

Thermochemistry of Homolytic C–C, C–H, and C–Cl Bond Dissociations in Polychloroethanes: Benchmark Electronic Structure Calculations

Jerzy Cioslowski,* Guanghua Liu, and David Moncrieff

Contribution from the Department of Chemistry and Supercomputer Computations Research Institute, Florida State University, Tallahassee, Florida 32306-3006

Received April 7, 1997. Revised Manuscript Received September 15, 1997[®]

Abstract: G2 and G2MP2 calculations on the $\text{C}_2\text{H}_{6-n}\text{Cl}_n$, $\text{C}_2\text{H}_{5-n}\text{Cl}_n^\bullet$, and $\text{CH}_{3-n}\text{Cl}_n^\bullet$ species produce benchmark thermochemical data for homolytic C–C, C–H, and C–Cl bond dissociations in ethane and its chloro derivatives. Without exception, the C–H bonds are found to be stronger than the C–C ones, which turn out to be barely stronger than their C–Cl counterparts. The standard enthalpies of the homolytic C–C, C–H, and C–Cl bond dissociations decrease sharply with the increasing number of chlorine atoms, the C–C bonds being affected the most. Wherever available, experimental data confirm the reliability of the G2 calculations. The G2MP2 predictions are found to follow closely those of the G2 method. At the same time, the present study uncovers a very poor performance of the BLYP and B3LYP functionals for systems with strong repulsions between chlorine atoms. Analysis of the computed enthalpies of bond dissociation in terms of substituent contributions leads to the conclusion that this poor performance is caused by a systemic exaggeration of the $\text{H}\cdots\text{Cl}$ and $\text{Cl}\cdots\text{Cl}$ repulsions. Most likely, this exaggeration is caused by the inability of the currently used density functionals to correctly describe dispersion interactions.

Pyrolysis of chlorinated aliphatic hydrocarbons is of great practical importance to fuel conversion, large-scale synthesis of chemicals, and environmental protection. Direct conversion of methane (the major component of natural gas) to more valuable hydrocarbons such as ethane, ethene, ethyne, and benzene that employs chlorination and pyrolysis has been developed recently.¹ Industrial production of vinyl chloride involves thermal decomposition of 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$.² Incineration of chlorine-containing chemical waste, which is widely used for its disposal,³ generates highly hazardous pollutants due to incomplete combustion. For example, pyrolysis of C_2Cl_4 yields a complex mixture of polychlorinated aromatic compounds, including polychlorinated biphenyls, that are well-known persistent soil contaminants and potent carcinogens.⁴

The chemical reactions that occur in the course of such pyrolytic processes are mostly of a free-radical nature.⁵ Bond cleavage, abstraction of atoms, and recombination of radicals are the major steps through which these reactions proceed. The initial stages of thermal decomposition are strongly dependent on the substrate. For example, rupture of the C–Cl bond initiates the decomposition of both CHCl_3 and CCl_4 .^{6–8} However, the CHCl_2^\bullet radical loses H^\bullet , producing dichlorocarbene:

CCl_2 that finally dimerizes to C_2Cl_4 ,⁶ whereas CCl_3^\bullet mostly recombines to form C_2Cl_6 .^{7,8} Pyrolysis of C_2HCl_5 yields primarily C_2Cl_4 through a sequence of C–H and C–Cl bond scissions,⁹ while dissociation of the C–C bond plays an important role in thermal decomposition of C_2Cl_6 ¹⁰ that ultimately produces C_2Cl_4 and CCl_4 .¹¹ The initial stages of high-temperature pyrolysis of C_2Cl_4 involve two consecutive C–Cl bond dissociations that lead to formation of dichloroacetylene C_2Cl_2 , which promptly polymerizes to yield polychlorinated aromatic hydrocarbons.¹²

Thanks to a combination of experimental measurements and cutting-edge electronic structure calculations,¹³ thermochemistry of the CH_n ($0 \leq n \leq 4$) species is now well established. The same is true for the CH_nCl_m ($0 \leq n + m \leq 4$) family of molecules.^{14–16} On the other hand, a survey of chemical literature reveals the scarcity of thermochemical data on polychloroethyl radicals (Table 1). The primary reason for this undesirable *status quo* is the difficulty of generating particular isomers of polychlorinated radicals and their propensity to decompose through a loss of chlorine atoms. In light of these experimental problems and the relevance of chlorinated alkyl radicals to pyrolytic reactions, and need for reliable quantum-chemical calculations on thermochemistry of these species is self-evident.

* To whom all the correspondence should be addressed. E-mail: jerzy@kyoko.chem.fsu.edu. Homepage: <http://www.scri.fsu.edu/~jerzy>.

[®] Abstract published in *Advance ACS Abstracts*, November 1, 1997.

(1) (a) Benson, S. W. *U.S. Patent* 4199533, 1980. (b) Benson, S. W.; Weissman, M. *Int. J. Chem. Kinet.* **1984**, *16*, 307. (c) Senkan, S. M. *U.S. Patent* 4714796, 1987.

(2) Cowfer, J. A.; Magistro, A. J. Vinyl Chloride. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Wiley: New York, 1984; p 865.

(3) (a) Senkan, S. M. *Environ. Sci. Technol.* **1988**, *22*, 368. Altwickler, E. A.; Schonberg, J. S.; Konduri, R. K. N.; and Milligan, M. S. *J. Hazard. Mater.* **1990**, *7*, 73. (b) Senkan, S. M. *Chem. Eng. Prog.* **1987**, *12*, 58.

(4) Ballschmitter, K.; Kirschmer, P.; and Zoller, W. *Chemosphere* **1986**, *15*, 1369.

(5) Hucknall, D. J. *Chemistry of Hydrocarbon Combustion*; Chapman and Hall: London, 1995.

(6) Won, Y. S.; Bozzelli, J. W. *Combust. Sci. Technol.* **1992**, *85*, 345.

