A benchmark *ab initio* study of the complex potential energy surfaces of the OH− + CH3CH2Y [Y = F, Cl, Br, I] reactions†

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We provide the first benchmark characterization of the OH− + CH3CH2Y [Y = F, Cl, Br, I] reactions utilizing the high-level explicitly-correlated CCSD(T)-F12b method with the aug-cc-pVnZ [n = 2(D), 3(T), 4(Q)] basis sets. We explore and analyze the stationary points of the elimination (E2) and substitution (Sn2) reactions, including anti-E2, syn-E2, back-side attack, front-side attack, and double inversion. In all cases, Sn2 is thermodynamically more preferred than E2. In the entrance channel of Sn2 a significant front-side complex formation is revealed, and in the product channel the global minimum of the title reactions is obtained at the hydrogen-bonded CH3CH2OH...Y− complex. Similar to the OH− + CH3Y reactions, double inversion can proceed via a notably lower-energy pathway than front-side attack, moreover, for Y = I double inversion becomes barrier-less. For the transition state of the anti-E2, a prominent ZPE effect emerges, giving an opportunity for a kinetically more favored pathway than back-side attack. In addition to Sn2 and E2, other possible product channels are considered, and in most cases, the benchmark reaction enthalpies are in excellent agreement with the experimental data.

I. Introduction

One of the main aims in chemistry is to understand chemical reactions at an atomic level. In organic chemistry the bimolecular nucleophilic substitution (Sn2) and the base-induced bimolecular elimination (E2) are elemental reactions and the competitions of these processes have been widely studied both experimentally and theoretically over the past 40 years.1−18 The traditional Walden-inversion and front-side attack mechanisms of Sn2 reactions were described by Ingold and co-workers in the middle of the 20th century.19,20

In a simple Sn2 reaction, X− + CH3Y → CH3X + Y−, the Walden-inversion mechanism goes through X−⋅⋅⋅CH3Y and XCH3⋅⋅⋅Y− minima connected by a central [X−⋅⋅⋅CH3−⋅⋅⋅Y−] transition state. Concerning the front-side attack, the mechanism is defined by a high-energy [XYCH3−]− transition state. In the last two decades, it has been recognized that the mechanisms of the Sn2 reactions are much more complex.5,21−25 Among the above-described traditional double-well Walden-inversion pathway and the front-side attack retention mechanism, several direct and indirect mechanisms can be found: roundabout,26 hydrogen-bond complex, front-side complex forming, double inversion,22 rebound, and stripping.23

In 2001, Gonzales and co-workers characterized the Walden-inversion pathway of the F− + CH3Y [Y = F, Cl, OH, SH, CN, PH2, NH2] Sn2 reactions.27 The geometries of the stationary points were optimized by CCSD(T)/TZ2P+dif, and the final single-point energies of the geometries were computed by the CCSD(T) method with the aug-cc-pVTZ basis set. Afterwards, focal-point analyses were made to obtain a more accurate description of the reaction profile.28 The OH− + CH3F Sn2 reaction was investigated by Hase and co-workers,29 and the dynamics simulations showed that in the exit channel the reaction occurs via the HOCH3⋅⋅⋅F− configuration, instead of the CH3OH⋅⋅⋅F− deep hydrogen-bonded minimum.30 In 1987, Jorgensen et al. determined an *ab initio* characterization of the OH− + CH3Cl Sn2 reaction using second and third-order Möller-Plesset perturbation theory,2 later direct dynamics simulations were performed by Tachikawa and co-workers.31,32 Regarding the OH− + CH3I reaction, several theoretical and experimental studies have been carried out.33−36 In 2012, Wester and co-workers unveiled various reaction mechanisms for OH−[H2O]n + CH3I → CH3OH + I− + nH2O [n = 0, 1, 2] using the crossed-beam imaging technique.33 Recently, the novel front-side complex mechanism of these latter reactions, along with several other nucleophiles [F−, Cl−, Br−, I−], was examined.37 The proton transfer and the traditional back-side attack pathways of the
OH\textsuperscript− + CH\textsubscript{3}I reaction were studied with density functional theory calculations by Xie et al.\textsuperscript{13} In 2018, we reported high-level \textit{ab initio} characterization of the OH\textsuperscript− + CH\textsubscript{3}Y [Y = F, Cl, Br, I] S\textsubscript{N}2 reactions, where the stationary points of the Walden-inversion, the front-side attack and the double-inversion pathways were computed at the CCSD(T)-F12b/aug-cc-pvQZ level of theory applying core- and post-CCSD(T) correlation corrections.\textsuperscript{38} Recently, we developed full-dimensional analytical potential energy surfaces for the OH\textsuperscript− + CH\textsubscript{3}I reaction with various \textit{ab initio} methods.\textsuperscript{39} It was found that at certain geometries of the potential energy surface the CCSD(T) energy breaks down resulting in an increase of the rejected unphysical trajectories in quasi-classical trajectory simulations. This problem was solved by proposing a Brueckner-type CCSD(T)-based composite method.\textsuperscript{39}

