Reaction Space Map Representation of the Chlorination/Dechlorination Reactions of Polychlorobenzenes

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The reaction space map (RESMAP) representation is proposed for the comprehensive description of the chlorination and dechlorination reactions of polychlorobenzenes. By using the B3LYP/6-311G** energies and by assuming the chemical reactions which govern the chlorination and dechlorination processes of polychlorobenzenes, the relative energies of polychlorobenzenes and polychlorophenyl radicals were defined artificially. They were collected as the RESMAP which has the relative energies of polychlorobenzenes at the diagonal parts and the polychlorophenyl radicals connecting two polychlorobenzenes at the off-diagonal parts. The RESMAPs created for three models for the chlorination/dechlorination processes provided a general view of the thermodynamically controlled isomer distributions and chlorination/dechlorination reaction patterns for benzene and (poly)chlorinated benzenes.

INTRODUCTION

The relationship between reactivity and structure of molecules constitutes a general interest in chemistry, and the knowledge of specific bond dissociation energies (BDE) contributes essential quantitative information to the reactivity-structure relationship. The polychlorinated compounds such as polychlorinated biphenyls (PCB) and polychlorinated dibenzo-p-dioxins (PCDD) are produced from diverse chlorine-containing organic substances by pyrolysis and combustion or from aromatic compounds in atmosphere by the reaction with the chlorine atoms which are generated by photochemical reaction by sunlight.[1−3] These environmental pollutants display toxic and carcinogenic actions, and the characterization of these compounds is greatly required.

To understand the chlorination and dechlorination reactions of aromatic compounds, the accurate estimation of BDE of the C−Cl bond is required for a variety of polychlorinated compounds. The BDE of the C−H bond in benzene and the C−Cl bond in chlorobenzene have been determined experimentally as 109.8−112.0 kcal/mol[4,5] and 93.0−93.6 kcal/mol,[6−8] respectively. The theoretical estimation of BDE requires the calculation of polychlorophenyl radicals. Recently density functional theory (DFT) calculations have improved the accuracy of free radicals, and the C−H BDE of C_6H_6 has been predicted successfully.[8,9] Cioslowski et al.[8] applied the BLYP/6-311G** level of DFT to polychlorobenzenes and examined energetics of the homolytic cleavages of the C−H and C−Cl bonds and showed that the bond dissociation energies correlate well with the number of the chlorine substituents at the *ortho*, *meta*, and *para* positions.

Another important property which is necessary to understand the chlorination and dechlorination reactions is the relative stability among polychlorobenzenes. The relative stability predicts the relative populations of polychlorobenzenes in the entire reaction system. Although the relative stability among isomers can be determined theoretically by comparing the total energies, the relative energy between polychlorobenzenes having a different number of chlorine atoms cannot uniquely be determined. They must be defined artificially by assuming the chemical reactions which govern the chlorination and dechlorination processes of polychlorobenzenes. The present paper proposes the representation of such relative energies among benzene and (poly)chlorobenzenes as a reaction space map (RESMAP). RESMAP is a diagram in a matrix form which displays the relative energies of a group of compounds at the diagonal parts and the relative energies of the intermediates, the phenyl and (poly)chlorophenyl radicals, connecting two of the compounds at the off-diagonal parts. The RESMAP of polychlorobenzenes will give a general view for the chlorination and dechlorination reactions of polychlorobenzenes.

DFT CALCULATION

The B3LYP/6-311G** level of theory[10−13] was employed, and geometries of benzene, polychlorobenzenes, phenyl radical, polychlorophenyl radicals, and the species involved in the assumed chemical reactions were fully optimized. The zero-point energies (ZPEs) were computed from unscaled vibrational frequencies. Cioslowski and co-workers have shown that this level of calculation is quite successful for the structure and energetics study of aryl radicals.[8] All calculations were carried out using GAUSSIAN 98 program.[14]

BOND DISSOCIATION ENERGIES

The calculated total energies and ZPEs for benzene and chlorinated benzenes are listed in Table 1. The calculated

