



## Elucidation of the dechlorination pathway of 1,2,3,4-TCDD through atomic charge calculation

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### ABSTRACT

The atomic charge of 1,2,3,4-TCDD as a model compound of dioxin using the Gaussian 03 program was compared with the radical dechlorination decomposition pathway reported in the literature. In the case of the atomic charge, the chlorine combined at the position of the carbon with a large negative charge value was found to have been dissociated first. Among the atomic charges, the CHelpG charge had the best agreement with the dechlorination degradation results in the literature. Based on the results, it is suggested that the radical dechlorination decomposition pathway of organic chlorinated compounds, including dioxins, can be predicted through atomic charge calculation.

*Keywords:* Dioxins; Atomic charge; Radical; Dechlorination pathway

### 1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are emitted when chlorine-containing fuels, chemical waste, hospital waste, and sewage sludge are burned [1,2]. There are 75 PCDD and 135 PCDF congeners. The dioxins included in the agrochemicals used in the past are also significant emission sources [3,4]. Much lower levels of PCDD and PCDF have been found in the exhaust from vehicles burning unleaded gasoline, presumably reflecting the low level of chlorine in fuel [5].

A number of methods for PCDD and PCDF decomposition have been examined. Five gallons of

sediments (initial conc.: 130 pg/g 2378-T4CDD, 193 pg/g total dioxins) was pretreated in a 600°C thermal desorption unit prior to injection into the gas phase thermal reduction chamber fired at 900°C. The removal efficiency of 2378-T4CDD was 25.5%, and that of the total dioxins was 61.5% [6]. The base catalyzed decomposition process can chemically decompose dioxin- and polychlorinated-biphenyl-contaminated soil at a removal efficiency rate of 99.9999% (initial conc.: 309 pg/g total dioxins) [7]. Small-scale thermal testing was done at an 815–980°C incineration temperature. A greater than 99.999% dioxin removal efficiency rate was obtained (initial conc.: 252 pg/g total dioxins) [8].

Dechlorination using a zero-valent metal has been reported [9]. Several studies have been conducted on

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the decomposition pathway, degradation intermediates, and degradation rates of dioxins using the various dechlorination methods mentioned earlier, but few studies have conducted theoretical or quantum chemical investigations on the dechlorination decomposition pathway of dioxin [10,11].

This study conducted a comparative examination of the results of a quantum chemical investigation into the decomposition pathway reported in the literature, using Gaussian 03, with 1,2,3,4-TCDD as a model material.

## 2. Methods

To predict the decomposition products of 1,2,3,4-TCDD using  $\cdot\text{OH}$  radical, the plane figures of all the molecules in this study were drawn using the ChemDraw program [12]. In addition, the three-dimensional features of these figures were confirmed with the Chem3D program, using the CS Chem3D program package [12]. The Gaussian program obtains the result file through execution by setting up the calculation method and best set after creating the input file using the Chem3D program [13].

Density functional theory calculations were also carried out with Becke's exchange functional (BLYP) [14], to obtain the optimized geometric parameters of the molecule at the level of BLYP/6-311++G(d,p). The  $\cdot\text{OH}$  radical attacks the atom on the benzene ring of each molecule, which has a strong electrophile.

Therefore, the atomic charge distributions were calculated for the carbon of benzene, using the CHelpG [15] and MK (Merz–Kollman/Singh) [16] methods with these optimized molecular structures.

## 3. Results and discussion

### 3.1. Literature research on the radical decomposition pathway

One of the many isomers of dioxin, 1,2,3,4-TCDD has a structure in which chlorine is not combined in positions 7 and 8. It has mostly been used in studies on the behaviors of dioxin as a model compound as it is known to be a nontoxic dioxin. The photochemical or radical decomposition pathway of 1,2,3,4-TCDD reported in the previous studies is summarized in Fig. 1 [9,17]. It is reported that a common characteristic of the decomposition pathways of 1,2,3,4-TCDD is that in general, 1,2,3,4-TCDD's benzene rings are not immediately destroyed or opened by photochemical or radical attacks [11]. The specific location of the benzene rings is attacked; however, dechlorination occurs. When this happens, 1,2,3,4-TCDD is gradually dechlorinated into low-chlorine dioxin, and finally, dibenzodioxin is generated.

