Ab Initio and DFT Benchmark Study for Nucleophilic Substitution at Carbon (S_N2@C) and Silicon (S_N2@Si)

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Abstract: To obtain a set of consistent benchmark potential energy surfaces (PES) for the two archetypal nucleophilic substitution reactions of the chloride anion at carbon in chloromethane (S_N2@C) and at silicon in chlorosilane (S_N2@Si), we have explored these PESes using a hierarchical series of ab initio methods [HF, MP2, MP4SDQ, CCSD, CCSD(T)] in combination with a hierarchical series of six Gaussian-type basis sets, up to g polarization. Relative energies of stationary points are converged to within 0.01 to 0.56 kcal/mol as a function of the basis-set size. Our best estimate, at CCSD(T)/aug-cc-pVQZ, for the relative energies of the [Cl^-/H11002,CH3Cl] reactant complex, the [Cl—CH3—Cl^-] transition state and the stable [Cl—SiH3—Cl^-] transition complex is —10.42, +2.52, and —27.10 kcal/mol, respectively. Furthermore, we have investigated the performance for these reactions of four popular density functionals, namely, BP86, BLYP, B3LYP, and OLYP, in combination with a large doubly polarized Slater-type basis set of triple-ζ quality (TZ2P). Best overall agreement with our CCSD(T)/aug-cc-pVQZ benchmark is obtained with OLYP and B3LYP. However, OLYP performs better for the S_N2@C overall and central barriers, which it underestimates by 2.65 and 4.05 kcal/mol, respectively. The other DFT approaches underestimate these barriers by some 4.8 (B3LYP) to 9.0 kcal/mol (BLYP).


Key words: ab initio benchmark; density functionals validation; nucleophilic substitution; potential energy surface; silicon

Introduction

Bimolecular nucleophilic substitution (S_N2) constitutes a class of elementary chemical reactions that play an important role in organic chemistry. Various theoretical and experimental studies have been conducted to obtain a detailed description of the potential energy surface (PES) of S_N2 reactions. The symmetric, thermoneutral S_N2 reaction between the chloride anion and chloromethane in the gas phase is generally used as the archetypal model for nucleophilic substitution [see eq. (1)]:

\[ \text{Cl}^- + \text{CH}_3\text{Cl} \rightarrow \text{CH}_3\text{Cl} + \text{Cl}^- \]  

(1)

This reaction proceeds preferentially through a backside nucleophilic attack of the chloride anion at the carbon atom (S_N2@C) which goes with concerted expulsion of the leaving group. Studying the S_N2@C reaction in the gas phase reveals the intrinsic behavior of this process, that is, its behavior without the interference of solvent molecules. This, in turn, can also shed light on the nature of S_N2@C reactions in solution, in particular the effect of the solvent, by comparing the gas-phase results with those from condensed-phase and microsolvation investigations. A well-known feature of gas-phase S_N2@C reactions is their double-well potential energy surface (PES) along the reaction coordinate, as shown in Figure 1, upper. This PES is characterized by two pronounced minima, associated with the reactant and

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The purpose of the present study is twofold. In the first place, we wish to obtain reliable benchmarks for the PESes of the two nucleophilic substitution reactions of eqs. (1) and (2). This is done by exploring these PESes with a hierarchical series of ab initio methods [HF, MP2, MP4SDQ, CCSD, CCSD(T)] in combination with a hierarchical series of Gaussian-type basis sets of increasing flexibility (up to quadruple-ζ + diffuse functions) and polarization (up to g functions). This provides the first solid benchmark for the $S_{n2}@Si$ reaction of $Cl^- + SiH_3Cl$. For the $S_{n2}@C$ reaction of $Cl^- + CH_3Cl$, an authoritative benchmark PES has been computed by Botschwina and coworkers, with CCSD(T) relative energies of $-10.26$ and $+2.65$ kcal/mol for RC and TS relative to reactants (see Table 1). This benchmark PES will be confirmed and thus further consolidated in the present investigation. The main purpose of our work is, however, to provide a consistent set of ab initio PES data for accurately estimating trends associated with going from $S_{n2}@C$ to $S_{n2}@Si$ substitution.

