

A Quantum and Deductive Chemical Study for All Congeners of Polybromo/Chlorodibenzo-*p*-dioxin and Polybromo/Chlorodibenzofuran

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We have performed semiempirical quantum chemical calculations to obtain the optimized structure and the free energy (ΔG) for all congeners (1701) of polybromo/chlorodibenzo-*p*-dioxins, which include all the isomers of all the homologues, and those for (3321) polybromo/chlorodibenzofurans. Then, to apply the “Quantum and Deductive Chemistry Approach” on the dioxin chemistry, we have carried out the multiple linear regression (MLR) as functions of temperature and the substituted numbers and positions of chlorine and bromine. The optimized structure of dibenzo-*p*-dioxin and the dibenzofuran ring is significantly influenced by the substitutions of the peri and lateral halogen atoms. The bond length between the aromatic ring and halogen atom also is influenced by the neighboring atoms. The bromine substitution at the 2 and 8 positions of dibenzofuran reduces the steric repulsion between the chlorine atoms at the 1 and 9 positions. The coefficients of the predicting equation of ΔG derived by MLR suggest that the probabilities of chlorine elimination from the peri and lateral positions for polychlorodibenzo-*p*-dioxin are nearly equal.

INTRODUCTION

Polychlorodibenzo-*p*-dioxins (PCDDs), polychlorodibenzofurans (PCDFs), and polychlorobiphenyls (PCBs) have attracted much attention for scientists in many areas because of their extremely high toxicity and effect on the ecology. These chemicals are widespread in the environment as byproducts of pesticides¹ and unintentional products generated in thermal processes such as in municipal and industrial solid-wastes incinerators (MSWIs) or other chemical plants.^{2,3} Many studies have pointed out that there are two dominant mechanisms, that is, *de novo* synthesis and reactions through various organic precursors, which generate the toxic dioxins in the thermal process.^{4–6} But, the relative importance of such pathways has been highly controversial, because the pathway depends on the combustion conditions.⁷

To know the formation or chemically synthetic procedure of dioxins, their thermodynamic data are crucially required. It should be noted, however, that dioxins themselves hardly exist in our surroundings even though there are so many congeners. Also, the standard enthalpy of formation^{8–10} and the solid-phase vapor pressure¹¹ have been measured only for several kinds of compounds of PCDDs and PCDFs. On the other hand, in reference to quantum chemical calculations for the physicochemical properties of dioxins, the computation needs much time and a high cost, and thus, few data were calculated. Shaub predicted the heat of formation, standard entropy of formation, and heat capacity by use of the group additivity method (GAM).¹² Saito and Fuwa calculated thermodynamic properties in their gaseous phase

for 76 PCDDs, 135 PCDFs, and 210 PCBs by using semiempirical calculations with the parametrization method 3 (PM3) Hamiltonian.¹³ León et al. reported the prediction of the enthalpy of formation for 76 PCDDs, by using the isodesmic reaction.¹⁴ Lee and Mhin calculated the enthalpy of formation for 76 PCDDs,¹⁵ and Li et al. obtained the enthalpy of formation for 76 polybromodibenzo-*p*-dioxins by density functional theory (DFT)-level calculations.¹⁶ Wang et al. calculated the gas-phase thermodynamic functions of 75 PCDDs by DFT-level calculations,¹⁷ discussing the parameters on the number and position of substituted chlorine. In some studies, quantum chemical calculations were used to predict the isomer or the homologue distribution pattern of PCDDs, PCDFs, or polychloronaphthalenes emitted from the thermal process.^{18–21}

Semiempirical quantum chemical calculations have been shown to be useful in studying the correlation between the biological activities and the structures of dioxins, the chemical hardness, or the molecular orbital properties.^{22–24} The quantitative structure–activity relationship approach is helpful for analyzing the toxicity and the physicochemical properties of dioxins.^{25,26} These methods claim strictly correct molecular structural information, although sophisticated quantum chemical computations such as high-level *ab initio* molecular orbital calculations have been emerging²⁷ for characterizing UV–vis absorption or emission spectra from dioxins.

In reference to the recent trend in dioxin problems, large home electronics, furniture, curtains, and carpets which are treated with fire retardants with brominated compounds have joined the family of dioxin-based toxic materials. Polybromo/chlorodibenzo-*p*-dioxins (PXDDs) and polybromo/chlorodibenzofurans (PXDFs) have been given as exhaust from wastes incinerators. Söderström and Marklund reported that,

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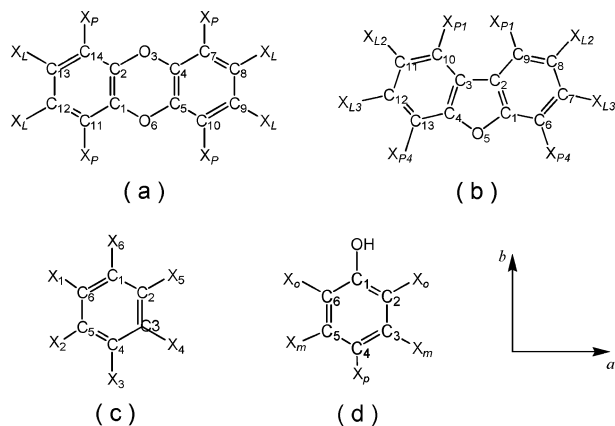


Figure 1. Defined labeling of the atoms and the definition of the axes: (a) PXDDs, (b) PXDFs, (c) PXBz's, and (d) PXPh's.

if the artificial municipal solid wastes containing the same molarity of chlorine and bromine are combusted in fluidized bed incinerators, the congener distributions of tetrahalogenated dibenzo-*p*-dioxin follow the numbers of their isomers.²⁸ There has been no database of the thermodynamic properties for PXDDs and PXDFs.