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Table 1. Total and Zero-Point Energies of Benzene and Its Chloro-Derivatives Calculated by the B3LYP/6-311G** Method

substituent(s)	symmetry	total energy (hartree)	ZPE (kcal/mol)
none (benzene)	D_{6h}	−232.30855	62.85
chloro	C_{2v}	−691.93057	56.91
1,2-dichloro	C_{2v}	−1151.54690	50.93
1,3-dichloro	C_{2v}	−1151.55081	50.88
1,4-dichloro	D_{2h}	−1151.55094	50.88
1,2,3-trichloro	C_{2v}	−1611.16174	44.87
1,2,4-trichloro	C_s	−1611.16599	44.84
1,3,5-trichloro	D_{3h}	−1611.16951	44.80
1,2,3,4-tetrachloro	C_{2v}	−2070.77576	38.80
1,2,3,5-tetrachloro	C_{2v}	−2070.77965	38.75
1,2,4,5-tetrachloro	D_{2h}	−2070.78032	38.79
pentachloro	C_{2v}	−2530.38881	32.70
hexachloro	D_{6h}	−2989.99648	26.59

Table 2. Total and Zero-Point Energies of Phenyl Radical and Its Chloro-Derivatives Calculated by the B3LYP/6-311G** Method

substituent(s)	symmetry	total energy (hartree)	ZPE (kcal/mol)
none (phenyl radical)	C_{2v}	−231.61942	54.61
2-chloro	C_s	−691.23888	48.73
3-chloro	C_s	−691.24101	48.66
4-chloro	C_{2v}	−691.23995	48.67
2,3-dichloro	C_s	−1150.85576	42.77
2,4-dichloro	C_s	−1150.85784	42.72
2,5-dichloro	C_s	−1150.85891	42.71
2,6-dichloro	C_{2v}	−1150.85668	42.80
3,4-dichloro	C_s	−1150.85609	42.69
3,5-dichloro	C_{2v}	−1150.86090	42.63
2,3,4-trichloro	C_s	−1610.46968	36.73
2,3,5-trichloro	C_s	−1610.47455	36.71
2,3,6-trichloro	C_s	−1610.47251	36.81
2,4,5-trichloro	C_s	−1610.47283	36.68
2,4,6-trichloro	C_{2v}	−1610.47422	36.72
3,4,5-trichloro	C_{2v}	−1610.47071	36.63
2,3,4,5-tetrachloro	C_s	−2070.08345	30.66
2,3,4,6-tetrachloro	C_s	−2070.08538	30.72
2,3,5,6-tetrachloro	C_{2v}	−2070.08740	30.78
pentachloro	C_{2v}	−2529.69531	24.68

Table 3. Total and Zero-Point Energies of the Species Involved in the Chlorination/Dechlorination Reactions Calculated by the B3LYP/6-311G** Method

species	total energy (hartree)	ZPE (kcal/mol)
HCl	−460.83349	4.19
Cl_2	−920.40568	0.73
CH_4	−40.53374	27.99
CH_3Cl	−500.15072	23.64
H	−0.50216	0.00
Cl	−460.16632	0.00
CH_3	−39.85376	18.56

total energies and ZPEs for phenyl radical and chlorinated phenyl radicals are listed in Table 2. In Table 3, the calculated energies for the species involved in the chlorination/dechlorination reactions are listed. The BDEs for homolytic C−H and C−Cl bond cleavages in benzene and chlorinated benzenes were computed from the total energies and ZPEs in Tables 1 and 2 and the total energies of H and Cl atoms in Table 3. They are listed in Table 4. The trends observed in the relative energies among isomers and in BDEs are similar to those reported by Cioslowski et al.[8] Slight difference was recognized in the C−H bond dissociation energies. The present B3LYP/6-311G** BDEs of the C−H bonds in chlorinated benzenes are larger than the corresponding BLYP/6-311G** values by about 2 kcal/mol. The calculated BDE of the C−H bond in benzene, 109.1 kcal/mol, is in better agreement with the experimental values

