

# Energetics of the Homolytic C–H and C–Cl Bond Cleavages in Polychlorobenzenes: The Role of Electronic and Steric Effects

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Geometries of (poly)chlorosubstituted benzenes and phenyl radicals are optimized at the BLYP/6-311G\*\* level of theory. The radicals, which are all planar and of the  $\sigma$ -type, possess geometries that are influenced by both electronic and indirect steric effects. The total energies of the species under study are quantitatively analyzed with simple additive schemes involving the chlorine–chlorine and chlorine–trivalent carbon interactions. Comparisons with the few available experimental data reveal that the computed C–H and C–Cl bond dissociation energies (BDEs) of benzene and its chloro- derivatives are systematically too low by ca. 5 kcal/mol and that the experimental C–Cl BDE of 1,3-dichlorobenzene is most probably in error. The substituents are predicted to facilitate the homolytic C–Cl bond cleavage by up to 6.6 kcal/mol while making the C–H cleavage less favorable by as much as 3.8 kcal/mol. The trends in BDEs are readily accounted for by a superposition of electronic and steric effects. In all cases, the C–Cl bond cleavages are found to require significantly less energy than the C–H ones, implying kinetic control of the aryl radical formation in the course of pyrolysis of (poly)chlorobenzenes.

## Introduction

Polychlorinated biphenyls (PCBs) are important end products of pyrolysis and combustion of diverse chlorine-containing organic substances such as trichloroethylene.<sup>1,2</sup> The formation of these persistent environmental pollutants, which are suspected to be precursors of much more toxic polychlorinated dibenzofurans,<sup>3</sup> is believed to proceed through four steps. The transient, highly unsaturated aliphatic compounds that are produced from the starting material by dehydrogenation and/or elimination of HCl undergo rapid polymerization/cyclization, yielding polychlorobenzenes and other polychlorinated arenes.<sup>2</sup> The subsequent abstraction of either H• or Cl• from polychlorobenzenes turns them into the corresponding substituted phenyl radicals, which finally dimerize or attack arene molecules, forming PCBs.<sup>1,4</sup>

Despite their prominence in the aforementioned environmentally important processes and many other reactions of organic chemistry,<sup>5</sup> substituted phenyl radicals have been the subject of surprisingly few electronic structure studies. This scarcity of theoretical investigations can be partially blamed on the grossly inadequate description of these systems afforded by the conventional UHF-based methods of quantum chemistry. The resulting inaccuracies in the computed properties are well documented for the prototype C<sub>6</sub>H<sub>5</sub>• radical, for which the large spin contamination of the UHF electronic wave function<sup>6</sup> leads to an error of over 30 kcal/mol in the C–H bond dissociation energy (BDE) of benzene.<sup>7</sup> Unfortunately, the ROHF calculations are found to fare only slightly better in this respect.

The recent advances in the modeling of electron correlation with density functionals have radically improved the accuracy of electronic structure calculations on aryl radicals,<sup>7,8</sup> the C–H BDE of C<sub>6</sub>H<sub>6</sub> being predicted, for example, within less than 5 kcal/mol from the experimental value. Taking advantage of these developments, we have recently undertaken a comprehensive study of the energetics of the homolytic C–H and C–Cl

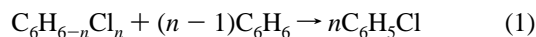
bond cleavages in benzene and its chloro- derivatives. The results of that investigation, together with their interpretation in terms of electronic and steric substituent effects, are presented in this paper.

## Details of Calculations

The BLYP/6-311G\*\* level of theory,<sup>9,10</sup> successfully used in previous calculations on aryl radicals,<sup>7,8</sup> was employed in the present study. Geometries of benzene, the phenyl radical, the 12 distinct (poly)chlorobenzenes, and the 19 distinct (poly)chlorophenyl radicals were fully optimized. The inspection of vibrational frequencies calculated within the same approximation confirmed all the optimized structures to be genuine minima. The zero-point energies (ZPEs) of the species under study were computed from unscaled vibrational frequencies. For the open-shell systems, the values of  $\langle \hat{S}^2 \rangle$  derived from the Kohn–Sham orbitals (which only approximate the actual expectation values) did not exceed 0.756. All calculations were carried out with the GAUSSIAN 94 suite of codes<sup>11</sup> running on an IBM SP2 computer.