(7) Shilov, A. E.; Sabirova, R. D. *Zh. Fiz. Khim.* **1959**, *33*, 1365.

(8) Michael, J. V.; Lim, K. P.; Kumaran, S. S.; and Kiefer, J. H. *J. Phys. Chem.* **1993**, *97*, 1914.

(9) Benson, S. W.; Weissman, M. *Int. J. Chem. Kinet.* **1982**, *14*, 1287 and references cited therein.

(10) White, M. L.; Kuntz, R. R. *Int. J. Chem. Kinet.* **1973**, *5*, 187.

(11) Weissman, M.; Benson, S. W. *Int. J. Chem. Kinet.* **1980**, *12*, 403.

(12) Taylor, P. H.; Tirey, D. A.; Dellinger, B. *Combustion Flame* **1996**, *104*, 260.

(13) Grev, R. S.; Schaefer, H. F., III. *J. Chem. Phys.* **1992**, *97*, 8389 and references cited therein.

(14) Rodriguez, C. F.; Böhme, D. K.; Hopkinson, A. C. *J. Phys. Chem.* **1996**, *100*, 2942 and the references cited therein.

(15) (a) Robles, E. S. J.; Chen, P. *J. Phys. Chem.* **1994**, *98*, 6919. Rodriguez, C. F.; Sirois, S.; Hopkinson, A. C. *J. Org. Chem.* **1992**, *57*, 4869. (b) Rayez, M.-T.; Rayez, J.-C.; Sawersyn, J.-P. *J. Phys. Chem.* **1994**, *98*, 11342.

(16) Berry, R. J.; Burgess, D. R. F., Jr.; Nyden, M. R.; Zachariah, M. R.; Melius, C. F.; Schwartz, M. *J. Phys. Chem.* **1996**, *100*, 7405.

Table 1. Summary of the Available Experimental Data on ΔH_f° of the Species Relevant to Homolytic Bond Dissociations in Polychloroethanes

species	ΔH_f° (kcal/mol)	species	ΔH_f° (kcal/mol)
H•	52.103 ± 0.001 ^a	Cl•	28.992 ± 0.002 ^a
CH ₃ •	35.06 ± 0.10 ^b	CH ₂ Cl•	29.1 ± 1.0, ^c 27.7 ± 2.0 ^d
CHCl ₂ •	23.5 ± 1.2, ^c 22.3 ± 2.0 ^d	CCl ₃ •	18.0 ± 2.0, ^d 17.0 ± 0.6 ^e
C ₂ H ₅ •	28.92 ± 0.36 ^f	CH ₂ ClCH ₂ •	22.8 ± 2.0 ^d
CH ₃ CHCl•	19.3 ± 2.0 ^d	C ₂ HCl ₄ • ^g	4.9 ^h
C ₂ Cl ₅ •	7.7 ± 1, ⁱ 8.4 ± 1.9 ^j		
C ₂ H ₆	−20.1 ± 0.1 ^k	C ₂ H ₅ Cl	−26.8 ± 0.2 ^k
CH ₃ CHCl ₂	−31.2 ± 0.7, ^k −30.52 ^l	CH ₂ ClCH ₂ Cl	−32.1 ± 0.3, ^k −30.33 ^l
CH ₃ CCl ₃	−34.56 ± 0.19 ^k	CH ₂ ClCHCl ₂	−34.58 ± 0.45, ^k −36.14 ^l
CCl ₃ CH ₂ Cl	−36.40 ± 0.33 ^k	CHCl ₂ CHCl ₂	−37.60 ± 0.72, ^k −35.66 ^l
C ₂ HCl ₅	−33.0, −34.2, −34.8, ^k −34.8 ^m	C ₂ Cl ₆	−32.9, −34.7, −33.0, −36.1, ^k −33.7 ⁱ

^a Reference 17. ^b Reference 18. ^c Reference 19. ^d Reference 20. ^e Reference 21. ^f Reference 22. ^g Unspecified isomer. ^h Reference 9. ⁱ Reference 11. ^j Reference 23. ^k Reference 24. ^l Reference 25. ^m Reference 26.

The contemporary electronic structure theory offers several extrapolation schemes that are capable of highly reliable predictions of standard enthalpies of formations. The G2²⁷ and G2MP2²⁸ approaches rely on the additivity of electron correlation contributions to the total energy computed at escalating levels of theory. The CBS methods, such as CBS-Q²⁹ or CBS-APNO,³⁰ employ a different formalism that is somewhat more empirical in nature. The recently published results of test calculations have demonstrated that, despite wide differences in the computational cost, these schemes possess similar accuracy (typically 1–2 kcal/mol).³¹

The lack of reliable thermochemical data on homolytic C–C, C–H, and C–Cl bond dissociations in polychloroethanes and the availability of the aforementioned quantum-chemical methods have prompted the research described in this paper. In addition to providing benchmarks for the standard enthalpies of bond dissociation, this research complements the recently published investigations of the relative accuracy of the G2-type and DFT-based electronic structure calculations.^{32,33} Comparison of the present G2 and G2MP2 predictions with those

obtained at the BLYP/6-311G** and B3LYP/6-311G** levels of theory reveals the excellent agreement between the two extrapolation schemes and the poor performance of the DFT approaches. Analysis of the computed data in terms of the contributions due to geminal and vicinal interactions allows the construction of a simple additive scheme for the standard enthalpies of homolytic C–C, C–H, and C–Cl bond dissociations and pinpoints the exaggeration of repulsions involving chlorine atoms as the primary reason behind the observed failure of the DFT-based methods.

