

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 $[Cl^-, CH_3Cl]$ reactant complex, the $[Cl-CH_3-Cl]^-$ transition state and the stable $[Cl-SiH_3-Cl]^-$ 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).

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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.^{1–3} Various theoretical^{4–21} and experimental^{22–32} 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)]:



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.^{5,6} Studying the $S_N2@C$ reaction in the gas phase reveals the intrinsic behavior of this process, that is, its behavior without the interfer-

ence 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^{1,2,33–37} and microsolvation^{38–43} investigations. A well-known feature of gas-phase $S_N2@C$ reactions is their double-well potential energy surface (PES) along the reaction coordinate,²⁵ shown in Figure 1, upper. This PES is characterized by two pronounced minima, associated with the reactant and

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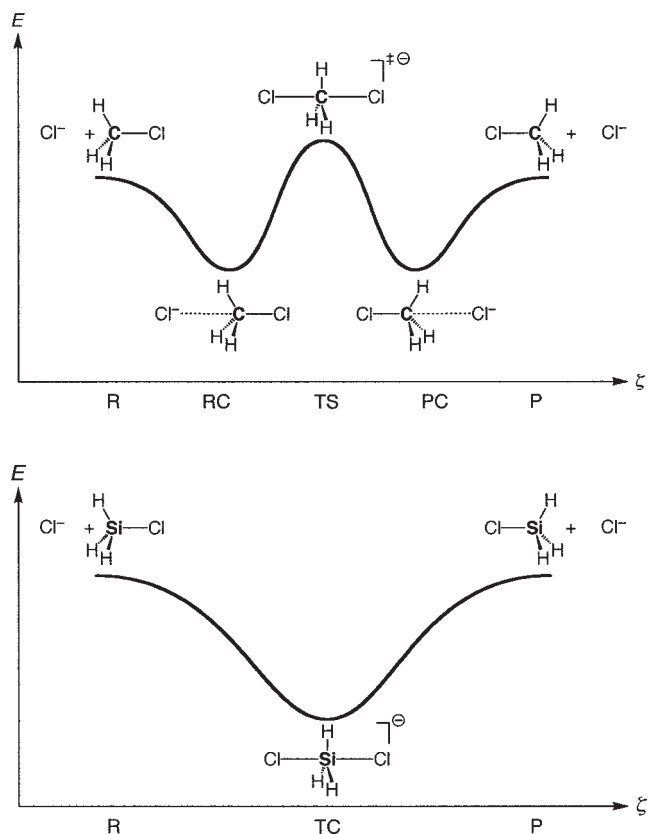
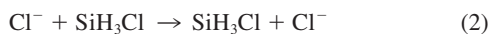


Figure 1. Double-well $S_N2@C$ (upper) and single-well $S_N2@Si$ potential energy surfaces along the reaction coordinate ζ (R = reactants, RC = reactant complex, TS = transition state, TC = stable transition complex, PC = product complex, P = products).

product ion–molecule complexes (RC and PC) that are interconverted through the transition state (TS) for nucleophilic substitution at carbon.

Thus, whereas the $S_N2@C$ reaction has been extensively studied, much less investigations both, experimental^{44–46} and theoretical,^{46–48} have been devoted to studying the nature and mechanism of gas-phase nucleophilic substitution at silicon ($S_N2@Si$). An example of an archetypal $S_N2@Si$ reaction is the symmetric, thermoneutral reaction between the chloride anion and chlorosilane [see eq. (2)]:



The structural transformation associated with the above $S_N2@Si$ substitution is equivalent to that of the $S_N2@C$ reaction of eq. (1). Further, both reaction systems are isoelectronic. A striking difference is however that $S_N2@Si$ proceeds via a single-well PES, as shown in Figure 1, lower, that is, it proceeds without encountering a first-order saddle point on the PES along the reaction coordinate. Thus, the D_{3h} symmetric transition structure $[Cl-AH_3-Cl]^-$ turns from a TS for $S_N2@C$ into a stable transition complex (TC) for $S_N2@Si$.

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,^{11,12} 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.^{49–56} 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;^{24,57} 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^{59–62} using the Amsterdam Density Functional (ADF) program.^{63–65} 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,^{66,67} BLYP,^{66,68} and OLYP.^{68,69} 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

Table 1. Selected Literature Values for Relative Energies (in kcal/mol) of Stationary Points along the Reaction Coordinate for the $S_N2@C$ and $S_N2@Si$ Reactions of $Cl^- + CH_3Cl$ and $Cl^- + SiH_3Cl$.

