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Theoretical degradation pathway analysis of hexachlorobenzene and 2,3,4-trichlorinated biphenyl by DFT

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ABSTRACT

This study calculated the atomic charge of carbon atoms combined with chlorine targeting hexachlorobenzene and 2,3,4-trichlorinated biphenyl, types of persistent organic pollutants. The comparison of the calculated atomic charge to the literature results showed that chlorine is dissociated first under the low atomic charge of carbon. Such a result agrees in principle with the literature results. Furthermore, since composites whose molecular shape is symmetrical have the same atomic charge, it is predicted that the dechlorination reaction will occur regardless of the location. Thus, it was possible to predict at which location of the carbon the dechlorination reaction would occur by calculating the atomic charge of the carbon atoms based on the density functional theory.

Keywords: Atomic charge distribution; Prediction of reaction site; CHelpG; DFT; Dechlorination pathway; Chlorinated compounds

1. Introduction

The Stockholm treaty, which includes the global restriction on the use and the appropriate management and disposal of persistent organic pollutants (POPs), was adopted in 1998 [1]. Required by the treaty is the phased prohibition of the manufacturing and usage of ten agricultural chemicals or industrial materials, including hexachlorobenzene (HCB). Also stipulated in the treaty is the establishment of a national emissions reduction plan of four materials, such as polychlorinated biphenyls (PCBs), which are by-products in various industrial activities. POPs are harmful materials that do not naturally decompose and accumulate in the body of plants and animals, disturbing the immune system and damaging the central nervous system. Most of them are produced in the industrial production process and low-temperature incineration process of waste [2,3]. Currently, various processes for organic chlorinated agricultural chemicals, including POPs, and waste are being conducted. Mechnochemical [4] and GeoMelt® [5] are discussed as some of the processing methods for stock files, and various tests are being carried out for commercialization. Moreover, the use of ionizing radiation [6], radical [7], ozone [8], or ultraviolet (UV) [9] have all been considered for processing relatively low-level pollution.

It is essential to determine not only the degradation ratio of the material itself but the byproducts from such a process in degrading and processing harmful substances like HCB and 2,3,4-trichlorinated biphenyl (2,3,4-TrCBi). It is generally predicted that there will be various types of degradation products from chemical degradation processes, and it is assumed that the main degradation product tends to have certain tendencies. By identifying such tendencies, it is believed it will then become possible to predict the degradation products. There have been reports on the theoretical analysis of the reaction mechanism based on the density functional theory (DFT). Xio et al. [10] evaluated the effect of the water chemistry factor on the photolysis of bisphenol A using the DFT, and Pu et al. [11] conducted a theoretical analysis of the photolysis degradation pathway of

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sulfonamide. Takeuchi et al. [12] proposed the dechlorination pathway by the electron beam irradiation of pentachlorobenzene in the calculation using B3LYP, cc-pVTZ ground state, Akai et al. [13] evaluated the photodegradation mechanism of mono ~ trichlorophenol under low temperatures at 15 K by the DFT [13].

Meanwhile, there have been relatively more studies on the degradation of HCB and TrCBi using radical, ozone, or UV [14–19]. However, existing studies on the process of HCB and TrCBi have discussed only the removal ratio and the qualification of degradation products. Thus, there are few studies for atomic charge comparison that have theoretically defined the degradation pathway of HCB and TrCBi.

This study, therefore, analyses the photo or radical degradation pathway of HCB and TrCBi based on the theoretical method using quantum chemistry calculations. Instead of calculating the transition state, we focused on the charge calculation which reduces computation and human time. Finally, the prediction performance of the proposed degradation pathway was verified by comparing the prediction results and the results reported previously in the existing literature.

2. Calculation method

To predict radical intermediates of HCB and tri-chlorinated biphenyl (TrCBi), the plane figures of all the molecules in this study were drawn and the three-dimensional features of these figures were confirmed with the Gauss View program [20]. With this Gauss View program, the Gaussian input files were created to run the Gaussian 09 program [21].

In this study, we carried out the density functional theory calculations with the Becke's exchange functional (B3LYP) [22] to obtain the optimized geometrical parameters of the molecule at the level of B3LYP/6-311++G(d,p). To discover that carbon in the benzene ring demonstrated a high minus charge, the atomic charge distributions were calculated using the CHelpG [23], MK [24], Mulliken and natural population analysis (NPA) methods with these optimized structures of molecules.