Table 4. Calculated C−H and C−Cl Bond Dissociation Energies (kcal/mol) of Benzene and (poly) Chlorobenzenes

molecule	BDE for the site					
	1	2	3	4	5	6
C_6H_6	109.09	109.09	109.09	109.09	109.09	109.09
1-C_6H_5Cl	88.58	110.75	109.35	110.02	109.35	110.75
1,2-$C_6H_4Cl_2$	86.72	86.72	110.43	110.14	110.14	110.43
1,3-$C_6H_4Cl_2$	87.82	112.38	87.82	111.58	109.57	111.58
1,4-$C_6H_4Cl_2$	88.57	110.98	110.98	88.57	110.98	110.98
1,2,3-$C_6H_3Cl_3$	85.54	84.99	85.54	111.02	110.28	111.02
1,2,4-$C_6H_3Cl_3$	86.88	86.20	112.03	87.95	111.69	110.65
1,3,5-$C_6H_3Cl_3$	87.12	113.11	87.12	113.11	87.12	113.11
1,2,3,4-$C_6H_2Cl_4$	85.63	83.93	83.93	85.63	111.18	111.18
1,2,3,5-$C_6H_2Cl_4$	85.05	85.26	85.05	112.52	87.38	112.52
1,2,4,5-$C_6H_2Cl_4$	86.48	86.48	111.69	86.48	86.48	111.69
1,2,3,4,5-C_6HCl_5	85.21	84.06	82.85	84.06	85.21	112.05
C_6Cl_6	82.71	82.71	82.71	82.71	82.71	82.71

(109.8 and 112.0 kcal/mol) than the previous BLYP/6-311G** value (106.9 kcal/mol[8]). The calculated BDE of the C−Cl bond in chlorobenzene is slightly better than the BLYP/6-311G** value (88.2 kcal/mol[8]).

Cioslowski et al. analyzed the effect of substituents on the BDEs of benzene and polychlorobenzenes and showed that the C−H BDEs of benzene and polychlorobenzenes are well correlated with the numbers of the Cl substituents at the *ortho* (N_o), *meta* (N_m), and *para* (N_p) positions with respect to the abstraction site.[8] Similar relations were obtained for the B3LYP/6-311G** BDEs in Table 4:

$$BDE(C−H) = 109.36 + 1.38\,N_o − 0.10\,N_m + 0.74\,N_p \text{ kcal/mol}$$

$$BDE(C−Cl) = 88.85 − 2.05\,N_o − 0.93\,N_m + 0.11\,N_p \text{ kcal/mol}$$

The first equation ($r^2 = 0.9538$) reproduces the calculated BDEs of the C−H bond within 0.59 kcal/mol, while the second equation ($r^2 = 0.9770$) does those of the C−Cl bond within 0.50 kcal/mol.

REACTION SPACE MAP

RESMAP is a diagram in a matrix form that represents the relative energies of a group of compounds in the diagonal parts of the matrix and those of the intermediates connecting the compounds in the off-diagonal parts. In the present case, benzene and 12 (poly)chlorobenzenes constitute the group, and the phenyl radical and 19 (poly)chlorophenyl radicals are the intermediates. The energies of these species are expressed as the relative values with respect to benzene.
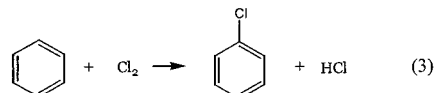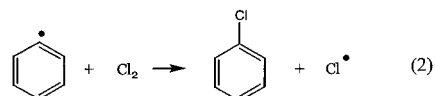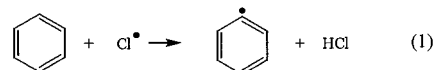
The following steps construct the RESMAP:

(i) The chlorination reaction processes must be assumed, for example, as in the two reaction steps (1) and (2) for

