduction

Cyclodienes are a well-known group of pesticides which are produced by the Diels-Alder condensation reaction between hexachlorocyclopentadiene (HCCP) and a substrate [1]. This group includes aldrin, dieldrin and endosulfan. Although the first two members were banned several years ago, and endosulfan is being phased out, large stockpiles, especially of endosulfan, are still in existence as well as large areas of contaminated vegetation and soils [2]. Accidental combustion of cyclodienes through wildfire or fires in stockpiles can produce significant amounts of highly toxic substances. There have been few detailed studies of toxic products of combustion of cyclodienes; one notable exception is the study by Chopra et al [3] in 1978 in which a large number of chlorinated benzenes and other aromatics was identified in the pyrolysis of endosulfan at 1173 K. Nevertheless, until our recent study of oxidative decomposition of endosulfan [4] there had been no reports of the emission of the highly toxic polychlorinated dibenzodioxins and dibenzofurans (PCDD/F) from combustion of cyclodienes. Our present experimental paper on pyrolysis of dieldrin [5] reports on the production of several toxic PCDD/F precursors. A better understanding of the mechanism of formation of toxic products, especially dioxins and their precursors is essential for determination of safe strategies for destruction of stockpiles of cyclodienes.

Our experimental study [5] of pyrolysis of dieldrin revealed the formation of several chlorinated aromatic toxic precursors of PCDD/F. This study was carried out in a silica flow reactor between 623 and 923 K and at a residence time of 5.0 s. Two

distinct temperature regions and sets of major products were observed – a low temperature region from 623 K to about 800 K and a high temperature region from about 800 K to 923 K. Major products at low temperatures comprised benzene, CO, HCCP and traces of octachloronaphthalene. At high temperatures, pentachlorostyrene (predominantly), hexachlorostyrene (lesser amounts), acetylene, CO and HCl were detected.

In order to unravel the complex chemistry involved in both low and high temperature regions, we have used quantum chemical calculation to identify major reaction pathways, intermediates and final products. We are aided in our pathways identification by a knowledge of the rates and mechanism of decomposition of HCCP from our previous study [6].

2 Computational Methodology

The Gaussian 09 suite of programs [7] was used for all quantum chemical computations. Optimization of species geometry was performed using the density functional M06-2X and the basis set 6-31+G(d,p). Improved energies were calculated at the M06-2X/GTLarge//M06-2X/6-31+G(d,p) level of theory. Transition states (TS) have been identified for each reaction step and the initial and final states linked by these TSs have been validated by IRC calculation [7].

3 Results and discussion

3.1 Low temperature pyrolysis mechanism

From our earlier studies [5,8], we have found that pyrolysis is initiated by retro Diels-Alder decomposition into HCCP and a substrate. In the case of dieldrin, the substrate is norbornadiene oxide (see Fig. 1a). The activation energy for the decomposition was found to be 228 kJ mol⁻¹, somewhat higher than the 212 kJ mol⁻¹ activation energy calculated for endosulfan. Hence dieldrin decomposition is predicted to commence at slightly higher temperatures than endosulfan in agreement with experiment [5,8].

As HCCP does not undergo significant Cl bond fission until a temperature of about 800 K is attained [6], the low temperature region is dominated by intramolecular reactions involving norbornadiene oxide (see Fig. 1b). This oxide first undergoes a concerted rearrangement to form a bicyclic aldehyde. This rearrangement, although not studied in the gas phase has been carried out experimentally in acid-catalysed liquid phase [9]. A facile rearrangement then takes place to form cyclohexa-2,4-diene aldehyde. Next, a hydrogen transfer to the ring leads to the elimination of CO and formation of 1,4-cyclohexadiene. 1,4-elimination of H₂ finally produces benzene.