Results

G2 and G2MP2 calculations on the H•, Cl•, and CH_{3–n}Cl_n• (0 ≤ n ≤ 3) radicals and all the species with the compositions C₂H_{6–n}Cl_n (0 ≤ n ≤ 6) and C₂H_{5–n}Cl_n• (0 ≤ n ≤ 5) were carried out (one should note that several of these G2 runs constitute the largest calculations of this type ever reported in the chemical literature). BLYP/6-311G** and B3LYP/6-311G** geometry optimizations and vibrational frequency calculations were also performed for the aforementioned molecules and radicals. The total energies (including ZPEs) as well as the standard energies, enthalpies, and free enthalpies of all the molecules under study, computed at the G2, G2MP2, BLYP/6-311G**, and B3LYP/6-311G** levels of theory with the GAUSSIAN94 suite of programs,³⁴ are reported in the Supporting Information.

Relative Energies of Isomers and Conformers of Polychloroethanes and Polychloroethyl Radicals. Most of the species under the present study possess several distinct rotamers. According to numerous experimental measurements, the *gauche* rotamer of 1,2-dichloroethane is less stable than its *anti* counterpart, the energy because of the large errors in the measured standard enthalpies of formation (Table 1).

Experimental studies of individual rotamers of polychloroethyl radicals are virtually nonexistent. The present calculations reveal a well-pronounced preference for conformations in which the *gauche* orientation of a chlorine atom with respect to the lone unpaired electron is avoided (one should be reminded that

(17) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. (Eds.) *CODATA Key Values for Thermodynamics*; Hemisphere Publishing Corp.: New York, 1989.

(18) Dobis, O.; Benson, S. W. *Int. J. Chem. Kinet.* **1987**, *19*, 691.

(19) Tschuikow-Roux, E.; Paddison, S. *Int. J. Chem. Kinet.* **1987**, *19*, 15.

(20) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1988**, *110*, 7343.

(21) Hudgens, J. W.; Johnson, R. D., III; Timonen, R. S.; Seetula, J. A.; Gutman, D. *J. Phys. Chem.* **1991**, *95*, 4400.

(22) Seakins, P. W.; Pilling, M. J.; Niiranen, J. T.; Gutman, D.; Krasnoperov, L. N. *J. Phys. Chem.* **1992**, *96*, 9847.

(23) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(24) Kolesov, V. P.; Papina, T. S. *Russ. Chem. Rev.* **1983**, *52*, 425, and references cited therein.

(25) Lide, D. R. (Ed.) *CRC Handbook of Chemistry and Physics* (1913–1995), 75th ed.; CRC Press: Boca Raton, FL, 1994; pp 5–9.

(26) (a) Chao, J.; Rodgers, A. S.; Wilhoit, R. C.; Zwolinski, B. J. *Ideal Gas Chemical Thermodynamic Properties of the Six Chloroethanes with Symmetric Top*; NBS: Washington, DC, 1972. (b) Rodgers, A. S.; Wilhoit, R. C.; Zwolinski, B. J. *Ideal Gas Chemical Thermodynamic Properties; The Eight Chloro- and Fluoromethanes*; NBS: Washington, DC, 1972.

(27) (a) Curtiss, A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221. (b) Curtiss, L. A.; Carpenter, J. E.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1992**, *96*, 9030.

(28) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293.

(29) Petersson, G. A.; Tensfeldt, T. G.; Montgomery, J. A., Jr. *J. Chem. Phys.* **1991**, *94*, 6091.

(30) Montgomery, J. A.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1994**, *101*, 5900.

(31) Ochterski, J. W.; Petersson, G. A.; Wiberg, K. B. *J. Am. Chem. Soc.* **1995**, *117*, 11299.

(32) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1053.

(33) Mole, S. J.; Zhou, X.; Liu, R. *J. Phys. Chem.* **1996**, *100*, 14665.

(34) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(35) Wiberg, K. B.; Murcko, M. A. *J. Phys. Chem.* **1987**, *91*, 3616 and the references cited therein.

(36) Hammarström, L.-G.; Liljefors, T.; Gasteiger, J. *J. Comput. Chem.* **1988**, *9*, 424 and references cited therein.

Table 2. Theoretical and Experimental Standard Enthalpies of Homolytic C–C Bond Dissociations in Ethane and Its Chloro Derivatives

species	products	ΔH_{C-C}° (kcal/mol)				exp. ^a
		G2	G2MP2	BLYP/6-311G**	B3LYP/6-311G**	
C ₂ H ₆	2CH ₃ •	90.81	91.07	85.61	86.04	90.2 ± 0.2
C ₂ H ₅ Cl	CH ₃ • + CH ₂ Cl•	90.99	91.28	83.67	84.77	89.8 ± 2.2
CH ₃ CHCl ₂	CH ₃ • + CHCl ₂ •	90.87	91.17	81.48	83.07	89.8 ± 3.3
CH ₂ ClCH ₂ Cl	2CH ₂ Cl•	89.87	90.20	79.59	81.28	87.2 ± 3.3
CH ₃ CCl ₃	CH ₃ • + CCl ₃ •	90.01	90.26	78.26	80.26	87.6 ± 2.0
CH ₂ ClCHCl ₂	CH ₂ Cl• + CHCl ₂ •	87.97	88.32	74.58	76.79	86.5 ± 4.0
CCl ₃ CH ₂ Cl	CCl ₃ • + CH ₂ Cl•	85.93	86.22	69.23	71.84	82.3 ± 3.0
CHCl ₂ CHCl ₂	2CHCl ₂ •	84.68	85.05	67.13	69.89	84.0 ± 4.7
C ₂ HCl ₅	CCl ₃ • + CHCl ₂ •	81.70	81.99	60.06	63.14	75.4 ± 3.9
C ₂ Cl ₆	2CCl ₃ •	77.56	77.72	50.98	54.34	70.1 ± 3.5

