Benchmark ab Initio Characterization of the Inversion and Retention Pathways of the OH$^-$ + CH$_3$Y [Y = F, Cl, Br, I] $S_N$2 Reactions

Domonkos A. Tasi, Zita Fábián, and Gábor Czakó*

Department of Physical Chemistry and Materials Science, Institute of Chemistry, University of Szeged, Rerrich Béla tér 1, Szeged H-6720, Hungary

Supporting Information

ABSTRACT: We study the Walden-inversion, front-side attack retention, and double-inversion retention pathways of the OH$^-$ + CH$_3$Y [Y = F, Cl, Br, I] $S_N$2 reactions using high-level ab initio methods. Benchmark stationary-point structures and frequencies are computed at the CCSD(T)-F12b/aug-cc-pVTZ level of theory and the best technically feasible relative energies are determined on the basis of CCSD(T)-F12b/aug-cc-pVQZ computations complemented with post-CCSD(T) correlation effects at the CCSDT(Q)/aug-cc-pVDZ level, core correlation corrections at the CCSD(T)/aug-cc-pwCVTZ level, scalar relativistic effects using effective core potentials for Br and I, and zero-point energy corrections at the CCSD(T)-F12b/aug-cc-pVTZ level. Walden inversion proceeds via hydrogen-bonded HO$^-$···HCH$_2$Y (Cl, Br, I) complex → hydrogen-bonded HO$^-$···HCH$_2$Y (Cl, Br, I) transition state → ion–dipole HO$^-$···HCY (F, Cl, Br) complex → Walden-inversion [HO···CH$_2$Y]$^-$ (F, Cl, Br) transition state → hydrogen-bonded CH$_3$OH···Y$^-$ (F, Cl, Br, I) complex, where the Y-dependent existence of the submerged stationary points is indicated in parentheses. Front-side HO$^-$···YCH$_3$ (Cl, Br, I) complexes are also found and HO$^-$···ICH$_3$ is a deeper minimum than HO$^-$···HCH$_2$Y. Front-side attacks go over high barriers of 42.8 (F), 28.7 (Cl), 22.4 (Br), and 17.2 (I) kcal/mol, well above the double-inversion barrier heights of 16.7 (F), 3.4 (Cl), 1.1 (Br), and −3.7 (I) kcal/mol.

I. INTRODUCTION

Bimolecular nucleophilic substitution ($S_N$2) is a widely known reaction class, playing central roles in chemical processes in textbooks, laboratories, and biological environments. The simplest examples of $S_N$2 reactions at carbon centers involve the six-atom X$^-$ + CH$_3$Y systems, where X and Y are halogens. The traditional textbook mechanism of the X$^-$ + CH$_3$Y $S_N$2 reactions goes through a prereaction complex, playing central roles in chemical processes in textbooks, laboratories, and biological environments.

Received: May 3, 2018
Revised: June 6, 2018
Published: June 7, 2018
been attracted considerable attention in the 21st century sometimes providing surprising results. Let us begin with the work of Gonzales et al. that reported in 2001 a hydrogen-bonded postreaction complex, CH$_3$OH···F$^-$, for the OH$^-$$^+$CH$_3$F reaction, whereas the traditional HOCH$_3$···F$^-$ ion–dipole complex was not found. In 2002 reaction dynamics simulations of Hase and co-workers revealed that the OH$^-$$^+$CH$_3$F reaction avoids the deep minimum corresponding to the hydrogen-bonded CH$_3$OH···F$^-$ complex and most of the trajectories proceed directly via the HOCH$_3$···F$^-$ region, highlighting the fact that dynamics may not follow the minimum-energy pathways. In 2003 two independent studies supported that postreaction ion–dipole complex does not exist for the OH$^-$$^+$CH$_3$F reaction.16 Gonzales et al. reported accurate ab initio data based on MP2/aug-cc-pV5Z and CCSD(T)/aug-cc-pVTZ energy computations considering core and scalar relativistic corrections for three stationary points along the SN$_2$ inversion pathway of the OH$^-$$^+$CH$_3$F reaction. For the OH$^-$$^+$CH$_3$I reaction Tachikawa and co-workers characterized the prereaction ion–dipole complex, the Walden-inversion TS, and the postreaction complex with MP2/6-311++G(2df,2pd) computations and performed direct dynamics simulations using the HF/3-21+G(d) level of theory. The OH$^-$$^+$CH$_3$I reaction has been under very recent experimental and theoretical investigations. In 2012 Wester and co-workers studied the effects of water molecules on the dynamics of the OH$^-$$^+$CH$_3$I reaction using the crossed-beam experimental technique. In 2013 Xie et al. characterized the stationary points of the OH$^-$$^+$CH$_3$I reaction reporting prereaction and postreaction minima connected by a first-order saddle point, all having hydrogen-bonded structures. Furthermore, a front-side complex, HO$^-$$^+$ICH$_3$, was also found at the B97-1/ECP/d level of theory. The dynamics and kinetics of the OH$^-$$^+$CH$_3$I reaction were investigated as well using direct dynamics simulations and the computed results were compared with crossed-beam experiments. In 2015 Hase and co-workers characterized the hydrogen-bonded prereaction complex for OH$^-$$^+$CH$_3$I using B97-1 and MP2 theories with double- and triple-ζ-quality basis sets. Finally, we note that the mechanisms of the OH$^-$$^+$CH$_3$Y [Y = F, Cl, Br] reactions were also studied in aqueous solution by Wang and co-workers using a quantum mechanical molecular mechanics method.