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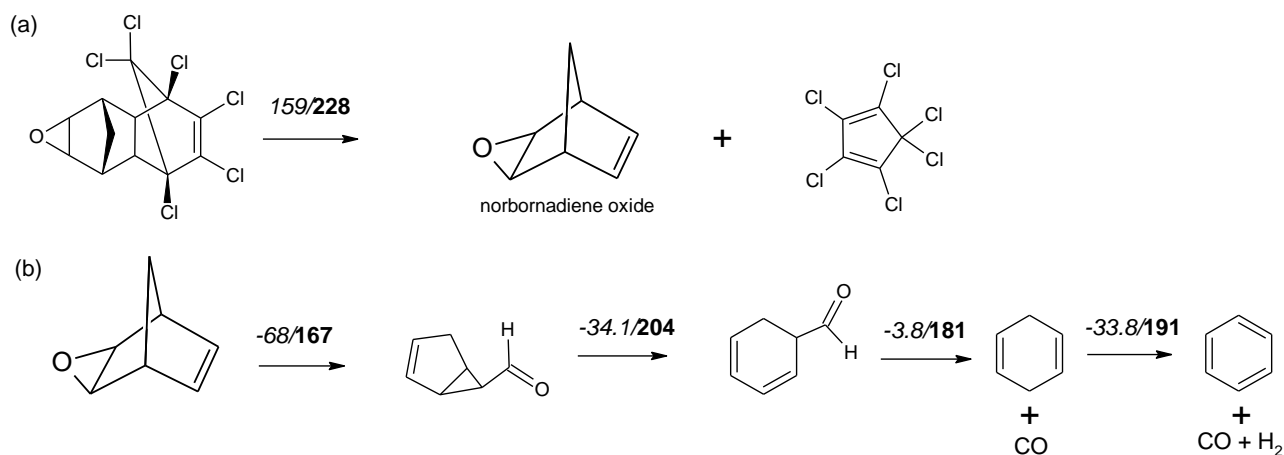


Figure 1 (a): Initial decomposition of dieldrin into norbornadiene oxide and hexachlorocyclopentadiene. (b): Low temperature decomposition mechanism of norbornadiene oxide. Numbers in italics are reaction energies; in bold, barrier heights. Both in kJ mol⁻¹ at 0 K.

After the initial barrier to formation of the bicyclic aldehyde is surmounted, the reaction to the final products of benzene, CO and H₂ should be facile and take place via chemical activation.

It should be pointed out that the retro Diels-Alder decomposition is reversible and equilibration will take place, such that the overall decomposition of dieldrin in the low temperature region will be slow. Between 673 and 773 K, the standard Gibbs free energy, $\Delta_r G^\circ_{c,298}$, ranges from 92.63 to 80.50 kJ mol⁻¹. It is only at temperatures where significant concentrations of Cl atoms become available from HCCP bond fission that dieldrin decomposition becomes accelerated.

3.2 High temperature pyrolysis mechanism

From our previous study [6] the rate constant for Cl fission from HCCP was found to be $k = 1.45 \times 10^{15} \exp(-222 \pm 9 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$. Thus, in our reactor [5], at 5 s residence time, Cl fission in HCCP becomes very rapid at temperatures above about 800 K. As a consequence, Cl atoms will attack residual dieldrin, abstracting an H atom to form HCl and a dieldrin radical.

There are, in fact, four different dieldrin radicals which may be produced by Cl atom abstraction. These are sketched in Fig. 2.

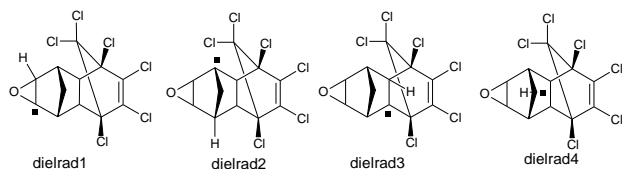


Figure 2: The four dieldrin radicals arising from H abstraction by Cl atom.

Formation of these radicals is facile with abstraction reaction energies between -18 and 22 kJ mol⁻¹ (at 0 K) with very small or zero barriers.

The pyrolysis mechanism has been studied by investigating the subsequent decomposition reactions of each of these four radicals. In general, secondary decomposition of a radical takes place by rupture of a so-called β -bond, i.e., a bond adjacent to the α -bond on which the radical site is located. The new radical formed by the fission is also subjected to β -bond fission and the

process continued until final products are produced or, in many cases, an intractable intermediate with no readily ruptured bonds is produced. Such a structure is considered to be a “dead end” and hence, an invalid reaction pathway.

It was found that just one of the four radicals underwent decomposition reaction resulting in final products. This was the radical labelled in Fig. 2 as dielrad1. The mechanism derived by quantum chemical calculation therefore commences with dielrad1 and is shown schematically in Fig. 3. In this figure Cl atoms are shown in green, O in red, C in grey and H in white.

Decomposition of dielrad1 commences with β -bond fission which converts the epoxy (-O-) moiety into a carbonyl (C=O) group which leads to facile elimination of the oxygen atom. This is not possible with the other three radicals, and is probably the reason why dielrad1 undergoes a complete passage to the final observed products. Next an H atom transfer from the bridging methylene (-CH₂-) group to the carbon atom adjacent to the carbonyl group precedes a C-C bond fission which then enables cleavage of the bond releasing ketene (CH₂=C=O). After a further C-C fission, a structure comprising a cyclopentadienyl radical attached to a pentachlorocyclopentadienyl radical results. Ring opening in the latter then takes place resulting in a cyclopentadiene with a chlorinated open chain radical attached. Direct opening of the cyclopentadiene ring has too large a barrier but after an H transfer this ring opens with a barrier of 229 kJ mol⁻¹, the largest barrier in the entire mechanism. A further H transfer to the allyl carbon (=C=) prepares the way for fission of acetylene to take place. Next, a facile rotation of the remaining moiety places the terminal vinyl radical conveniently to undergo six-membered ring closure with a very modest barrier. Finally the extremely weakly bonded Cl atom in the trichlorocyclohexadienyl moiety easily fissions to produce the final product, the major observed species, pentachlorostyrene.