^a Computed from the data listed in Table 1.**Table 3.** Theoretical and Experimental Standard Enthalpies of Homolytic C–H Bond Dissociations in Ethane and Its Chloro Derivatives

species	product	ΔH_{C-H}° (kcal/mol)				exp. ^a
		G2	G2MP2	BLYP/6-311G**	B3LYP/6-311G**	
C ₂ H ₆	C ₂ H ₅ •	102.61	102.67	97.98	99.09	101.1 ± 0.4
C ₂ H ₅ Cl	CH ₃ CHCl•	99.09	99.17	93.91	95.48	98.2 ± 2.0
	CH ₂ ClCH ₂ •	103.11	103.18	95.97	98.36	101.7 ± 2.0
CH ₃ CHCl ₂	CH ₃ CCl ₂ •	96.63	96.72	91.29	93.08	n/a
	CHCl ₂ CH ₂ •	104.51	104.61	97.16	99.54	n/a
CH ₂ ClCH ₂ Cl	CH ₂ ClCHCl•	98.98	99.06	91.28	94.24	n/a
CH ₃ CCl ₃	CCl ₃ CH ₂ •	105.51	105.62	97.86	100.32	n/a
CH ₂ ClCHCl ₂	CH ₂ ClCCl ₂ •	95.56	95.66	87.68	90.69	n/a
	CHCl ₂ CHCl•	99.44	99.55	91.38	94.32	n/a
CCl ₃ CH ₂ Cl	CCl ₃ CHCl•	100.10	100.19	91.99	94.89	n/a ^b
CHCl ₂ CHCl ₂	CHCl ₂ CCl ₂ •	95.66	95.76	87.37	90.39	94.0 ± 1.3
C ₂ HCl ₅	C ₂ Cl ₅ •	96.97	97.05	88.81	91.83	94.5 ± 2.2

^a Computed from the data listed in Table 1. ^b The C₂HCl₄• species listed in Table 1 are assumed to be CHCl₂CCl₂•.

the *gauche* and *anti* designations for conformations of alkyl radicals are only approximate due to the almost planar arrangement of atoms bonded to the formally trivalent carbon). For example, the C_s rotamer of the CHCl₂CCl₂• radical is predicted to be less stable than its C₁ counterpart by as much as 3.6 (G2), 3.5 (G2MP2), 4.8 (BLYP/6-311G**), and 4.2 kcal/mol (B3LYP/6-311G**). At all the four levels of theory, the *gauche* rotamers of CH₂ClCH₂•, CH₂ClCHCl• (the conformer with the *gauche* arrangement of the Cl atoms), and CHCl₂CHCl• are not even energy minima. In the cases of CH₂ClCCl₂• and CH₂ClCHCl• (the conformer with the *anti* arrangement of the Cl atoms), such rotamers are minima on the G2 and G2MP2 potential energy hypersurfaces but not on the BLYP or B3LYP ones.

Trends in the Standard Enthalpies of Homolytic Bond Dissociations. Introduction of multiple chlorine atoms into organic molecules brings about a substantial increase in steric repulsions that manifests itself in the markedly reduced stability of such species with respect to homolytic bond cleavages. Thus, although alkanes with arbitrary numbers of carbon atoms can be synthesized, C₃Cl₈ readily loses Cl₂,³⁷ C₄Cl₁₀ is very unstable,³⁸ the initial report³⁹ of the synthesis of C₅Cl₁₂ has never been confirmed, and higher perchloroalkanes are unknown at present. The limited experimental data on the standard enthalpies of homolytic C–C, C–H, and C–Cl bond dissociations, ΔH_{C-C}° , ΔH_{C-H}° , and ΔH_{C-Cl}° , in ethane and its chloro derivatives confirm these observations. For example, the C–C bond in C₂Cl₆ is ca. 20 kcal/mol weaker than that in C₂H₆ (Table 2). The analogous effects on ΔH_{C-H}° and ΔH_{C-Cl}° are smaller in general (Tables 3 and 4).

The G2 and G2MP2 methods are equally successful at reproducing the available experimental values of ΔH_{C-C}°

(Table 2). The standard enthalpy of the homolytic C–C bond dissociation in ethane is predicted with an error of less than 1 kcal/mol by both approaches. The agreement between the experimental and theoretical ΔH_{C-C}° worsens somewhat with increasing degree of chlorination. It is unclear at present whether this worsening reflects the reduced quality of the experimental data or it is caused by the neglect of spin–orbit effects that is known to diminish the accuracy of G2 predictions for molecules with multiple heavy atoms.³² In all cases, the G2MP2 data deviate by less than 0.4 kcal/mol from their G2 counterparts. On the other hand, both the BLYP and B3LYP density functionals badly underestimate ΔH_{C-C}° . Although the BLYP/6-311G** standard enthalpy of the homolytic C–C bond dissociation in the C₂H₆ molecule is too low by 4.6 kcal/mol (which is much less than the error of more than 8 kcal/mol in the computed ΔH_{C-C}° for C₆H₅–C₆H₅),⁴⁰ the underestimation becomes more severe upon chlorine substitution, amounting to at least 20 kcal/mol for C₂Cl₆. The B3LYP/6-311G** results are only marginally better.

The standard enthalpy of the homolytic C–H bond dissociation in C₂H₆ is well reproduced at both the G2 and G2MP2 levels of theory (Table 3). The B3LYP/6-311G** estimate is ca. 2 kcal/mol too low, whereas the BLYP/6-311G** calculations produce ΔH_{C-H}° that deviates by ca. 3 kcal/mol from the experimental value (which is similar to the ca. 5 kcal/mol error in ΔH_{C-H}° for C₆H₅–H).^{41,42} Comparison of the computed data with the limited experimental results reveals a pattern similar to that observed for the C–C bond dissociation, i.e. the reliability of the G2 and G2MP2 levels of theory, and a marked

(40) Cioslowski, J.; Piskorz, P.; Liu, G.; Moncrieff, D. *J. Phys. Chem.* **1996**, *100*, 19333.(41) Cioslowski, J.; Liu, G.; Martinov, M.; Piskorz, P.; Moncrieff, D.; *J. Am. Chem. Soc.* **1996**, *118*, 5261. Cioslowski, J.; Liu, G.; Moncrieff, D. *J. Org. Chem.* **1996**, *61*, 4111.(42) Cioslowski, J.; Liu, G.; Moncrieff, D. *J. Phys. Chem. A* **1997**, *101*, 957.(37) Khalaf, H. *Tetrahedron Lett.* **1971**, *45*, 4229.(38) Roedig, A. *Ann. Chem.* **1951**, *574*, 122. Miller, W. *J. Am. Chem. Soc.* **1940**, *62*, 341.(39) Motsarev, G. V.; Inshakova, V. T.; Raskina, A. D.; Rozenberg, V. R.; Kolbasov, V. I. *Zh. Obshch. Khim.* **1990**, *60*, 1623.

