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Isomer Test of DFT: Chlorofluoroethenes

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DFT calculations have been performed for all isomeric chlorofluoroethenes. The relative stabilities of different isomers have been calculated and compared with experimental enthalpies of formation. The DFT method, which uses the non-local density approximation (NLDA) and Becke-Lee-Yang-Parr functional, has been found to be a fairly reliable method for predicting relative thermodynamic stabilities.

INTRODUCTION

The density functional theory (DFT) based methods are now recognized as cost-effective and accurate alternatives to HF and post-HF methods (*e.g.* MP2 or CISD) for electronic structure calculations.¹ A meaningful test of the quality of a quantum chemical method consists of comparing predicted molecular properties with experimental ones. The commonly used properties include: geometries, atomization energies, dissociation energies and harmonic vibrational frequencies. Several such comparisons have been reported for the DFT method,² but mostly for small, diatomic or polyatomic molecules. There are two principal reasons for choosing small molecules: scarcity of good quality experimental thermodynamic data and computational cost in dealing with large molecules at high level of theory, *i.e.* non-local density approximation. In this work, we report a DFT study of a complete set of isomeric chlorofluoroethenes ($C_2F_2Cl_2$, $C_2H_2F_2$, $C_2H_2Cl_2$, C_2H_2FCl , C_2HFCl_2 and C_2HClF_2). We have deliberately tested thermodynamic properties and not geometries because the molecular structure data can be more readily obtained by experiment than formation enthalpies. Thus, one may have to rely on the calculated values of thermodynamic properties to assess the relative stability (and synthesizability) of new compounds.

METHOD OF CALCULATION

The density functional theory calculations were performed with DGauss program,³ which is a part of the UniChem package from Cray Research Inc.⁴ The calculations were carried out at NLDA level and the non-local correction was included self-consistently. Two different functionals: Becke-Lee-Yang-Parr (BLYP) and Becke-Perdew (BP) were used in the calculations. The basis sets were DZVP and TZVP, which are of double zeta and triple zeta quality; they contain polarization functions and are specially optimized for DFT calculations ensuring reduction of basis set superposition error (BSSE). A complete geometry optimization was performed for each molecule and the structure obtained was confirmed to be a genuine minimum on potential energy surface by the absence of imaginary vibrational frequencies.

The calculated total energy for each molecule was ZPE corrected using unscaled calculated harmonic frequencies. The relative formation enthalpies $\Delta_f H^\circ$ (0 K) are shown in Figures 1–3.