It should be pointed out that ketene, predicted by this mechanism, was not observed experimentally amongst the products. This is because ketene is a highly reactive species and decomposes rapidly on most surfaces. Our silica flow reactor with its relatively long residence time would make detection of ketene unlikely. Its initial products of decomposition are CO and the methylene biradical (:CH₂). The latter rapidly forms

ethylene and acetylene, both of which are observed.

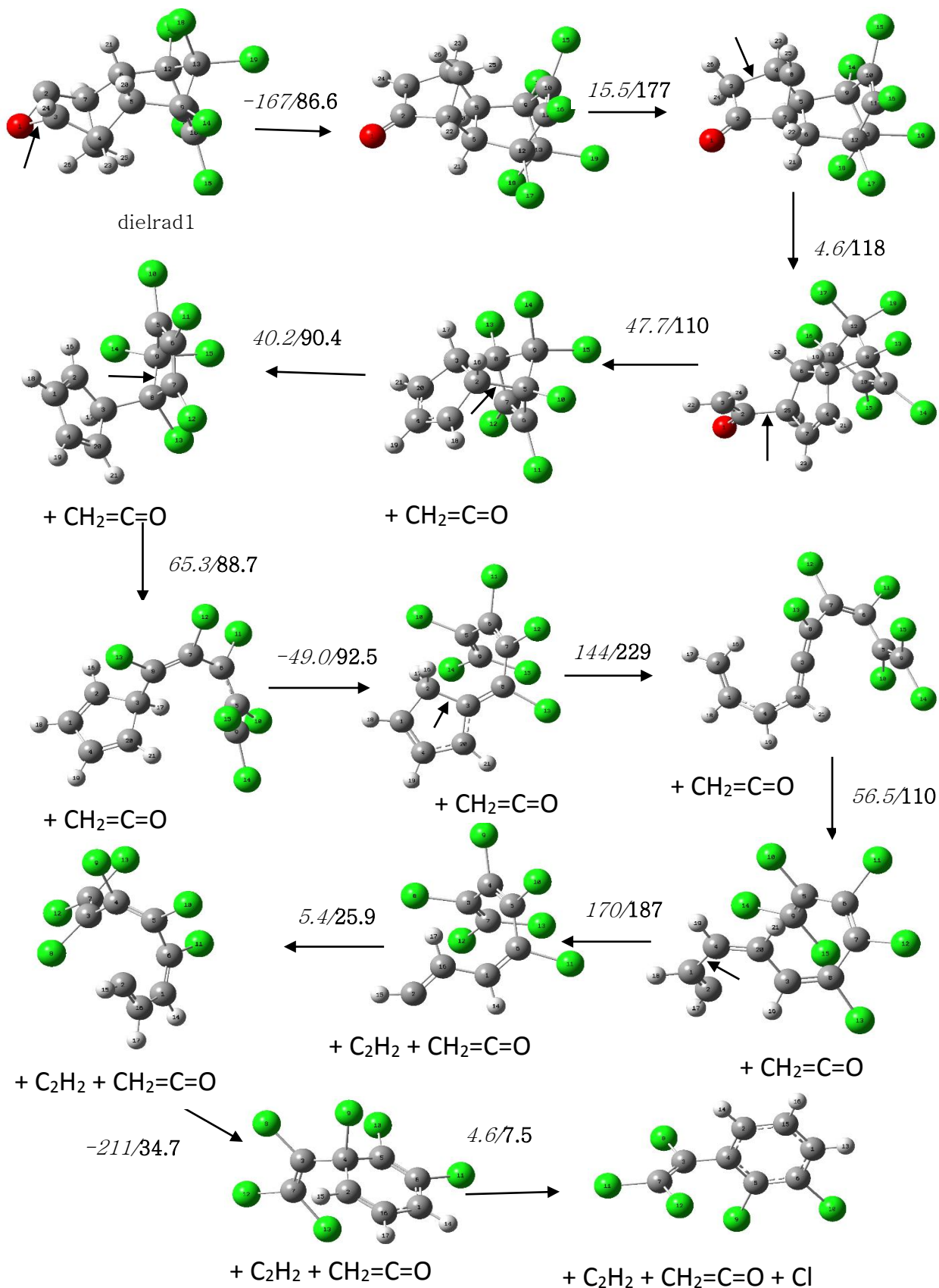


Figure 3: Mechanism of decomposition of dielrad1. Figures in italics: Reaction energies. In bold: Barrier heights both at 0 K. Arrows pointing to bonds represent sites of β -bond fissions.