The representative physical and chemical characteristics of dioxins, including 1,2,3,4-TCDD are summarized in Table 1 [18]. It was found that as the number of chlorine substitutions increases, the melting

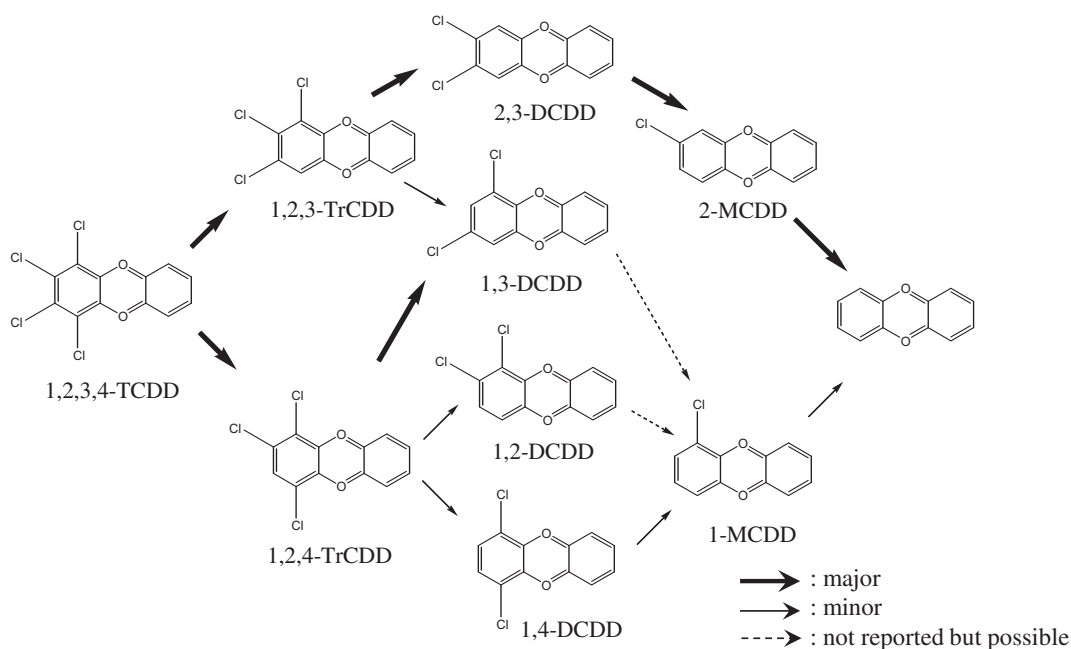


Fig. 1. Literature summary of the radical degradation pathway of 1,2,3,4-TCDD.

Table 1  
Chemical properties of 1,2,3,4-TCDD and its degradation products

Compound	Molecular weight	Melting point (°C)	Boiling point (°C)	Vapor pressure (mm Hg, 25°C)	Log $K_{ow}$ (25°C)
1,2,3,4-TCDD	320	188	419	$6.4 \times 10^{-6}$	6.60
1,2,4-TrCDD	286	128	375	$1.0 \times 10^{-4}$	6.35
2,3-DCDD	252	163	358	$3.9 \times 10^{-4}$	5.60
1-MCDD	218	105	325	$1.2 \times 10^{-2}$	5.00

and boiling points become higher, and the vapor pressure becomes lower. Therefore, it turned out that as the number of chlorine substitutions increases, the volatilization decreases. In addition, it was found that the  $K_{ow}$  value, which represents the degree of bioaccumulation, becomes higher as the number of chlorine substitutions increases, which indicates that the bioaccumulation through the food chain of highly chlorinated dioxins is high.

### 3.2. Atomic charge calculation

In general, various theoretical studies on the decomposition pathway of dioxins have been proposed, and the electronic cloud [19], HOMO & LUMO [20], and local energy [21], etc., have been used. In this study, the charge values of each carbon position of dioxins were calculated under the observation that electrophilic reaction occurs as dioxin is substituted by chlorine. As for the charge, the Mulliken, CHelpG, and MK values, which are commonly used, were calculated. Table 2 shows the atomic charges of 1,2,3,4-TCDD and TrCDD. In each of the carbon atoms in Table 2, the larger the negative value of the atomic charge is, the greater the reactivity with photochemical or ·OH radicals, which means that as the value of the negative charge of the carbon atoms in the benzene

ring becomes larger, the positive charge of the hydrogen atoms (H) bonded to the carbon atoms increases, thereby contributing to the enhancement of the electron affinity. In the case of 1,2,3,4-TCDD, the Mulliken, CHelpG, and MK charge values turned out to be higher in positions 1 and 4 than in positions 2 and 3. In the decomposition pathway of 1,2,3,4-TCDD reported in the literature and shown in Fig. 1, 1,2,3-TrCDD, in which the chlorine in position 4 is dissociated, was reported, and its results turned out to be in good agreement with the calculation results. In addition, as a dechlorination product of 1,2,3,4-TCDD, 1,2,3-TrCDD was reported to generate more than 1,2,4-TrCDD (53:47%), which was in good agreement with the calculation results. The reason that the charge values of positions 1 and 2 are the same as those of positions 2 and 3 in the Mulliken, CHelpG, and MK charges of 1,2,3,4-TCDD is its structural symmetry.