In this study, the “quantum and deductive chemistry approach” is applied to the PXDDs’ chemistry as a simple expression in order to predict the thermal properties for them. We deal with the optimized molecular structures and the calculated free energies, ΔG , for all kinds of the congeners (the isomers of all of the homologues) for 1701 PXDDs and 3321 PXDFs, for the first time, by use of the quantum chemical calculation with the PM3 Hamiltonian, providing the predicted ΔG , that is, the predicting equations based on multiple linear regression (MLR). The purpose of this study was to verify the utility of quantum and deductive chemistry, which was derived from the quantum chemical calculation for a lot of molecules. Thus, *ab initio* molecular orbital calculations and the density functional method have not been performed to reduce time and cost. In GAM, polybromo/chlorobenzenes (PXBz's) and polybromo/chlorophenols (PXPh's) were exploited as references, while in MLR, dummy variables were used. The influence of halogen substitution on the molecular structure was estimated in terms of the position and number of the substitution. The abundance of the five groups of tetrachlorodibenzo-*p*-dioxin congeners can be predicted.

The approach under study is part of deduction chemistry or chemometrics science, contributing particularly to dioxin chemistry and environmental sciences from the theoretical side.

COMPUTATIONAL PROCEDURE

Semiempirical quantum chemical calculations have been performed with the Gaussian03W package²⁹ for all of the molecules under study. The structural parameters were fully optimized using with the PM3 Hamiltonian, and ΔG was calculated with the FREQ keyword.³⁰ The labeling of atoms for 92 PXBz's, 135 PXPh's, 1701 PXDDs, and 3321 PXDFs and molecular axes for PXDDs and PXDFs are defined as given in Figure 1. The chemically equivalent halogen atoms are labeled to have the same numbers.

The temperature dependence of ΔG was calculated at seven points, 373, 473, 573, 773, 1073, 1273 K, and room

temperature (298 K), for all 92 PXBz's and all 135 PXPh's. But, the congeners of only 225 PXDDs and only 405 PXDFs, in which the congeners with $X_i = \text{H}$, Cl, and Br are excluded, were calculated for the temperature dependence.

The GAM referred to in Schemes 1 and 2, based on the dibenzo-*p*-dioxin ring (DD), and the GAM referred to in Scheme 3, based on the dibenzofuran ring (DF), were applied without any correction. It was necessary to consider the 81 ($= 3^4$) combinations for both PXBz's and PXPh's. It is noted that there are 79 congeners which have the same kind of halogen atoms substituted on both X_1 and X_2 for PXBz's, and there are also 117 compounds in which the chlorine or bromine atoms are substituted on the X_0 position for PXPh's.

As for MLR, we need to take the dummy variables, which depend on both the kind of halogen atom and its substituted positions. It should be noted that some kinds of molecules with a superimposable image derived by a symmetry operation such as rotation or mirror reflection were treated as distinguishable molecules. Thus, for the MLR calculation, there are 729 ($= 3^6$) PXBz's, 243 ($= 3^5$) PXPh's, 6561 ($= 3^8$) PXDDs, and 6561 ($= 3^8$) PXDFs. Because of mathematical reasons, it is required to assume a single coefficient to be zero. To obtain the predicting equation for ΔG , we took zero for the coefficient of hydrogen.

RESULTS AND DISCUSSION

1. Optimized Structure. 1.1. Optimized Structure of Aromatic Rings. The optimized structures of aromatic rings, the DD and DF rings, are respectively summarized in Figures S1 and S2 in the Supporting Information. The aromatic rings were optimized to be planar.

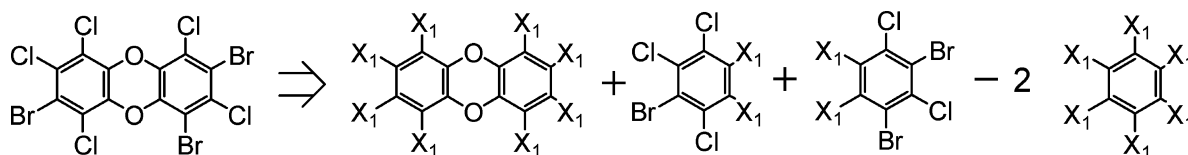
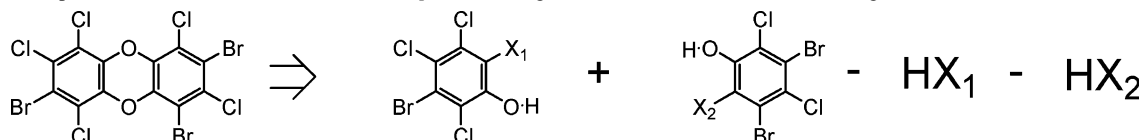
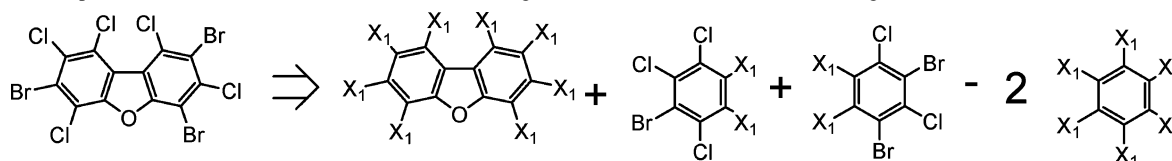
The influence on the DD and DF ring sizes by the halogen substitution was studied in terms of the optimized structures of all kinds of the congeners for PXDDs and PXDFs. The general trends along with both the *a* axis and *b* axis of the DD ring and those with the DF ring are given in the Supporting Information. The trends are described by the numbers and position of halogen substitution.