Table 4. Theoretical and Experimental Standard Enthalpies of Homolytic C–Cl Bond Dissociations in Ethane and Its Chloro Derivatives

species	product	$\Delta H_{\text{C-Cl}}^{\circ}$ (kcal/mol)				
		G2	G2MP2	BLYP/6-311G**	B3LYP/6-311G**	exp. ^a
C ₂ H ₅ Cl	C ₂ H ₅ •	86.49	87.63	78.27	78.05	84.7 ± 0.4
CH ₃ CHCl ₂	CH ₃ CHCl•	82.25	83.41	71.70	71.51	79.5 ± 2.1
CH ₂ ClCH ₂ Cl	CH ₂ ClCH ₂ •	85.70	86.85	74.13	75.11	83.2 ± 2.3
CH ₃ CCl ₃	CH ₃ CCl ₂ •	77.47	78.56	64.78	64.58	n/a
CH ₂ ClCHCl ₂	CH ₂ ClCHCl•	80.36	81.52	66.25	67.47	n/a
	CHCl ₂ CH ₂ •	85.31	86.50	72.50	73.49	n/a
CCl ₃ CH ₂ Cl	CH ₂ ClCCl ₂ •	75.23	76.32	59.03	60.05	n/a
	CCl ₃ CH ₂ •	85.13	86.33	71.07	72.13	n/a
CHCl ₂ CHCl ₂	CHCl ₂ CHCl•	79.43	80.61	63.92	65.15	n/a
C ₂ HCl ₅	CHCl ₂ CCl ₂ •	74.38	75.47	57.01	57.95	67.8 ^b
	CCl ₃ CHCl•	79.15	80.30	62.80	63.92	n/a ^c
C ₂ Cl ₆	C ₂ Cl ₅ •	74.53	75.53	56.44	57.34	71.5 ^d

^a Computed from the data listed in Table 1. ^b Uncertainty of the experimental data difficult to assess, definitely greater than 0.9 kcal/mol. ^c The C₂HCl₄• species listed in Table 1 assumed to be CHCl₂CCl₂•. ^d Uncertainty of the experimental data difficult to assess, estimated at about 2.8 kcal/mol.

deterioration in the accuracy of the BLYP and B3LYP predictions upon the increase in the number of chlorine atoms.

The overall agreement between the theoretical and experimental data is somewhat worse for the homolytic C–Cl bond dissociation (Table 4). The G2 prediction for $\Delta H_{\text{C-Cl}}^{\circ}$ of C₂H₅–Cl is ca. 2 kcal/mol too high, and there is a difference of over 1 kcal/mol between the G2 and G2MP2 estimates. These discrepancies (which are similar to those previously encountered in analogous calculations on chlorofluoromethanes)¹⁶ persist for polychloroethanes, for which the DFT-based methods again fail. In particular, although $\Delta H_{\text{C-Cl}}^{\circ}$ of C₂H₅Cl is calculated too low by 6.5 kcal/mol at the BLYP/6-311G** level of theory (which can be compared with the error of ca. 5 kcal/mol for C₆H₅–Cl),⁴² the error in the computed $\Delta H_{\text{C-Cl}}^{\circ}$ of C₂Cl₆ amounts to 15 kcal/mol.

It should be emphasized that the aforescribed poor performance of the BLYP/6-311G** and B3LYP/6-311G** levels of theory does not stem from the moderate size of the basis set. In fact, the agreement between the experimental and theoretical standard enthalpies of the homolytic C–C bond dissociations worsens slightly upon the augmentation of the present basis set with diffuse and additional polarization functions. In particular, the predicted values of $\Delta H_{\text{C-C}}^{\circ}$ in C₂Cl₆ are 48.13 and 51.70 at the BLYP/6-311+G(3df,2p) and B3LYP/6-311+G(3df,2p) levels of theory, respectively, i.e., almost 3 kcal/mol lower than their BLYP/6-311** and B3LYP/6-311** counterparts. On the other hand, a minor improvement is observed in the corresponding $\Delta H_{\text{C-Cl}}^{\circ}$ values that rise by ca. 2 kcal/mol to 58.19 and 59.42 kcal/mol.

Analysis of Substituent Effects on the Standard Enthalpies of Homolytic Bond Dissociations. The standard enthalpies discussed in the preceding section of this paper refer to “adiabatic” bond dissociations, i.e. those involving the parent molecules and the resulting radicals in their lowest-energy conformations. A much more detailed picture of substituent effects on the energetics of homolytic bond dissociations is provided by “vertical” (or site-specific) $\Delta H_{\text{C-X}}^{\circ}$, where X = C, H, or Cl, that are computed from the standard enthalpies of formation of specific rotamers and those of the corresponding radicals with the arrangement of substituents kept intact after bond dissociation (Table 5). The computed values of site-specific $\Delta H_{\text{C-X}}^{\circ}$ can be readily analyzed by enumerating the geminal and vicinal pairs of substituents in the parent molecules.