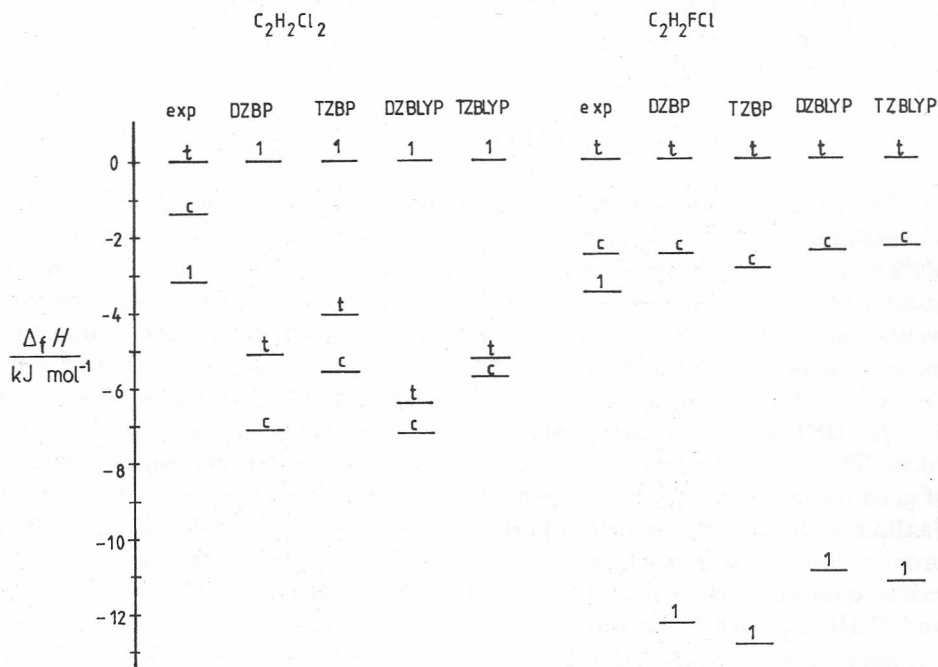


Figure 1. Relative $\Delta_f H^\circ$ (0 K) values for C₂H₂Cl₂ and C₂H₂FCl at different levels of theory.

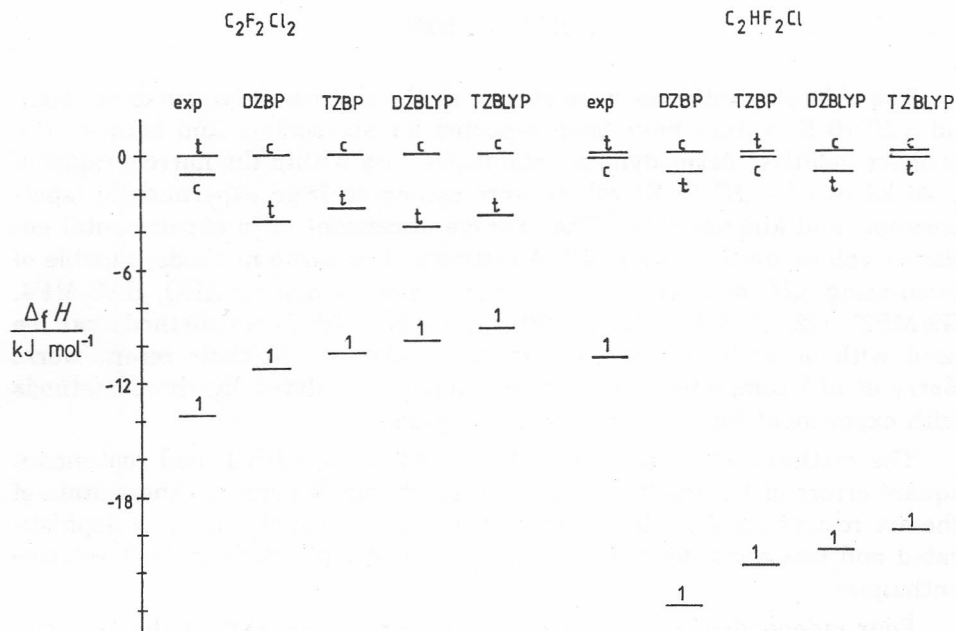


Figure 2. Relative $\Delta_f H^\circ$ (0 K) values for $C_2F_2Cl_2$ and CHF_2Cl at different levels of theory.

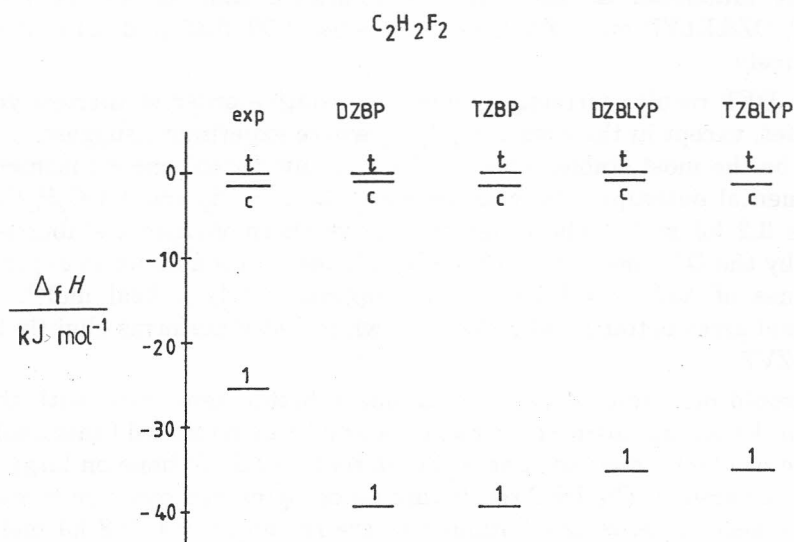


Figure 3. Relative $\Delta_f H^\circ$ (0 K) values for $C_2H_2F_2$ at different levels of theory.