The goal of the present study is to provide a benchmark ab initio characterization of the OH$^-$$^+$CH$_3$Y [Y = F, Cl, Br, I] SN$_2$ reactions moving beyond the previous work in several aspects: (a) We provide a comprehensive study of the above four reactions at the same level of theory, (b) investigate the front-side attack and double-inversion TSs for the first time to the best of our knowledge, (c) use the explicitly correlated CCSD(T)-F12b method ensuring fast basis set convergence for geometry, frequency, and energy computations, and (d) consider core–valence and post-CCSD(T) correlation effects, which were usually neglected in previous studies. The computational details are described in detail in section II. In section III the results are presented and discussed in both qualitative and quantitative points of view. The paper ends with summary and conclusions in section IV.

II. COMPUTATIONAL DETAILS

The stationary points of the potential energy surfaces of the OH$^-$$^+$CH$_3$Y [Y = F, Cl, Br, I] SN$_2$ reactions are searched and preoptimized at the MP2/aug-cc-pVQZ and CCSD(T)/aug-cc-pVTZ energy computations considering core and scalar relativistic corrections for three stationary points along the SN$_2$ inversion pathway of the OH$^-$$^+$CH$_3$I reaction. For the OH$^-$$^+$CH$_3$F reaction Tachikawa and co-workers characterized the prereaction ion–dipole complex, the Walden-inversion TS, and the postreaction complex with MP2/6-311++G(2df,2pd) computations and performed direct dynamics simulations using the HF/3-21+G(d) level of theory. The OH$^-$$^+$CH$_3$I reaction has been under very recent experimental and theoretical investigations. In 2012 Wester and co-workers studied the effects of water molecules on the dynamics of the OH$^-$$^+$CH$_3$I reaction using the crossed-beam experimental technique. In 2013 Xie et al. characterized the stationary points of the OH$^-$$^+$CH$_3$I reaction reporting prereaction and postreaction minima connected by a first-order saddle point, all having hydrogen-bonded structures. Furthermore, a front-side complex, HO$^-$$^+$ICH$_3$, was also found at the B97-1/ECP/d level of theory. The dynamics and kinetics of the OH$^-$$^+$CH$_3$I reaction were investigated as well using direct dynamics simulations and the computed results were compared with crossed-beam experiments. In 2015 Hase and co-workers characterized the hydrogen-bonded prereaction complex for OH$^-$$^+$CH$_3$I using B97-1 and MP2 theories with double- and triple-ζ-quality basis sets. Finally, we note that the mechanisms of the OH$^-$$^+$CH$_3$Y [Y = F, Cl, Br] reactions were also studied in aqueous solution by Wang and co-workers using a quantum mechanical molecular mechanics method.