In the case of 1,2,3-TrCDD, the Mulliken charge was higher in position 3, and the CHelpG and MK charges turned out to be higher in position 1. Even in the literature, 2,3-DCDD, in which the chlorine in position 1 of 1,2,3-TrCDD was dissociated, and 1,3-DCDD, in which the chlorine in position 2 was dissociated, were reported to be dechlorination intermediates of 1,2,3-TrCDD, which was in good agreement with the literature results. In addition, the

Table 2  
Calculated atomic charge distributions of 1,2,3,4-TCDD and TrCDD<sup>a</sup>

Position	1,2,3,4-TCDD			1,2,3-TrCDD			1,2,4-TrCDD		
	Mulliken	CHelpG	MK	Mulliken	CHelpG	MK	Mulliken	CHelpG	MK
1	-0.389	-0.032	-0.177	-0.129	-0.128	-0.250	0.093	-0.024	-0.082
2	-0.022	0.047	0.040	0.282	0.129	0.115	-0.158	0.058	-0.049
3	-0.022	0.047	0.040	-0.531	-0.058	-0.125	-	-	-
4	-0.389	-0.032	-0.177	-	-	-	0.491	-0.024	-0.268

<sup>a</sup>Charges in electron, energies in Hartree.

Table 3  
Calculated atomic charge distributions of 2,3-, 1,3-, 1,2-, and 1,4-DCDD<sup>a</sup>

Position	2,3-DCDD			1,3-DCDD		
	Mulliken	CHelpG	MK	Mulliken	CHelpG	MK
1	–	–	–	0.557	–0.031	–0.251
2	0.300	0.082	0.036	–	–	–
3	0.299	0.082	0.036	0.585	0.066	–0.079
4	–	–	–	–	–	–

Position	1,2-DCDD			1,4-DCDD		
	Mulliken	CHelpG	MK	Mulliken	CHelpG	MK
1	0.291	0.012	–0.080	0.732	–0.029	–0.171
2	0.691	0.035	–0.021	–	–	–
3	–	–	–	–	–	–
4	–	–	–	0.732	–0.029	–0.171

<sup>a</sup>Charges in electron, energies in Hartree.

production ratios of 2,3-DCDD and 1,3-DCDD were 88 and 12%, respectively, which were in good agreement with the literature results. In the case of 1,2,4-TrCDD, the Mulliken, CHelpG, and MK charges turned out to be higher in positions 2, 1 and 4, respectively. Even in the literature, 1,3-DCDD, in which the chlorine in position 1 of 1,2,4-TrCDD was dissociated, 1,2-DCDD, in which the chlorine in position 4 was dissociated, and 1,4-DCDD, in which the chlorine in position 2 was dissociated, were reported to be dechlorination intermediates of 1,2,4-TrCDD, which was in good agreement with the literature results. According to the literature reports, the production ratios of 1,3-DCDD, 1,2-DCDD, and 1,4-DCDD were 88, 9, and 3%, respectively, and the CHelpG charge value in Table 3 turned out to be the highest in position 1, which was in good agreement with the calculation results, in which the main product of 1,2,4-TrCDD was 1,3-DCDD.

As described earlier, as 2,3- and 1,3-DCDD were reported to be major dechlorination intermediates of 1,2,3-TrCDD, their charge values were calculated as shown in Table 3. In the case of 2,3-DCDD, as its molecular structure is symmetric, its Mulliken, CHelpG, and MK charge values turned out to be the same in positions 2 and 3, which leads to the expectation that dechlorination will occur in one of the two

positions. In the case of 1,3-DCDD, the Mulliken, CHelpG, and MK charge values turned out to be higher in position 1 than in position 3, and 2-MCDD, in which the chlorine in position 1 was dissociated, was reported to be a dechlorination intermediate, which was in good agreement with the literature results.

As 1,3-, 1,2-, and 1,4-DCDD were reported to be major dechlorination intermediates of 1,2,4-TrCDD, their charge values were calculated as shown in Table 3. In the case of 1,4-DCDD, as its molecular structure is symmetric, its Mulliken, CHelpG, and MK charge values turned out to be the same in positions 1 and 4, which leads to the expectation that dechlorination will occur in one of these two positions. In the case of 1,3- and 1,2-DCDD, their Mulliken, CHelpG, and MK charge values turned out to be higher in position 1 than in position 2 or 3, and 2-MCDD, in which the chlorine in position 1 was dissociated, was reported to be a dechlorination intermediate, which was in good agreement with the literature results.