A second purpose is to evaluate and validate the performance of four popular density functionals, BP86, BLYP, B3LYP, and OLYP, for describing the above $S_{n2}@C$ and $S_{n2}@Si$ substitution reactions against our ab initio benchmark PESes for the two model reactions. Although the ab initio approach turns out to be satisfactory in terms of accuracy and reliability, it is at the same time prohibitively expensive if one wishes to study more realistic model reactions involving larger nucleophiles and substrates. Thus, our survey of density functionals serves to validate one or more of these density functional theory (DFT) approaches as a computationally more efficient alternative to high-level ab initio theory in future investigations. A general concern associated with the application of DFT to the investigation of chemical reactions is its notorious tendency to underestimate activation energies. Thus, we arrive at a ranking of density functional approaches in terms of the accuracy with which they describe the PES of our model reaction, in particular, the activation energy. We focus on the overall activation energy, that is, the difference in energy between the TS and the separate reactants, which is decisive for the rate of chemical reactions in the gas phase, in particular, if they occur under low-pressure conditions in which the reaction system is (in good approximation) thermally isolated. Thus, see also Section II of ref. 58. But we also address the central barrier, that is, the difference in energy between the TS and the reactant complex. Here, we anticipate that the (nonhybrid) functional OLYP is found to perform very satisfactorily, in fact, as good as the much advocated hybrid functional B3LYP.

**Methods**

**DFT Geometries and Potential Energy Surfaces**

All geometry optimizations have been done with DFT using the Amsterdam Density Functional (ADF) program. The performance for computing the geometries and relative energies of the stationary points along the PESes of our model reaction (see Fig. 1) was compared for the following density functionals: BP86, BLYP, B3LYP, and OLYP. They were used in combination with the TZ2P basis set, which is a large uncontracted set of Slater-type orbitals (STOs) containing diffuse functions, which is of triple-ζ...
quality and has been augmented with two sets of polarization functions: 2p and 3d on hydrogen, 3d and 4f on carbon, silicon, and chlorine. The core shells of carbon (1s), silicon (1s2s2p) and chlorine (1s2s2p) were treated by the frozen-core approximation. An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular density and to represent the Coulomb and exchange potentials accurately in each SCF cycle. The importance of relativistic effects was investigated in case of the OLYP functional using the zeroth-order regular approximation, that is, at ZORA-OLYP. Relativistic effects were found to be negligible. For each of the four approaches, that is, BP86, BLYP, OLYP, and ZORA-OLYP, all stationary points were confirmed to be equilibrium structures (no imaginary frequencies) or a transition state (one imaginary frequency) through vibrational analysis. In addition, based on both BLYP/TZ2P and OLYP/TZ2P geometries, we have computed the relative energies of stationary points along the PES for the B3LYP hybrid functional. For technical reasons, our basis sets were defined and their values collected in Figure 2 (see also Fig. 1). At each level of theory, a hierarchical series of six Gaussian-type basis sets was used: Pople’s 6-31+G*, 6-311+G**, 6-311+G** basis sets, and Dunning’s aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets.

**Results and Discussion**

**Geometries of Stationary Points**

Based on the ZORA-OLYP/TZ2P geometries, energies of the stationary points were computed in a series of single-point calculations with the program package Gaussian. Using the following hierarchy of quantum chemical methods: Hartree–Fock (HF), Møller–Plesset perturbation theory through the second order (MP2) and fourth order with omission of the triple substitutions (MP4SDQ), and coupled-cluster theory with single and double excitations (CCSD) and with triple excitations treated perturbatively [CCSD(T)]. At each level of theory, a hierarchical series of six Gaussian-type basis sets was used: Pople’s 6-31+G*, 6-311+G**, 6-311+G** basis sets, and Dunning’s aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ.

### Ab Initio Potential Energy Surfaces

Based on the ZORA-OLYP/TZ2P geometries, energies of the stationary points were computed in a series of single-point calculations with the program package Gaussian. Using the following hierarchy of quantum chemical methods: Hartree–Fock (HF), Møller–Plesset perturbation theory through the second order (MP2) and fourth order with omission of the triple substitutions (MP4SDQ), and coupled-cluster theory with single and double excitations (CCSD) and with triple excitations treated perturbatively [CCSD(T)]. At each level of theory, a hierarchical series of six Gaussian-type basis sets was used: Pople’s 6-31+G*, 6-311+G**, 6-311+G** basis sets, and Dunning’s aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ.
directly, without a barrier to a $D_{3h}$ symmetric TC, that is, a stable pentavalent silicate intermediate, which corresponds structurally and is isoelectronic with the TS of the SN2@C reaction. From this TC the products, which are equivalent to the reactants, are reached without the occurrence of a reverse barrier. These results agree well with earlier experimental and theoretical work (see Introduction). All species have been verified through a vibrational analysis to represent equilibrium structures (no imaginary frequencies) or a transition state (one imaginary frequency, only in the case of SN2@C). The imaginary frequency in the SN2@C TS, associated with the normal mode that connects RC and PC, varies, depending on the functional, between 282 and 356 $\text{cm}^{-1}$ (for BP86, BLYP, OLYP, and ZORA-OLYP it amounts to 316, 282, 356, and 354 $\text{cm}^{-1}$).