	0	1	2a	2b	2c	3a	3b	3c	4a	4b	4c	5	6
C₆H₆ (0)	0.00	9.73											
C₆H₅Cl (1)	9.73	-33.75	-22.35	-23.76	-23.08								
1,2-C₆H₄Cl₂ (2a)		-22.35	-63.97			-52.90	-53.18						
1,3-C₆H₄Cl₂ (2b)		-23.76		-66.47		-53.44	-54.25	-56.26					
1,4-C₆H₄Cl₂ (2c)		-23.08			-66.55		-54.93						
1,2,3-C₆H₃Cl₃ (3a)			-52.90	-53.44		-93.33			-81.66	-82.41			
1,2,4-C₆H₃Cl₃ (3b)			-53.18	-54.25	-54.93		-96.03		-83.36	-84.74	-83.69		
1,3,5-C₆H₃Cl₃ (3c)				-56.26				-98.28		-84.52			
1,2,3,4-C₆H₂Cl₄ (4a)						-81.66	-83.36		-122.19			-110.36	
1,2,3,5-C₆H₂Cl₄ (4b)						-82.41	-84.74	-84.52		-124.68		-111.51	
1,2,4,5-C₆H₂Cl₄ (4c)							-83.69				-125.06	-112.72	
C₆HCl₅ (5)									-110.36	-111.51	-112.72	-150.47	-137.78
C₆Cl₆ (6)												-137.78	-175.38

Figure 1. RESMAP matrix representation for the chlorination/dechlorination reactions of benzene and (poly)chlorobenzenes initiated by the Cl atom. The diagonal elements (i,i) in the matrix display the relative energies (in kcal/mol) of (poly)chlorobenzenes with respect to benzene, which are defined as the energy changes of the reactions, $C_6H_6 + nCl_2 \rightarrow C_6H_{6-n}Cl_n + nHCl$. The off-diagonal elements display the relative energies of the intermediate (poly)chlorophenyl radicals with respect to benzene; the (i,j) element shows the relative energy of the intermediate radical of the interconversion reaction between i and j compounds.

benzene. The reverse steps are the dechlorination processes. These two steps are expected to occur when there is a constant supply of Cl atoms and then Cl_2 molecules as in the combustion of chlorinated organic compounds. Sokolov et al. studied the gas-phase reaction of Cl atoms with benzene and found that the H-atom abstraction by Cl atoms produces phenyl radicals which then react with Cl_2 to give chlorobenzene, although the effective rate constant for the reaction of Cl with benzene is small.[15] The above reaction processes can be a model of the gas-phase reactions which produce polychlorobenzenes. The formation of chlorobenzene from benzene is written formally by reaction 3, and the phenyl radical is the intermediate species for the chlorination of benzene and also for the dechlorination of chlorobenzene.

(ii) The relative energy of chlorobenzene with respect to benzene is defined by the energy change associated with reaction 3. The energy change associated with reaction 3 can be calculated from Table 1 and the energies of Cl_2 and HCl in Table 3 as -33.75 kcal/mol including the zero-point energy. This energy is assigned to chlorobenzene as the relative energy and displayed at the (1,1) diagonal element of the RESMAP in Figure 1. Similarly, the relative energies of other polychlorobenzenes can be determined successively, and they are collected at the diagonal parts of Figure 1.

(iii) The relative energy of the phenyl radical with respect to benzene is defined by the energy change associated with reaction 1. The energy change of reaction 1, 9.73 kcal/mol, is assigned to the phenyl radical. This energy is listed at the (0,1) and (1,0) off-diagonal elements, since the phenyl radical is the intermediate for the interconversion reaction between benzene and chlorobenzene whose energies are listed as the (0,0) and (1,1) elements. In Figure 1, the energy difference between chlorobenzene at the (1,1) diagonal element and the phenyl radical at the (0,1) off-diagonal element, -43.48 kcal/mol, corresponds to the energy change of reaction 2.