3. Results and discussion

3.1. Literature review on radical degradation

The $^{\bullet}OH$ radical is produced by the ozone degradation in the water under the ozone oxidation reaction or by H_2O_2 in the coexistence of the catalyst (Fe^{2+} etc.) and under the catalyst, such as the Fenton reaction. Produced as such, the $^{\bullet}OH$ radical attacks the bonding of chlorine atoms and carbon that have high electronegativity. As a result, the chlorine atom bound with the benzene ring is broken from the chloride ion. Further on, the benzene ring attacked by the $^{\bullet}OH$ radical can create products in open form, which are then attacked by the $^{\bullet}OH$ or radicals to create the final products that are further oxidized [25].

3.2. Physiochemical properties of the target material

Table 1 shows the physicochemical properties of the target materials of the study, HCB and 2,3,4-TrCBi, and the radical degradation products. All radical degradation products reported in the literature show the structure of the compound with the dissociated chlorine. As shown in Table 1, all target materials have a relatively higher boiling point and thus the possibility of volatilization is determined to be low in the ozone and Fenton oxidation reaction in the open system reported in the literature. Moreover, both materials have a relatively higher octanol-water partition coefficient and it is, therefore, determined that the materials can cause biological concentration through the food chain, making them important research subjects. Finally, the less the amount of chlorine in HCB and 2,3,4-TrCBi, the lower the boiling point and the octanol-water partition coefficient becomes.

Table 1
Chemical properties of HCB and 2,3,4-TrCBi [26,27]

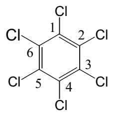
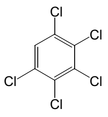
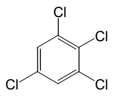
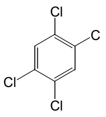
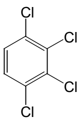
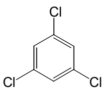
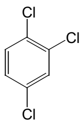
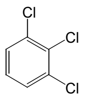
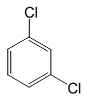
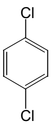
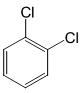
Name	Molecular weight (g)	Boiling point (°C)[a]	Octanol-water partition coefficient (log K_{ow})[a]
HCB	284.8	325	6.18
PeCB	250.3	277	5.18
TeCB	213.8	246	4.66
TrCB	181.4	218	4.05
DCB	146.9	174	3.44
MCB	112.5	132	2.84
TrCBi	257.5	321	5.42
DCBi	222.0	299	4.97
MCBi	188.6	291	4.50

[a] Average value of isomers.

3.3. Calculation of the atomic charge

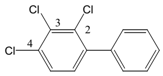
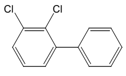
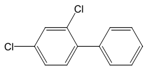
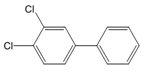
The degradation of HCB and TrCBi by the $^{\bullet}OH$ radical oxidization starts with the electron deficiency of the carbon in the benzene ring, which causes strong electrophilic $^{\bullet}OH$ to attack the carbon in the benzene. Thus, the examination of the electron density of the carbon in the benzene ring is efficient in analyzing the oxidization reaction. In other words, the higher the negative charge of the carbon that forms the benzene ring of HCB and TrCBi, the more susceptible it is to being attacked by the electrophilic $^{\bullet}OH$ radical. In this study, therefore, we calculated the atomic charge partition of each carbon atom using the CHelpG, MK, Mulliken, and NPA charge methods on the molecular structure acquired from B3LYP/6-311++G(d,p) optimization. However, the results of all three methods were shown to be identical and so Table 3 only shows the value from the CHelpG charge. While it was a natural result, the electric charge value in all locations of the symmetrical HCB was almost the same ranged from –0.615 to –0.617 as shown in Table 2. The CHelpG charge of 1,2,3,4,5-PeCB, which is one chlorine dissociated from HCB, shows that that the electric charge of the no. 3 carbon was the lowest at –0.578, followed by no. 1 and no. 5 carbon at –0.540 and no. 2 and no. 4 at 0.084. It was determined that the electric charge of no. 1, 3, and 5 carbon were similar to each other so that the chlorine bound with these carbons would be broken. The experimental

Table 2
Calculated mulliken charge distributions of HCB[a]

Position	Compounds										
											
1	–0.615	–0.540	–0.317	0.094	–0.246	0.440	–0.008	–0.085	0.441	0.495	0.264
2	–0.617	0.084	0.247	0.094	–0.194	–	0.186	0.191	–	–	0.264
3	–0.616	–0.578	–0.317	–	–0.194	0.441	–	–0.085	0.441	–	–
4	–0.616	0.084	–	0.094	–0.246	–	0.543	–	–	0.495	–
5	–0.617	–0.540	0.479	0.094	–	0.440	–	–	–	–	–
6	–0.616	–	–	–	–	–	–	–	–	–	–

[a]Charges in electron.