1.2. Bond Lengths between Aromatic Ring and Halogen Atoms. The bond lengths between the halogen atom and the aromatic ring are summarized in Table S2 in the Supporting Information with mean values and standard deviations. The C- X_L length for PXDDs and the C- X_{L2} length for PXDFs were chosen for clarity in Table S3 in the Supporting Information.

In the case of hydrogen ($X = \text{H}$), there is no difference between the two lengths despite the neighboring atom for PXDDs. Moreover, the C-X bond length becomes shorter when bromine atoms are substituted. In contrast, it becomes longer when chlorine atoms are substituted.

In the case of chlorine ($X = \text{Cl}$), the difference is about 1.2 pm due to the existence of the neighboring atom for PXDDs. The bond length is the longest when both of the neighboring atoms are hydrogen. If one of them is substituted by a bromine or chlorine atom, the length becomes shorter by 0.5 pm. When both of them are substituted, the distance becomes shorter by a further 0.3 pm. There is no significant difference whether the hydrogen atoms are at the peri or lateral position.

In the case of bromine ($X = \text{Br}$), the difference was about 1.2 pm due to the neighboring atom for PXDDs. The C-X

Scheme 1. Examples for the Reaction to Form a Dibenzo-*p*-dioxin Congener from Two Kinds of Benzene Congeners**Scheme 2.** Examples for the Reaction to Form a Dibenzo-*p*-dioxin Congener from Two Kinds of Phenol Congeners**Scheme 3.** Examples for the Reaction to Form a Dibenzofuran Congener from Two Kinds of Benzene Congeners

bond length is the shortest when both of the neighboring atoms are bromine. If one of them is substituted by chlorine, the bond length becomes longer by 0.5 pm. If the neighboring atoms are hydrogen, it becomes 0.5 pm longer. A similar tendency of the neighboring atom effect is obtained not only for PXDDs but also for PXDFs and PXBz's. The above tendency indicates that there must be some significant reason for it based on quantum chemical considerations. An attempt using more sophisticated approaches by the use of nonempirical molecular orbital calculations of a high level is underway.³¹

1.3. Spatial Distance between Cl_{P1} and Cl_{P1} of Dibenzofuran. It is interesting to know the influence of the bromine substitution on the spatial distance between two X_{P1} atoms of PXDFs. The statistical treatments link the influence through the steric repulsion with the two halogen atoms. Figure S6 in the Supporting Information shows, in the case of X_{P1} = chlorine, the relation between the distances and the numbers of the substituted bromine atom at the X_{L2} position, denoted by an open circle. The distance ranges from 285.5 to 288.5 pm (3.0 pm or 1.0% difference) with no Br_{L2} , from 286.9 to 292.1 pm (5.2 pm or 1.8% difference) with one Br_{L2} , and from 288.5 to 296.1 pm (7.6 pm or 2.6% difference) with two Br_{L2} 's, showing that the neighboring bromine reduces the steric repulsion of the two chlorines at the $P1$ position. The reduced steric effect gives a rationale for the subtle difference in the magnitude of the coefficient of the predicting equation for the free energy of PXDFs, as will be discussed in section 3.2.

2. Prediction of ΔG for PXBz's and PXPh's. The calculated results, as a function of temperature, for the ΔG of PXBz's and PXPh's are given in Tables S4 and S5 in the Supporting Information. The values for ΔG are given in units of kJ mol^{-1} in Tables S4 and S5 instead of the units of hartree particle⁻¹ which are originally given in the PM3 calculation. The MLR approach has been applied to predict ΔG both for PXBz's and for PXPh's with dummy variables, which correspond to the functions of the substituted position. The coefficients are temperature-dependent, as expected. In

PXBz's, the coefficient of the halogen is the same because all substitution positions are equivalent.

It depends only on the number of substituted halogen atoms. In PXPh's, it depends on the number of halogen atoms at the ortho, meta, and para positions with respect to the OH group.

For instance, the values for the ΔG of PXBz's and PXPh's at room temperature are given by eqs 1a and 1b, respectively:

$$\Delta G(\text{PXBz's}) = 268.388 - 50.017N_{\text{Cl}} + 7.943N_{\text{Br}} \quad (1a)$$

where N_{Cl} and N_{Br} , for example, stand for the numbers of

$$\Delta G(\text{PXPh's}) = 96.135 - 49.988N_{\text{Cl-o}} - 50.102N_{\text{Cl-m}} - 50.259N_{\text{Cl-p}} + 8.759N_{\text{Br-o}} + 7.483N_{\text{Br-m}} + 6.980N_{\text{Br-p}} \quad (1b)$$

substituted chlorine and bromine atoms in eq 1a, respectively. Naturally, as the number of parameters increases, the better the correlation constant (RRT) that is obtained, comparing those for PXBz's with those for PXPh's.