(iv) The relative energy of the 2-chlorophenyl radical with respect to chlorobenzene is calculated from the energy change of reaction 4 as 11.40 kcal/mol. Since the relative energy of chlorobenzene with respect to benzene is -33.75 kcal/mol, the relative energy of the 2-chlorophenyl radical with respect to benzene is -22.35 kcal/mol. This is listed as the (1,2a) and (2a,1) off-diagonal elements connecting chlorobenzene and 1,2-dichlorobenzene in Figure 1. Simi-

larly, the relative energies of other (poly)chlorophenyl radicals were determined successively and are collected as the off-diagonal elements of Figure 1.
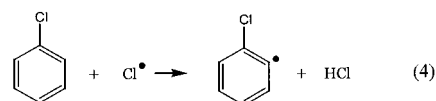

Figure 1 is called a reaction space map, RESMAP, of the chlorination/dechlorination reactions for benzene and (poly)-chlorobenzenes. The diagonal elements represent relative energies of benzene and (poly)chlorobenzenes, and the off-diagonal elements represent the relative energies of the intermediate radicals connecting the corresponding two diagonal elements.

Figure 1 indicates that the relative energies of polychloro-benzenes become low as the chlorination step proceeds. It also indicates that the chlorination reaction becomes slightly more difficult as the number of Cl atoms in (poly)chloro-benzene is increased. Reaction 2 is highly exothermic since the bond dissociation energy of the Cl–Cl bond (45.1 kcal/mol from Table 3) is much less than that of the C–Cl bond (88.6 kcal/mol from Table 4). Sokolov et al. proposed that the phenyl radicals produced in reaction 1 react rapidly with Cl_2 to give chlorobenzene if an appreciable amount of Cl_2 is included in the reaction system.[15] This is well reflected in Figure 1.

As is seen from Figure 1, the energy change for the H-abstraction in chlorobenzene by a Cl atom is 9.99-11.40 kcal/mol. On the other hand, the energy change for the Cl-abstraction in chlorobenzene by a Cl atom (the reverse of reaction 2) is 43.48 kcal/mol. This may seem to be strange since the BDE of the C–H bond is larger than the C–Cl bond by about 22 kcal/mol (Table 4). However, the selectivity of dehydrogenation or dechlorination is controlled not only by the homolytic bond dissociation energies of the C–H and C–Cl bonds in chlorobenzene but also by the bond dissociation energies of the reaction products, HCl and Cl_2. The bond dissociation energies of HCl and Cl_2 are estimated from Table 3 as 99.4 and 45.1 kcal/mol, respectively. This supports the preferable C–H bond dissociation, and chlorobenzene undergoes the C–H bond cleavage rather than the C–Cl bond cleavage in the above reaction processes.

	0	1	2a	2b	2c	3a	3b	3c	4a	4b	4c	5	6
C$_6$H$_6$ (0)	0.00	6.90											
C$_6$H$_5$Cl (1)	6.90	-4.75	3.82	2.41	3.08								
1,2-C$_6$H$_4$Cl$_2$ (2a)		3.82	-5.97			2.27	1.98						
1,3-C$_6$H$_4$Cl$_2$ (2b)		2.41		-8.48		1.72	0.91	-1.10					
1,4-C$_6$H$_4$Cl$_2$ (2c)		3.08			-8.56		0.23						
1,2,3-C$_6$H$_3$Cl$_3$ (3a)			2.27	1.72		-6.34			2.50	1.75			
1,2,4-C$_6$H$_3$Cl$_3$ (3b)			1.98	0.91	0.23		-9.04		0.80	-0.58	0.47		
1,3,5-C$_6$H$_3$Cl$_3$ (3c)				-1.10				-11.29		-0.36			
1,2,3,4-C$_6$H$_2$Cl$_4$ (4a)						2.50	0.80		-6.20			2.79	
1,2,3,5-C$_6$H$_2$Cl$_4$ (4b)						1.75	-0.58	-0.36		-8.70		1.64	
1,2,4,5-C$_6$H$_2$Cl$_4$ (4c)							0.47				-9.08	0.43	
C$_6$HCl$_5$ (5)									2.79	1.64	0.43	-5.49	4.38
C$_6$Cl$_6$ (6)												4.38	-1.41