The goal of the present study is to provide a benchmark ab initio characterization of the OH$^-$$^+$CH$_3$Y [Y = F, Cl, Br, I] SN$_2$ reactions moving beyond the previous work in several aspects: (a) We provide a comprehensive study of the above four reactions at the same level of theory, (b) investigate the front-side attack and double-inversion TSs for the first time to the best of our knowledge, (c) use the explicitly correlated CCSD(T)-F12b method ensuring fast basis set convergence for geometry, frequency, and energy computations, and (d) consider core–valence and post-CCSD(T) correlation effects, which were usually neglected in previous studies. The computational details are described in detail in section II. In section III the results are presented and discussed in both qualitative and quantitative points of view. The paper ends with summary and conclusions in section IV.
coupled cluster singles, doubles, and perturbative triples CCSD(T)-F12b method\textsuperscript{27} with the correlation-consistent aug-cc-pVDZ and aug-cc-pVTZ basis sets.\textsuperscript{28} To obtain the best technically feasible relative energies, the following single-point energy computations are performed at the most accurate CCSD(T)-F12b/aug-cc-pVTZ geometries: (a) CCSD(T)-F12b/aug-cc-pVQZ, (b) CCSD(T),\textsuperscript{29} CCSDT,\textsuperscript{30} and CCSDT(Q)\textsuperscript{31} with the aug-cc-pVDZ basis set, and (c) CCSD(T)/aug-cc-pwCVTZ with both frozen-core and all-electron approaches. For Br and I small-core relativistic effective core potentials,\textsuperscript{32} replacing the inner-core $1s^22s^22p^6$ and $1s^22s^22p^63s^23p^63d^{10}$ electrons, respectively, are used with the corresponding aug-cc-pVDZ-PP, aug-cc-pVTZ-PP, aug-cc-pVQZ-PP, and aug-cc-pwCVTZ-PP basis sets.\textsuperscript{32} The frozen-core (FC) computations, used as default unless otherwise noted, correlate the valence electrons only, whereas in the all-electron (AE) approach the $1s^2$ (C, O, F), $2s^22p^6$ (Cl), $3s^2p^63d^{10}$ (Br), and $4s^2p^64d^{10}$ (I) electrons are also correlated. All the ab initio computations are performed with the Molpro program package,\textsuperscript{33} except CCSDT and CCSDT(Q) that are carried out with the MRCC code\textsuperscript{34} interfaced to Molpro.

The benchmark classical relative energies of the stationary points are obtained at the CCSD(T)-F12b/aug-cc-pVTZ geometries as

\[
\Delta E(\text{CCSD(T)-F12b/aug-cc-pVQZ}) + \delta(\text{CCSDT}) + \Delta \text{core} + \Delta \text{ZPE}
\]

where

\[
\delta(\text{CCSDT}) = \Delta E(\text{CCSDT/aug-cc-pVDZ}) - \Delta E(\text{CCSD(T)/aug-cc-pVQZ})
\]

\[
\Delta \text{core} = \Delta E(\text{AE-CCSD(T)/aug-cc-pwCVTZ}) - \Delta E(\text{FC-CCSD(T)/aug-cc-pwCVTZ})
\]

The benchmark adiabatic relative energies are computed as

\[
\Delta E(\text{CCSD(T)-F12b/aug-cc-pVQZ}) + \delta(\text{CCSDT}) + \delta(\text{CCSDT(Q)}) + \Delta \text{core} + \Delta \text{ZPE}
\]

where \(\Delta \text{ZPE}\) is the harmonic zero-point energy correction obtained at the CCSD(T)-F12b/aug-cc-pVTZ level of theory.

### III. RESULTS AND DISCUSSION

A schematic potential energy surface (PES) of the OH\textsuperscript{−} + CH\textsubscript{3}Y [Y = F, Cl, Br, I] \textit{S}_\text{N}2 reactions showing the most important distances (Å) and angles (deg) obtained at the CCSD(T)-F12b/aug-cc-pVTZ level of theory. All the geometries have C\textsubscript{1} point-group symmetry, except the nonsymmetric FSTS (Y = F) and HTS (Y = Br, I); see Figure 3.

![Figure 2. Benchmark stationary-point structures for the OH\textsuperscript{−} + CH\textsubscript{3}Y [Y = F, Cl, Br, I] \textit{S}_\text{N}2 reactions showing the most important distances (Å) and angles (deg) obtained at the CCSD(T)-F12b/aug-cc-pVTZ level of theory. All the geometries have C\textsubscript{1} point-group symmetry, except the nonsymmetric FSTS (Y = F) and HTS (Y = Br, I); see Figure 3.](image-url)
Table 1. Benchmark Classical and Adiabatic Energies (kcal/mol) of the Stationary Points (Figure 1) Relative to the Reactants for the OH$^+$ + CH$_3$Y [Y = F, Cl, Br, I] $S_n$2 Reactions