Reaction	Method	RC	TS	Reference
$Cl^- + CH_3Cl$	MP2/6-311++G(2d, p)	-10.64	3.05	17
	MP2/6-31+G*	-9.66	7.66	18
	MP2/6-31G**	-10.96	4.55	18
	MP-SAC2/6-31G**//MP2/6-31G**	-11.04	4.56	18
	G2(+)	-10.50	2.75	10
	RHF/6-31+G*//RHF/6-31+G*	-8.87	6.60	13
	MP2/6-31+G*//RHF/6-31+G*	-9.44	8.49	13
	MP3/6-31+G*//RHF/6-31+G*	-9.46	9.04	13
	MP4/6-31+G*//RHF/6-31+G*	-9.53	6.48	13
	CBS-QB3//B3LYP/6-311G(2d, d, p)	-10.6	2.0	15
	QCISD(T)/6-31++G(3df, 2pd)	-10.84	3.0	19
	HF		7.65	^a
	MP2		4.02	^a
	CCSD		5.07	^a
	CCSD(T)	-10.26	2.65	^a
	$Cl^- + SiH_3Cl$	MNDO//RHF/6-31G*	-35.2	^b
RHF/6-31G*		-21.0	^b	46
MP4/6-31++G(d, p)//MP2/6-31++G(d,p)		-22.4	^b	48

^aFor RC: aug-cc-pVQZ(Cl), cc-pVQZ(C), (H: sp aug-cc-pVTZ, d cc-pVTZ) basis set; see ref. 11. For TS, aug-cc-pV5Z(Cl), cc-pV5Z(C), cc-pVQZ(H) basis set; see ref. 12.

^bNo first-order saddle point exists.

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.⁶³ 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.⁶³ The importance of relativistic effects was investigated in case of the OLYP functional using the zeroth-order regular approximation,⁷⁰ 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.^{68,71} For technical reasons, our B3LYP/TZ2P energies are computed in a post-SCF manner, that is, using the electron density obtained at BLYP/TZ2P. Recently, we have extensively tested this approximation and have shown that it introduces an error in the computed B3LYP energies of a few tenths of a kcal/mol.^{72,73}

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 Gaussian⁷⁴ using the following hierarchy of quantum chemical methods: Hartree-Fock (HF), Møller-Plesset perturbation theory⁷⁵ through the second order

(MP2) and fourth order with omission of the triple substitutions (MP4SDQ),^{76,77} and coupled-cluster theory⁷⁸ with single and double excitations (CCSD)⁷⁹ and with triple excitations treated perturbatively [CCSD(T)].⁸⁰ At each level of theory, a hierarchical series of six Gaussian-type basis sets was used: Pople's 6-31+G*, 6-31++G**, 6-311++G**, basis sets, and Dunning's^{81,82} augmented correlation consistent polarized valence basis sets of double-, triple-, and quadruple- ζ quality, that is, aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ.

Results and Discussion

Geometries of Stationary Points

First, we examine the geometries of stationary points along the reaction coordinate of the $S_N2@C$ reaction of $Cl^- + CH_3Cl$ and the $S_N2@Si$ reaction of $Cl^- + SiH_3Cl$, computed with the GGA functionals BP86, BLYP, OLYP, and ZORA-OLYP in combination with the TZ2P basis set. The computed geometry parameters are defined and their values collected in Figure 2 (see also Fig. 1). For each of the functionals, the $S_N2@C$ reaction proceeds, not unexpectedly, from the reactants via formation of a stable C_{3v} symmetric reactant complex (RC), in which Cl^- sticks in an η^3 fashion to the three hydrogen atoms of chloromethane, followed by the D_{3h} symmetric TS. The latter leads to the product complex (PC) and finally the products (P), which in this thermoneutral automerization are equivalent to RC and R, respectively. On the other hand, the $S_N2@Si$ reaction proceeds from the reactants

