Benchmark ab Initio Energy Profiles for the Gas-Phase S_N2 Reactions $Y^- + CH_3X \rightarrow CH_3Y + X^-$ (X,Y = F,Cl,Br). Validation of Hybrid DFT Methods

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The energetics of the gas-phase S_N2 reactions $Y^- + CH_3X^- \rightarrow CH_3Y + X^-$ (where X,Y = F,Cl,Br), were studied using (variants on) the recent W1 and W2 ab initio computational thermochemistry methods. These calculations involve CCSD and CCSD(T) coupled cluster methods, basis sets of up to spdfgh quality, extrapolations to the one-particle basis set limit, and contributions of inner-shell correlation, scalar relativistic effects, and (where relevant) first-order spin−orbit coupling. Our computational predictions are in excellent agreement with experimental data where these have small error bars; in a number of other instances reexamination of the experimental data may be in order. Our computed benchmark data (including cases for which experimental data are unavailable altogether) are used to assess the quality of a number of compound thermochemistry schemes such as G2 theory, G3 theory, and CBS-QB3, as well as a variety of density functional theory methods. Upon applying some modifications to the level of theory used for the reference geometry (adding diffuse functions, replacing B3LYP by the very recently proposed mPW1K functional [Lynch, B. J.; Fast, P. L.; Harris, M.; Truhlar, D. G. *J. Phys. Chem. A* **2000**, *104*, 4811]), the compound methods appear to perform well. Only the "half-and-half" functionals BH&HLYP and mPWH&HPW91, and the empirical mPW1K functional, consistently find all required stationary points; the other functionals fail to find a transition state in the F/Br case. BH&HLYP and mPWH&HPW91 somewhat overcorrect for the tendency of B3LYP (and, to a somewhat lesser extent, mPW1PW91) to underestimate barrier heights. The Becke97 and Becke97-1 functionals perform similarly to B3LYP for the problem under study, while the HCTH and HCTH-120 functionals both appear to underestimate central barriers. HCTH underestimates complexation energies; this problem is resolved in HCTH-120. mPW1K appears to exhibit the best performance of the functionals considered, although its energetics are still inferior to the compound thermochemistry methods. mPW1K, however, appears to be very suitable for generating reference geometries for more elaborate thermochemical methods in kinetics applications.

I. Introduction

Due to the central importance of bimolecular nucleophilic substitution (S_N2) reactions in organic chemistry,[1,2] the prototype S_N2 reactions

$$Y^- + CH_3X \rightarrow CH_3Y + X^- \ (X,Y = F,Cl,Br) \qquad (1)$$

have aroused considerable interest in the past three decades. (Halomethanes have also received considerable attention in the area of atmospheric chemistry in connection with global warming[3] and ozone layer destruction.[4]) Both theoretical and experimental studies (see refs 5,6 for reviews) indicate that the preferred gas-phase reaction pathway involves a backside attack of the halide ion, Y^-, at the carbon atom followed by the familiar "Walden inversion" of the CH_3 group. The resulting reaction profile (Figure 1) exhibits two local minima, i.e., entry and exit channel ion−molecule complexes $Y^-\cdots CH_3X$ and $YCH_3\cdots X^-$, connected by a central transition state $[Y\cdots CH_3\cdots X]^-$, which has D_{3h} and C_{3v} symmetries in the identity (X = Y) and nonidentity (X ≠ Y) cases, respectively. Although the qualitative form of this reaction pathway is widely accepted for substitution reactions in the gas phase, there is still considerable uncertainty about the exact energetics.

Böhme et al.[7] and Brauman et al.[8] were the first to investigate the gas-phase S_N2 reactions experimentally. Brauman and coworkers concluded that the measurements were best explained by a double-well potential with a central barrier. Subsequent experimental studies[9−12] for a series of anionic nucleophiles with alkyl halides revealed that changes in the nucleophile, leaving group, and alkyl moiety lead to a wide variation of reaction rate constants; their observed variation was attributed to the central barrier height.

The double-well S_N2 potential energy surface also finds abundant theoretical support from ab initio calculations, which are currently one of the most useful tools for evaluating reaction potential energy profiles. For instance, Chandrasekhar et al.[13] presented a comprehensive examination of Cl/Cl identity S_N2 reaction at the HF/6-31G* level, and Tucker and Truhlar[14] examined the S_N2 reactions at the MP2/6-31G* level. Wladkowski et al.[15] studied the F/F identity S_N2 reaction by large-scale coupled cluster theory involving single and double excitation operators with an a posteriori a quasiperturbative treatment of the effects of connected triple substitutions (CCSD(T)) (see refs 16,17 for reviews). Later, Radom, Pross, and coworkers have carried out ab initio molecular orbital calculations at the G2(+) level of theory for the backside identity[18] and

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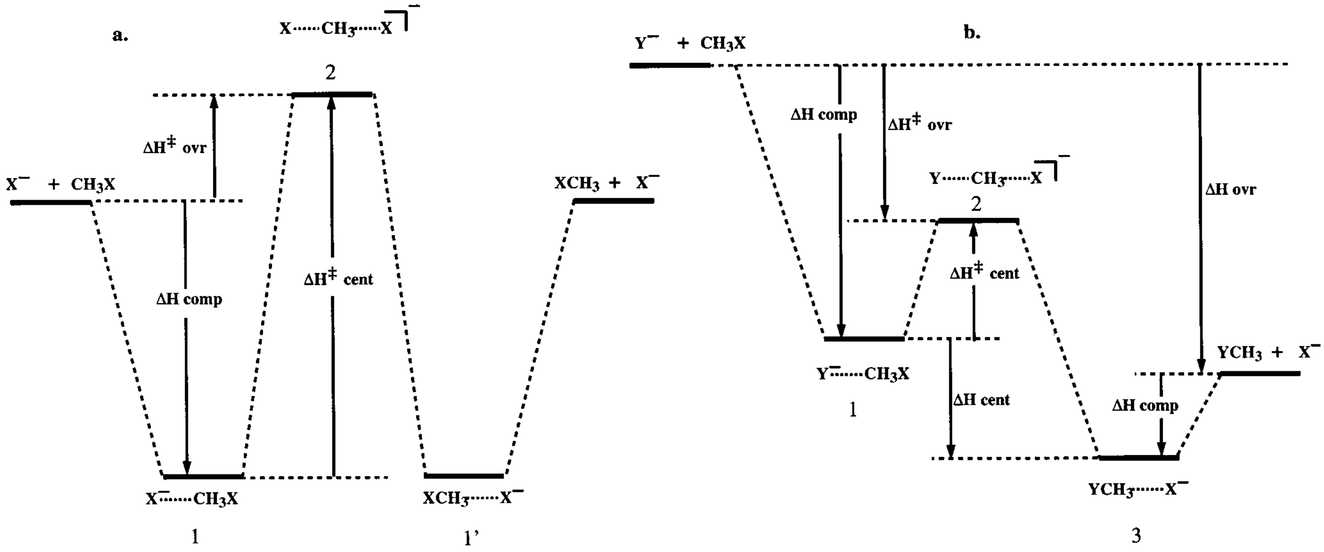

Figure 1. Schematic representation of potential energy surface for the (a) identity and (b) nonidentity S_N2 reactions.

nonidentity[19] S_N2 reactions. These authors have also investigated the identity front-side S_N2 reactions with retention of configuration.[20] The G2(+) theory is essentially G2 theory carried out from MP2/6-31+G* (rather than MP2/6-31G*) geometries and employing scaled HF/6-31+G* (rather than HF/6-31G*) zero-point energies. For the bromine- and iodine-containing systems, these authors employed Hay–Wadt[21] relativistic effective core potentials (RECPs). Botschwina and co-workers examined the stationary points of the potential surface for the F/Cl nonidentity S_N2 reaction[22] and for the Cl/Cl identity S_N2 reaction[23] by means of large-scale CCSD(T) calculations. Finally, a referee brought a very recent large-scale coupled cluster study by Schmatz et al.[24] on the Cl/Br system to our attention.