<table>
<thead>
<tr>
<th>Y</th>
<th>DZ$^{ad}$</th>
<th>TZ$^{ad}$</th>
<th>QZ$^{ad}$</th>
<th>$\delta T$</th>
<th>$\delta (Q)$</th>
<th>$\delta \text{core}$</th>
<th>$\Delta \text{classical}$</th>
<th>$\Delta \text{ZPE}$</th>
<th>$\delta \text{adiabatic}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>$-13.87$</td>
<td>$-13.87$</td>
<td>$-13.74$</td>
<td>$-0.03$</td>
<td>$+0.00$</td>
<td>$+0.01$</td>
<td>$-13.76$</td>
<td>$+0.60$</td>
<td>$-13.16$</td>
</tr>
<tr>
<td>Cl</td>
<td>$-2.44$</td>
<td>$-2.71$</td>
<td>$-2.59$</td>
<td>$-0.10$</td>
<td>$-0.18$</td>
<td>$+0.27$</td>
<td>$-2.60$</td>
<td>$+0.81$</td>
<td>$-1.79$</td>
</tr>
<tr>
<td>Br</td>
<td>$-50.32$</td>
<td>$-50.19$</td>
<td>$-50.05$</td>
<td>$+0.08$</td>
<td>$+0.08$</td>
<td>$-0.16$</td>
<td>$-50.05$</td>
<td>$+1.75$</td>
<td>$-48.31$</td>
</tr>
<tr>
<td>I</td>
<td>$42.56$</td>
<td>$42.44$</td>
<td>$42.74$</td>
<td>$-0.13$</td>
<td>$-0.43$</td>
<td>$+0.32$</td>
<td>$42.49$</td>
<td>$+0.36$</td>
<td>$42.85$</td>
</tr>
<tr>
<td>F + CH$_3$OH</td>
<td>$17.00$</td>
<td>$17.23$</td>
<td>$17.45$</td>
<td>$-0.04$</td>
<td>$-0.10$</td>
<td>$17.29$</td>
<td>$-0.55$</td>
<td>$16.73$</td>
<td></td>
</tr>
<tr>
<td>Cl + CH$_3$OH</td>
<td>$-9.76$</td>
<td>$-19.82$</td>
<td>$-19.95$</td>
<td>$+0.11$</td>
<td>$-0.15$</td>
<td>$19.97$</td>
<td>$+2.19$</td>
<td>$-17.78$</td>
<td></td>
</tr>
<tr>
<td>Br + CH$_3$OH</td>
<td>$-52.10$</td>
<td>$-52.37$</td>
<td>$-52.65$</td>
<td>$+0.26$</td>
<td>$+0.08$</td>
<td>$-52.25$</td>
<td>$+3.17$</td>
<td>$-49.08$</td>
<td></td>
</tr>
<tr>
<td>I + CH$_3$OH</td>
<td>$-60.59$</td>
<td>$-60.41$</td>
<td>$-60.80$</td>
<td>$+0.29$</td>
<td>$+0.32$</td>
<td>$-60.13$</td>
<td>$+3.58$</td>
<td>$-56.55$</td>
<td></td>
</tr>
</tbody>
</table>