The geometries obtained with the various density functionals (BP86, BLYP, and OLYP) do not show significant mutual discrepancies, and they agree reasonably well with gas-phase experimental values obtained through microwave (MW) spectroscopy (compare Fig. 2 and Table 2). The C—H and Si—H bond distance values are very robust with respect to changing the functional, with variations in the order of a few thousandths of an Å. Variations in the length of the C—Cl and Si—Cl bonds are in the order of a few hundredths of an Å. Relativistic effects on geometry parameters are virtually negligible (compare OLYP and ZORA-OLYP in Fig. 2): bond distances values change by 0.001 Å or less and bond angles change by 0.1° or less. Comparison with MW experiments for CH3Cl and SiH3Cl (Table 2) furthermore shows that all three density functionals somewhat overestimate bond distances, by up to 0.003 (C—H), 0.008 (Si—H), 0.04

Table 2. Experimental Geometries (in Å, deg) of CH3Cl and SiH3Cl.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Method</th>
<th>R(A—Cl)</th>
<th>R(A—H)</th>
<th>$\angle$ClAH</th>
<th>$\angle$HAH</th>
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<td>MW, IR</td>
<td>2.048</td>
<td>1.481</td>
<td>108.0</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2. Geometries (in Å, deg.) of stationary points along the potential energy surfaces for SN2@C and SN2@Si substitution of Cl$^- + \text{CH}_3\text{Cl}$ and Cl$^- + \text{SiH}_3\text{Cl}$, respectively, optimized at BP86, BLYP, OLYP, and ZORA-OLYP in combination with the TZ2P basis set.
(C—Cl), and 0.041 Å (Si—Cl), whereas bond angles agree with 1° for all methods. OLYP (or ZORA-OLYP) performs overall slightly better than the other functionals with bond-length overestimations of 0 (C—H), 0.008 (Si—H), 0.007 (C—Cl), and 0.019 Å (Si—Cl). Likewise, OLYP (or ZORA-OLYP) compares slightly better than the other functionals with CCSD(T) geometries\textsuperscript{11,12} for CH\textsubscript{3}Cl (C—H and C—Cl are 1.0853 and 1.7821 Å at CCSD(T), function of the basis-set size (at aug-cc-pVQZ) to within 0.01 kcal/mol computed by Botschwina and coworkers.\textsuperscript{11,12} Further-

mates the stability of the TC, that is, by 9 kcal/mol! The three

and CCSD(T), see Table 3. Note how HF dramatically underesti-

mates that of the SN\textsubscript{2}@C transition state in the sense

stable (ZORA-OLYP/TZ2P, to compute the

Later on, in the section hereafter, we show that OLYP also per-

forms excellently in terms of relative energies of stationary points.

Based on these findings, and the fact that OLYP is numerically

robust and agrees slightly better with available experimental and

CCSD(T) geometries, we choose the geometries of this functional,

that is, ZORA-OLYP/TZ2P, to compute the \textit{ab initio} benchmark

potential energy surfaces, which are summarized as relative ener-

gies in Table 3 (total energies in a.u. of all species occurring at the

stationary points are collected in Table S1 in the supplementary

material).

The energy of the \textit{S}\textsubscript{2}@C reactant complex computed with our

best basis set (aug-cc-pVQZ) varies relatively little along the range

of methods, that is, from

\[ -8.77 \text{ to } -10.30 \text{ to } -10.02 \text{ to } -10.00 \text{ to } -10.42 \text{ kcal/mol for HF, MP2, MP4SDQ, CCSD, and CCSD(T),} \]

and the three highest level values are equal to each other within

less than half a kcal/mol, see Table 3. At variance, the energy of

the \textit{S}\textsubscript{2}@C transition state depends more delicately on the level at

which correlation is treated. This TS energy computed again with

our best basis set (aug-cc-pVQZ) varies from

\[ 7.44 \text{ to } 4.34 \text{ to } 4.80 \text{ to } 4.89 \text{ to } 2.52 \text{ kcal/mol along HF, MP2, MP4SDQ, CCSD, and CCSD(T),} \]

and CCSD(T), see Table 3. Thus, not unexpectedly, HF signifi-

cantly overestimates the barrier, which is significantly lowered by

the incorporation of Coulomb correlation into theoretical treat-

ment. Note that for the TS the three highest level values are distrib-

uted over a range of 2.37 kcal/mol. Furthermore, the CCSD(T) values

are converged as a function of the basis-set size (at aug-cc-pVQZ)

to within a few hundredths of a kcal/mol for the RC and to about

half a kcal/mol for the TS. Thus, our best estimates at CCSD(T) of

\[ 25.71 \text{ to } 27.64 \text{ kcal/mol for the RC and TS of the S}\textsubscript{2}@C reaction agree excellently with and further consolidate the corre-

sponding CCSD(T) benchmark values of \[ 25.84 \text{ kcal/mol computed by Botschwina and coworkers.}\textsuperscript{11,12}