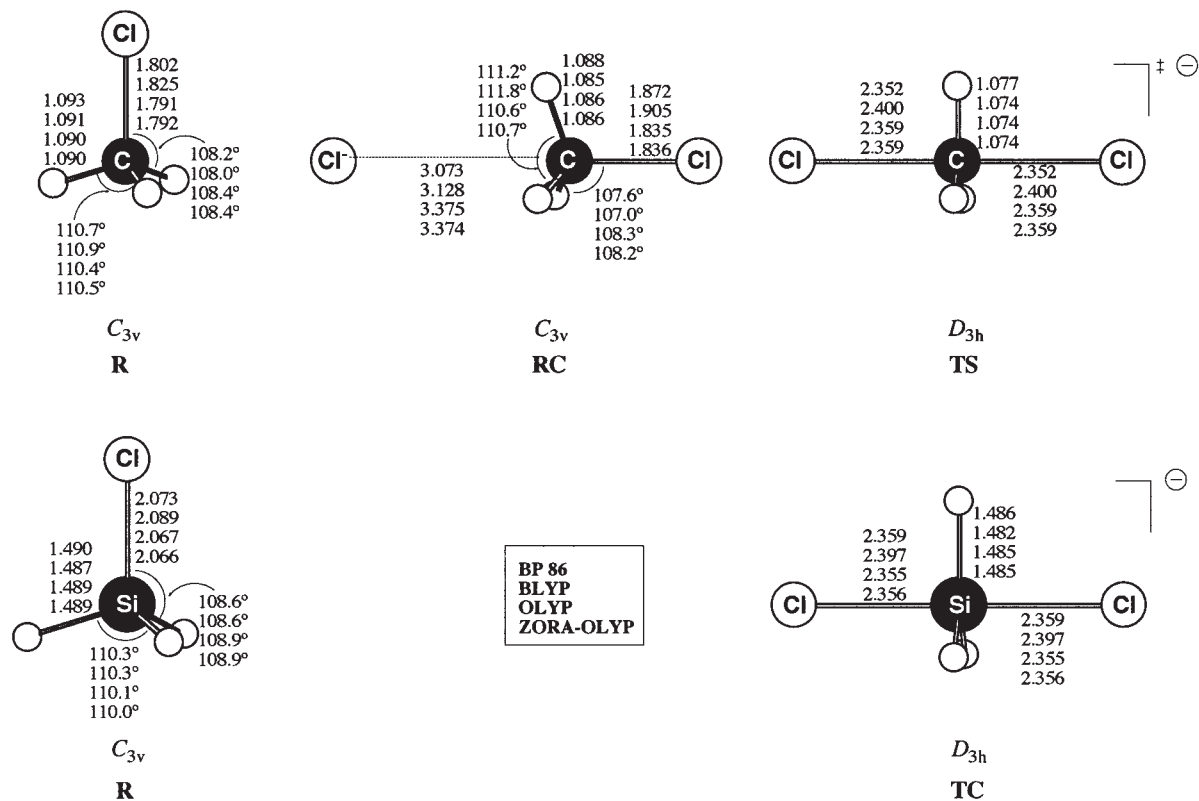


Figure 2. Geometries (in Å, deg.) of stationary points along the potential energy surfaces for $S_N2@C$ and $S_N2@Si$ substitution of $Cl^- + CH_3Cl$ and $Cl^- + SiH_3Cl$, respectively, optimized at BP86, BLYP, OLYP, and ZORA-OLYP in combination with the TZ2P basis set.

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 $S_N2@C$ 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 $S_N2@C$). The imaginary frequency in the $S_N2@C$ TS, associated with the normal mode that connects RC and PC, varies, depending on the functional, between 282 and 356 $i\text{ cm}^{-1}$ (for BP86, BLYP, OLYP, and ZORA-OLYP it amounts to 316, 282, 356, and 354 $i\text{ cm}^{-1}$).

The geometries obtained with the various density functionals (BP86, BLYP, and OLYP) do not show significant mutual dis-

crepancies, and they agree reasonably well with gas-phase experimental values^{83,84} 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 (Fig. 2). The same holds for H—C—Cl and H—Si—Cl (or H—C—H and H—Si—H) angles, which typically vary by a few tenths of a degree; only in the case of the RC of $Cl^- + CH_3Cl$ they vary up to ca. 1°. 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 CH_3Cl and SiH_3Cl (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 CH_3Cl and SiH_3Cl .