Figure 2. RESMAP matrix representation for the chlorination/dechlorination reactions of benzene and (poly)chlorobenzenes initiated by the CH$_3$ radical. The diagonal elements (i,i) in the matrix display the relative energies (in kcal/mol) of (poly)chlorobenzenes with respect to benzene, which are defined as the energy changes of the reactions, C$_6$H$_6$ + nCH$_3$Cl → C$_6$H$_{6-n}$Cl$_n$ + nCH$_4$. The off-diagonal elements display the relative energies of the intermediate (poly)chlorophenyl radicals with respect to benzene; the (i,j) element shows the relative energy of the intermediate radical of the interconversion reaction between i and j compounds.

Experiment supports this consideration; the pyrolysis of pure 1,2-dichlorobenzene produced mostly tetrachlorobiphenyls,[2] suggesting the preferable C−H bond cleavage despite the energetic advantage of the homolytic C−Cl bond cleavage over the C−H one. Figure 1 demonstrates clearly how the conversion proceeds among (poly)chlorobenzenes on the assumption that the chlorination and dechlorination reactions proceed by the reaction steps such as (1) and (2).

The relative energies of isomers, which have same atomic constitutions, are obtained directly from their total energies and ZPEs. However, the energies of the polychlorobenzenes having a different number of chlorine atoms cannot be compared directly to one another. The RESMAP defines the relative energy between such compounds artificially as the energy change associated with appropriate chemical reactions and provides immediate estimation of the favorable reaction path in the chlorination/dechlorination processes. The following are the advantages of the RESMAP representation of chemical reactions:

(i) The energies of (poly)chlorobenzenes and the intermediate (poly)chlorophenyl radicals are expressed as the relative values with respect to benzene. The relative energies in the RESMAP represent the thermodynamic stability of each species under the given reaction system.

(ii) The energy changes associated with the interconversion reactions among the species can be derived easily from the difference between the corresponding matrix elements in the RESMAP. In the present chlorination/dechlorination reaction system, the energy changes for 40 chemical reactions are involved in Figure 1.

(iii) The reaction path can be postulated easily from the RESMAP. For example, chlorination of chlorobenzene is expected to occur at the *meta* position, although 1,3-dichlorobenzene is not the most stable isomer of three dichlorobenzenes, since the 3-chlorophenyl radical, (1,2b), is more stable than the 2-chlorophenyl, (1,2a), and 4-chlorophenyl, (1,2c), radicals.

H-ABSTRACTION BY THE CH$_3$ RADICAL

The hydrogen abstraction by Cl is faster from CH$_4$ than from benzene.[15] If the reaction system involves chlorine-containing aliphatic organic compounds, it is expected that the Cl atom abstracts hydrogen atoms from alkyl groups and

the alkyl radical produced undergoes the H-abstraction from benzene. Thus another reaction system considered here to construct a RESMAP involves CH$_3$, CH$_4$, and CH$_3$Cl, which is a model for the chlorination/dechlorination reactions of (poly)chlorobenzenes including chlorine-containing organic compounds. The chlorination reaction of 1,2-dichlorobenzene to 1,2,4-trichlorobenzene, reaction 5, is described as an example to construct the RESMAP. The reaction was assumed to proceed in two steps, (6) and (7), and the RESMAP is shown in Figure 2.
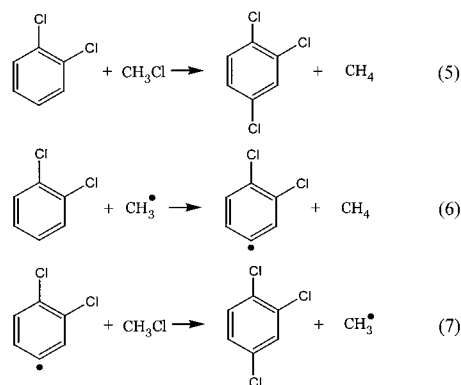
The calculated energy change for reaction 6 is 7.95 kcal/mol and that for reaction 7 is −11.02 kcal/mol. We thus define the relative energy of the intermediate 3,4-dichlorophenyl radical with respect to 1,2-dichlorobenzene to be 7.95 kcal/mol, while the relative energy of 1,2,4-trichlorobenzene with respect to the 3,4-dichlorophenyl radical is −11.02 kcal/mol. From these two quantities, the relative energy of 1,2,4-trichlorobenzene with respect to 1,2-dichlorobenzene is obtained as −3.07 kcal/mol. Since the relative energy of 1,2-dichlorobenzene with respect to benzene, the (2a,2a) element in Figure 2, is calculated to be −5.97 kcal/mol, the relative energy of 1,2,4-trichlorobenzene, the (3b,3b) element in Figure 2, is −9.04 kcal/mol. Similarly, the relative energy of the 3,4-dichlorophenyl radical, the off-diagonal (2a,3b) element which connects 1,2-dichlorobenzene and 1,2,4-trichlorobenzene, is 1.98 kcal/mol. The relative energies of other species were obtained similarly.

