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Data Article

A dataset of homolytic C–Cl bond dissociation energies obtained by means of W1w theory

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ABSTRACT

We herein report a dataset of 28 homolytic C–Cl bond dissociation energies (BDEs) (to be known as the CCl28 dataset), obtained using the benchmark-quality W1w thermochemical protocol. This set contains chlorinated organic molecules that consist of either sp^3-, sp^2- or sp-hybridized C–Cl bonds. The species in this set have C–Cl BDEs (at 298 K) that differ by as much as 168.4 kJ mol^{-1}, with allyl chloride having the lowest BDE (291.7 kJ mol^{-1}) and 1-chloroprop-1-yne having the largest (460.1 kJ mol^{-1}). Given the benchmark quality of the CCl28 dataset, it may serve as a useful reference for assessing the performance of more approximate quantum chemical methods, such as density functional theory (DFT) and double-hybrid DFT methods.

Specifications Table

Subject area	*Computational Chemistry*
Compounds	*Chlorinated organic molecules*
Data category	*High-level quantum chemical calculations*
Data acquisition format	*W1w thermochemical protocol*
Data type	*Simulated*
Procedure	*W1w thermochemical protocol*
Data accessibility	*Data is provided in article, and geometries of all species (in Cartesian coordinates) are provided as supporting information*

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1. Rationale

Chlorinated organic molecules are ubiquitous, and as such, knowledge of their fundamental thermodynamic properties is desirable. Of particular importance are the energies necessary to induce homolytic cleavage of the C–Cl bonds of such species (i.e., the homolytic bond dissociation energies, BDEs), which culminates in the formation of carbon-centered radicals and chlorine atom. The radicals arising from dissociation of the C–Cl bonds of chlorinated organic molecules may then undergo additional reactions. From the perspective of atmospheric chemistry, photodecomposition of chlorofluorocarbons results in the formation of Cl•, which depletes ozone in the stratosphere [1]. In the context of synthetic organic chemistry, radical formation via homolysis of chlorinated precursor molecules has also been instrumental in the preparation of, for example, 2,2-dichlorovinylcyclopentanes [2], benzo[*c*]naphthyridinones [3], and 2-trifluoromethyl-3-acylindoles [4].

Although a number of experimentally-determined homolytic C–Cl BDEs have been reported [5], the chemical diversity of the species for which data is available is relatively limited, and for the most part, the reported BDEs are associated with (i) large uncertainties (or no uncertainties at all) and/or (ii) or are obtained indirectly using either heats of formation ($\Delta_f H^o$) or by way of correlations. In this light, obtaining such quantities by way of quantum chemical calculations has become a valuable alternative to the use of experimental methods. The most recent and comprehensive example of the application of quantum chemical calculations to the study of the effect of substituents in governing the energetics of C–Cl dissociation is the work by Coote et al. [6] who obtained a wide range of BDEs for sp^3-hybridized C–Cl bonds. Further examples of computational studies focusing on the determination of C–Cl BDEs include the study of chlorinated benzene derivatives [7–9], polychloroethanes [10], chlorinated heterocyclic species [11], as well as chlorofluorocarbons and hydrofluorocarbons [12]. It is also worth noting that quantum chemical methods have also recently been employed in order to obtain a comprehensive dataset of homolytic C–Br BDEs [13].

As in any quantum chemical study, one is confronted with the choice of method to use, invariably requiring a consideration of the cost to performance ratio. In the abovementioned studies, C–Cl BDEs have been obtained by way of more approximate methods (i.e., of lower computational cost) such as density functional theory (DFT), and to a lesser extent, empirical Gaussian-*n* protocols [14]. However, the performance of such methods for the calculation of C–Cl BDEs has, to the best of our knowledge, yet to be established. To be able to critically assess the performance of such methods, and in so doing, identify suitable lower-cost procedures that may be used to afford reliable C–Cl BDEs, it is first necessary to have a test set of accurate BDEs by which to reliably assess such methods. To address this, we herein report a chemically-diverse dataset of 28 accurate homolytic C–Cl BDEs (to be known as the CCl28 dataset) obtained using the benchmark-quality W1w [15] thermochemical protocol (which represents a layered extrapolation to the all-electron, relativistic CCSD(T) basis-set-limit), for species that contain sp^3-, sp^2- and *sp*-hybridized C–Cl bonds. The W1w protocol has shown reliable performance for the calculation of BDEs more generally. For example, when assessed against the 99 BDEs found in the W4-11 dataset, W1w achieved a mean absolute deviation (MAD) of just 2.1 kJ mol^{-1} [16]. On this basis, the CCl28 dataset may therefore serve as a reference by which to critically assess the performance of more approximate lower-cost theoretical procedures, such as DFT and double hybrid DFT. Such lower cost methods may then be used for studying larger species for which W1w would be prohibitively costly in terms of both time and computational resources.

2. Procedure

The geometries of all species were obtained at the B3LYP/A’VTZ level (where A’V*n*Z indicates the combination of cc-pV*n*Z basis sets [17] on H atom, aug-cc-pV*n*Z basis sets [18] for first row atoms, and aug-cc-pV(*n*+d)Z basis sets [19] for second-row elements), and were confirmed to be equilibrium structures (i.e., consisting of all real frequencies) by way of harmonic vibrational frequency calculations, which were performed at the same level of theory. The zero-point vibrational energy (ZPVE) and enthalpy ($H_{\mathrm{vib}}(298\,\mathrm{K})$) corrections resulting from these frequency calculations have been used in later steps to correct the BDEs to 0 K and 298 K. These corrections have been scaled according to literature scaling factors [20], namely 0.9884 for the ZPVE and