Despite the well-known successes (e.g., refs 25,26) of the increasingly popular DFT (density functional theory) methods,[27] their performance for transition state structures and reaction barrier heights leaves something to be desired. For instance, Durant[28] found that the B3LYP, B3P86, and B3PW91 functionals all systematically underestimated barrier heights, while only the Becke half-and-half/Lee, Yang, and Parr (BH&HLYP)[29] functional predicted transition state barrier heights reasonably well—despite the fact that its performance for thermochemical and other properties is generally substantially poorer than that of B3LYP and B3PW91. Baker et al.[30] arrived at a similar conclusion stating that the currently available density functionals are unable to provide a correct description of the transition states. For the prototype S_N2 reactions (Cl/Cl and Cl/Br) considered here, Radom and co-workers[31] found that the popular B3LYP[32,33] exchange-correlation functional significantly underestimated the overall and central barrier heights compared to the G2(+) and experimental results.

Nevertheless, the size of the systems involved in kinetic and mechanistic problems of organic and organometallic interest often makes DFT the only practical option. As a matter of fact, our group has recently reported DFT studies of the mechanism of competitive intramolecular C–C and C–H bond activation in rhodium(I) pincer complexes[34] and of the Heck reaction.[35]

Aside from BH&HLYP, better performance for barrier heights has been claimed for a number of newer exchange-correlation functionals. For example, Adamo and Barone[36] found that their mPW1PW91 (modified Perdew–Wang 1991 1-parameter hybrid exchange with Perdew–Wang 1991 correlation[37]) at least correctly predicts a positive overall barrier for the Cl/Cl identity S_N2 reaction, although it is still being underestimated. Very recently, Truhlar and co-workers[38] proposed a new hybrid model called the modified Perdew–Wang 1-parameter model for kinetics (mPW1K). In this empirical functional, the coefficient X for admixture of "exact" Hartree–Fock exchange

$$V_{XC} = XV_{X,HF} + (1-X)V_{X,mPW1} + V_{C,PW91} \tag{2}$$

(where $X = 1/4$ for standard mPW1PW91) was determined (using the fairly small 6-31+G* basis set) by minimizing the average deviation from a set of 40 barrier heights (20 forward, 20 reverse) obtained from a combination of experiment and theory (see ref 38 for details). (Note that the Walden inversion, or for that matter cationic or anionic reactions of any kind, were not part of the parametrization set.) It was found that mPW1K reduced the mean unsigned error in reaction barrier heights by a factor of 2.4 over mPW1PW91 and by a factor of 3 over B3LYP.

Theoretical models such as transition state theory (TST)[39] and Rice–Ramsperger–Kassel–Marcus (RRKM)[40] theory were also employed to examine the S_N2 reactions. Results from such studies (see ref 41 and references therein) suggested that the assumption of statistical behavior in ion–molecule intermediate complexes is not valid. This "nonstatistical" behavior has been documented for several halide–methyl halide reactions and a thorough discussion is given by Hase.[5] Classical trajectory simulations performed by Hase and co-workers[42] questioned the basic assumptions of statistical theories and found that the trajectory calculations are very useful in interpreting the kinetics and dynamics of S_N2 reactions.

Despite the enormous amount of work in the past, there are still significant gaps in the experimental data for the gas-phase S_N2 reactions and, even where data are available, the results often possess large uncertainties. Recently, two computational thermochemistry methods known as W1 and W2 (Weizmann-1 and Weizmann-2) theory[43] have been developed in our laboratory. These are free of parameters derived from experiment and on average can claim "benchmark accuracy" (defined in ref 43 as a mean absolute error of 1 kJ/mol, or 0.25 kcal/mol) for molecular total atomization energies (TAEs) of first- and second-row compounds. The primary objective of the present study is to obtain high-quality energetic data for reaction 1 by means of W1 and W2 theory. Using these benchmark data, we shall then examine the performance of various DFT methods and ab initio computational thermochemistry methods such as G1,[44] G2,[45] G3,[46] and CBS-QB3[47] theories.

II. Computational Methods

All calculations were carried out on the 4-processor Compaq ES40 of our research group, and on the 12-CPU SGI Origin 2000 of the Faculty of Chemistry.

Energetics for the gas-phase stationary points for all six surfaces (i.e., F/F, Cl/Cl, Br/Br, F/Cl, F/Br, and Cl/Br) were obtained by means of the W1′ method described in refs 43,48. The W1′ method[48] is a minor variation on W1 theory[43] that exhibits improved accuracy for second-row systems at no additional computational cost. For a detailed description and theoretical and empirical arguments for each step, see ref 43. We shall merely summarize the main points here for the sake of clarity. The basis sets employed are mostly Dunning's augmented correlation consistent *n*-tuple ζ^{49-51} (aug-cc-pV*n* Z) basis sets; for second-row atoms high-exponent d and f functions were added (denoted "+2d" or "+2d1f") as recommended in ref 52 for accommodating inner polarization. Since the standard aug-cc-pV*n*Z basis sets for bromine[53] already contain quite high-exponent d functions in order to describe the 3d orbitals, no "inner polarization" functions were deemed to be necessary on Br. We may distinguish the following six components in the "bottom-of-the-well" TAE at the W1′ level:

- The SCF component of the TAE is obtained using the aug-cc-pVDZ+2d, aug-cc-pVTZ+2d, and aug-cc-pVQZ+2d1f basis sets, and extrapolated to the infinite-basis limit using the geometric expression[54] $A + B \cdot C^{-L}$, where the "cardinal number" $L = \{2,3,4\}$ for these three basis sets. (It is identical to the maximum angular momentum present for nonhydrogen atoms. Regular cc-pV*n*Z basis sets were used on hydrogen atoms throughout.)
- The CCSD (coupled cluster with all singles and doubles[55]) valence correlation contribution to TAE is obtained using the aug-cc-pVTZ+2d and aug-cc-pVQZ+2d1f basis sets, then extrapolated to the infinite basis limit using the expression $A + B/L^{3.22}$.
- The (T) connected triple excitations component[56] of TAE was computed using the aug-cc-pVDZ+2d and aug-cc-pVTZ+2d basis sets, and extrapolated to the infinite basis limit using the expression $A + B/L^{3.22}$.
- The inner-shell correlation contribution was computed as the difference between CCSD(T)/MTsmall[43] values with and without constraining the inner-shell orbitals to be doubly occupied. The very deep-lying chlorine (1s) and bromine (1s,2s,2p) orbitals were doubly occupied throughout; the "inner-shell correlation" thus represents carbon (1s), chlorine (2s,2p) and bromine (3s,3p,3d) correlation. (Basis set superposition error, BSSE, can be an issue for inner-shell correlation energies in heavier element systems;[57] our experience[43] suggests that BSSE in the W1/W2 inner shell correlation contributions largely cancels with basis set incompleteness.)
- The scalar relativistic contribution was computed as expectation values of the one-electron Darwin and mass-velocity (DMV) operators[58,59] for the ACPF/MTsmall (averaged coupled pair functional[60]) wave function, with all inner-shell electrons correlated except for chlorine (1s) and bromine (1s,2s,2p).
- The spin−orbit contribution to TAE, in the present case of all-closed-shell systems, is nothing more than the sum of the atomic fine structure corrections.