It is important to derive the temperature dependence of $\Delta G(T)$ as the quadratic function. In deriving the dependence, the unit of temperature was taken as kiloKelvin to prevent the coefficients of these equations from being so large. The temperature dependence of the coefficients of the predicted equation are summarized in the Supporting Information. The values for $\Delta G(T)$ of PXBz's and PXPh's are obtained by the following equations, as given by eqs 2a and 2b, respectively:

$$\Delta G(T, \text{PXBz's}) = [346.960 - 226.217(10^{-3}T) - 119.919(10^{-3}T)^2] + [-39.752 - 31.506(10^{-3}T) - 7.696(10^{-3}T)^2]N_{\text{Cl}} + [20.899 - 40.530(10^{-3}T) - 7.540(10^{-3}T)^2]N_{\text{Br}} \quad (2a)$$

Table 1. Relation between ΔG and Abundance among the Several Kinds of PCDDs and PCDFs Congeners

compound	$\Delta G/\text{kJ mol}^{-1}$		abundance/%			
	PM3	MLR	ref 33	MSWI ^a 34	MSWI ^b 34	FA ³⁴
1,3,6,8-T4CDD	95.004	98.955	13	14.6	19.2	24.2
1,3,7,9-T4CDD	95.093	98.955	8.7	8.3	11.3	11.2
1,4,6,9-T4CDD	106.267	104.803	5.2	4.3	3.8	4.6
2,3,7,8-T4CDD	91.262	93.107	3.5	4.8	4.6	1.1
1,2,3,4,6,7,8-H7CDD	-44.715	-46.321	50	44.2	50.9	45.7
1,2,3,4,6,7,9-H7CDD	-42.790	-43.397	50	55.8	49.1	54.3
1,2,3,4,6,7,8-H7CDF	90.572	92.793	68	65.5	64.9	57.3
1,2,3,4,6,7,9-H7CDF	97.839	95.946	13	11.8	14.0	14.5
1,2,3,4,6,8,9-H7CDF	98.314	96.364	13	12.3	13.0	15.9
1,2,3,4,7,8,9-H7CDF	95.938	92.712	6	10.4	8.1	12.3

^a Exhaust gas at the outlet of the Electron Participator at the municipal solid-wastes incinerator in Osaka City ^b Exhaust gas at the inlet of the Electron Participator at the municipal solid-wastes incinerator in Osaka City

$$\begin{aligned} \Delta G(T, \text{PXPh's}) = & [182.966 - 249.018(10^{-3}T) - \\ & 134.294(10^{-3}T)^2] + [-40.264 - 29.759(10^{-3}T) - \\ & 7.609(10^{-3}T)^2]N_{\text{Cl-o}} + [-40.034 - 30.903(10^{-3}T) - \\ & 7.626(10^{-3}T)^2]N_{\text{Cl-m}} + [-40.227 - 30.785(10^{-3}T) - \\ & 7.628(10^{-3}T)^2]N_{\text{Cl-p}} + [21.586 - 40.130(10^{-3}T) - \\ & 7.653(10^{-3}T)^2]N_{\text{Br-o}} + [20.942 - 42.194(10^{-3}T) - \\ & 7.795(10^{-3}T)^2]N_{\text{Br-m}} + [19.621 - 39.465(10^{-3}T) - \\ & 7.653(10^{-3}T)^2]N_{\text{Br-p}} \quad (2b) \end{aligned}$$

Figure 2 shows the relation of $\Delta G(T)$ values between the MLR result along the y axis and the result by the PM3 calculation along the x axis. The diagonal line shows the linear relation of $y = x$. The bar graph shows the distribution range of $\Delta G(T)$ at a given temperature. Figure 2 shows that the prediction method based on the MLR with dummy variables gives a reasonably good approximation with a correlation above 0.99.

For both PXBz's and PXPh's, the general tendencies for $\Delta G(T)$ were as follows:

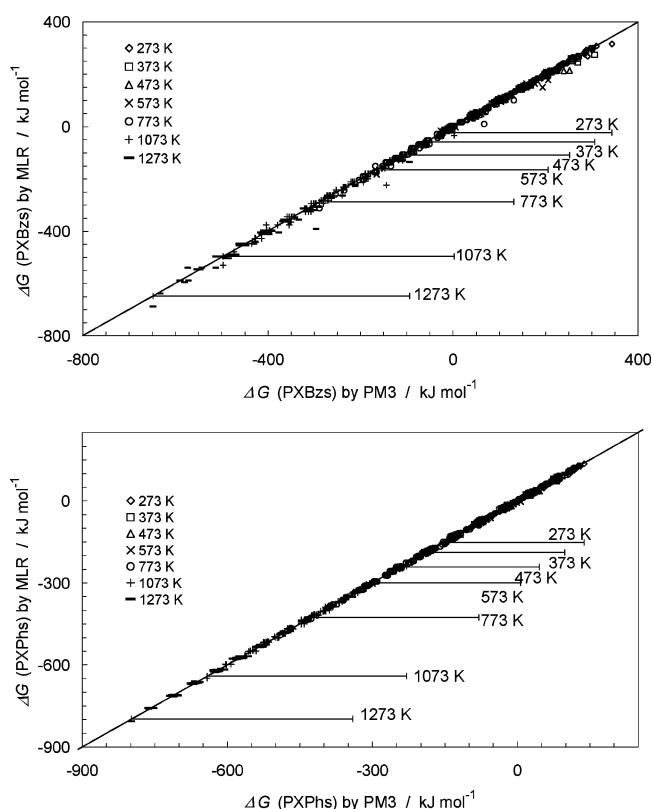
If chlorine is substituted to the benzene or phenol ring, the values for $\Delta G(T)$ become lower, but if bromine is substituted, they become larger.

When the temperature is high, the distribution range of $\Delta G(T)$ becomes wide because of the translation and rotation energy distribution of the molecules, but $\Delta G(T)$ becomes less. It changes from positive to negative between 473 and 573 K.