The reaction pathway, and all of them are below the reactant asymptote. The global minimum of the PESs corresponds to exit-channel complexes, which are not the usual ion–dipole complexes with Y···CH$_3$OH structures, but hydrogen-bonded CH$_3$OH···Y complexes (PostHMIN) as seen in Figure 1. For Y = F, a hydrogen-bonded F···HCH$_3$OH complex (Table S4) is also found with an energy ~21 kcal/mol higher than that of CH$_3$OH···F$^-$. As mentioned earlier, trajectory simulations showed that the OH$^+$ + CH$_3$F reaction avoids this PostHMIN configuration and proceeds via the usual backward scattering mechanism. The F$^-$ leaving group forms the strongest OH···Y$^-$ hydrogen bond with a dissociation energy (D$_0$) of 30.5 kcal/mol, whereas the D$_0$ values are 16.0, 13.8, and 11.6 kcal/mol for Y = Cl, Br, and I, respectively. These dissociation energies are in accord with the trends of the H···Y$^-$ distances of 1.345, 2.097, 2.303, and 2.584 Å for Y = F, Cl, Br, and I, respectively (Figure 2). The entrance channels of the title reactions are also nontraditional, except for Y = F. The OH$^+$ + CH$_3$F reaction proceeds via an ion–dipole complex (PreMIN) followed by a usual Walden-inversion TS (WaldenTS), as seen in Figure 1. Here the barrier is just slightly submerged by 2.6 kcal/mol without (with) ZPE correction. In the cases of Cl and Br leaving groups, a hydrogen-bonded prereaction complex (HMIN) also exists besides PreMIN and a first-order saddle point (HTS) connects the two minima. HMIN is below PreMIN by 0.6–0.8 kcal/mol, and the barrier between them is negligible. For Y = Cl the classical (adiabatic) energy of the WaldenTS is ~13.2 (~12.6) kcal/mol relative to the reactants, which is 2.4 kcal/mol above PreMIN. For Y = Br the energies of PreMIN and WaldenTS, ~16.4 (~15.9) and ~16.3 (~15.9) kcal/mol, are the same within 0.1 kcal/mol. Moreover, for Y = I the traditional PreMIN and WaldenTS do not exist anymore and the reaction proceeds via HMIN $\rightarrow$ HTS $\rightarrow$ PostHMIN. Here HMIN is at ~18.5 (~18.1) kcal/mol, below HTS by 1.9 kcal/mol. This finding is in qualitative agreement with the DFT/B97-1/ECP/d results of Xie et al. 26,27, though our benchmark energies are above the DFT values by 1.5–2 kcal/mol. As Figure 2 shows, the H···OH hydrogen bond is decreasing as 1.764, 1.717, and 1.654 Å for Y = Cl, Br, and I in accord with the leaving-group dependence of the depth of HMIN. The corresponding HTS values of 2.059, 2.025, and 2.034 Å are longer and do not show significant Y dependence.
However, we have found a qualitative difference between the HTSs of the Y = Cl and Y = Br, I systems, because the former has C_s symmetry, whereas the latter structures have C_3 symmetry, as shown in Figure 3.

For the OH\(^-\) + CH\(_3\)Y \([Y = Cl, Br, I]\) systems, we find front-side complexes (FSMIN) in the entrance channels, where OH\(^-\) connects to Y. As Figure 2 shows, FSMIN complexes have C\(_s\) structures with almost collinear C—Y···O arrangements and Y···O distances of 2.593, 2.399, and 2.366 Å for Y = Cl, Br, and I, respectively. For Y = Cl FSMIN is just slightly bonded with dissociation energy around 2 kcal/mol, whereas for Y = Br and I, respectively, stretched by 0.369, 0.481, 0.461, and 0.454 Å relative to the corresponding bond length in CH\(_3\)Y. The C—O distances are longer by 0.497, 0.660, 0.698, and 0.724 Å than the C—O bond length of 1.420 Å in CH\(_2\)OH. The Y—C—O angles are around 80° for all four systems. For Y = Cl, Br, and I FSTS has C\(_s\) symmetry, whereas in the case of Y = F the symmetry is slightly broken, as shown in Figure 3. The double-inversion transition state (DITS) has C\(_s\) symmetry, where the CH\(_2\)Y— unit is almost planar and H\(_2\)O connects to the C atom with a hydrogen bond of around 2.1 Å length in all four cases. The DITSs have substantial imaginary frequencies of 983i (F), 864i (Cl), 889i (Br), and 846i (I) cm\(^{-1}\) at the CCSD(T)-F12b/aug-cc-pVTZ level of theory, whereas the corresponding FSTS values are 729i, 627i, 578i, and 545i cm\(^{-1}\), in order, as seen in the Supporting Information. The large imaginary frequencies of the DITSs may make these TSs stand out from the other proton-transfer-like stationary points of the OH\(^-\) + CH\(_3\)Y systems. At this point, we should note that the double-inversion pathway shown in Figure 1 may be a non-IRC pathway as Hase and co-workers\(^{11}\) pointed out in the case of the F\(^-\) + CH\(_3\)I reaction.

The detailed data presented in Table 1 and shown in Figures 4 and 5 allow estimating the accuracy of the new benchmark relative energies. Figure 4 shows the fast basis-set convergence of the explicitly correlated CCSD(T)-F12b method, since both the aug-cc-pVDZ and aug-cc-pVTZ basis sets provide similar quality results with 0.1 kcal/mol deviations from the aug-cc-pVQZ relative energies. The large imaginary frequencies of the DITSs may make these TSs stand out from the other proton-transfer-like stationary points of the OH\(^-\) + CH\(_3\)Y systems. At this point, we should note that the double-inversion pathway shown in Figure 1 may be a non-IRC pathway as Hase and co-workers\(^{11}\) pointed out in the case of the F\(^-\) + CH\(_3\)I reaction.