#### 4. Conclusions

As a result of the comparison of the atomic charge values of 1,2,3,4-TrCDD using the Gaussian 03 program

and those in the literature on the radical decomposition pathway, the following conclusions were obtained:

- (1) The atomic charge values CHelpG, MK, Mulliken, in that order, were in good agreement with the radical decomposition pathway reported in existing literature;
- (2) The atomic charge values showed that chlorine is dissociated by the attack of  $\cdot\text{OH}$  radicals on the carbon-bonded hydrogen with a high negative charge value. The chlorine that bonded to carbon with a high charge value is subsequently dissociated; and
- (3) The atomic charge calculation can provide us with a more profound understanding about reaction pathway and can be a useful tool for predicting reaction intermediate(s) and final product(s).

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### References

- [1] H. Fiedler, O. Hutzinger, C. Timms, Dioxins: Sources of environmental load and human exposure, *Toxicol. Environ. Chem.* 29 (1990) 157–234.
- [2] G. Lindner, A. Jenkins, J. McCormack, R. Adrian, Dioxins and furans in emissions from medical waste incinerators, *Chemosphere* 20 (1990) 1793–1800.
- [3] R. Dupont, J. McLean, R. Hoff, W. Moore, Evaluation of the use of solar irradiation for the decontamination of soils containing wood treating wastes, *J. Air Waste Manage. Assoc.* 40 (1990) 1257–1265.
- [4] S. Masunaga, T. Takasuga, J. Nakanishi, Dioxin and dioxin-like PCB impurities in some Japanese agrochemical formulations, *Chemosphere* 44 (2001) 873–885.
- [5] S. Marklund, R. Andersson, M. Tysklind, C. Rappe, K.-E. Egebäck, E. Björkman, V. Grigoriadis, Emissions of PCDDs and PCDFs in gasoline and diesel fueled cars, *Chemosphere* 20 (1990) 553–561.
- [6] Eco Logic International Inc., Pilot-scale Demonstration of Contaminated Harbor Sediment Treatment Process, Final Report, Rockwood, Canada, 1992, pp. 109–115.
- [7] S. Taniguchi, S. Iimura, K. Usukura, S. Ozawa, M. Hosomi, A. Murakami, Chemical decomposition of toxic organic chlorine compounds, *Organohalogen Compound* 19 (1994) 325–330.
- [8] Acurex Environmental Corporation, Test plan for evaluating the thermal treatability of contaminated New York harbor sediments, incineration research facility, Acurex Environmental Corporation, Jefferson, MO, 1992.
- [9] Z. Wang, W. Huang, D.E. Fennell, P. Peng, Kinetics of reductive dechlorination of 1,2,3,4-TCDD in the presence of zero-valent zinc, *Chemosphere* 71 (2008) 360–368.
- [10] Y. Okamoto, A new dioxin decomposition process based on a hybrid density-functional calculation, *Chem. Phys. Lett.* 310 (1999) 355–360.
- [11] L. Wang, A. Tang, The oxidation mechanism of polychlorinated dibenzo-p-dioxins under the atmospheric conditions—A theoretical study, *Chemosphere* 89 (2012) 950–956.
- [12] CS Chem3D Pro. CambridgeSoft Co., Cambridge, MA, 1999.
- [13] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Jr. Montgomery, T. Vreven, K.N. Kudin, J.C. Burant, J.C. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, *Exploring chemistry with electronic structure methods*, Gaussian, Inc., Pittsburgh, PA, 2003.
- [14] A.D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, *Phys Rev. A* 38 (1988) 3098–3100.
- [15] C.M. Breneman, K.B. Wiberg, Determining atom-centered monopoles from molecular electrostatic potentials, The need for high sampling density in formamide conformational analysis, *J. Comp. Chem.* 11 (1990) 361–373.
- [16] B.H. Besler Jr, K.M. Merz, P.M. Kollman, Atomic charges derived from semiempirical methods, *J. Comp. Chem.* 11 (1990) 431–439.
- [17] M. Takeuchi, K. Tsuchiya, K. Hatanak, A. Kitajima, K. Harada, T. Hirashima, Decomposition properties of chlorinated benzene and T4CDD by electron beam radiation, *Haikibutsugakaironbunshi* 14 (2002) 109–115 (in Japanese).
- [18] <http://ncis.nier.go.kr/ncis/Index>.
- [19] M.M. Branda, N.J. Castellani, S.H. Tarulli, DFT Study of electronic structure of saccharin, thiosaccharin, and their respective ions: Effects of metal coordination on thiosaccharinate electronic structure, *Int. J. Quantum Chem.* 89 (2002) 525–534.
- [20] B.-D. Lee, M. Iso, M. Hosomi, Prediction of Fenton oxidation positions in polycyclic aromatic hydrocarbons by frontier electron density, *Chemosphere* 42 (2001) 431–435.
- [21] M. Solimannejad, DFT study of the local molecular properties for the electrophilic substitution in 2 substituted benzenes, *J. Mol. Struct.* 589–590 (2002) 315–319.