## Results and Discussion

The computed total energies of benzene and its chloro-derivatives are listed in Table 1 together with the respective ZPEs. The energies of the isodesmic transchlorination reactions



which measure the extents of interactions between the chlorine substituents, exhibit easily recognizable regularities, with each pair of chlorines at the *ortho*, *meta*, and *para* positions destabilizing the C<sub>6</sub>H<sub>6-n</sub>Cl<sub>n</sub> molecule by ca. 3.7, 1.1, and 1.1 kcal/mol, respectively. Steric interactions between the bulky chlorine atoms are undoubtedly the contributing factor to the larger destabilizing effect of the *ortho* pair. The *meta* and *para* effects, which are of predominantly electronic origin, are much smaller. The ZPEs of the C<sub>6</sub>H<sub>6-n</sub>Cl<sub>n</sub> molecules are additive to an even greater degree, accurately following the simple expres-

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**TABLE 1: BLYP/6-311G\*\* Total and Zero-Point Energies of Benzene and Its Chloro- Derivatives**

substituent(s)	symm	total energy (au)	ZPE (au)
none	$D_{6h}$	-232.197 309	0.097 244
chloro	$C_{2v}$	-691.810 663	0.087 933
1,2-dichloro	$C_{2v}$	-1151.418 178	0.078 564
1,3-dichloro	$C_{2v}$	-1151.422 228	0.078 485
1,4-dichloro	$D_{2h}$	-1151.422 332	0.078 498
1,2,3-trichloro	$C_{2v}$	-1611.024 270	0.069 072
1,2,4-trichloro	$C_s$	-1611.028 617	0.069 031
1,3,5-trichloro	$D_{3h}$	-1611.032 235	0.068 931
1,2,3,4-tetrachloro	$C_{2v}$	-2070.629 573	0.059 568
1,2,3,5-tetrachloro	$C_{2v}$	-2070.633 545	0.059 497
1,2,4,5-tetrachloro	$D_{2h}$	-2070.634 168	0.059 527
pentachloro	$C_{2v}$	-2530.233 875	0.050 009
hexachloro	$D_{6h}$	-2989.832 761	0.040 455

**TABLE 2: BLYP/6-311G\*\* Total and Zero-Point Energies of Phenyl Radical and Its Chloro- Derivatives**

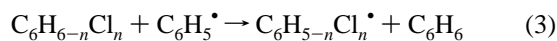
substituent(s)	electronic			ZPE (au)
	symm	state	total energy (au)	
none	$C_{2v}$	$^2A_1$	-231.516 424	0.084 333
2-chloro	$C_s$	$^2A'$	-691.127 435	0.075 086
3-chloro	$C_s$	$^2A'$	-691.129 499	0.074 993
4-chloro	$C_{2v}$	$^2A_1$	-691.128 136	0.075 045
2,3-dichloro	$C_s$	$^2A'$	-1150.735 777	0.065 757
2,4-dichloro	$C_s$	$^2A'$	-1150.737 582	0.065 691
2,5-dichloro	$C_s$	$^2A'$	-1150.738 882	0.065 669
2,6-dichloro	$C_{2v}$	$^2A_1$	-1150.736 757	0.065 789
3,4-dichloro	$C_s$	$^2A'$	-1150.735 668	0.065 661
3,5-dichloro	$C_{2v}$	$^2A_1$	-1150.740 909	0.065 563
2,3,4-trichloro	$C_s$	$^2A'$	-1610.340 910	0.056 291
2,3,5-trichloro	$C_s$	$^2A'$	-1610.346 067	0.056 276
2,3,6-trichloro	$C_s$	$^2A'$	-1610.344 049	0.056 403
2,4,5-trichloro	$C_s$	$^2A'$	-1610.343 967	0.056 223
2,4,6-trichloro	$C_{2v}$	$^2A_1$	-1610.345 538	0.056 271
3,4,5-trichloro	$C_{2v}$	$^2A_1$	-1610.341 739	0.056 146
2,3,4,5-tetrachloro	$C_s$	$^2A'$	-2069.946 096	0.046 786
2,3,4,6-tetrachloro	$C_s$	$^2A'$	-2069.948 184	0.046 868
2,3,5,6-tetrachloro	$C_s$	$^2A'$	-2069.950 438	0.046 982
pentachloro	$C_{2v}$	$^2A_1$	-2529.549 606	0.037 419

sion

$$\text{ZPE} = 0.09724 - 0.0095n \text{ au} \quad (2)$$

The observed negative correlation between the ZPE and the number of chlorine substituents stems from the lowering of vibrational frequencies upon the replacement of the C–H bonds by the C–Cl ones.