DISCUSSION

The chlorofluorethenes were chosen as the test case because experimental $\Delta_f H^\circ$ (0 K) values have been reported for all isomers and because the isomers' relative thermodynamic stabilities vary within the narrow range of ≤ 26 kJ mol⁻¹. $\Delta_f H^\circ$ (0 K) values were estimated from experimental (spectroscopic and kinetic) data.⁵ The average uncertainties in experimental enthalpy values were ± 7 kJ mol⁻¹. A plethora of *ab initio* methods, capable of calculating $\Delta_f H^\circ$ directly, exist and carry unusual names: AEQ, BAC-MP4, G2(MP2), G2, CBS-4, CBS-Q, CBS-QCI/APNO. *Ab initio* methods can be used with or without isodesmic reaction schemes. In their recent work, Berry *et al.*⁶ compared formation enthalpies calculated by these methods with experiment for a series of fluoromethanes.

The methods which performed best, BAC-MP4, CBS-4, had root-mean-square errors of 1.2 and 2.8 kJ mol⁻¹, respectively. We can use these state-of-the-art results as a yardstick against which to compare our less sophisticated and less accurate (but computationally less demanding) DFT relative enthalpies.

Four independent calculations were performed for each of the 18 molecules using different basis sets and functionals: DZVP & BP, TZVP & BP, DZVP & BLYP, TZVP & BLYP. The results are shown in graphic form (Figures 1–3) in order to emphasize the trends more clearly than it is possible by tabulation of numerical values. We have also calculated rms errors for different functional & basis set combinations. Rms errors for DZ&BP, TZ&BP, DZ&BLYP and TZ&BLYP were 4.04, 3.50, 3.45 and 3.13 kJ mol⁻¹, respectively.

The DFT results correctly predict the relative order of thermodynamic stabilities, except in the case of C₂H₂Cl₂ where experiment suggests 1,1 isomer to be the most stable, while all DFT results favour the *cis* isomer. The experimental enthalpy difference between *cis*-C₂H₂Cl₂ and 1,1-C₂H₂Cl₂ isomers is 3.2 kJ mol⁻¹. The order of relative thermodynamic stabilities obtained by the DFT method can thus be considered reliable up to experimental values of $\Delta_f H^\circ > 4$ kJ mol⁻¹, *i.e.* approximately 1 kcal mol⁻¹. BLYP functional gives better results than BP, while TZVP performs slightly better than DZVP.

It would of course be possible to obtain better agreement with the experiment by enlargement of the basis set and by using mixed functionals but we have used only methods applicable to routine calculations on large molecules (> 20 atoms). The DFT results are encouraging and compare favourably with the best *ab initio* calculations,⁶ where reliability was 2.8 kJ mol⁻¹.

In conclusion, we suggest that the NLDA algorithm and BLYP functional should always be employed. The basis set choice is not so critical, although TZVP is of course preferred.

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SAŽETAK

Izomerni test metode DFT: klorofluoroeteni

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DFT računi izvedeni su za sve izomere klorofluoroetena. Relativne termodinamičke stabilnosti tih spojeva uspoređene su s eksperimentalnim vrijednostima entalpija stvaranja. Metoda DFT pouzdano predviđa relativnu stabilnost spojeva čije se entalpije stvaranja razlikuju za više od 4 kJ mol⁻¹. Pri upotrebi metode DFT preporučuje se uporaba algoritma NLSCF te funkcionala BLYP.