Table 3
Calculated mulliken charge distributions of 2,3,4-TrCBi[a]

Position	Compounds			
				
2	–0.731	–0.904	–0.215	–
3	–0.192	0.443	–	0.082
4	–0.046	–	0.474	0.377

[a]Charges in electron.

result of the literature reported that the main degradation products were 1,2,4,5-TeCB and 1,2,3,5-TeCB with the chlorine detached from no. 3 and no. 4 carbons [14]. Despite the electric charge of no. 4 carbon being higher than that of no. 1, 3, and 5 carbon, the literature reported that 1,2,3,5-TeCB was the degradation product with the chlorine dissociated from no. 4. Furthermore, while the calculation result predicted that 1,2,3,4-TeCB (same as 2,3,4,5-TeCB) would be the main degradation product, the literature reported it to be a minor product. These results demonstrate that while there were some differences between the results from the CHelpG charge results and the actual radical degradation products, they were generally well matched. For the 1,2,4,5-TeCB, the major product reported in the literature, the chemical structure is symmetrical and so the charge value was identical in all carbon locations. In the literature, 1,2,4-TrCB was reported to be the major product, satisfying the calculating result. Another major product reported in the literature, 1,2,3,5-TeCB had the lowest electric charge on no. 1 and no. 3 carbon. Again, in the literature, 1,2,4-TrCB which had the dissociated chlorine combined with no.1 and no. 3 carbon was the major product, and 1,3,5-TrCB which had the dissociated chlorine with no. 2 carbon was the minor product, satisfying the calculation results. The calculation results on 1,2,3,4-TeCB showed that the electric charge of the no. 1 and no. 4 carbon was the lowest at –0.246, followed by no. 2 and no. 3 carbon at –0.194. The literature also reported that 1,2,3-TrCB and 1,2,4-TrCB which had the dissociated chlorine with no. 3 and no. 4 carbon were the major products. 1,2,3-TrCB showed the lower electric charge with no. 1 and no. 3 location and the literature also reported that 1,2-dichlorinated biphenyl (1,2-DCB) which had the dissociated chlorine combined with no. 3 carbon was the major product, and 1,3-DCB with the dissociated chlorine combined with no. 2 carbon was the minor product, satisfying the calculated results exactly. 1,2,4-TrCB had the low electric charge on no. 1 and no. 2 (i.e., the closest to the negative value) locations and the literature also reported that 1,3-DCB (same as 2,4-DCB) which had the dissociated chlorine combined with no. 1 carbon was the major product and 1,4-DCB which had the dissociated chlorine combined with no. 2 carbon was the minor product, satisfying the calculated results. 1,3,5-TrCB is symmetrical, and the electric charge on no. 1, 3, and 5 locations were identical to each other, and the literature also reported 1,3-DCB as the only major product. 1,2, 1,3, 1,4-DCB are all symmetrical, and the electric charge in all carbon locations were identical. Therefore, it is predicted that the dechlorination from DCB to MCB would continue regardless of the carbon location in the molecule.

Meanwhile, Table 3 displays the CHelpG charge calculation results on 2,3,4-TrCBi, which had three chlorine substituted on biphenyl. The negative electric charge on no. 2 was largest at –0.731, followed by no. 3 at –0.192. However, the degradation product reported in the literature was 2,4-DCBi, which had the dissociated chlorine on no. 3 carbon, was the major product, and 2,3-DCBi and 3,4-DCBi, which had the dissociated chlorine on no. 4 and no. 2, respectively, were the minor products. While there were some differences between the literature and the calculated charge values, these were believed to be acceptable in scope. The calculation of 2,4-DCBi, the major product reported by the literature, showed that no. 2 had a considerably higher electric charge than no, 4, and the literature also reported that 4-MCBi, which had the dissociated chlorine on no. 2 carbon, was the major product, showing that the two results were identical to each other. Furthermore, the calculation of 2,3-DCBi, the degradation products of 2,3,4-TrCBi, estimated from the charge calculation, resulted in the estimation of 3-MCBi with the dissociated chlorine on no. 2 location. However, the experiment value in the literature reported 2-MCBi which had the dissociated chlorine on no. 3 location. For the 3,4-DCBi, 4-MCBi with the dissociated chlorine on no. 3 was estimated, but the literature reported 3-MCBi with the dissociated chlorine in the no. 4 location. It showed that 2,3- and 3,4-DCBi were not identical to the experimental results from the literature, and it was determined that further research would be required. For the 2,3,4-TrCBi, it is believed that the reason for the considerably low electric charge with the chloride on no. 2 location was because three chlorines were crowded together, and also because there was the effect of the benzene ring on the other side. Therefore, it is predicted that the dechlorination reaction on the no. 2 location would be more advantageous than the reaction at the other locations.