The energy of the stable \textit{S}\textsubscript{2}@Si transition complex shows a similar behavior as that of the \textit{S}\textsubscript{2}@C transition state in the sense that it also delicately depends on the level at which correlation is treated. The energy of this TC computed with our best basis set (aug-cc-pVQZ) varies from

\[ -18.08 \text{ to } -27.64 \text{ to } -25.87 \text{ to } -25.71 \text{ to } -27.10 \text{ kcal/mol along HF, MP2, MP4SDQ, CCSD, and CCSD(T),} \]

and CCSD(T), see Table 3. Note how HF dramatically underesti-

mates the stability of the TC, that is, by 9 kcal/mol! The three

highest level values are within a range of 1.39 kcal/mol. Further-

more, the CCSD(T) values for the stable TC are converged as a function of the basis-set size (at aug-cc-pVQZ) to within 0.01 kcal/mol. Thus, our best estimate at CCSD(T) of \[ -27.10 \text{ kcal/mol for the TC of the S}\textsubscript{2}@Si reaction is 4.7 kcal/mol more bonding than the best value of \[ -22.4 \text{ kcal/mol obtained previously by Gordon and coworkers}\textsuperscript{48} \text{ at MP4/6-31+}+\text{G(d,p)}/\text{MP2/6-31+}+\text{G(d,p). Note that the latter value closely agrees with our MP4SDQ/6-31+}+\text{G**}/\text{OLYP/TZ2P value of } -21.46 \text{ kcal/mol. We conclude that the pentavalent silicate intermediate (i.e., TC) displays the same strong correlation phenomena, associated with three-center-four-electron bonding,}\textsuperscript{16,53} \text{ as the transition state of the } S\textsubscript{2}@C \text{ reaction.}

Validation of DFT Potential Energy Surfaces

Next, we examine the relative energies of stationary points com-

puted with the density functionals BP86, BLYP, OLYP, ZORA-

OLYP, and B3LYP in combination with the TZ2P basis set. Note

that for all density functional but B3LYP we use consistently the

geometries optimized with that functional, for example, OLYP//

OLYP. In the case of B3LYP, we have carried out single-point

computations using both the BLYP and the OLYP geometries.

\[
\text{Table 3. Relative Energies (in kcal/mol) of Stationary Points along the Reaction Coordinate for the } S\textsubscript{2}@C \text{ and } S\textsubscript{2}@Si \text{ Reactions of } \text{Cl}^+ + \text{CH}_3\text{Cl} \text{ and } \text{Cl}^- + \text{SiH}_3\text{Cl}, \text{ Computed at Several Levels of the } \text{Ab Initio} \text{ and Hybrid Density Functional Theory.}
\]

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<th>Method</th>
<th>RC</th>
<th>TS</th>
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First, we focus on the overall activation energy, that is, the difference in energy between the TS and the separate reactants. This barrier, as pointed out in the introduction, is decisive for the rate of chemical reactions in the gas phase, in particular, if they occur under low-pressure conditions.\textsuperscript{24,57,58} The central barrier, that is, the difference in energy between the TS and the reactant complex is discussed thereafter. The DFT relative energies are collected in Table 4. The performance of the various density functional approaches is assessed by a systematic comparison of the resulting potential energy surfaces with our CCSD(T)/aug-cc-pVQZ benchmark values (see Table 3).