An evident way to extend the complexity of the X\textsuperscript− + CH\textsubscript{3}Y reactions is to replace CH\textsubscript{3}Y with CH\textsubscript{3}CH\textsubscript{2}Y. In these cases, the E2 reaction can also occur competing with the S\textsubscript{N}2 reaction. In 1988, for F\textsuperscript− + CH\textsubscript{3}CH\textsubscript{2}Cl and X\textsuperscript− + CH\textsubscript{3}CH\textsubscript{2}X [X = F, Cl] reactions, Yamabe and co-workers determined the stationary points of the S\textsubscript{N}2 and the E2 reactions by \textit{ab initio} calculations, in order to analyze structure-reactivity variation.\textsuperscript{14} Later, Mugnai \textit{et al.} investigated the competition between S\textsubscript{N}2 and E2 in the F\textsuperscript− + CH\textsubscript{3}CH\textsubscript{2}Cl reaction by molecular dynamics simulations and revealed that the initial velocity of fluoride has a different effect on the two reaction mechanisms.\textsuperscript{10} Bento \textit{et al.}\textsuperscript{3} and Zhao \textit{et al.}\textsuperscript{41} defined the E2 and S\textsubscript{N}2 pathways of the X\textsuperscript− + CH\textsubscript{3}CH\textsubscript{2}X [X = F, Cl] reactions, comparing the accuracy of numerous \textit{ab initio} methods and density functionals. In 2009, the reactivity order of twelve nucleophiles [F\textsuperscript−, Cl\textsuperscript−, Br\textsuperscript−, OH\textsuperscript−, SH\textsuperscript−, SeH\textsuperscript−, NH\textsubscript{2}\textsuperscript−, PH\textsubscript{3}\textsuperscript−, AsH\textsubscript{3}\textsuperscript−, CH\textsubscript{3}\textsuperscript−, SiH\textsubscript{3}\textsuperscript−, and GeH\textsubscript{3}\textsuperscript−] toward ethyl-chloride was studied by Wu \textit{et al.}, and a strong correlation was found between the electronegativity of the attacking atom of the nucleophiles and the barrier heights of the S\textsubscript{N}2 and E2 reactions.\textsuperscript{42} Recently, our group characterized the potential energy surface of the F\textsuperscript− + CH\textsubscript{3}CH\textsubscript{2}Cl reaction using a series of \textit{ab initio} methods, up to the CCSD(T)-F12b method with the aug-cc-pVQZ basis set.\textsuperscript{43} Comparing the benchmark results of the stationary points with lower-level methods showed that the MP2 method has an inaccuracy of 1.5–2.5 kcal mol\textsuperscript{−1}, in fact for some products an inaccuracy of 4.0–4.5 kcal mol\textsuperscript{−1} can be recognized. In 2018, the effects of various solvents were studied for the reaction of fluoride with bromo-ethane by Satpathy \textit{et al.}, and the gas-phase reaction was also investigated at the CCSD(T) level.\textsuperscript{44} Hase and co-workers examined the microsolvated F\textsuperscript−(CH\textsubscript{3}OH)\textsubscript{n} + CH\textsubscript{3}CH\textsubscript{2}Br [n = 0–2] reactions and direct dynamics simulations showed that by adding methanol to the reaction, the transition states of the S\textsubscript{N}2 reactions become more stabilized, therefore substitution dominates over elimination.\textsuperscript{45} The F\textsuperscript− + CH\textsubscript{3}CH\textsubscript{2}I reaction was described by Yang \textit{et al.} using several electronic structure calculations,\textsuperscript{46} and an experimental and theoretical reaction dynamics study was performed by the collaboration of Hase and Wester groups.\textsuperscript{7}