Molecule	Method	R(A—Cl)	R(A—H)	∠CIAH	∠HAH	Ref.
CH_3Cl	MW	1.778	1.086	108.2	110.7	84
	MW, IR	1.785	1.090		110.8	83
SiH_3Cl	MW	2.048	1.482	107.9	111.0	84
	MW, IR	2.048	1.481	108.0		83

(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 0.018 Å (Si—Cl). Likewise, OLYP (or ZORA-OLYP) compares slightly better than the other functionals with CCSD(T) geometries^{11,12} for CH₃Cl (C—H and C—Cl are 1.0853 and 1.7821 Å at CCSD(T), which is close to the MW experimental values, see Table 2) and for the TS of the S_N2@C reaction [C—H and C—Cl are 1.0704 and 2.3071 Å at CCSD(T)].

Ab Initio Benchmark Potential Energy Surfaces

The various functionals thus yield essentially the same geometries. Later on, in the section hereafter, we show that OLYP also performs 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 *ab initio* benchmark potential energy surfaces, which are summarized as relative energies 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 S_N2@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 to -10.30 to -10.02 to -10.00 to -10.42 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 S_N2@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 to 4.34 to 4.80 to 4.89 to 2.52 kcal/mol along HF, MP2, MP4SDQ, CCSD, and CCSD(T), see Table 3. Thus, not unexpectedly, HF significantly overestimates the barrier, which is significantly lowered by the incorporation of Coulomb correlation into theoretical treatment. Note that for the TS the three highest level values are distributed 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 -10.42 and +2.52 kcal/mol for the RC and TS of the S_N2@C reaction agree excellently with and further consolidate the corresponding CCSD(T) benchmark values of -10.26 and 2.65 kcal/mol computed by Botschwina and coworkers.^{11,12}

The energy of the stable S_N2@Si transition complex shows a similar behavior as that of the S_N2@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 to -27.64 to -25.87 to -25.71 to -27.10 kcal/mol along HF, MP2, MP4SDQ, CCSD, and CCSD(T), see Table 3. Note how HF dramatically underestimates 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. Furthermore, 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 kcal/mol

Table 3. Relative Energies (in kcal/mol) of Stationary Points along the Reaction Coordinate for the S_N2@C and S_N2@Si Reactions of Cl⁻ + CH₃Cl and Cl⁻ + SiH₃Cl, Computed at Several Levels of the *Ab Initio* and Hybrid Density Functional Theory.

Method		CH ₃ Cl + Cl ⁻		SiH ₃ Cl + Cl ⁻
		RC	TS	TC
HF	6-31+G*	-8.83	6.77	-17.41
	6-31++G**	-8.92	6.65	-17.33
	6-311++G**	-9.13	7.05	-18.05
	aug-cc-pVDZ	-9.32	5.23	-19.69
	aug-cc-pVTZ	-8.89	6.94	-18.40
MP2	aug-cc-pVQZ	-8.77	7.44	-18.08
	6-31+G*	-9.39	7.87	-21.70
	6-31++G**	-9.42	7.91	-22.15
	6-311++G**	-9.66	8.43	-24.06
	aug-cc-pVDZ	-10.78	2.54	-27.27
MP4SDQ	aug-cc-pVTZ	-10.36	3.88	-27.67
	aug-cc-pVQZ	-10.30	4.34	-27.64
	6-31+G*	-9.37	7.48	-21.01
	6-31++G**	-9.40	7.42	-21.46
	6-311++G**	-9.64	8.01	-23.35
CCSD	aug-cc-pVDZ	-10.58	2.71	-25.98
	aug-cc-pVTZ	-10.07	4.31	-25.98
	aug-cc-pVQZ	-10.02	4.80	-25.87
	6-31+G*	-9.35	7.40	-20.89
	6-31++G**	-9.39	7.26	-21.35
CCSD(T)	6-311++G**	-9.66	7.73	-23.23
	aug-cc-pVDZ	-10.57	2.66	-25.84
	aug-cc-pVTZ	-10.06	4.34	-25.82
	aug-cc-pVQZ	-10.00	4.89	-25.71
	6-31+G*	-9.54	5.80	-21.29
	6-31++G**	-9.59	5.62	-21.80
	6-311++G**	-9.88	5.93	-23.83
	aug-cc-pVDZ	-10.95	0.54	-26.80
	aug-cc-pVTZ	-10.48	1.96	-27.11
	aug-cc-pVQZ	-10.42	2.52	-27.10

for the TC of the S_N2@Si reaction is 4.7 kcal/mol more bonding than the best value of -22.4 kcal/mol obtained previously by Gordon and coworkers⁴⁸ at MP4/6-31++G(d,p)//MP2/6-31++G(d,p). Note that the latter value closely agrees with our MP4SDQ/6-31++G**//OLYP/TZ2P value of -21.46 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,^{16,53} as the transition state of the S_N2@C reaction.