Where our computational hardware permitted (in practice, for F/F, Cl/Cl, and the Br/Br transition state), we also carried out even more demanding W2h calculations. In W2 theory, the same steps occur as above, except that the three valence basis sets are aug-cc-pVTZ+2d1f, aug-cc-pVQZ+2d1f, and aug-cc-pV5Z+2d1f (with $L = 3$, 4, and 5, respectively) and that the extrapolation formula[61] used for the CCSD and (T) steps is simply $A + B/L^3$. The W2h variant[62] indicates, in this particular case, the use of unaugmented cc-pV*n*Z basis sets on carbon. The largest basis set CCSD step was carried out using the direct algorithm of Lindh, Schütz, and Werner.[63] All these calculations were performed using MOLPRO 98.1[64] and a driver for the W1/W2 calculations[65] written in MOLPRO's scripting language. Reference geometries were obtained primarily using the B3LYP[32,33] density functional method, which employs the Lee−Yang−Parr[33] correlation functional in conjugation with a hybrid exchange functional first proposed by Becke.[32]

A number of lower-level procedures were validated against the W1′ and W2h results. These include the following set of DFT exchange-correlation functionals and basis sets: B3LYP/cc-pVTZ(+X), BH&HLYP/cc-pVTZ(+X), mPW1PW91/cc-pVTZ(+X), mPW1K/6-31+G*, mPW1K/cc-pVDZ(+X), mPW1K/cc-pVTZ(+X), where (+X) indicates that diffuse functions are included only for halogens. BH&HLYP[29] is essentially the B3LYP method, with the exception that the fraction of HF exchange is 50% (H&H denotes "half and half"). Analogous to BH&HLYP, we have also performed mPWH&HPW91.[66] In addition, we carried out calculations using the standard G1, G2, G3, and CBS-QB3 model chemistries. The MP2/6-31G* and B3LYP/6-311G(2d,d,p) levels of theory (used for the reference geometries in G3[46] and CBS-QB3,[47] respectively) fail to find stationary points for several of the ion−molecule complexes in the nonidentity cases (because of the absence of diffuse functions). Therefore, we have defined, by analogy with Radom and co-workers,[18−20] G3(+) and CBS-QB3(+) model chemistries where MP2/6-31+G* and B3LYP/6-311+G(2d,d,p) reference geometries, respectively, are used. The G2(+) results quoted in the tables are taken from Radom and co-workers.[18,19] All of these calculations were carried out using Gaussian 98 rev. A7[67] or trivial modifications thereof. Following the recommendations in ref 68, larger grids than the default were used in the DFT calculations if necessary, specifically a pruned (99,590) grid for integration and gradients, and a pruned (50,194) grid for the solution of the coupled perturbed Kohn−Sham equations.

Finally, following very recent suggestions in the literature[69] that some of these functionals may perform better for transition states, some calculations using the novel B97 (Becke-1997),[70] B97-1 (reparametrized Becke-1997),[71] HCTH (Hamprecht−Cohen−Tozer−Handy),[71] and HCTH-120 (reparametrization of HCTH including anions and weakly interacting systems)[72] functionals were carried out by means of a slightly modified version of NWCHEM 3.3.1.[73]

III. Results and Discussion

A. Reference Geometries. Reference geometries for the W1′ calculations were mostly obtained at the B3LYP/cc-pVTZ+1 level, where the "+1" signifies the addition of a high-exponent d function on second-row elements.[74] (The Br basis set already includes high-exponent d functions to cover the (3d) orbital.) It was previously shown[26] that B3LYP/cc-pVTZ geometries for stable molecules are generally within a few thousandths of an Å from experiment, as well that the use of B3LYP/cc-pVTZ+1 rather than much costlier CCSD(T)/cc-pVQZ+1 reference geometries insignificantly affects computed energies.[43] (Modifications of popular computational thermochemistry methods that use DFT reference geometries include variants[75,76] of G2

TABLE 1: Components of Computed Electron Affinities of X and Total Atomization Energies (kcal mol^{-1}) of CH_3X (X = F,Cl,Br)

species	SCF limit	CCSD limit	(T) limit	core corr.	spin−orbit splitting	scalar rel. effects	final energy
				W1′			
F^-	30.21	44.76	4.17	0.17	−0.39	−0.26	78.66
Cl^-	58.35	24.16	2.28	0.02	−0.84	−0.34	83.63
Br^-	58.37	21.76	1.98	0.31	−3.51	−0.90	78.02
CH_3F	319.57	97.39	5.41	1.12	−0.47	−0.37	422.65
CH_3Cl	303.73	86.14	5.27	1.19	−0.93	−0.42	394.98
CH_3Br	292.99	85.48	5.25	1.45	−3.60	−0.79	380.78
				W2h			
F^-	30.08	44.71	4.15	0.17	−0.39	−0.26	78.46
Cl^-	58.33	23.82	2.26	0.02	−0.84	−0.34	83.25
Br^-	58.31	21.49	1.91	0.31	−3.51	−0.90	77.62
CH_3F	319.82	96.89	5.34	1.14	−0.47	−0.37	422.34
CH_3Cl	303.90	86.03	5.28	1.21	−0.93	−0.42	395.07
CH_3Br	293.14	85.45	5.21	1.49	−3.60	−0.79	380.91

TABLE 2: Components of Relative Energies (kcal mol^{-1}) of Ion−Molecule Complexes and Transition State Structures with Respect to Reactants

species	SCF limit	CCSD limit	(T) limit	core corr.	scalar rel. effects	final energy
			W1′			
$F^-\cdots CH_3F$	−10.63	−2.54	−0.56	0.09	−0.02	−13.66
$[F\cdots CH_3\cdots F]^-$	8.23	−6.23	−2.65	0.36	−0.08	−0.37
$Cl^-\cdots CH_3Cl$	−8.08	−1.93	−0.62	0.08	0.01	−10.54
$[Cl\cdots CH_3\cdots Cl]^-$	7.81	−2.62	−2.37	0.35	−0.10	3.07
$Br^-\cdots CH_3Br$	−7.55	−1.92	−0.65		0.09	−10.03[a]
$[Br\cdots CH_3\cdots Br]^-$	5.71	−2.43	−2.36	0.26	−0.16	1.02
			W2h			
$F^-\cdots CH_3F$	−11.16	−2.17	−0.45	0.07	−0.02	−13.72
$[F\cdots CH_3\cdots F]^-$	8.58	−6.61	−2.58	0.35	−0.08	−0.34
$Cl^-\cdots CH_3Cl$	−8.01	−2.39	−0.65	0.10	0.01	−10.94
$[Cl\cdots CH_3\cdots Cl]^-$	8.55	−3.63	−2.46	0.33	−0.11	2.67
$[Br\cdots CH_3\cdots Br]^-$	6.57	−3.41	−2.38	0.21	−0.21	0.77
			W1′			
$F^-\cdots CH_3Cl$	−13.67	−1.16	−0.76	0.18	−0.02	−15.43
$[F\cdots CH_3\cdots Cl]^-$	−10.39	−0.84	−1.60	0.36	−0.07	−12.54
$Cl^-\cdots CH_3F$	−7.08	−2.03	−0.42	0.03	0.00	−9.51
$F^-\cdots CH_3Br$	−15.08	−1.24	−0.72		0.03	−17.01[a]
$[F\cdots CH_3\cdots Br]^-$	−13.85	−1.02	−1.43		−0.07	−16.37[a]
$Br^-\cdots CH_3F$	−6.63	−1.69	−0.24		0.05	−8.51[a]
$Cl^-\cdots CH_3Br$	−8.89	−2.02	−0.59		−0.41	−11.91[a]
$[Cl\cdots CH_3\cdots Br]^-$	2.24	−2.69	−2.28		−0.57	−3.30[a]
$Br^-\cdots CH_3Cl$	−7.38	−2.03	−0.45		−0.46	−10.32[a]

[a] W1′ − without inner-shell correlation.

theory, G3//B3LYP,[77] and CBS-QB3.[47]) In some cases where B3LYP fails to locate the required stationary point, we used mPW1K/cc-pVTZ(+X) reference geometries. For the W2h calculations, CCSD(T)/cc-pVQZ+1 reference geometries were used. The geometries of all the structures involved in the present study calculated at various levels of theory are provided in the Supporting Information.