Figure 2 shows that trichlorobenzenes are more stable than other polychlorobenzenes, and 1,3,5-trichlorobenzene is the

	0	1	2a	2b	2c	3a	3b	3c	4a	4b	4c	5	6
C₆H₆ (0)	0.00	0.00											
C₆H₅Cl (1)	0.00	0.00	1.67	0.26	0.93								
1,2-C₆H₄Cl₂ (2a)		1.67	3.53			4.87	4.58						
1,3-C₆H₄Cl₂ (2b)		0.26		1.03		4.32	3.52	1.51					
1,4-C₆H₄Cl₂ (2c)		0.93			0.95		2.84						
1,2,3-C₆H₃Cl₃ (3a)			4.87	4.32		7.92			9.85	9.11			
1,2,4-C₆H₃Cl₃ (3b)			4.58	3.52	2.84		5.22		8.16	6.78	7.83		
1,3,5-C₆H₃Cl₃ (3c)				1.51				2.97		7.00			
1,2,3,4-C₆H₂Cl₄ (4a)						9.85	8.16		12.81			14.90	
1,2,3,5-C₆H₂Cl₄ (4b)						9.11	6.78	7.00		10.32		13.75	
1,2,4,5-C₆H₂Cl₄ (4c)							7.83				9.93	12.54	
C₆HCl₅ (5)									14.90	13.75	12.54	18.27	21.24
C₆Cl₆ (6)												21.24	27.11

Figure 3. RESMAP of benzene and (poly)chlorobenzenes for the isodesmic reactions initiated by the phenyl radical. The diagonal elements display the relative energies (kcal/mol) of the compounds with respect to benzene and the off-diagonal elements do those of the intermediate phenyl and (poly)chlorophenyl radicals.

most stable. This indicates that the chlorination of benzene proceeds step by step to trichlorobenzenes. However, the formation of tetra-, penta-, and hexachlorobenzenes is rather restricted. In other words, the dechlorination reactions precede the chlorination reactions in tetra-, penta-, and hexachlorobenzenes under the assumed reaction system.

ISODESMIC REACTIONS

The use of isodesmic reactions may be a standard method to define the relative energy between two compounds having different number and species of constituent atoms. In isodesmic reactions, the same number and type (atomic species and hybridization) of chemical bonds are included in the reactants and reaction products. For the conversion of 1,2-dichlorobenzene to 1,2,4-trichlorobenzene, for example, the following is an isodesmic reaction:

(8)
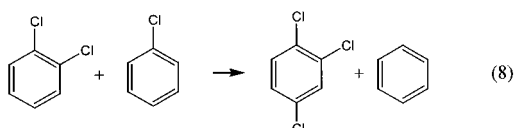
The energy difference of this reaction is calculated from Table 1 as 1.69 kcal/mol, which corresponds to the difference between the (3b,3b) element for 1,2,4-trichlorobenzene and the (2a,2a) element for 1,2-dichlorobenzene in Figure 3. This energy difference is strongly related to the BDEs. It is the sum of two energy differences, the difference between the BDE of the C−H bond at the 4 position in 1,2-dichlorobenzene and that of benzene and the difference between the BDE of the C−Cl bond at the 4 position in 1,2,4-trichlorobenzene and that of chlorobenzene.