Like their unsubstituted prototype,<sup>7,12,13</sup> all the polychlorophenyls are planar,  $\sigma$ -type radicals (Table 2). Substituent effects in these species are readily assessed with the isodesmic hydrogen abstraction reactions



Since these reactions conserve the numbers of chlorine pairs, their energies (computed from the total energies listed in Tables 1 and 2) measure the extents of interactions between the substituents and the electron holes at the formally trivalent carbons. By means of a least-squares fitting, each chlorine substituent at the *ortho*, *meta*, and *para* position is found to contribute, respectively, ca. 1.20, -0.24, and 0.79 kcal/mol to these energies, the contributions being fully ascribable to electronic effects. The exact nature of these effects cannot be unequivocally identified because of the smallness of the above energy contributions. However, the observed pattern of slight stabilization at the *meta* position and larger destabilization at the *ortho* and *para* ones, together with the  $\sigma$  character of the radicals under study, points out the importance of inductive

**TABLE 3: Dependence of the Calculated C–H and C–Cl Bond Dissociation Energies on the Parent Molecule and the Abstraction Site**

parent molecule	C–X BDE (kcal/mol) for the site					
	1	2	3	4	5	6
$\text{C}_6\text{H}_6$	106.94	106.94	106.94	106.94	106.94	106.94
$\text{C}_6\text{H}_5\text{Cl}$	88.18	108.45	107.10	107.98	107.10	108.45
1,2- $\text{C}_6\text{H}_4\text{Cl}_2$	86.06	86.06	107.96	107.96	107.96	107.96
1,3- $\text{C}_6\text{H}_4\text{Cl}_2$	87.30	109.95	87.30	109.37	107.21	109.37
1,4- $\text{C}_6\text{H}_4\text{Cl}_2$	88.24	108.60	108.60	88.24	108.60	108.60
1,2,3- $\text{C}_6\text{H}_3\text{Cl}_3$	84.75	84.16	84.75	108.57	107.96	108.57
1,2,4- $\text{C}_6\text{H}_3\text{Cl}_3$	86.33	85.50	109.43	87.51	109.37	108.08
1,3,5- $\text{C}_6\text{H}_3\text{Cl}_3$	86.50	110.74	86.50	110.74	86.50	110.74
1,2,3,4- $\text{C}_6\text{H}_2\text{Cl}_4$	84.88	82.98	82.98	84.88	108.65	108.65
1,2,3,5- $\text{C}_6\text{H}_2\text{Cl}_4$	84.17	84.50	84.17	109.93	86.81	109.93
1,2,4,5- $\text{C}_6\text{H}_2\text{Cl}_4$	85.83	85.83	108.95	85.83	85.83	108.95
$\text{C}_6\text{HCl}_5$	84.36	83.10	81.76	83.10	84.36	109.26
$\text{C}_6\text{Cl}_6$	81.58	81.58	81.58	81.58	81.58	81.58

effects of the chlorine substituents. As in the case of polychlorobenzenes, the calculated ZPEs (Table 2) decrease linearly with the number of chlorine atoms while being almost completely insensitive to their positions.

The BDEs for homolytic C–H and C–Cl bond cleavages in benzene and its chloro- derivatives are easily computed from the total energies and ZPEs of the species under study. These BDEs (at  $T = 0$  K) are compiled in Table 3. As mentioned previously, the predicted C–H BDE of  $\text{C}_6\text{H}_6$ , which equals 106.9 kcal/mol,<sup>7</sup> is a few kilocalories per mole lower than the experimental values of  $112.0 \pm 0.6$ <sup>14</sup> and  $109.8 \pm 0.8$  kcal/mol.<sup>15</sup> Taking the former experimental energy as a benchmark produces the correction of roughly 5 kcal/mol to be applied to the theoretical BDEs. This correction works well for the C–Cl BDE of chlorobenzene, for which it yields the value of 93.2 kcal/mol, in good agreement with the experimental estimates (obtained from the respective  $\Delta H_{298}$  data by subtracting  $(5/2)RT \approx 1.5$  kcal/mol to account for thermal effects<sup>16</sup>) of  $93.6$ ,<sup>17</sup>  $93.0$ ,<sup>18</sup> and  $94.2 \pm 2$  kcal/mol.<sup>19</sup>