Following the above-mentioned studies, in this work, we provide benchmark \textit{ab initio} characterization of the OH\textsuperscript− + CH\textsubscript{3}CH\textsubscript{2}Y [Y = F, Cl, Br, I] S\textsubscript{N}2 and E2 reactions presenting the benchmark geometries of the stationary points of the OH\textsuperscript− + CH\textsubscript{3}CH\textsubscript{2}Y [Y = F, Cl, Br, I] reactions are preoptimized using the second-order Møller–Plesset perturbation theory\textsuperscript{47} (MP2) with the augmented correlation-consistent polarized-valence-double-\textsuperscript{5} (aug-cc-pVQZ) basis set. The benchmark harmonic vibrational frequencies of the stationary points are computed using the explicitly-correlated coupled-cluster singles, doubles, and perturbative triples (CCSD(T)-F12b) method\textsuperscript{49} with the aug-cc-pVQZ basis set. To obtain the most accurate geometries for the stationary points, the CCSD(T)-F12b method is utilized with the aug-cc-pVTZ basis set.\textsuperscript{48} The best relative energies of the stationary points are determined using the CCSD(T)-F12b method with the quadruple-\textsuperscript{5} aug-cc-pVQZ basis set at the CCSD(T)-F12b/aug-cc-pVQZ geometries. Note that performing CCSD(T)-F12b/aug-cc-pVQZ geometry optimizations is not feasible and also unnecessary as the geometry effects on the relative energies are usually significantly less than 0.01 kcal mol\textsuperscript{−1} as ref. 43 showed. For the open-shell systems [CH\textsubscript{3}CH\textsubscript{2}OY \textsuperscript−; Y = F, Cl, Br, I] restricted MP2 (RMP2) and unrestricted UCCSD(T)-F12b methods are used based on restricted open-shell Hartree–Fock (ROHF) orbitals. For Br and I, we apply small-core relativistic effective core potentials,\textsuperscript{50} replacing the inner-core 1s\textsuperscript{2}2s\textsuperscript{2}2p\textsuperscript{6} and 1s\textsuperscript{2}2s\textsuperscript{2}2p\textsuperscript{3}3s\textsuperscript{2}3p\textsuperscript{6} electrons, respectively, with the appropriate aug-cc-pVnZ-PP [n = 2–4] basis sets.

The benchmark adiabatic relative energies of the stationary points are computed as:

\[
\Delta E_{\text{CCSD(T)-F12b/aug-cc-pVQZ}} + \Delta ZPE_{\text{CCSD(T)-F12b/aug-cc-pVQZ}}
\]

(1)

where \(\Delta E\) is the benchmark classical relative energy and \(\Delta ZPE\) is the harmonic zero-point energy correction. All the \textit{ab initio} computations are performed with the MOLPRO program package.\textsuperscript{51}

II. Computational details

The geometries of the stationary points of the OH\textsuperscript− + CH\textsubscript{3}CH\textsubscript{2}Y [Y = F, Cl, Br, I] reactions are characterized using several electronic structure calculations,\textsuperscript{46} and an experimental and theoretical reaction dynamics study was performed by the collaboration of Hase and Wester groups.\textsuperscript{7}
classical and adiabatic relative energies of the stationary points are shown in Fig. 1 and 2, respectively. The geometries of the stationary points along with the most important structural parameters are given in Fig. 3 and 4. The relative energies of the minima and transition states determined at the MP2/aug-cc-pVDZ, CCSD(T)-F12b/aug-cc-pVDZ, CCSD(T)-F12b/aug-cc-pVTZ, and CCSD(T)-F12b/aug-cc-pVQZ levels of theory are presented in Table 1. Fig. 5 shows the structures of the examined product channels with the relevant bond lengths and angles. The reaction enthalpies of several product channels obtained by the above-defined levels of theory are shown in Table 2. The most accurate Cartesian coordinates of the minima, transition states, reactants, and products are given in the ESI.†