The additional energy is nearly equal if the temperature is the same, in the case of PXBz's and PXPh's.

It is believed that the de novo synthesis of dioxins in MSWIs occurs around 573 K.³² It is suggested that the reaction is related to the $\Delta G(T)$ of PXBz's and that the sign of $\Delta G(T)$ changes at around 573 K for PXPh's.

3. Prediction of ΔG for PXDDs and PXDFs. 3.1 Predicting ΔG at Room Temperature on the Basis of GAM. Figure 3 shows the relation of ΔG for PXDDs and PXDFs calculated from PM3 calculation, given along the x axis, and ΔG predicted by GAM, given along the y axis. The values of the y axis in Figure 3a–c are predicted on the basis of Schemes 1–3, respectively. The diagonal line is the linear relation of $y = x$. All of the points are above the linear relation of $y = x$. In the case of $X_a = \text{Cl}$ and $X_b = \text{Cl}$ in Scheme 2, the equilibrium constant becomes positive. If the

**Figure 2.** Comparison of ΔG for PXBz's and PXPh's calculated from the PM3 calculation with those predicted by MLR.

system has excess energy above the activation energy, it is predicted that the reaction occurs forward. It is estimated that the abundance of PXDDs is on the order of parts per thousand of PXPh's from the equilibrium constant of this reaction.

3.2. Predicting Equations for ΔG at Room-Temperature on the Basis of MLR. It is possible to predict the values of ΔG for PXDDs and PXDFs as follows:

$$\begin{aligned} \Delta G(\text{PXDDs}) = & 290.707 - 46.476N_{\text{Cl-p}} - \\ & 49.400N_{\text{Cl-L}} + 12.713N_{\text{Br-p}} + 7.918N_{\text{Br-L}} \quad (3a) \end{aligned}$$

$$\begin{aligned} \Delta G(\text{PXDFs}) = & 432.174 - 46.585N_{\text{Cl-p1}} - \\ & 46.504N_{\text{Cl-p4}} - 49.738N_{\text{Cl-L2}} - 50.156N_{\text{Cl-L3}} + \\ & 6.439N_{\text{Br-p1}} + 15.126N_{\text{Br-p4}} + 5.872N_{\text{Br-L2}} + \\ & 6.922N_{\text{Br-L3}} \quad (3b) \end{aligned}$$

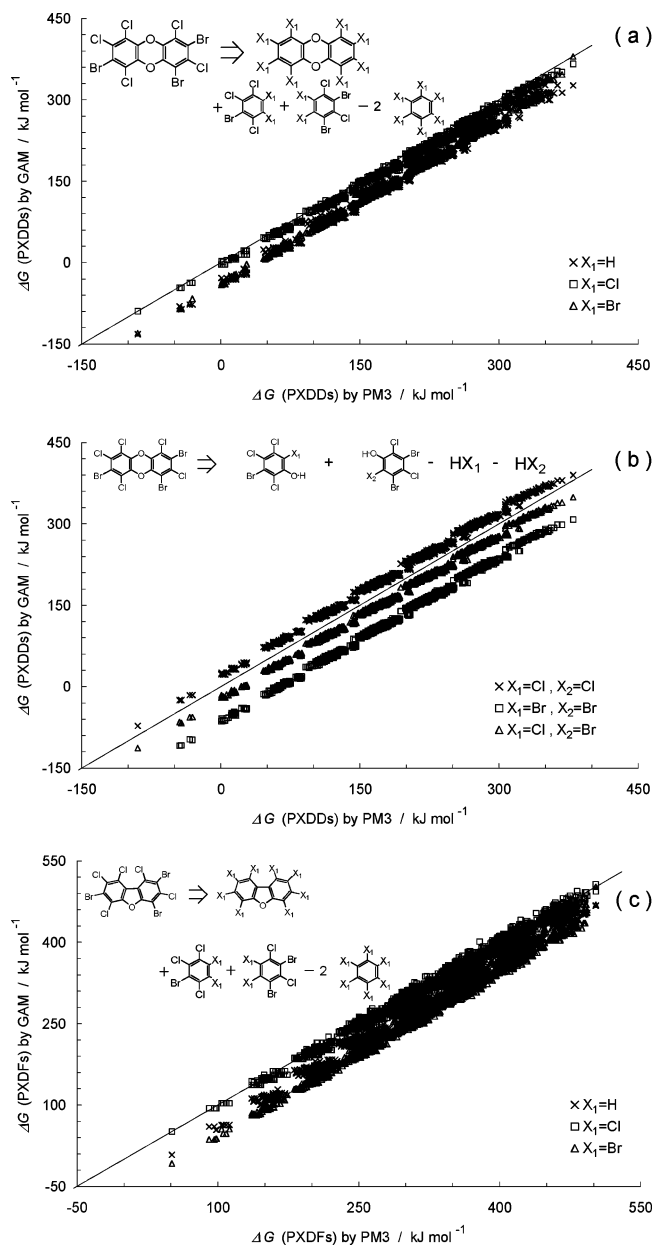


Figure 3. Comparison of ΔG for PXDDs and PXDFs calculated by the PM3 calculation with those predicted by GAM: (a) Scheme 1, (b) Scheme 2, and (c) Scheme 3.