Shown in Figs. 1 and 2 are the comparison of the HCB and TrCBi degradation pathways based on the CHelpG charge calculation, according to the above results, to the reported results from the literature.

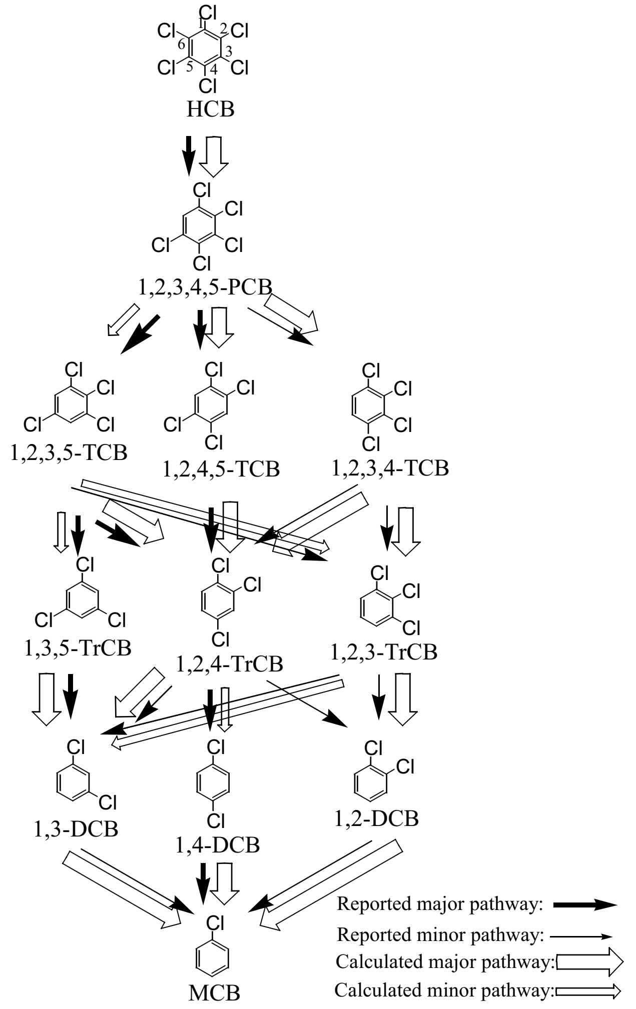


Fig. 1. Comparison of HCB radical decomposition pathway between literature [14–16] and atomic charge calculation.

4. Conclusion

The comparison of the CHelpG charge values calculated from HCB and 2,3,4-TrCBi using DFT to the degradation products of these compounds reported in the literature produced the following results.

- That the chlorine is dissociated and converted to hydrogen at the location of the carbon with the large negative charge distribution among the benzene ring of the target compounds was compared to the experimental results and was confirmed.
- It was believed that the reason for the electric charge of the chlorine in the no. 2 location of 2,3,4-TrCBi being considerably low was not only because three chlorines were crowded together but that it was also affected by the benzene ring on the other side. Therefore, it was expected that the dechlorination reaction in the no. 2 location would be more advantageous than the reaction on the other locations.
- The structure of dichlorobenzene is symmetrical and the electric charge on all carbon locations was identical, so it was estimated that the dechlorination from dichlorobenzene to monochlorobenzene would continue regardless of the location of carbon in the molecule.

When the experimental results from the literature and the calculation results on the two materials were compared, they were generally well-matched in spite of some differences in the calculation results. Therefore, it was determined that the calculation of the CHelpG charge values would be useful in estimating the dechlorination reaction location.

Acknowledgments

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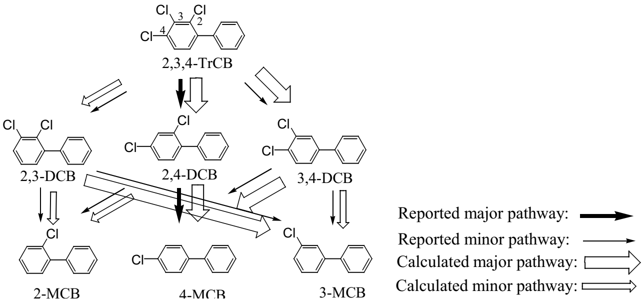

Fig. 2. Comparison of 2,3,4-TrCBi radical decomposition pathway between literature [17–19] and atomic charge calculation.

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