Experimental measurements of the BDEs of polychlorobenzenes are scarce. The C–Cl BDEs of 90.7, 92.2, 93.0, and 92.9 kcal/mol obtained for 1,2- $\text{C}_6\text{H}_4\text{Cl}_2$ , 1,4- $\text{C}_6\text{H}_4\text{Cl}_2$ , 1,3,5- $\text{C}_6\text{H}_3\text{Cl}_3$ , and 1,2,4,5- $\text{C}_6\text{H}_2\text{Cl}_4$ , respectively, from dissociative thermal electron attachment experiments<sup>17</sup> agree within the error bars with the corresponding (corrected) theoretical values of 91.1, 93.2, 91.5, and 90.8 kcal/mol, but such agreement is lacking in the case of the C–Cl BDE of 1,3- $\text{C}_6\text{H}_4\text{Cl}_2$  (88.4 vs 92.3 kcal/mol). No experimental data for the C–H BDEs of (poly)chlorobenzenes are available at present.

The inspection of BDEs for the 20 distinct homolytic C–H cleavages listed in Table 3 leads to the conclusion that the abstraction of single hydrogen radicals from (poly)chlorosubstituted benzenes is invariably more difficult than that from benzene itself. Conversely, the abstraction of  $\text{Cl}^\bullet$  is facilitated by the chlorine substituents in almost all cases (the only exception being the C–Cl bond cleavage in 1,4- $\text{C}_6\text{H}_4\text{Cl}_2$ ). The aforesaid approximate additivity of the substituent contributions to the energies of reactions 1 and 3 readily accounts for these trends. In particular, since the energies of the latter reactions are equal to the respective differences between the C–H BDEs of substituted benzenes and that of  $\text{C}_6\text{H}_6$ ,

$$\text{BDE}(\text{C–H}) \approx 107.24 + 1.20N_o - 0.24N_m + 0.79N_p \text{ kcal/mol} \quad (4)$$

where  $N_o$ ,  $N_m$ , and  $N_p$  are the numbers of the chlorine substituents at the *ortho*, *meta*, and *para* positions with respect to the abstraction site. Despite considerable residual errors, eq

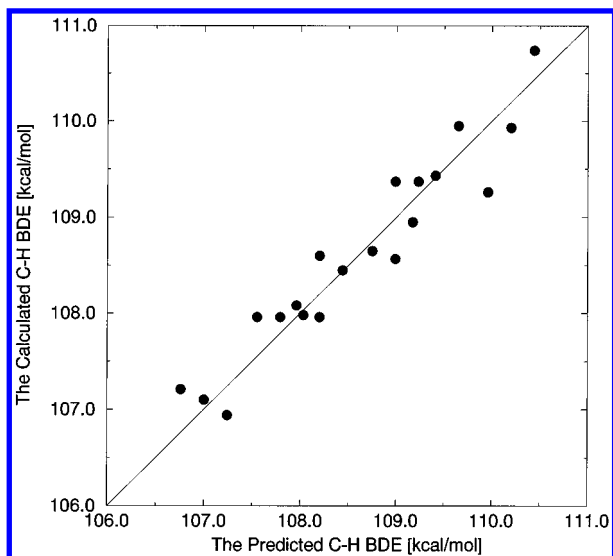


Figure 1. Calculated C–H BDEs vs those predicted from eq 4.

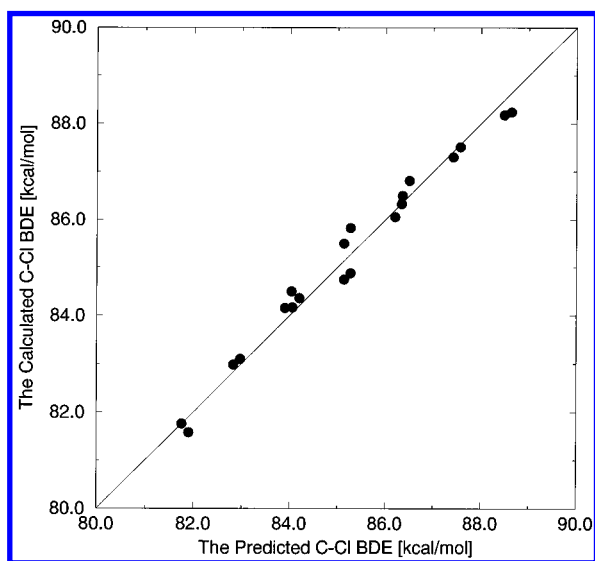


Figure 2. Calculated C–Cl BDEs vs those predicted from eq 5.