B. Energetics. To assess the accuracy of W1′ and W2h results, we consider first the total atomization energies (TAEs) of CH_3X and electron affinities (EAs) of X^-. A summary of our computed results and their components for the reactants/products of the S_N2 reactions is presented in Table 1. The final energies presented in the last column of the Table correspond to EAs of X (X = F,Cl,Br) and TAEs without zero-point vibrational energy (ZPVE) of CH_3X. The inner-shell correlation contributions are all positive and the largest is 1.49 kcal/mol for CH_3Br. The core correlation contribution for TAE(CH_3X) is found to increase in the order F < Cl < Br, while for EA(X) it increases in the order Cl < F < Br. The importance of Darwin and mass−velocity corrections increases, as expected, with increasing atomic number (Z) of X and its contribution becomes substantial when X = Br.

It is perhaps more pertinent for our purposes to examine the relative energies (with respect to reactants) of the ion−molecule complexes and transition state structures. Table 2 presents W1′ and W2h results for identity reactions and only W1′ results for nonidentity reactions. W2h calculations for the nonidentity reactions are extremely expensive as the reaction intermediates are less symmetric. Moreover, the size of the bromine atoms prevents us from performing a W2h calculation on the identity $Br^-\cdots CH_3Br$ ion−molecule complex. Likewise, we could not obtain the core correlation contributions for the $Br^-\cdots CH_3Br$ ion−molecule complex at the W1′ level of theory. It was previously established[78] that the inclusion of connected triple excitations in CCSD(T) is absolutely necessary for reliable core correlation contributions: the n^3N^4 CPU time dependence of the (T) step dominates the required CPU time for Cl and Br. Both the size of the halogen atoms and the reduced symmetry prevented us from performing core-correlation calculations for nonidentity S_N2 reactions, except for the F/Cl nonidentity case.

From Table 2, it can be seen that the final W1′ and W2h energy values for the identity reactions are very close to each other. Considering the very close agreement between W1′ and W2h results, the conclusion is warranted that the results from W1′ theory can be used as reference values to compare the results from other methods when W2h results are not available. As a general observation, the core contributions for the transition state structures are noticeably larger than for the ion−molecule complexes (see Table 2). Although the core-correlation contribution is small in absolute terms, its relative contribution to the likewise small overall barrier heights can be substantial. For example, it is 0.36 kcal/mol for $[F\cdots CH_3\cdots F]^-$, while the total energy is −0.37 kcal/mol. Likewise, the core correlation contributions for $[Cl\cdots CH_3\cdots Cl]^-$ and $[Br\cdots CH_3\cdots Br]^-$ are nearly 10% and 25% of the overall barrier (relative to reactants), respectively. At the W2h level, the core correlation contribution to the total energy increases slightly. Scalar relativistic effects exhibit similar trends as those of core correlation, but the effects are fairly small. Only $Cl^-\cdots CH_3Br$, $[Cl\cdots CH_3\cdots Br]^-$, and $Br^-\cdots CH_3Cl$ exhibit noticeable scalar relativistic contributions, due to the presence of the heavy halogen Br.

Among the identity reactions only $[F\cdots CH_3\cdots F]^-$ has a transition state below the reactants energy level. In the nonidentity case all the transition state structures lie below the reactants.

The computed final heats of formation (ΔH_f°) of CH_3X in kcal/mol are compared with experiment in Table 3. Both W1′ and W2h values are presented after accounting for ZPVEs and thermal corrections calculated at the B3LYP/cc-pVTZ+1 level. At this level the ZPVEs, after scaling by 0.985,[43] are found to be 24.16, 23.26, and 22.89 kcal/mol, respectively, for CH_3F, CH_3Cl, and CH_3Br. The corresponding thermal corrections are −1.92, −1.89, and −3.68 kcal/mol. The computed (ΔH_f°) value for CH_3Cl lies within the experimental error bar: the experimental value for CH_3F is a crude estimate (±7 kcal/mol) and our computed value is certainly more reliable. Our calculated value for CH_3Br is slightly outside the experimental error bar: some of the discrepancy could be due to the limitations of the scalar relativistic treatment. As shown by Bauschlicher,[79] the simple DMV correction starts to exhibit minor deficiencies for third-row compounds; for first- and second-row compounds, it is in excellent agreement with more rigorous treatments.[80,81]

Also included in Table 3 are calculated electron affinities of X (X = F,Cl,Br) in eV together with experimental results. Using a similar approach, but with even larger spdfghi basis sets as

TABLE 3: Calculated and Experimental Heats of Formation (kcal mol^{-1}) of CH_3X and Electron Affinities (eV) of X (X = F,Cl,Br)

	heat of formation				electron affinity		
species	W1′	W2h	experiment	species	W1′	W2h	experiment
CH_3F	−57.06	−56.75	−56(7)[87]	F	3.411	3.402	3.401 190(4)[88]
CH_3Cl	−20.14	−20.23	−20.00(50)[87]	Cl	3.627	3.610	3.612 69(6)[88]
CH_3Br	−8.50	−8.63	−8.20(19)[87]	Br	3.383	3.366	3.363 583(44)[89]

well as full CI corrections, we were able[82] to reproduce the experimental EAs of the first- and second-row atoms to within ±0.001 eV on average. The presently calculated W2h results of F and Cl EAs differ by only about 0.001 eV from these benchmark values (EA(F) = 3.403 eV and EA(Cl) = 3.611 eV), and the W2h results for F, Cl, and Br are all within 0.003 eV of experiment. Although the W1′ values differ about 0.01 eV for F and Cl and 0.02 eV for Br, this is comparable to the W1/W2 target accuracy (0.25 kcal/mol on average). The performance of the W1′ and W2h methods for the reactants and products is obviously encouraging for the study of the problem at hand.

C. S_N2 Reactions. The reaction mechanism with the double-well potential energy surface for the gas-phase S_N2 reactions is shown in Figure 1. Obviously, the energy profile is symmetric for the identity reactions (Figure 1a), and asymmetric for the nonidentity reactions (Figure 1b). The complexation energy (ΔH_{comp}), central barrier ($\Delta H^{\ddagger}_{cent}$), and overall activation barrier relative to the separated reactants ($\Delta H^{\ddagger}_{ovr}$) are defined in Figure 1. In the nonidentity case, the following additional quantities are defined in Figure 1b: overall enthalpy change for the reaction (ΔH_{ovr}) and the central enthalpy difference ΔH_{cent} between product and reactant ion−molecule complexes, **3** and **1**.

D. Identity Reactions. Complexation energies (ΔH_{comp}), overall barrier heights ($\Delta H^{\ddagger}_{ovr}$), and central barriers ($\Delta H^{\ddagger}_{cent}$) obtained from W1′ and W2h methods are compared in Table 4 with DFT, Gn, and CBS-QB3 methods together with available experimental values.