In the C₂H_{6-n}Cl_n species (Figure 1), there are 6 geminal (X₁–X₂, X₂–X₃, X₃–X₁, X₄–X₅, X₅–X₆, and X₆–X₄), 6 *gauche* vicinal (X₁–X₅, X₁–X₆, X₂–X₄, X₂–X₆, X₃–X₄, and X₃–X₅), and 3 *anti* vicinal (X₁–X₄, X₂–X₅, and X₃–X₆) pairs of substituents (note that both the H and Cl atoms are regarded as

substituents whereas the C–C fragment constitutes the molecular frame).⁴³ A similar situation is encountered in the C₂H_{5-n}Cl_n• radicals, in which the well-localized free electron can be formally treated as a “substituent”. On the other hand, all the 6 substituent pairs in the CH_{3-n}Cl_n• radicals are of the geminal type.

Considerations employing cluster expansions⁴³ for the standard enthalpies of formation of the C₂H_{6-n}Cl_n•, C₂H_{5-n}Cl_n•, and CH_{3-n}Cl_n• species (see the Supporting Information) lead to the following approximate expression for the site-specific standard enthalpies of homolytic C–C bond dissociations in ethane and its chloro derivatives:

$$\Delta H_{\text{C-C}}^{\circ} \approx \sigma_{\text{C-C}}^{\circ} + n_{\text{Cl}}\sigma_{\text{C-C}} + n_{\text{ClCl}}^{\text{g}}\sigma_{\text{C-C}}^{\text{g}} + n_{\text{ClCl}}^{\text{vg}}\sigma_{\text{C-C}}^{\text{vg}} + n_{\text{ClCl}}^{\text{va}}\sigma_{\text{C-C}}^{\text{va}} \quad (1)$$

where n_{Cl} , $n_{\text{ClCl}}^{\text{g}}$, $n_{\text{ClCl}}^{\text{vg}}$, and $n_{\text{ClCl}}^{\text{va}}$ are, respectively, the numbers of the chlorine atoms and the geminal, *gauche* vicinal, and *anti* vicinal Cl–Cl pairs in the parent molecule. Analogous formulae can be derived for $\Delta H_{\text{C-H}}^{\circ}$ and $\Delta H_{\text{C-Cl}}^{\circ}$:

$$\Delta H_{\text{C-H}}^{\circ} \approx \sigma_{\text{C-H}}^{\circ} + m_{\text{HCl}}^{\text{g}}\sigma_{\text{C-H}}^{\text{g}} + m_{\text{HCl}}^{\text{vg}}\sigma_{\text{C-H}}^{\text{vg}} + m_{\text{HCl}}^{\text{va}}\sigma_{\text{C-H}}^{\text{va}} \quad (2)$$

and

$$\Delta H_{\text{C-Cl}}^{\circ} \approx \sigma_{\text{C-Cl}}^{\circ} + m_{\text{ClCl}}^{\text{g}}\sigma_{\text{C-Cl}}^{\text{g}} + m_{\text{ClCl}}^{\text{vg}}\sigma_{\text{C-Cl}}^{\text{vg}} + m_{\text{ClCl}}^{\text{va}}\sigma_{\text{C-Cl}}^{\text{va}} \quad (3)$$

where $m_{\text{HCl}}^{\text{g}}$, $m_{\text{HCl}}^{\text{vg}}$, $m_{\text{HCl}}^{\text{va}}$ ($m_{\text{ClCl}}^{\text{g}}$, $m_{\text{ClCl}}^{\text{vg}}$, $m_{\text{ClCl}}^{\text{va}}$) are the numbers of the chlorine atoms present in the parent molecule that are in the geminal, *gauche* vicinal, and *anti* vicinal positions with respect to the dissociating C–H (C–Cl) bond.

Inspection of Figure 2 reveals accurate reproduction of the computed standard enthalpies of homolytic C–C bond dissociations by the five-parameter regression (1) at all the four levels of theory. However, the parameters $\sigma_{\text{C-C}}^{\circ}$, $\sigma_{\text{C-C}}$, $\sigma_{\text{C-C}}^{\text{g}}$, $\sigma_{\text{C-C}}^{\text{vg}}$, and $\sigma_{\text{C-C}}^{\text{va}}$ obtained from the G2 and G2MP2 data differ significantly from their BLYP and B3LYP counterparts (Table 6). The DFT-based methods produce smaller values of $\sigma_{\text{C-C}}^{\circ}$, reflecting the general underestimation of bond dissociation enthalpies. The $\sigma_{\text{C-C}}$ parameter, which describes the overall lowering of $\Delta H_{\text{C-C}}^{\circ}$ upon chlorination, is much too negative at the BLYP/6-311G** and B3LYP/6-311G** levels of theory. On the other hand, the three other parameters that measure nonadditivities among the H•••H, H•••Cl, and Cl•••Cl nonbond-