It is clear from the data in Table 4 that OLYP outperforms both BP86 and BLYP and, furthermore, that it performs similarly well as the much advocated B3LYP hybrid functional. The mean absolute errors (MAE) in energies of stationary points relative to reactants for OLYP (2.2 kcal/mol) and B3LYP (2.3–2.5 kcal/mol) are equal within a few tenths of a kcal/mol and clearly smaller than those of BP86 (3.4 kcal/mol). Note that these MAE values are merely to be used as a rough indicator of overall performance for relative energies of the stationary points (i.e., RC and TS for \( \text{Sn}_2@\text{C} \), and TC for \( \text{Sn}_2@\text{Si} \), which need to be inspected individually. OLYP performs particularly well for the overall activation energy (i.e., TS relative to R) of the \( \text{Sn}_2@\text{C} \) reaction, which it understimates by only 2.65 kcal/mol compared to an underestimation of 4.7 to 4.9 kcal/mol for B3LYP and of ca. 8–9 kcal/mol for BP86 and BLYP. Relativistic effects on the OLYP energies are negligible, that is, one-tenth of a kcal/mol or less. Note also that the effect of using either BLYP or OLYP geometries for the computation of B3LYP energies is 0.3 kcal/mol at most (namely, for the \( \text{Sn}_2@\text{C} \) central barrier, i.e., TS relative to RC) and even much less for all other relative energies. Thus, the OLYP potential energy surfaces for \( \text{Sn}_2@\text{C} \) (−9.0 and −0.1 kcal/mol for RC and TS relative to R) and \( \text{Sn}_2@\text{Si} \) (−24.4 kcal/mol for TC relative to R) appear to be as good as that of B3LYP and both compare reasonably well (although not perfect) with the \textit{ab initio} benchmark PES. This agrees with the work of Baker and Pulay for other organic reactions.\textsuperscript{51}

Finally, we address the central barrier, that is, the difference in energy between the TS and the reactant complex, which becomes decisive in the high-pressure regime, when termolecular collisions are sufficiently efficient to cool the otherwise rovibrationally hot reactant complex, causing it to be in thermal equilibrium with the environment.\textsuperscript{24,57,58} Also, for the central barrier of the \( \text{Sn}_2@\text{C} \) reaction, OLYP outperforms both BP86 and BLYP, and it performs also slightly better than the much advocated B3LYP hybrid functional. Thus, OLYP underestimates this central activation energy (i.e., TS relative to RC) by 4.1 kcal/mol compared to an underestimation of 5.0 to 5.4 kcal/mol for B3LYP and of ca. 7–8 kcal/mol for BP86 and BLYP. On the other hand, if one examines the overall performance in terms of the mean absolute error in energies of stationary points relative to the reactant complex, it is B3LYP (with an error of 2.4–2.6), which is slightly better than OLYP (with an error of 2.7–2.8 kcal/mol). All together, we conclude that both OLYP and B3LYP are reasonable approaches for tackling the \( \text{Sn}_2@\text{C} \) and \( \text{Sn}_2@\text{Si} \) reactions.

**Conclusions**

We have computed \textit{ab initio} benchmarks for the archetypal nucleophilic substitution of chloride at chloromethane carbon (\( \text{Sn}_2@\text{C} \)) and chlorosilane silicon (\( \text{Sn}_2@\text{Si} \)) and, thus, for the trend from \( \text{Sn}_2@\text{C} \) to \( \text{Sn}_2@\text{Si} \). These benchmarks derive from a hierarchical series of methods up to CCSD(T)/aug-cc-pVQZ, which is converged with respect to the basis-set size within a few tenths of a kcal/mol. Previous benchmarks for the \( \text{Sn}_2@\text{C} \) reaction,\textsuperscript{11,12} in particular the activation energy, are confirmed and thus further consolidated. The previous best \textit{ab initio} estimate of the stability of the \( \text{D}_{2h} \) symmetric transition complex (TC) occurring in the \( \text{Sn}_2@\text{Si} \) reaction is shown to be too weakly bonding by ca. 5 kcal/mol.

This benchmark is used to evaluate the performance of four popular density functionals, BP86, BLYP, B3LYP, and OLYP, for describing the above \( \text{Sn}_2@\text{C} \) and \( \text{Sn}_2@\text{Si} \) substitution reactions.
Relativistic effects (ZORA) are shown to be negligible. Interestingly, the relatively new OLYP functional, which features Handy’s improved exchange functional OPTX,\(^{69}\) performs satisfactorily with a mean absolute error of 2.2 and 2.7 kcal/mol (in energies of stationary points of both reactions relative to reactants, R, and reactant complex, RC, respectively) and an underestimation of the overall \(S_{2,2}@C\) barrier (i.e., TS relative to R) by about 2.5 kcal/mol and of the central \(S_{2,2}@C\) barrier (i.e., TS relative to RC) by 4.1 kcal/mol. The B3LYP hybrid functional too performs well with a mean absolute error of about 2.4 and 2.5 kcal/mol (in energies relative to R and RC, respectively), an underestimation of the overall \(S_{2,2}@C\) barrier by ca. 4.8 kcal/mol and an underestimation of the central \(S_{2,2}@C\) barrier of 5.0 –5.4 kcal/mol. Thus, OLYP/TZ2P emerges from this investigation as a sound and efficient approach for the routine investigation of trends in nucleophilic substitution reactions at carbon and silicon, also in larger, more realistic model systems.

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