Hexachlorostyrene is also observed experimentally at high temperatures. This can arise through the propensity of Cl atom to add to ring carbon atoms and displace H atoms. Experimental yields of hexachlorostyrene are greatest at temperatures above which hexachlorocyclopentadiene has completely decomposed. Traces of octachloronaphthalene are also observed in the high temperature region. In our previous study of pyrolysis of HCCP we identified the mechanism of formation of octachloronaphthalene as arising from the recombination of two pentachlorocyclopentadienyl radicals resulting from fission of a Cl atom.

Octachloronaphthalene is an acknowledged persistent toxic industrial contaminant [10]. The polychlorostyrenes, though not industrial products, arise as byproducts of other chlorinated substances, especially from incineration, and are bioaccumulative and potential endocrine disruptors [11].

In addition to its uses in unravelling the complex pathways of thermal decomposition of dieldrin and similar cyclodienes, quantum chemical calculation of the thermodynamic functions of transition states, reactants and products should enable future development of detailed reaction kinetic schemes. Detailed kinetic modelling should be useful in determining combustion conditions which minimize the emissions of toxic products and precursors of PCDD/F to enable safe strategies to be developed for destruction of unwanted pesticides.

4 Conclusions

Thermal decomposition of dieldrin has been shown by quantum chemical computation to be initiated by retro Diels-Alder decomposition into hexachlorocyclopentadiene and norbornadiene oxide. As this is a reversible reaction, equilibration will take place at temperatures below which hexachlorocyclopentadiene can fission a chlorine atom. This leads to a low temperature mechanism in which norbornadiene oxide decomposes by intramolecular rearrangement and loss of CO. The other major products under these conditions are benzene and molecular hydrogen. Once temperatures are attained whereby hexachlorocyclopentadiene rapidly fissions Cl atoms (around 800 K in a flow reactor of 5 s residence time), a high temperature free radical mechanism takes over in which Cl atoms abstract an H atom from dieldrin, forming HCl which becomes a major product. Of four possible dieldrin radicals, we find that just one of these, viz., dielrad1, can undergo a sequence of reactions of modest energy barriers to lead to the major observed high temperature products pentachlorostyrene and acetylene. Ketene was also predicted to be a major product at high temperatures but was not observed experimentally because of its considerable reactivity. Rather, its products of decomposition, CO, acetylene and ethylene, are observed.

5 Acknowledgment

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References

- [1] G. Matolcsy, M. Nadasy, V. Andriska, *Pesticide Chemistry*, Elsevier: Amsterdam, The Netherlands, 1988.
- [2] X. Wang, K. Kennedy, J. Powell, M. Keywood, P. Thai, P.

Bridgen, S. Broomhall, C. Paxman, F.K. Waniae, J.F. Muellera, *Environ. Sci –Processes & Impacts*, 17 (2015) 525-532.

[3] N. M. Chopra, B. S Campbell, J. C.Hurley, J. Agric. Food Chem. 26 (1978) 255-258.

[4] N.K. Dharmarathne, J.C. Mackie, E.M. Kennedy, M. Stockenhuber, *Environmental Science & Technology*, 50 (2016) 10106-10113.

[5] N.K. Dharmarathne, J.C. Mackie, E.M. Kennedy, M. Stockenhuber, submitted to 11th Asia-Pacific Conference on Combustion, The University of Sydney, NSW, Australia, 10th-14th December, 2017.

[6] N.K. Dharmarathne, J.C. Mackie, E.M. Kennedy, M. Stockenhuber, *J. Phys. Chem. A*. 121 (2017) 5871-5883.

[7] M. J. Frisch, G. W. Trucks, H. B. Schlegel et al, *Gaussian 09*, Revision D.01, Gaussian, Inc., Wallingford CT, 2013.

[8] N.K. Dharmarathne, J.C. Mackie, E.M. Kennedy, M. Stockenhuber, *Proceedings of the Combustion Institute*, 36 (2017) 1119-1127.

[9] R. Grigg, D. Shelton, *Chem. Communications* (1971) 1247-1248.

[10] H. Park, J.-H. Kang, S.-Y. Baek, Y.-S. Chang, *Environmental Pollution*, 158 (2010) 1420-1427.

[11] D. Carrizo, J. O. Grimalt, *J. Chromatography A* 1216 (30) (2009) 5723-5729.