It should be emphasized that the experimental data for the S_N2 reactions are insufficient and the available data are subject to large uncertainties. Therefore, it would be appropriate to analyze the performance of various methods with respect to W*n* methods. First of all, note that the mPW1K/6-31+G* ΔH_{comp} (13.55 kcal/mol) for the F/F case is very close to the W1′ and W2h results (13.66 and 13.72 kcal/mol, respectively). mPW1K/cc-pVDZ(+X) and mPW1K/cc-pVTZ(+X) methods, however, predict lower ΔH_{comp} values. In fact, the B3LYP, B97, HCTH-120, mPW1PW91, mPWH&HPW91, and mPW1K methods all predict roughly 1 kcal/mol lower complexation energies, while BH&HLYP and B97-1 agree well with W1′ and W2h. (The HCTH ΔH_{comp} is much lower than the others, vide infra.) G2 and CBS-QB3 values are close to the W*n* results while the G3 method predicts higher complexation energy compared to the W*n* methods. Inclusion of diffuse functions for the G*n* and CBS-QB3 reference geometries (i.e., G*n*(+) and CBS-QB3(+)) increases the ΔH_{comp} value by 0.4−0.6 kcal/mol.

A comparison of overall barrier heights is presented in the third column of Table 4. Both W1′ (−0.37 kcal/mol) and W2h (−0.34 kcal/mol) theories predict negative barrier heights in the F/F case and the values are very close. The CBS-QB3(+) result is in excellent agreement therewith; all G*n* theories predict barrier heights that are lower by 1 kcal/mol, with further lowering seen at the G2(+) and G3(+) levels. Among the DFT methods considered, only mPW1K/6-31+G* and HCTH/cc-pVDZ(+X) fortuitously predict overall barrier heights close to the W*n* results: basis set extension for mPW1K leads to positive overall barrier heights, which are likewise found for the "half-and-half" functionals. B3LYP, B97(-1) and HCTH-120 all significantly underestimate the barrier, mPW1PW91 to a lesser extent.

For the chlorine identity gas-phase S_N2 reactions, fairly accurate experimental values are available and are presented in Table 4. The experimental values reported by Li and co-workers[11] correspond to the standard state. Hence, thermal corrections and ZPVEs are subtracted from experimental values in order to compare with the "bottom of the well" calculated values. It is noteworthy that the W1′ (10.54 kcal/mol) and W2h (10.94 kcal/mol) complexation energies are in good agreement with the experimental value (10.53 kcal/mol). CBS-QB3 results are also in agreement with the W*n* and experimental values, while those from DFT calculations are less satisfactory as they are about 1 kcal/mol lower. Also note that the G1 and G2 methods reproduce the complexation energy well, while G3 results are 0.5 kcal/mol higher than the W*n* and experimental values.

The overall barrier height for the Cl/Cl reaction is found to be 3.07 and 2.67 kcal/mol at the W1′ and W2h levels of theory. Note first that the experimental value (2.90 kcal/mol) is very close and lies between the W1′ and W2h values. The $\Delta H^{\ddagger}_{ovr}$ value calculated at the mPW1K/6-31+G*, and CBS-QB3 levels of theory as well as the G2(+) value by Radom et al.[18] and the CCSD(T)/spdfg value by Botschwina[23] agree well with the W2h result. The mPW1K exchange-correlation functional with the cc-pVDZ(+X) and cc-pVTZ(+X) basis sets predict somewhat higher $\Delta H^{\ddagger}_{ovr}$ values, while the G1, G2MP2, and G3(+) values are about 1 kcal/mol lower. B3LYP, B97, B97-1, and HCTH-120 all predict a negative overall barrier for the Cl/Cl system, in disagreement with all other methods considered and with experiment. BH&HLYP performs moderately well, while mPWH&HPW91 predicts a larger barrier height (4.50 kcal/mol) than W*n*. The central barrier values presented in the last column of the Table 4 reveal that the agreement between W*n* theories (13.61 kcal/mol) and experiment (13.66 kcal/mol) is excellent. The G2MP2, G2(+), and CBS-QB3 methods also reproduce the central barriers very well. As expected from the overall barrier heights, the DFT results are less satisfactory, except for mPW1K/cc-pVDZ(+X) and mPW1K/cc-pVTZ(+X) which are in good agreement with the W*n* values.

For the bromine identity S_N2 reaction, W1′ theory predicts 10.03 kcal/mol for ΔH_{comp}. Note that the G2(+) value is in close agreement with W1′ theory. The reported experimental value (11.34 ± 0.4 kcal/mol) agrees fairly well. Most DFT levels of theory considered suggest a complexation energy about 1 kcal/mol lower than the W1′ value, except mPW1K/6-31+G** which is higher (12.78 kcal/mol, probably an artifact of the small basis set); B97 and B97-1 which closely bracket the W1′ value; HCTH-120 which is close to the W1′ value (see below); and HCTH which is 2.5 kcal/mol lower than the latter. The complexation energies for $X^- \cdots CH_3X$ are found to decrease in the order F > Cl > Br. This trend was noted previously by Radom and co-workers,[18] who attributed it to the electronegativities of the halogens.

The overall barrier height for the Br/Br reaction is found to be 1.02 and 0.77 kcal/mol at the W1′ and W2h levels of theory.

TABLE 4. Comparison of Complexation Energies (ΔH_{Comp}) of the Ion−Molecule Complexes, Overall Barrier Heights Relative to Reactants ($\Delta H^{\ddagger}_{Ovr}$), and Central Barriers ($\Delta H^{\ddagger}_{Cent}$) of Identity S_N2 Reactions, $X^- + CH_3X \rightarrow XCH_3 + X^-$, Calculated at Various Levels of Theory (all values in kcal/mol)

X	method	ΔH_{comp}	$\Delta H^{\ddagger}_{ovr}$	$\Delta H^{\ddagger}_{cent}$
F	W1′	13.66	−0.37	13.29
	W2h	13.72	−0.34	13.38
	B3LYP/cc-pVTZ(+X)	12.72	−2.58	10.15
	BH&HLYP/cc-pVTZ(+X)	13.22	1.31	14.53
	mPW1PW91/cc-pVTZ(+X)	12.49	−0.95	11.55
	mPWH&HPW91/cc-pVTZ(+X)	12.77	2.60	15.38
	B97/cc-pVDZ(+X)	12.48	−2.47	10.01
	B97-1/cc-pVDZ(+X)	13.21	−3.29	9.92
	HCTH/cc-pVDZ(+X)	9.87	−0.60	9.27
	HCTH-120/cc-pVDZ(+X)	12.39	−4.20	8.18
	mPW1K/6-31+G*	13.55	−0.30	13.26
	mPW1K/cc-pVDZ(+X)	12.63	0.36	13.00
	mPW1K/cc-pVTZ(+X)	12.66	1.69	14.36
	G1	13.01	−1.37	11.64
	G2	13.34	−1.15	12.19
	G2MP2	13.41	−0.63	12.78
	G3	14.23	−1.97	12.26
	CBS-QB3	13.46	−0.85	12.61
	G3(+)	14.59	−2.68	11.90
	CBS-QB3(+)	14.15	−0.52	13.63
	G2(+)[a]	13.81	−1.86	11.95
	CCSD(T)/spdf[c]	13.73	−0.92	12.81
Cl	W1′	10.54	3.07	13.61
	W2h	10.94	2.67	13.61
	B3LYP/cc-pVTZ(+X)	9.50	−0.48	9.02
	BH&HLYP/cc-pVTZ(+X)	9.67	3.17	12.84
	mPW1PW91/cc-pVTZ(+X)	9.59	1.23	10.82
	mPWH&HPW91/cc-pVTZ(+X)	9.69	4.50	14.19
	B97/cc-pVDZ(+X)	10.10	−0.66	9.44
	B97-1/cc-pVDZ(+X)	10.74	−1.46	9.28
	HCTH/cc-pVDZ(+X)	7.91	1.45	9.36
	HCTH-120/cc-pVDZ(+X)	9.96	−1.93	8.03
	mPW1K/6-31+G*	9.75	3.20	12.95
	mPW1K/cc-pVDZ(+X)	9.65	3.63	13.28
	mPW1K/cc-pVTZ(+X)	9.64	3.66	13.30
	G1	10.52	1.79	12.31
	G2	10.77	3.06	13.83
	G2MP2	10.89	2.74	13.63
	G3	11.15	1.79	12.95
	CBS-QB3	10.65	2.47	13.12
	G3(+)	11.04	1.80	12.83
	CBS-QB3(+)	10.69	2.40	13.09
	G2(+)[a]	10.71	3.01	13.72
	CCSD(T)/spdfg[b]		2.75	
	experiment	10.53(40)[d]	2.90[e]	13.66(2.01)[f]
Br	W1′-core	10.03	1.02[i]	10.79
	W2h		0.77	
	B3LYP/cc-pVTZ(+X)	9.06	−2.42	6.64
	BH&HLYP/cc-pVTZ(+X)	9.04	1.25	10.29
	mPW1PW91/cc-pVTZ(+X)	9.21	−1.03	8.18
	mPWH&HPW91/cc-pVTZ(+X)	9.19	2.22	11.40
	B97/cc-pVDZ(+X)	9.62	−2.29	7.33
	B97-1/cc-pVDZ(+X)	10.24	−3.02	7.22
	HCTH/cc-pVDZ(+X)	7.56	−0.70	6.86
	HCTH-120/cc-pVDZ(+X)	9.73	−4.06	5.68
	mPW1K/6-31+G*	12.78	−1.95	10.83
	mPW1K/cc-pVDZ(+X)	9.34	0.68	10.02
	mPW1K/cc-pVTZ(+X)	9.16	1.38	10.54
	G1	9.68	1.11	10.78
	G2	9.85	1.52	11.38
	G2MP2	9.83	1.83	11.66
	G2(+)[a]-ECP	10.17	1.48	11.65
	experiment	11.34(40)[d]	1.73[g]	11.68[h]