Besides the Walden-inversion pathways, the title reactions have different stationary points of the OH\(^-\) + CH\(_3\)Y systems. At this point, we should note that the double-inversion pathway shown in Figure 1 may be a non-IRC pathway as Hase and co-workers\(^{11}\) pointed out in the case of the F\(^-\) + CH\(_3\)I reaction.

The detailed data presented in Table 1 and shown in Figures 4 and 5 allow estimating the accuracy of the new benchmark relative energies. Figure 4 shows the fast basis-set convergence of the explicitly correlated CCSD(T)-F12b method, since both the aug-cc-pVDZ and aug-cc-pVTZ basis sets provide similar quality results with 0.1–0.2 kcal/mol deviations from the aug-cc-pVQZ relative energies for most of the stationary points. The largest deviation of about 0.6 kcal/mol is found for the I\(^-\) + CH\(_2\)OH product channel, whereas the mean absolute deviations of the aug-cc-pVDZ and aug-cc-pVTZ data, relative to aug-cc-pVQZ, are only 0.22 and 0.16 kcal/mol, respectively, considering all 31 stationary points shown in Figure 4. As Table 1 and Figure 5 show, the post-CCSD(T) correlation effects are usually small, typically between 0 and ±0.3 kcal/mol. The most significant effects are found for FSTS, where the post-CCSD(T) correlation energy contributions are –0.56, –0.85, –0.87, and –0.90 kcal/mol for Y = F, Cl, Br, and I, respectively. As Figure 5 shows, the signs of the δ[CCSDT] and δ[CCSDT(Q)] energy increments are almost always the same and the latter is usually larger, whereas the core correlation corrections often have opposite signs and magnitudes similar to those of the post-CCSD(T) corrections; thus the post-CCSD(T) and core corrections can partially cancel each other. This is not always the case, especially for the OH\(^-\) + CH\(_3\)I reaction.
Y\(^-\) + CH\(_3\)Y \([Y = \text{Cl}, \text{Br}, \text{and} \text{I}]\) product channels, where the post-CASSD(T) and core-correlation effects are both positive and result in cumulative energy corrections of 0.40, 0.68, and 1.07 kcal/mol, respectively. Thus, these results show that these traditionally neglected effects should be taken into account if subchemical accuracy is desired for some of the reaction enthalpies. Relativistic effects are expected to be significant for Br and I, where scalar relativity is involved in the effective core potentials used in the present study. For the other atoms the scalar relativistic corrections are likely to be small, usually 10\(^-\)\text{a} \pm \text{b}\kcal/mol.10,11,12 The new ab initio reaction enthalpies are seen, all the AT\(_c\)T and the new ab initio reaction enthalpies are around 0.5 kcal/mol for most of the stationary points, except \([\text{Y} = \text{Cl}, \text{Br, I}]\) SN\(_2\) reactions. On the basis of the above analysis of the subchemical accuracy is desired for some of the reaction enthalpies. Relativistic effects are both positive and result in cumulative energy corrections of 0.40, 0.68, and 1.07 kcal/mol, respectively. Thus, these results show that these closed-shell systems. As Table 1 shows, ZPE effects are taken into account. The latter is not always important, because the core and post-CASSD(T) correlation corrections. We show that most of the new benchmark energies are accurate within about 0.3 kcal/mol, because the explicitly correlated CASSD(T)-F12b method has fast basis set convergence and the core and post-CASSD(T) effects are both positive and result in cumulative energy corrections of 0.40, 0.68, and 1.07 kcal/mol, respectively. Among the other three reactions, perhaps the most notable results are the B97-1 energies corresponding to the Walden-inversion pathway of the OH\(^-\) + CH\(_3\)I reaction, which usually have an error of about 2 kcal/mol relative to the present benchmark energies. The front-side attack and double-inversion pathways are reported for the first time for the title reactions; therefore, their properties cannot be compared to literature data.