4 reproduces the general trends in the C–H BDEs of the molecules under study reasonably well ( $r^2 = 0.928$ , Figure 1).

Homolytic cleavage of the C–Cl bonds in polychlorobenzenes decrease the numbers of chlorine pairs. Consequently, one expects the chlorine substituents at the *ortho*, *meta*, and *para* positions to contribute ca.  $-2.5$  ( $=1.2-3.7$ ),  $-1.3$  ( $=-0.2-1.1$ ), and  $-0.3$  ( $=0.8-1.1$ ) kcal/mol, respectively (compare the contributions to the energies of reactions 1), to the C–Cl BDEs in these species. The coefficients of the linear regression ( $r^2 = 0.978$ )

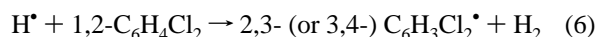
$$\text{BDE}(\text{C}-\text{Cl}) \approx 88.49 - 2.30N_o - 1.07N_m + 0.14N_p \text{ kcal/mol} \quad (5)$$

obtained by a least-squares fitting of the data for the 20 distinct homolytic C–Cl cleavages listed in Table 3, turn out to be reasonably close to these estimates. Good agreement between the computed BDEs and those predicted from eq 5 is observed (Figure 2).

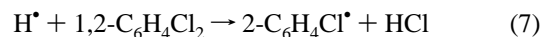
In summary, the substituent effects on the C–H BDEs of (poly)chlorobenzenes are, irrespective of the substituent position(s), of a purely electronic origin. On the other hand, the lowering of the C–Cl BDEs brought about by the *ortho* chlorines stems from a competition between the substituent-

induced electronic destabilization of the aryl radicals and the relief of the Cl–Cl steric repulsions in the parent arenes upon the removal of chlorine, the latter being clearly the prevailing factor. The respective *meta* and *para* effects are the consequence of a differential electronic destabilization of arenes and the corresponding aryl radicals by the chlorine substituents.

Pyrolysis of 1,2-dichlorobenzene at 1100–1400 K produces mostly tetrachlorobiphenyls, some trichlorobiphenyls, and no detectable amounts of dichlorobiphenyls.<sup>1,4</sup> Such a distribution of products implies the preferential formation of the dichlorophenyl radicals despite the 22 kcal/mol energetic advantage of the homolytic C–Cl bond cleavage over the C–H one (Table 3; note that the dissociation energies of the two distinct C–H bonds in 1,2- $\text{C}_6\text{H}_4\text{Cl}_2$  are practically identical). An attempt to rationalize this surprising finding has been made<sup>1</sup> by presuming the hydrogen abstraction



to be thermodynamically favored over the chlorine abstraction



However, this presumption is easily proven to be incorrect. The difference between the standard enthalpies of the reactions 7 and 6 is simply

$$\begin{aligned} \Delta(\Delta H) &= \\ \Delta H_f(\text{C}_6\text{H}_4\text{Cl}^\bullet) + \Delta H_f(\text{HCl}) - \Delta H_f(\text{C}_6\text{H}_3\text{Cl}_2^\bullet) - \Delta H_f(\text{H}_2) &= \\ \text{BDE}(\text{C}-\text{Cl}) - \text{BDE}(\text{H}-\text{Cl}) - \text{BDE}(\text{C}-\text{H}) + \text{BDE}(\text{H}-\text{H}) &= \end{aligned} \quad (8)$$

At  $T = 298$  K, the experimentally determined difference between the BDEs of  $\text{H}_2$  and  $\text{HCl}$  equals 1.1 kcal/mol,<sup>15</sup> whereas the computed difference between the two BDEs of 1,2-dichlorobenzene amounts to  $-21.9$  kcal/mol (Table 3). Combining these data affords  $\Delta(\Delta H) = -20.8$  kcal/mol, clearly in favor of reaction 7. This conclusion is not expected to be qualitatively altered by taking into account the higher temperatures at which the reactions 6 and 7 takes place and/or by including the entropic terms. Therefore, one must conclude that the relative product yields of the thermal dehydrogenation/dechlorination reactions of polychlorobenzenes are kinetically controlled.