[a] G2(+) values are from ref 18. [b] CCSD(T)/spdfg values are from ref 23. [c] Ref 15. [d] Exptl. values from ref 11. [e] Exptl. values from ref 90. [f] Exptl. values from ref 10. [g] Exptl. values from ref 83. [h] Exptl. values from ref 84. [i] Core contribution included.

Of the various exchange-correlation functionals considered, only BH&HLYP, mPWH&HPW91, and mPW1K find positive barriers (as do the G*n* theories). It should be pointed out that the DFT results for this system display appreciable basis set sensitivity: for instance, the mPW1K/6-31+G* overall barrier has the wrong sign. It is interesting to note that the complexation energy derived from the experimental overall (1.73 kcal/mol[83]) and central (11.68 kcal/mol[84]) barrier heights is 9.95 kcal/mol while the reported experimental complexation energy (11.34 kcal/mol)[11] is inconsistent with the derived value. In fact, the derived value is in excellent agreement with the W1′ value (10.03 kcal/mol). This clearly suggests that the experimental data should be reexamined.

The performance of both B97 and B97-1 for the identity reactions is quite similar to that of B3LYP. While the "pure DFT" HCTH functional appears to yield markedly better overall barrier heights, this comes at the expense of significantly underestimated complexation energies (and severely overestimated ion−molecule distances, see Supporting Information). It was previously noted[85] that HCTH severely underestimates interaction energies of H-bonded complexes; this was ascribed to the absence of anions and H-bonded dimers in the original HCTH parametrization set. A reparametrization[72] against an enlarged sample of high-quality ab initio energies, denoted HCTH-120, eliminates this particular problem.[85] For the identity S_N2 reactions, we find that complexation energies (and ion−molecule distances) are dramatically improved compared to HCTH: no corresponding improvement is, however, seen for the central barrier heights, and the overall barrier heights deteriorate accordingly.

Overall, the DFT methods are less satisfactory for barrier height calculations. Although the performance of mPW1K/6-31+G* method for F/F and Cl/Cl reactions was excellent, it is not the ultimate low cost method for barrier heights as it has predicted a negative barrier for the Br/Br system. This behavior illustrates the inadequacy of the 6-31+G* basis set for Br: the more extended correlation consistent basis sets with the mPW1K exchange-correlation functional do predict the sign correctly. In addition, G*n*(+) and CBS-QB3(+) provide an acceptable account of reaction energetics.

E. Nonidentity Reactions. A comparison of computed and experimental complexation energies for the nonidentity S_N2 reactions is provided in Table 5. For the $F^-\cdots CH_3Cl$ ion−molecule complex we could find a stationary point neither at the MP2/6-31G* level of theory used for the G2 and G3 reference geometries nor at the B3LYP/6-311G(2d,d,p) level used for the CBS-QB3 reference geometries; at these levels of theory, the optimization leads to $Cl^-\cdots CH_3F$ even if the initial geometries were chosen to correspond to $F^-\cdots CH_3Cl$. Addition of diffuse functions to the basis set for the reference geometry remedies the problem. Similarly, in the F/Br case only the $Br^-\cdots CH_3F$ complex is found as a stationary point at the MP2/6-31G* level of theory, and the transition state and second ion−molecule complex only appear when diffuse functions are added to the basis set. Furthermore, and regardless of the basis set employed, none of the DFT functionals except mPW1K, mPWH&HPW91, and BH&HLYP find a transition state or a $F^-\cdots CH_3Br$ complex. (The CBS-QB3 method is not defined for Br and hence no CBS-QB3 data are presented for the F/Br and Cl/Br ion−molecule complexes.) Table 5 also presents large-scale CCSD(T) energetics for the F/Cl[22] and Cl/Br[24] cases reported by Botschwina and co-workers. Available experimental values are presented at the end of the Table with uncertainties in parentheses.

Examination of Table 5 indicates that the ΔH_{comp} values strongly depend on the nucleophile (Y^-), decreasing in the order $F^- > Cl^- > Br^-$. They also depend on the leaving group (X^-),

TABLE 5: Comparison of Complexation Energies (ΔH_{comp}, kcal/mol) of the Ion−Molecule Complexes for the Nonidentity S_N2 Reactions, Calculated at Various Levels of Theory

method	$F^-\cdots CH_3Cl$	$Cl^-\cdots CH_3F$	$F^-\cdots CH_3Br$	$Br^-\cdots CH_3F$	$Cl^-\cdots CH_3Br$	$Br^-\cdots CH_3Cl$
W1′−core	15.43[a]	9.51[a]	17.01	8.51	11.91	10.32
B3LYP/cc-pVTZ(+X)	15.37	8.09		7.18	10.24	8.42
BH&HLYP/cc-pVTZ(+X)	15.39	8.42	16.65	7.45	10.23	8.56
mPW1PW91/cc-pVTZ(+X)	15.06	8.13		7.27	10.32	8.54
mPWH&HPW91/cc-pVTZ(+X)	15.03	8.32	16.28	7.42	10.30	8.65
B97/cc-pVDZ(+X)	15.43	8.49		7.69	10.66	9.13
B97−1/cc-pVDZ(+X)	16.26	9.05		8.21	11.32	9.74
HCTH/cc-pVDZ(+X)	12.66	6.56		5.82	8.56	7.00
HCTH-120/cc-pVDZ(+X)	15.42	8.48		7.69	10.78	9.01
mPW1K/6-31+G*	15.32	8.79	17.63	9.12	12.97	10.56
mPW1K/cc-pVDZ(+X)	14.52	8.46	16.25	7.62	10.41	8.68
mPW1K/cc-pVTZ(+X)	14.97	8.25	16.30	7.37	10.27	8.60
G1		9.58		8.35	11.17	9.10
G2		9.68		8.42	11.35	9.36
G2MP2		9.71		8.40	11.37	9.45
G3		10.03				
CBS-QB3		9.33				
G3(+)	16.34	9.97				
CBS-QB3(+)	15.85	9.51				
G2(+)[b]	15.62	9.64	16.74	8.56	11.47	9.64
CCSD(T)/large[c]	16.07	9.75			11.31	9.71
experiment		11.41(2.01)[d]			12.54(40)[e]	11.01 (40)[e]