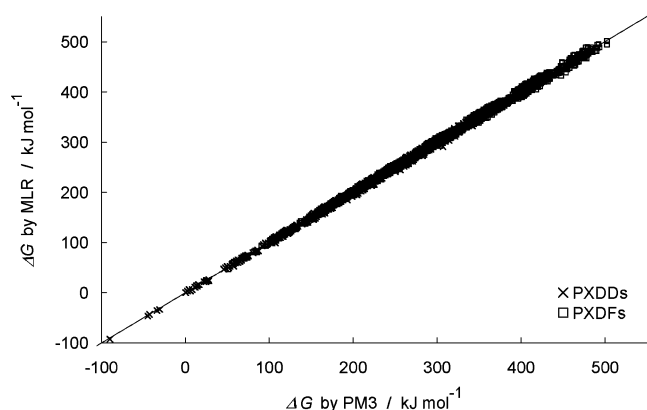


Figure 4. Comparison of ΔG for PXDDs and PXDFs calculated by the PM3 calculation with those predicted by MLR.

Figure 4 shows the relation of ΔG between the predicted value from MLR and the one from the PM3 calculation. The

tendency observed in PXBz's and PXPh's was confirmed also in PXDDs and PXDFs. The MLR method gives more simple and accurate results than GAM. Thus, MLR with dummy variables is the more efficient prediction method of ΔG for PXDDs and PXDFs than GAM. Temperature dependence of the predicting equations of $\Delta G(T)$ for PXDDs and PXDFs is discussed in the Supporting Information. Referring to ref 17, ΔG of PCDDs was obtained by using the least-squares method. The derived equation shows that the total energy of PCDD with chlorine substituted at the lateral position is lower than that at the peri position, agreeing with our present study.

But, as shown in Table 1, the dominant isomers of tetrachlorodibenzo-*p*-dioxin (T4CDDs) emitted from MSWIs were 1,3,6,8-T4CDD and 1,3,7,9-T4CDD, which have two peri chlorine atoms and two lateral ones. The abundance of the isomer with the four peri chlorine atoms, 1,4,6,9-T4CDD, and that of the isomer with the four-lateral ones, 2,3,7,8-T4CDD, were less than 5%. For the case of heptachlorodibenzo-*p*-dioxin (H7CDD), the abundances of the two isomers were of nearly the same ratio, from 40 to 60%. For the case of heptachlorodibenzofuran (H7CDF), the dominant isomer 1,2,3,4,6,7,8-H7CDF, which has no chlorine atom at the 9 position, and the other three isomers, which have a chlorine atom at both the 1 and 9 positions, had abundances of less than 15%.

The ΔG for 1,2,3,4,6,7,8-H7CDD, 1,2,3,4,6,7,9-H7CDD, and 1,2,3,4,6,7,8,9-octachlorodibenzo-*p*-dioxin at 1273 K is -972.748 , -971.346 , and -1057.703 kJ mol $^{-1}$, calculated by the PM3 calculation, respectively. The difference in ΔG between the two isomers of H7CDD is 1.402 kJ mol $^{-1}$, which is much smaller than their absolute value. This finding reveals that chlorine atoms eliminated from both the peri and lateral positions have nearly equal probabilities of dechlorination. Thus, the abundances of the two H7CDD isomers are quite equal. If this postulate is applied to all of the homologue's dechlorination procedure, the abundance of the five groups of the T4CDD congener obeys the following ratio: (0, 4):(1, 3):(2, 2):(3, 1):(4, 0) = 1:4:6:4:1. In the notation of (*a*, *b*), *a* stands for the number of Cl_P and *b* stands for the number of Cl_L. Similarly, the abundance of the four groups of the pentachloro-*p*-dioxin (P5CDD) congener is in a ratio of (1, 4):(2, 3):(3, 2):(4, 1) = 1:3:3:1, and the abundance of the three groups of the hexachloro-*p*-dioxin (H6CDD) congener is in a ratio of (2, 4):(3, 3):(4, 2) = 1:2:1. The distribution patterns of PCDDs in the fly ash from the MSWI in Osaka City³⁴ reveal the very tendency above, as given in Figure S7 of the Supporting Information; in Figure S7, we took the summation of the abundances of all of the isomers in each group. In Figure S7, the abundance measured from the overlapped peaks appearing in the gas chromatograph was simply assumed to be equal among the isomers. As seen in Figure 5, the mean value of the abundance for each group reveals that the results give a rationale for the postulate in a semiquantitative manner, suggesting that the dechlorination procedure and de novo synthesis simultaneously occur at the electron participator in the incinerator. Thus, it turns out that the absolute values of ΔG do not allow us to evaluate the isomer distribution patterns or give fingerprints emitted from thermal plants in a straightforward manner.

The abundance of PCDFs with two Cl_P's is small, less than 15% as shown in Table 1. The coefficient of the

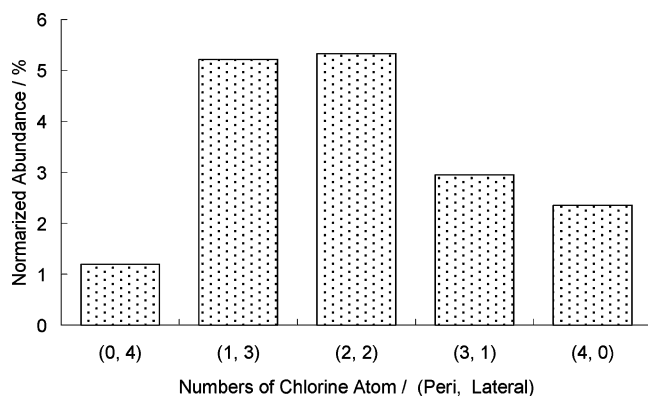


Figure 5. Abundance of the five groups of tetrachloro-*p*-dioxin congeners emitted from MSWI.

predicting equation of ΔG for PCDFs at the *P1* position is the largest in Table 1. On the other hand, the coefficient for PXDFs at the *P4* position is larger than that at the *P1* position in eq 3b. It can be rationalized in terms of the discussion in section 1.3 that the neighboring bromine at the *L2* position stabilizes the steric repulsion between two chlorine atoms at the *P1* position. The coefficient of eq 3b contains this effect.