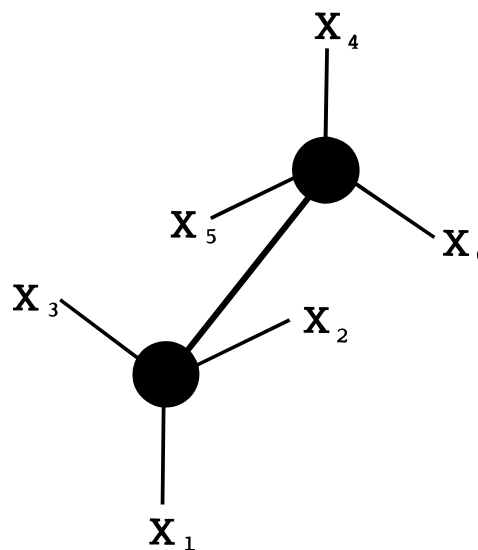
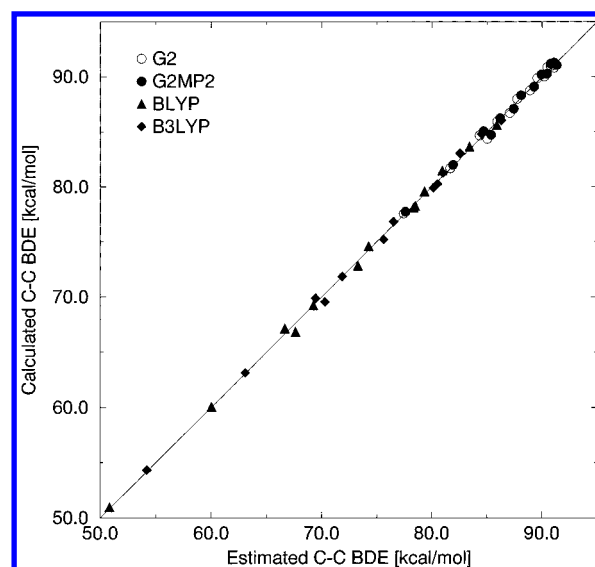
Table 5. Site-Specific Standard Enthalpies of Homolytic C–H, C–Cl, and C–C Bond Dissociations in Ethane and Its Chloro Derivatives

						ΔH_{C-X}° (kcal/mol)			
substituents ^a									
X ₁	X ₂	X ₃	X ₄	X ₅	X ₆	site ^b	G2	G2MP2	BLYP/ 6-311G**
H	H	H	H	H	H	1	102.61	102.67	97.98
						CC	90.81	91.07	85.61
Cl	H	H	H	H	H	1	86.49	87.63	78.27
						2	99.09	99.17	93.91
						4	103.11	103.18	95.97
						5	n/a	n/a	n/a
						CC	90.99	91.28	83.67
Cl	H	H	H	H	Cl	1	n/a	n/a	n/a
						2	n/a	n/a	n/a
						3	97.86	97.95	89.81
						CC	88.75	89.10	78.12
Cl	H	H	Cl	H	H	1	85.70	86.85	74.13
						2	100.90	100.98	n/a
						CC	89.87	90.20	79.59
Cl	Cl	H	H	H	H	1	82.25	83.41	71.70
						3	96.63	96.72	91.29
						4	104.51	104.61	97.16
						6	105.59	105.68	98.96
						CC	90.87	91.17	81.48
H	Cl	Cl	Cl	H	H	1	94.31	94.42	85.92
						2	n/a	n/a	n/a
						4	85.13	86.33	72.54
						5	98.80	98.88	90.75
						CC	86.71	87.08	72.82
Cl	H	Cl	Cl	H	H	1	80.36	81.52	66.25
						2	97.85	97.94	n/a
						3	82.28	83.44	n/a
						4	85.31	86.50	72.50
						5	n/a	n/a	n/a
						6	99.44	99.55	91.38
						CC	87.97	88.32	74.58
Cl	Cl	Cl	H	H	H	1	77.47	78.56	64.78
						4	105.51	105.62	97.86
						CC	90.01	90.26	78.26
H	Cl	Cl	H	Cl	Cl	1	98.91	98.96	91.92
						2	79.11	80.31	63.64
						CC	84.36	84.74	66.86
Cl	Cl	Cl	Cl	H	H	1	75.23	76.32	59.03
						2	77.51	78.60	n/a
						4	85.13	86.33	71.07
						5	100.10	100.19	91.99
						CC	85.93	86.22	69.23
Cl	Cl	H	H	Cl	Cl	1	n/a	n/a	n/a
						2	80.05	81.19	65.04
						3	95.66	95.76	87.37
						CC	84.68	85.05	67.13
Cl	Cl	Cl	Cl	Cl	H	1	74.38	75.47	57.01
						3	77.96	78.97	61.84
						4	79.15	80.30	62.80
						6	96.97	97.05	88.81
						CC	81.70	81.99	60.06
Cl	Cl	Cl	Cl	Cl	Cl	1	74.53	75.53	56.44
						CC	77.56	77.72	50.98

^a See Figure 1 for atom numbering. ^b The symmetry-unequivalent sites of the C–H and C–Cl bond dissociations are listed under numbers 1–6, whereas the C–C bond dissociations are denoted by CC.

ing interactions vary less from one method to another. In other words, the observed discrepancies among the values of σ_{C-C} computed at various levels of theory single out the systemic exaggeration of the nonbonding H···Cl and Cl···Cl repulsions as the main source of the gross underestimation of ΔH_{C-C}° in polychloroethanes by DFT-based methods.

The lesser accuracy of the predictions for ΔH_{C-H}° and ΔH_{C-Cl}° based on eqs 2 and 3 (Figures 3 and 4) hampers unambiguous interpretation of the trends in the computed values of the σ_{C-H}° , σ_{C-H}^g , σ_{C-H}^{vg} , σ_{C-H}^{va} , σ_{C-Cl}° , σ_{C-Cl}^g , σ_{C-Cl}^{vg} , and σ_{C-Cl}^{va} parameters (Tables 6 and 7). In general, these param-

**Figure 1.** Numbering of substituents in polychloroethanes and polychloroethyl radicals.**Figure 2.** Computed C–C bond dissociation enthalpies (BDEs) vs those predicted from eq 1.**Table 6.** Substituent Effects on ΔH_{C-C}° (eq. 1)

level of theory	σ_{C-C}°	σ_{C-C}	σ_{C-C}^g	σ_{C-C}^{vg}	σ_{C-C}^{va}
G2	91.08	−2.28	−0.01	0.77	0.44
G2MP2	91.32	−2.28	0.02	0.78	0.44
BLYP	85.91	−5.85	−0.01	1.29	0.80
B3LYP	86.33	−5.35	0.07	1.28	0.85

eters are again found to be substantially underestimated by the DFT-based methods.