The reaction may involve the C−H bond cleavage, which is followed by the C−Cl bond formation, and can be expressed by two isodesmic reactions by

(9)

(10)
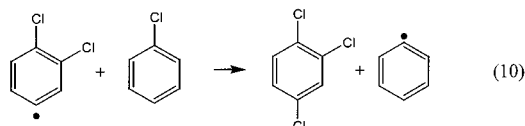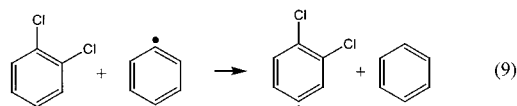
The RESMAP of this reaction system is shown in Figure 3. The relative energy of the 3,4-dichlorophenyl radical with respect to 1,2-dichlorobenzene is defined by the energy change for reaction 9 as 1.05 kcal/mol. Since the relative energy of 1,2-dichlorobenzene with respect to benzene, the (2a,2a) element, is 3.53 kcal/mol, the relative energy of the 3,4-dichlorophenyl radical with respect to benzene is 4.58 kcal/mol, which is given at the (2a,3b) element. Similarly, the relative energy of 1,2,4-trichlorobenzene is 0.64 kcal/mol with respect to the 3,4-dichlorophenyl radical and 5.22 kcal/mol with respect to benzene. The isodesmic reactions 8−10 are unfavorable thermodynamically for the successive chlorination reaction of benzene. The RESMAP for the isodesmic reactions rather gives information on the BDE for the C−H and C−Cl bonds in benzene and polychlorobenzenes.

Three RESMAPs for the chlorination/dechlorination reactions of benzene and polychlorobenzenes were obtained for three different reaction processes. These reaction processes are idealized ones and may be far from what occurs in the experimental conditions of the chlorination reactions or in the combustion of aromatic compounds. However, the real reaction processes are expected to be much complicated, and the exact simulation for such reaction system is almost impossible. The RESMAP is easily created from Tables 1 and 2 by modeling the chlorination/dechlorination reactions and is very useful for the primary and basic consideration on the chlorination and dechlorination processes of benzene and polychlorobenzenes in real reaction systems.

CONCLUSION

Total energies obtained by quantum chemical calculations cannot be compared between two compounds which have different atomic constituents. They can be transformed into relative energies by assuming the chemical reactions which convert the two compounds to each other. In other words, relative stability among molecules with different constituents depends on what reactions we consider to relate them to each other. This means that the reactions can be chosen arbitrarily depending on our particular purpose and the definition of relative energies is necessarily artificial. The artificially defined relative energies for a group of compounds are collected at the diagonal parts of the RESMAP. The relative energies of the intermediates connecting two of the com-

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pounds are stored at the off-diagonal parts. When the conversion between two compounds is kinetically controlled, the off-diagonal parts of the RESMAP can be replaced by the transition state energies. In the present study, the RESMAPs were created for the chlorination and dechlorination reactions of benzene and polychlorobenzenes using three model reactions. Each RESMAP provided a general view of the thermodynamically controlled isomer distributions and chlorination/dechlorination patterns for benzene and polychlorobenzenes. It is easy to create a RESMAP if the total energies of a group of compounds and the intermediates are given. Only a few additional species which are involved in the postulated reactions must be calculated by the same level of theory as used in the total energy calculations for the group of compounds; in the first example of this study, calculations were required for Cl, Cl_2, and HCl. The RESMAP representation will be applied successfully to understand the comprehensive description of the chlorination/dechlorination patterns in PCB or PCDD. Also the RESMAP representation provides a good use of computational output resources in Tables 1 and 2, since the RESMAP can be created for any reaction system from these data by adding a small number of data specific for the reactions considered.

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