CONCLUSIONS

We have applied the “quantum and deductive chemistry approach” to dioxin chemistry. The calculations have been made for all congeners (1701) of PXDDs, which include all of the isomers of all of the homologues, and for those (3321) of PXDFs. The aromatic ring sizes are influenced by the kinds and the numbers of halogen atoms substituted at the lateral and peri positions. The bond lengths between the aromatic rings and substituted halogen atom are varied according to the neighboring effects. The steric repulsion between two chlorine atoms at the 1 and 9 positions of the PXDF congeners can be stabilized by the neighboring bromine atom at the 2 and 8 positions.

It was shown that MLR with dummy variables is an efficient and accurate method to predict the ΔG of the dioxin molecules only by allocating the substituted position of the halogen atom. A comparison of the calculated ΔG with the experimental data suggests that the absolute value of ΔG cannot predict the isomer distribution patterns of the polychlorodibenzo-*p*-dioxin congeners emitted from municipal solid-waste incinerators. On the other hand, the predicting equation of ΔG for the PXDD congeners suggests that chlorine atoms eliminated from both the peri and lateral positions have nearly equal probabilities of dechlorination. According to this postulate, the abundance of the five groups of the tetrachlorodibenzo-*p*-dioxin congeners can be predicted.

ACKNOWLEDGMENT

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Supporting Information Available: The optimized structures of aromatic rings and the bond length between carbon and halogen atoms at either the peri or lateral position; a figure and tables related to the “Optimized Structure” section in the Results and Discussion; a table of ΔG values for PXBzs

and PXPhs by PM3 calculation; the temperature dependence of the coefficients of the predicting equation of ΔG for PXBzs, PXPhs, PXDDs, and PXDFs; and the experimental data for the group distribution pattern of some kinds of dibenzo-*p*-dioxin congeners. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

REFERENCES AND NOTES

- Masunaga, S. The Origin of and Change in Dioxin Pollution in Japan. *Waste Manage. Res.* **2000**, *11*, 173–181.
- Olie, K.; Vermeulen, P. L.; Hutzinger, O. Chlorodibenzo-*p*-dioxins and chlorodibenzofurans are trace components of fly ash and flue gas of some municipal incinerators in The Netherlands. *Chemosphere* **1977**, *6*, 455–459.
- Ministry of the Environment, Japan, Web Site, *News Release and Speeches* (2003.12.05). <http://www.env.go.jp/press/press.php3?serial=3790> (accessed Dec 2003 and Jan 2006).
- Bumb, R. R.; Crummett, W. B.; Cutie, S. S.; Gledhill, J. R.; Hummel, R. H.; Kagel, R. O.; Lamparski, L. L.; Luoma, E. V.; Miler, D. L.; Nestruck, T. J.; Shadoff, L. A.; Stehl, R. H.; Woods, J. S. Trace chemistries of fire: A source of chlorinated dioxins. *Science* **1980**, *210*, 385–390.
- Hagenmaier, H.; Brunner, H.; Haag, R.; Kraft, M. Catalytic effects of fly ash from waste incineration facilities on the formation and decomposition of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans. *Environ. Sci. Technol.* **1987**, *21*, 1085–1088.
- Tuppurainen, K.; Halonen, I.; Ruokojärvi, P.; Tarhanen, J.; Ruuskanen, J. Formation of PCDDs and PCDFs in municipal waste incineration and its inhibition mechanisms: A review. *Chemosphere* **1998**, *36*, 1493–1511.
- Dickson, L. C.; Lenoir, D.; Hutzinger, O. Quantitative comparison of *de novo* and precursor formation of polychlorinated dibenzo-*p*-dioxins under simulated municipal solid waste incinerator postcombustion condition. *Environ. Sci. Technol.* **1992**, *26*, 1822–1828.
- Papina, T. S.; Kolesov, V. P.; Vorobieva, V. P.; Golovkov, V. F. The standard molar enthalpy of formation of 2-chlorodibenzo-*p*-dioxin. *J. Chem. Thermodyn.* **1996**, *28*, 307–311.
- Papina, T. S.; Luk'yanova, V. A.; Kolesov, V. P.; Golovkov, V. F.; Chernov, C. A.; Vorob'eva, V. P. Standard enthalpy of formation of 1-chlorodibenzo-*p*-dioxin. *Zh. Fiz. Khim.* **1998**, *72*, 7–10.
- Papina, T. S.; Kolesov, V. P.; Lukyanova, V. A.; Golovkov, V. F.; Chernov, C. A.; Vorobieva, V. P. The standard molar enthalpy of 2,3-dichlorodibenzo-*p*-dioxin. *J. Chem. Thermodyn.* **1998**, *30*, 431–436.
- Mader, B. T.; Pankow, J. F. Vapor pressures of the polychlorinated dibenzodioxins (PCDDs) and the polychlorinated dibenzofurans (PCDFs). *Atmos. Environ.* **2003**, *37*, 3103–3114.
- Shaub, W. M. Procedure for Estimating the Heats of Formation of Aromatic Compounds: Chlorinated Benzenes, Phenols and Dioxins. *Thermochim. Acta* **1982**, *55*, 59–73.
- Saito, N.; Fuwa, A. Prediction for thermodynamic function of dioxins for gas phase using semiempirical molecular orbital method with PM3 Hamiltonian. *Chemosphere* **2000**, *40*, 131–145.
- León, L. A.; Notario, R.; Quijano, J.; Sánchez, C. Structure and enthalpies of formation in the gas phase of the most toxic polychlorinated dibenzo-*p*-dioxins. A DFT study. *J. Phys. Chem. A* **2002**, *106*, 6618–6627.
- Lee, J. E.; Mhin, B. J. DFT Calculation on the Thermodynamic Properties of Polychlorinated Dibenzo-*p*-dioxins: Intramolecular Cl–Cl Repulsion Effects and Their Thermochemical Implications. *J. Phys. Chem. A* **2003**, *107*, 2693–2699.
- Li, X. W.; Shibata, E.; Nakamura, T. Theoretical calculation of thermodynamic properties of polybrominated dibenzo-*p*-dioxins. *J. Chem. Eng. Data* **2003**, *48*, 727–735.
- Wang, Z. Y.; Zhai, Z. C.; Wang, L. S.; Chen, J. L.; Kikuchi, O.; Watanabe, T. Prediction of gas phase thermodynamic function of polychlorinated dibenzo-*p*-dioxins using DFT. *J. Mol. Struct.* **2004**, *672*, 97–104.
- Thompson, D. An evaluation of the heat of formation of chlorinated dioxins and its application to isomer abundance predictions. *Chemosphere* **1994**, *29*, 2545–2554.
- Iino, F.; Tsuchiya, K.; Imagawa, T.; Gullett, B. K. An Isomer Prediction Model for PCNs, PCDD/Fs, and PCBs from Municipal Waste Incinerators. *Environ. Sci. Technol.* **2001**, *35*, 3175–3181.
- Khachatryan, L.; Burcat, A.; Dellinger, B. An elementary reaction-kinetic model for the gas-phase formation of 1,3,6,8- and 1,3,7,9-tetrachlorinated dibenzo-*p*-dioxin from 2,4,6-trichlorophenol. *Combust. Flame* **2003**, *132*, 406–421.
- Tan, P.; Hürtado, I.; Neuschütz, D. Predictions for isomer distributions of toxic dioxins and furans in selected industrial combustion processes. *Chemosphere* **2002**, *46*, 1287–1292.