[a] Core contribution included. [b] G2(+) values are from ref 19. [c] F/Cl: CCSD(T)/spdfg values from ref 22; Cl/Br: CCSD(T)/spdfgh values from ref 24. [d] Exptl. values from ref 86. [e] Exptl. values from ref 11.

in the order $CH_3F < CH_3Cl < CH_3Br$. Similar observations were made earlier by Radom and co-workers.[19]

Comparison of the complexation energies obtained from various methods with W1′ theory indicates that all DFT results for $Cl^-\cdots CH_3F$ are lower by 1 kcal/mol. The only available experimental value[86] for $Cl^-\cdots CH_3F$ ($\Delta H^o = 11.41$ kcal/mol) has an uncertainty of 2.01 kcal/mol. Comparison of this value with the calculated values suggest that more accurate measurements are in order. For $Cl^-\cdots CH_3Br$ and $Br^-\cdots CH_3Cl$, rather more accurate high-pressure mass spectrometry data are available (12.54 and 11.01 kcal/mol). The W1′ values (11.91 and 10.32 kcal/mol) are very close to the experimental results, considering the experimental uncertainty of 0.4 kcal/mol. While the mPW1K/6-31+G* values for $Cl^-\cdots CH_3Br$ and $Br^-\cdots CH_3Cl$ are fortuitously within the experimental error bars, the other DFT methods predict lower values. Also note that G2(+) predicts complexation energies close to W1′ and experiment for $Cl^-\cdots CH_3Br$, while the $Br^-\cdots CH_3Cl$ value is small. A complete assessment of CBS-QB3 is not possible as it could not be applied to the bromine-containing systems.

As for the identity reactions, complexation energies are significantly underestimated (and ion−molecule distances overestimated by up to 0.3 Å: see Supporting Information) by HCTH, and this problem is mostly remedied by HCTH-120. B97 and especially B97-1 appear to represent an improvement over B3LYP for the complexation energies.

Calculated overall reaction enthalpies, central enthalpy differences between reactant and product ion−molecule complexes, overall barrier heights, and central barrier heights for the nonidentity S_N2 reactions are presented with available experimental results in Table 6. It needs to be reemphasized that all values are "bottom-of-the-well" (i.e., zero-point exclusive): that is, the experimental values are presented after subtracting the ZPVEs (scaled by 0.985) and thermal corrections obtained using the B3LYP method.

The overall reaction enthalpies of the three nonidentity reactions, viz F/Cl, F/Br, and Cl/Br, calculated at the W1′ level are −32.65, −41.43, and −8.56 kcal/mol, respectively. The corresponding experimental values are available and are presented in Table 6. The experimental value for the F/Cl reaction (−33.34 kcal/mol) is in close agreement with the W1′ value. B3LYP, B97(-1), mPW1PW91, G*n*, and CCSD(T)/spdfg results are all in close agreement with the W1′ value, but mPW1K, "half-and-half" and CBS-QB3 theories predict 3−5 kcal/mol higher exothermicity. For the F/Br reaction, the mPW1K/6-31+G* and mPW1PW91/cc-pVTZ(+X) methods yield overall reaction enthalpies which are quite close to the W1′ result. The experimental result (−40.20 kcal/mol) is in good agreement with the best calculated values considering the uncertainty of 1 kcal/mol. The G*n* theories predict exothermicities below, and mPW1K/cc-pV*n* Z(+X) above, the W1′ value. Concerning the Cl/Br nonidentity reaction, the reported experimental value (−6.86 kcal/mol) differs from the W1′ value by 2 kcal/mol. As expected, the very recent CCSD(T)/spdfgh results of Botschwina and co-workers[24] are in close agreement with our predictions. Our results suggest that the Cl/Br experimental data may need to be reconsidered. Note the significant basis set dependence in the mPW1K results, which illustrates the inadequacy of the 6-31+G* basis set.

As a general observation, 50:50 admixture of HF exchange in the DFT theories increases the magnitude of the overall reaction enthalpy, and the increase is greater in BH&HLYP than in mPWH&HPW91. Performance of B97 and B97-1 for the overall reaction enthalpies is similar to B3LYP, while HCTH and HCTH-120 represent underestimates in absolute value.

At the W1′ level of theory, the calculated central barrier ($\Delta H^{\ddagger}_{cent}$) for the F/Cl system is 2.89 kcal/mol. G*n*(+), CBS-QB3(+), BH&HLYP, mPWH&HPW91, and mPW1K all reproduce the W1′ value moderately well, while B3LYP, mPW1PW91, B97, B97-1, HCTH, and HCTH-120 all underestimate the central barriers. The experimental central barrier for the F/Cl system is nearly 4 kcal/mol higher than the calculated values. Judging from the performance of the various methods for the identity S_N2 reactions, it is almost certain that the experimental F/Cl central barrier is in error and unambiguous new measurements are in order. For the F/Cl and Cl/Br systems, the B3LYP, mPW1PW91, B97, B97-1, HCTH, and HCTH-120 central barriers are all underestimated, while these exchange-correlation functionals find no barrier at all for the F/Br case. As for the identity case, mPW1K/cc-pVTZ(+X) and BH&HLYP/cc-pVTZ(+X) central barriers agree well with the benchmark

TABLE 6: Comparison of Overall Reaction Enthalpies (ΔH_{ovr}), Central Enthalpy Differences between Reactant and Product Ion−Molecule Complexes (ΔH_{cent}), Overall Barrier Heights ($\Delta H^{\ddagger}_{over}$) and Central Barrier Heights ($\Delta H^{\ddagger}_{cent}$) for Exothermic $Y^- + CH_3X \rightarrow YCH_3 + X^-$ Reactions, Calculated at Various Levels of Theory (all values in kcal/mol)