The abstraction of the hydrogen radical from unsubstituted arenes is accompanied by a widening of the *ipso* C–C–C bond angle  $\alpha_{\text{ipso}}$  by an almost constant amount.<sup>7</sup> Although the geometries of the systems under the present study do not exhibit such regularities, the substituent contributions to  $\alpha_{\text{ipso}}$  in the radical species can be extracted from the differences between  $\alpha_{\text{ipso}}$  in  $\text{C}_6\text{H}_5^\bullet$  (equal to  $125.9^\circ$ ) and those in 2- $\text{C}_6\text{H}_4\text{Cl}^\bullet$  ( $125.2^\circ$ ), 3- $\text{C}_6\text{H}_4\text{Cl}^\bullet$  ( $126.8^\circ$ ), and 4- $\text{C}_6\text{H}_4\text{Cl}^\bullet$  ( $125.6^\circ$ ). The resulting increments of  $-0.7^\circ$ ,  $0.9^\circ$ , and  $-0.3^\circ$  for the chlorine substituents at the *ortho*, *meta*, and *para* positions, respectively, work reasonably well for polychlorophenyl radicals that lack chlorine atoms attached to neighboring carbons (*ortho* chlorine pairs). In particular, the values of  $124.9$ ,  $126.1$ ,  $124.5$ ,  $127.7$ , and  $124.2^\circ$  are predicted for  $\alpha_{\text{ipso}}$  in the 2,4- $\text{C}_6\text{H}_3\text{Cl}_2^\bullet$ , 2,5- $\text{C}_6\text{H}_3\text{Cl}_2^\bullet$ , 2,6- $\text{C}_6\text{H}_3\text{Cl}_2^\bullet$ , 3,5- $\text{C}_6\text{H}_3\text{Cl}_2^\bullet$ , and 2,4,6- $\text{C}_6\text{H}_2\text{Cl}_3^\bullet$  radicals, in good agreement with the respective actual values of  $125.0$ ,  $126.1$ ,  $124.6$ ,  $127.7$ , and  $124.4^\circ$ . However, no such agreement is observed for  $\alpha_{\text{ipso}}$  in radicals with *ortho* chlorine pairs, such as 2,3- $\text{C}_6\text{H}_3\text{Cl}_2^\bullet$  (the predicted angle of  $124.9^\circ$  vs the actual angle of  $126.9^\circ$ ), 2,3,4- $\text{C}_6\text{H}_2\text{Cl}_3^\bullet$  ( $125.8^\circ$  vs  $126.4^\circ$ ), or  $\text{C}_6\text{Cl}_5^\bullet$  ( $126.0^\circ$  vs  $127.3^\circ$ ). This absence of universal additivity indicates the

comparable importance of electronic and indirect steric effects as the factors determining the geometries around the formally trivalent carbon atoms in substituted phenyl radicals.

## Conclusions

In analogy to their unsubstituted prototype, (poly)chlorophenyls are planar,  $\sigma$ -type radicals. Their total energies are well approximated by a simple additive model that accounts for the chlorine–chlorine and chlorine–trivalent carbon interactions. The same model (without the latter interactions) accurately reproduces the total energies of polychlorobenzenes.

The BLYP/6-311G\*\* level of theory produces the C–H and C–Cl bond dissociation energies (BDEs) of benzene and its chloro- derivatives that are too low by ca. 5 kcal/mol. When corrected for this systematic error, the computed BDEs match their measured counterparts within experimental uncertainties except for the C–Cl BDE of 1,3-dichlorobenzene, for which the experimental value appears to be incorrect. The chlorine (poly)substitution is predicted to facilitate the homolytic C–Cl bond cleavage by up to 6.6 kcal/mol (see the difference between the C–Cl BDEs in  $C_6H_5Cl$  and  $C_6Cl_6$ ) while making the C–H cleavage less favorable by as much as 3.8 kcal/mol (see the difference between the C–H BDEs in  $C_6H_6$  and 1,3,5- $C_6H_3Cl_3$ ). In all cases, the C–Cl bond cleavages require significantly less energy than the C–H ones.

Simple thermochemical considerations rule out the thermodynamic control of the aryl radical formation in the course of pyrolysis of (poly)chlorobenzenes. This conclusion demonstrates the usefulness of electronic structure calculations in studies of reaction mechanisms that are of importance to combustion processes involving chlorine-containing environmental pollutants.

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