IV. SUMMARY AND CONCLUSIONS
We have performed a high-level ab initio study for the OH\(^-\) + CH\(_3\)Y \([Y = \text{F, Cl, Br, I}]\) S\(_n\)2 reactions providing qualitatively and quantitatively new results. On the qualitative side, we have characterized the front-side attack and double-inversion retention pathways for the first time in the case of the title reactions, to the best of our knowledge. The computations reveal that double inversion has a smaller barrier than front-side attack. Moreover, for \(Y = \text{I}\) double inversion is a barrierless process via a submerged transition state. Furthermore, in agreement with, and in some cases, extending previous studies,13,14,15 we find that the Walden-inversion pathways of the OH\(^-\) + CH\(_3\)Y S\(_n\)2 reactions are nontraditional in several aspects: (1) In the postreaction region hydrogen-bonded CH\(_3\)OH•••Y complexes exist instead of the traditional ion–dipole complexes. (2) For \(Y = \text{Cl and Br}\) there are hydrogen-bonded HO•••HCH\(_3\)Y complexes in the entrance channels, whose energies are slightly below the ion–dipole HO•••H\(_2\)CH\(_3\)Y minima and hydrogen-bonded transition states connect the HO•••HCH\(_3\)Y and HO•••H\(_2\)CH\(_3\)Y minima. (3) For \(Y = \text{I}\) the traditional ion–dipole complex and Walden-inversion TS are not found and the OH\(^-\) + CH\(_3\)I reaction proceeds via the hydrogen-bonded minimum and transition state. (4) For \(Y = \text{Cl, Br, I, HO}^-\)–YCH\(_3\) front-side complexes are found and in the case of \(Y = \text{I}\) this front-side complex is the global minimum of the entrance channel. On the quantitative side, we provide new benchmark data based on CASSD(T)-F12b/aug-cc-pVTZ geometries and vibrational frequencies as well as energies obtained at CASSD(T)-F12b/aug-cc-pVQZ with additive core and post-CASSD(T) correlation corrections. We show that most of the new benchmark energies are accurate within about 0.3 kcal/mol, because the explicitly correlated CASSD(T)-F12b method has fast basis set convergence and the core and post-CASSD(T) effects are taken into account. The latter is not always important, because the core and post-CASSD(T)
corrections of about 0.3 kcal/mol often partially cancel each other, except for most of the postreaction complexes and products, where these auxiliary corrections can add up to 1 kcal/mol. ZPE effects are also considered, which are found essential for accurate reaction enthalpies.

In the present study we have focused on the most important reaction channel of the OH\(^-\) + CH\(_3\)Y reactions. Besides S\(_2\)2, proton transfer can also occur and, on the basis of previous studies, many stationary points are involved in the proton-abstraction process.\(^{21}\) The detailed ab initio study of this higher-energy channel may be considered in a future work. Furthermore, as some previous work revealed,\(^{14,11}\) the title reactions, and similar systems, may not follow IRC pathways; thus reaction dynamics simulations would be desired to gain deeper insights into the dynamics of the title reactions. As mentioned earlier, Hase and co-workers\(^{14,20,21}\) reported trajectory studies for OH\(^-\) + CH\(_3\)Y reactions using the direct dynamics approach. We plan to use our analytic-PES-based method\(^{35}\) to study the dynamics of the OH\(^-\) + CH\(_3\)I reaction, which may provide double inversion without activation energy. PES development is underway in our group, for which the present benchmark stationary-point properties provide a definitive guidance.

**ASSOCIATED CONTENT**

1. Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.8b04218.

Energies, structures, and frequencies of the stationary points at different levels of theory (PDF)

**AUTHOR INFORMATION**

Corresponding Author

*G. Czako. E-mail: gczako@chem.u-szeged.hu.

**ORCID**

Gábor Czako: 0000-0001-5136-4777

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

G.C. thanks the National Research, Development and Innovation Office—NKFIH, K-125317 for financial support. We acknowledge the National Information Infrastructure Development Institute for awarding us access to resource based in Hungary at Szeged.

**REFERENCES**


(9) Szabó, I.; Czako, G. Revealing a Double-Inversion Mechanism for the F\(^-\) + CH\(_3\)I S\(_2\)2 Reaction. *Nat. Commun.* 2015, 6, 5972.


(18) Tachikawa, H.; Igarashi, M. Direct ab Initio Molecular Dynamics Study on a S\(_2\)2 Reaction OH\(^-\) + CH\(_3\)Cl \(\rightarrow\) CH\(_3\)OH + Cl\(^-\): Effect of Non-Zero Impact Parameter on the Reaction Dynamics. *Chem. Phys.* 2006, 324, 639–646.