Y,X	method	ΔH_{ovr}	ΔH_{cent}	$\Delta H^{\ddagger}_{over}$	$\Delta H^{\ddagger}_{cent}$
F/Cl	W1′	−32.65	−26.73	−12.54	2.89
	B3LYP/cc-pVTZ(+X)	−32.77	−25.49	−14.69	0.67
	BH&HLYP/cc-pVTZ(+X)	−37.02	−30.05	−12.86	2.53
	mPW1PW91/cc-pVTZ(+X)	−33.08	−26.15	−13.43	1.63
	mPWH&HPW91/cc-pVTZ(+X)	−36.45	−29.73	−11.51	3.52
	B97/cc-pVDZ(+X)	−32.90	−25.95	−14.70	0.73
	B97−1/cc-pVDZ(+X)	−33.13	−25.92	−15.60	0.66
	HCTH/cc-pVDZ(+X)	−30.77	−24.67	−11.95	0.71
	HCTH-120/cc-pVDZ(+X)	−30.58	−23.64	−15.14	0.27
	mPW1K/6-31+G*	−36.59	−30.07	−13.02	2.30
	mPW1K/cc-pVDZ(+X)	−34.74	−28.68	−11.95	2.57
	mPW1K/cc-pVTZ(+X)	−35.50	−28.78	−11.97	3.01
	G1	−30.62			
	G2	−31.59			
	G2MP2	−32.25			
	G3	−33.00			
	CBS-QB3	−35.21			
	G3(+)	−32.86	−26.50	−14.04	2.30
	CBS-QB3(+)	−35.15	−28.81	−13.77	2.07
	G2(+)[a]	−31.44	−25.46	−12.63	2.98
	CCSD(T)/spdfg[b]	−32.34	−26.36	−11.84	3.89
	experiment	−33.34(72)[c]			7.52(1.20)[d]
F/Br	W1′−core	−41.43	−32.93	−16.37	0.64
	B3LYP/cc-pVTZ(+X)	−40.78			
	BH&HLYP/cc-pVTZ(+X)	−46.13	−36.93	−16.33	0.32
	mPW1PW91/cc-pVTZ(+X)	−41.65			
	mPWH&HPW91/cc-pVTZ(+X)	−45.90	−37.05	−15.42	0.85
	B97/cc-pVDZ(+X)	−40.41			
	B97-1/cc-pVDZ(+X)	−40.68			
	HCTH/cc-pVDZ(+X)	−38.18			
	HCTH-120/cc-pVDZ(+X)	−37.96			
	mPW1K/6-31+G*	−42.35	−33.84	−16.92	0.71
	mPW1K/cc-pVDZ(+X)	−44.76	−36.13	−16.08	0.18
	mPW1K/cc-pVTZ(+X)	−44.70	−35.77	−15.76	0.54
	G1	−40.87			
	G2	−40.02			
	G2MP2	−40.35			
	G2(+)[a]	−39.47	−31.29	−15.90	0.84
	experiment	−40.20(96)[c]			
Cl/Br	W1′−core	−8.56	−6.97	−1.82	8.61
	B3LYP/cc-pVTZ(+X)	−8.01	−6.19	−5.25	4.99
	BH&HLYP/cc-pVTZ(+X)	−9.11	−7.43	−2.15	8.08
	mPW1PW91/cc-pVTZ(+X)	−8.57	−6.79	−3.99	6.33
	mPWH&HPW91/cc-pVTZ(+X)	−9.45	−7.79	−1.17	9.14
	B97/cc-pVDZ(+X)	−7.52	−5.99	−5.06	5.60
	B97-1/cc-pVDZ(+X)	−7.54	−5.97	−5.83	5.48
	HCTH/cc-pVDZ(+X)	−7.41	−5.85	−3.18	5.38
	HCTH-120/cc-pVDZ(+X)	−7.38	−5.62	−6.52	4.26
	mPW1K/6-31+G*	−5.75	−3.34	−3.12	9.85
	mPW1K/cc-pVDZ(+X)	−10.02	−8.30	−6.60	3.81
	mPW1K/cc-pVTZ(+X)	−9.20	−7.53	−1.88	8.38
	G1	−10.25	−8.18	−3.45	7.72
	G2	−8.43	−6.44	−1.82	9.53
	G2MP2	−8.11	−6.18	−1.67	9.70
	G2(+)[a]	−8.04	−6.21	−1.71	9.76
	CCSD(T)/spdfgh[b]	−8.53	−6.93	−2.33	8.98
	experiment	−6.86(72)[c]		−1.83(5)[e] −1.69(33)[f] −1.52[g] −1.11[h] −0.61[i]	

[a] G2(+) values are from ref 19. [b] Ref 22 (F/Cl) and ref 24 (Cl/Br). [b′] Table 2 of ref 24. [c] Exptl. values from ref 91. [d] Exptl. values from ref 84. [e] Exptl. values from ref 9. [f] Exptl. values from ref 92. [g] Exptl. values from ref 93. [h] Exptl. values from ref 90. [i] Exptl. values from ref 94.

ab initio values, although the basis set sensitivity of particularly the Cl/Br results argues against using small basis sets such as 6-31+G*.

Several studies have reported experimental overall barrier heights ($\Delta H^{\ddagger}_{ovr}$), but only for the Cl/Br system, and the experimental data range from −0.61 to −1.83 kcal/mol. To our knowledge, no experimental data are available for the F/Cl and F/Br systems. For the Cl/Br system, the theoretical values span a range from −1.17 to −6.60 kcal/mol. Nevertheless, it is worth noting that the W1′ value (−1.82 kcal/mol) for the Cl/Br system is in excellent agreement with the experimental overall barrier height reported by Caldwell and co-workers[9] (−1.83 kcal/mol, after accounting for ZPVE and thermal corrections). Some caution should be exercised as the W1′ value does not include the core correlation contribution. Also note that G2 theory (−1.82 kcal/mol) reproduces the W1′ value very well. Except for mPW1K/cc-pVTZ(+X), mPWH&HPW91/cc-pVTZ(+X), and BH&HLYP/cc-pVTZ(+X), all the DFT methods perform poorly, consistent with the preceding discussion.

IV. Conclusions

A benchmark study using the W1′ and W2h methods has been carried out for the potential surface of the gas-phase *S*$_N$2 reactions $Y^- + CH_3X \rightarrow CH_3Y + X^-$. A number of more approximate (and less expensive) methods—both compound models (like G2/G3 theory and CBS-QB3) and density functional methods—have been applied in an attempt to assess their performance for barrier heights in S_N2 reactions. We arrive at the following conclusions.

(1) Our best calculations are in excellent agreement with experiment for the (ΔH_f°) values of the methyl halides (where available) and the electron affinities of the halogens. Where accurate experimental data are available for the title reactions (e.g., for the Cl/Cl case), our best calculations agree with experiment to within overlapping uncertainties. Our calculations, however, suggest that more reliable experimental data are in order for most of the reactions considered.

(2) The nonidentity S_N2 reactions and F/F identity reaction possess transition state structures below the reactants energy while Cl/Cl and Br/Br transition structures are above the reactants energy. The complexation energies for identity S_N2 reactions are found to increase in the order Br < Cl < F while the barrier heights follow the order F $\lesssim$ Br < Cl. The complexation energies for the nonidentity S_N2 reactions indicate that the ΔH_{comp} values strongly depend on the nucleophile and leaving group.

(3) The B3LYP, and to a lesser extent mPW1PW91, exchange-correlation functionals systematically underestimate barrier heights and, in the F/Br case, are not even able to locate the correct stationary points on the potential surface. The latter problem is remedied by using the corresponding “half-and-half” functionals BH&HLYP and mPWH&HPW91, which however appear to somewhat overcorrect the barrier height. The B97 and B97-1 functionals perform similarly to B3LYP for the problem under study. The “pure DFT” HCTH and HCTH-120 functionals both underestimate central barrier heights; HCTH in addition underestimates complexation energies (and severely overestimates ion−molecule distances), which are however well reproduced by HCTH-120. Overall, the mPW1K functional appears to put in the best performance of all DFT methods considered, especially when using extended basis sets.

(4) The performance of G2(+), G3(+), and CBS-QB3(+) methods for the energetics still appears to be superior to the DFT methods. (The “(+)” stands for the addition of diffuse functions to the basis set used in obtaining the reference geometries; this is mandatory to get transition states at all in the F/Br and Cl/Br cases.) The limitations for transition states of the B3LYP exchange-correlation functional suggest its replacement—at least for kinetics applications—by mPW1K in thermochemistry methods that employ DFT reference geometries, e.g., G3B3, CBS-QB3, and W1 theory. (In addition, larger basis sets than 6-31+G* should definitely be considered for the Br compounds.)

The present calculations illustrate the power of state-of-the-science theoretical methods in providing both qualitative and quantitative information regarding the reaction energetics. In the absence of accurate experimental data, our high quality results should be useful to future experimental and theoretical studies.

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Supporting Information Available: Calculated geometries of species involved in the S_N2 reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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