Conclusions

The present calculations provide benchmark thermochemical data for homolytic C–C, C–H, and C–Cl bond dissociations in ethane and in its chloro derivatives. In light of the very limited experimental data available at present and the involvement of (poly)chloroethyl radicals in a wide variety of chemical reactions of practical interest, the computed standard enthalpies of bond dissociations are particularly useful. Without exception, the C–H bonds are found to be stronger than either the C–C or C–Cl ones. In addition, they are affected the least by the presence of chlorine atoms. In general, the calculations predict

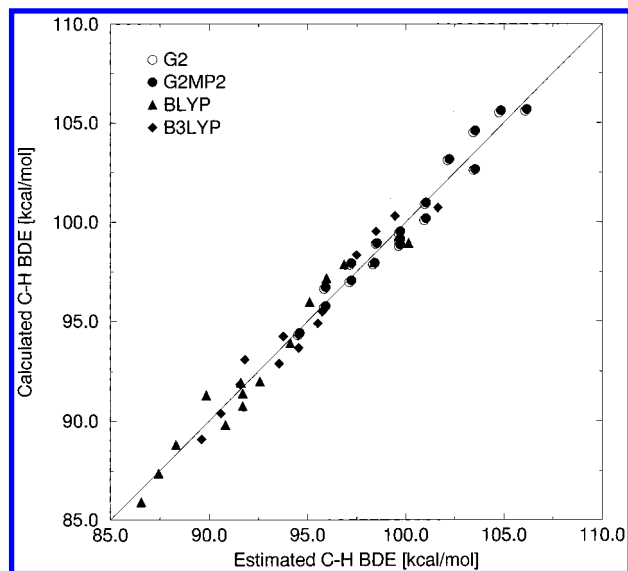


Figure 3. Computed C–H bond dissociation enthalpies (BDEs) vs those predicted from eq 2.

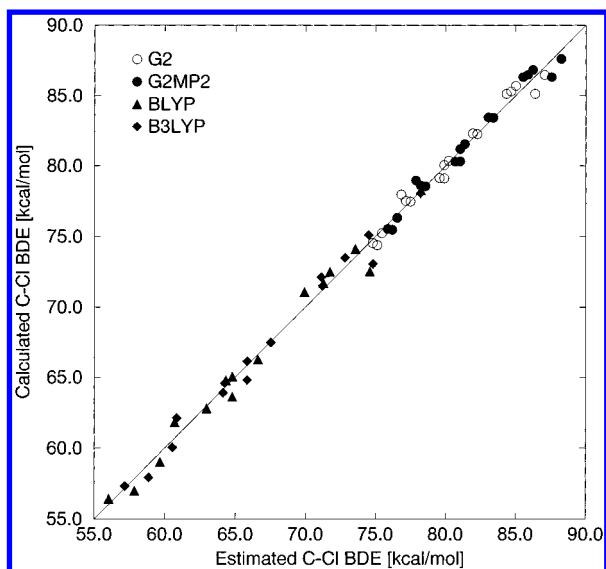


Figure 4. Computed C–Cl bond dissociation enthalpies (BDEs) vs those predicted from eq 3.

the C–C bonds to be barely stronger than their C–Cl counterparts, accounting for the experimentally observed competition between thermally induced bond scissions.¹⁰

Wherever available, experimental data confirm the reliability of the G2 calculations. The G2MP2 predictions are found to follow closely those of the G2 method, opening an avenue to

Table 7. Substituent Effects on ΔH_{C-H}° (eq 2)

level of theory	σ_{C-H}°	σ_{C-H}^g	σ_{C-H}^{vg}	σ_{C-H}^{va}
G2	103.46	−3.81	1.31	−1.33
G2MP2	103.54	−3.81	1.31	−1.31
BLYP	98.37	−4.26	0.88	−3.29
B3LYP	99.68	−3.94	0.98	−2.19

Table 8. Substituent Effects on ΔH_{C-Cl}° (eq. 3)

level of theory	σ_{C-Cl}°	σ_{C-Cl}	σ_{C-Cl}^{vg}	σ_{C-Cl}^{va}
G2	87.05	−4.78	−0.33	−2.04
G2MP2	88.25	−4.84	−0.34	−2.03
BLYP	78.22	−6.94	−1.82	−4.67
B3LYP	78.20	−6.98	−1.70	−3.69

accurate theoretical studies of thermochemistry of higher perchlorinated alkanes for which G2 calculations are presently out of question. At the same time, the present investigation uncovers a very poor performance of the BLYP and B3LYP functionals for systems with strong repulsions between chlorine atoms. Contrary to the recent claims of its overall superiority,^{32,33} the B3LYP functional is found in this instance to perform only marginally better than the BLYP one. It appears that the difference in the accuracy of these functionals is significant only for “easy” systems but is quite irrelevant for “difficult” cases.

Analysis of the site-specific ΔH_{C-C}° in terms of substituent contributions leads to the conclusion that the gross underestimation of bond dissociation enthalpies by the DFT-based methods is caused by a systematic exaggeration of the $H\cdots Cl$ and $Cl\cdots Cl$ repulsions. Most probably this exaggeration is caused by the inability of the currently used density functionals such as BLYP and B3LYP to correctly describe dispersion interactions.⁴⁴ In light of this observation, the recently reported large errors in the DFT predictions for the standard enthalpies of formation of systems such as $SiCl_4$ ³² come as no surprise.

Acknowledgment. The research described in this publication has been supported by the Office of Energy Research, Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy under the grant DE-FG02-97ER14758. Support by Florida State University through the allocation of supercomputer resources on the SGI Power Challenge computer is acknowledged.

Supporting Information Available: Appendix describing cluster expansion for bond dissociation energies and 12 tables of G2, G2MP2, BLYP/6-311G**, and B3LYP/6-311G** results (15 pages). See any current masthead page for ordering and Internet access information.

JA971108Q

(44) Pulay, P. personal communication, March 1997.