- (22) Lewis, D. F. V.; Ioannides, C.; Parke, D. V. Validation of a novel molecular orbital approach (COMPACT) for the prospective safety evaluation of chemicals, by comparison with rodent carcinogenicity and Salmonella mutagenicity data evaluated by the U. S. NCI/NTP. *Mutat. Res.* **1993**, *291*, 61–77.
- (23) Kobayashi, S.; Sameshima, K.; Ishii, Y.; Tanaka, A. Toxicity of Dioxins: Role of an Absolute Hardness–Absolute Electronegativity Diagram (η – χ Diagram) as a New Measure in Risk Assessment. *Chem. Pharm. Bull.* **1995**, *43*, 1780–1790.
- (24) Lynam, M. M.; Kutty, M.; Damborsky, J.; Koca, J.; Adriaens, P. Molecular Orbital Calculations to Describe Microbial Reductive Dechlorination of Polychlorinated Dioxins. *Environ. Toxicol. Chem.* **1998**, *17*, 988–997.
- (25) Mekenyan, O. G.; Veith, G. D.; Call, D. J.; Ankley, G. T. A QSAR Evaluation of Ah Receptor Binding of Halogenated Aromatic Xenobiotics. *Environ. Health Perspect.* **1996**, *104*, 1302–1310.
- (26) Consonni, V.; Todeschini, R.; Pavan, M.; Gramatica, P. Structure/Response Correlations and Similarity/Diversity Analysis by GETAWAY Descriptors. 2. Application of the Novel 3D Molecular Descriptors to QSAR/QSPR Studies. *J. Chem. Inf. Comput. Sci.* **2002**, *42*, 693–705.
- (27) Koto, T.; Toyota, K.; Sato, K.; Shiomi, D.; Takui, T. *Angew. Chem., Int. Ed.* Submitted for publication.
- (28) Söderström, G.; Marklund, S. Pxdd and pxdf from combustion of bromflameretardant containing MSW. *Organohalogen Compd.* **2000**, *47*, 225–228.
- (29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Akatsuki, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; *Gaussian03*, revision A. 1; Gaussian, Inc.: Pittsburgh, PA, 2003.
- (30) The Z-matrix data of all of the compounds have been constructed by the homemade program written in the FORTRAN language.
- (31) We have studied these tendencies for simple molecules such as chlorobenzene and chlorophenol.
- (32) Addink, R.; Olie, K. Mechanisms of Formation and Destruction of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in Heterogeneous Systems. *Environ. Sci. Technol.* **1995**, *29*, 1425–1435.
- (33) Ryu, J. Y.; Mulholland, J. A.; Dunn, J. E.; Iino, F.; Gullett, B. K. Potential Role of Chlorination Pathways in PCDD/F Formation in a Municipal Waste Incinerator. *Environ. Sci. Technol.* **2004**, *38*, 5112–5119.
- (34) Sakai, M.; Takakura, A.; Nishitani, T.; Tsuruho, K. Unpublished data, measured at the municipal solid waste incinerator in Osaka City.

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