Validation of DFT Potential Energy Surfaces

Next, we examine the relative energies of stationary points computed 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.

Table 4. Relative Energies (in kcal/mol) of Stationary Points along the Reaction Coordinate for the $S_N2@C$ and $S_N2@Si$ Reactions of $Cl^- + CH_3Cl$ and $Cl^- + SiH_3Cl$, Computed at Several Levels of the Density Functional Theory.^a

Method	$Cl^- + CH_3Cl$				$Cl^- + SiH_3Cl$		
	RC	TS	(Err. in Barr. Rel. to R ^b)	(Err. in Barr. Rel. to RC ^b)	TC	(Mean Abs. Err. Rel. to R ^b)	(Mean Abs. Err. Rel. to RC ^b)
BP86	-10.98	-5.32	(-7.84)	(-7.28)	-28.75	(3.35)	(3.16)
BLYP	-11.19	-6.46	(-8.98)	(-8.21)	-25.92	(3.64)	(3.39)
OLYP	-9.02	-0.13	(-2.65)	(-4.05)	-24.42	(2.24)	(2.71)
ZORA-OLYP	-8.99	-0.22	(-2.74)	(-4.17)	-24.36	(2.30)	(2.78)
B3LYP//BLYP	-10.07	-2.17	(-4.69)	(-5.04)	-25.29	(2.28)	(2.40)
B3LYP//OLYP	-9.93	-2.35	(-4.87)	(-5.36)	-25.11	(2.45)	(2.61)

^aComputed with TZ2P basis set (see Methods section). Geometries (see Fig. 2) and energies computed at the same level of theory, unless indicated otherwise.

^bError in Overall Barrier (TS relative to R) and Central Barrier (TS relative to RC) and mean absolute error for the energies of the two stationary points of $Cl^- + CH_3Cl$ (i.e., RC and TS) plus that of $Cl^- + SiH_3Cl$ (i.e., TC) both relative to R and relative to RC, compared with the CCSD(T)/aug-cc-pVQZ benchmark values from this work (see Table 3).

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.^{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 $S_N2@C$, and TC for $S_N2@Si$), which need to be inspected individually. OLYP performs particularly well for the overall activation energy (i.e., TS relative to R) of the $S_N2@C$ reaction, which it underestimates 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 $S_N2@C$ central barrier, i.e., TS relative to RC) and even much less for all other relative energies. Thus, the OLYP potential energy surfaces for $S_N2@C$ (-9.0 and -0.1 kcal/mol for RC and TS relative to R) and $S_N2@Si$ (-24.4 kcal/mol for TC relative to R) appears to be as good as that of B3LYP and both compare reasonably well (although not perfect) with the *ab initio* benchmark PES. This agrees with the work of Baker and Pulay for other organic reactions.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.^{24,57,58} Also, for the central barrier of the $S_N2@C$ 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 $S_N2@C$ and $S_N2@Si$ reactions.

Conclusions

We have computed *ab initio* benchmarks for the archetypal nucleophilic substitution of chloride at chloromethane carbon ($S_N2@C$) and chlorosilane silicon ($S_N2@Si$) and, thus, for the trend from $S_N2@C$ to $S_N2@Si$. 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 $S_N2@C$ reaction,^{11,12} in particular the activation energy, are confirmed and thus further consolidated. The previous best *ab initio* estimate of the stability of the D_{3h} symmetric transition complex (TC) occurring in the $S_N2@Si$ 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 $S_N2@C$ and $S_N2@Si$ 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_N2@C barrier (i.e., TS relative to R) by about 2.5 kcal/mol and of the central S_N2@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_N2@C barrier by ca. 4.8 kcal/mol and an underestimation of the central S_N2@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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