The SN2 reactions are more exothermic than the corresponding E2 reactions, submerged by classical (adiabatic) energies of 14.6 (9.6) kcal mol\(^{-1}\), at 0 K, in all cases, as seen in Fig. 1 and 2. The back-side attack substitution can occur via the traditional PreMIN → WaldenTS → Sn2 PostHMIN and/or Sn2 PostMIN pathway. For the Sn2 reactions, similar to

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**Fig. 1** Schematic potential energy surfaces of the OH\(^{-}\) + CH\(_3\)CH\(_2\)Y \([Y = F, Cl, Br, I]\) SN2 reactions showing the classical (adiabatic) CCSD(T)-F12b/aug-cc-pVQZ (±AZPE[CCSD(T)-F12b/aug-cc-pVDZ]) relative energies (kcal mol\(^{-1}\)) of the stationary points along the different reaction pathways, see Table 1. Results indexed by * correspond to CCSD(T)-F12b/aug-cc-pVDZ structures.

**Fig. 2** Schematic potential energy surfaces of the OH\(^{-}\) + CH\(_3\)CH\(_2\)Y \([Y = F, Cl, Br, I]\) E2 reactions showing the classical (adiabatic) CCSD(T)-F12b/aug-cc-pVQZ (±AZPE[CCSD(T)-F12b/aug-cc-pVDZ]) relative energies (kcal mol\(^{-1}\)) of the stationary points along the different reaction pathways, see Table 1.
OH\textsuperscript{−} + CH\textsubscript{3}CH\textsubscript{2}Y\textsuperscript{−}\textsuperscript{−} the global minimum of the potential energy surfaces is $S_{\text{MIN}}$ PostMIN. $S_{\text{MIN}}$ PostMIN is above $S_{\text{MIN}}$ PostHMIN by 18.9 (19.8), 8.8 (8.6), 7.4 (7.0) and 5.8 (5.7) kcal mol\textsuperscript{−1} for $Y = F$, Cl, Br and I, in order. Note that the $S_{\text{MIN}}$ PostHMIN is the global minimum for the complex multi-channel potential energy surfaces also. In the entrance channel only one minimum is found (PreMIN), unlike the F\textsuperscript{−} + CH\textsubscript{3}CH\textsubscript{2}Cl reaction,\textsuperscript{43} where a H-bonded complex was also obtained. The barrier of the Walden-inversion mechanism is significantly submerged, except for $Y = F$, where the classical barrier height is only $0.6$ kcal mol\textsuperscript{−1}, and with ZPE correction it is even above the reactant asymptote by $0.1$ kcal mol\textsuperscript{−1}. In the F\textsuperscript{−} + CH\textsubscript{3}CH\textsubscript{3}I reaction for the transition state of the back-side attack substitution, a classical energy of $−16.9$ kcal mol\textsuperscript{−1} was revealed relative to the reactants,\textsuperscript{46} while for the OH\textsuperscript{−} + CH\textsubscript{3}CH\textsubscript{2}I reaction, a value of $−19.1$ kcal mol\textsuperscript{−1} is identified. The difference of these latter classical energies, $2.2$ kcal mol\textsuperscript{−1}, is similar to the cases of the X\textsuperscript{−} + CH\textsubscript{3}CH\textsubscript{2}Cl [X = F, OH] reactions,\textsuperscript{43} where a difference of $1.4$ kcal mol\textsuperscript{−1} is determined. As Fig. 3 shows, at WaldenTS the Y–C bond is stretched by 0.362, 0.285, 0.218 and 0.204 Å, respectively.

Fig. 3 Structures of the minima and transition states corresponding to the OH\textsuperscript{−} + CH\textsubscript{3}CH\textsubscript{2}Y [Y = F, Cl, Br, I] $S_{\text{MIN}}$ reactions showing the relevant bond lengths (Å) and angles (degree) obtained at the CCSD(T)-F12b/aug-cc-pVTZ level of theory. Results indexed by * correspond to the CCSD(T)-F12b/aug-cc-pVDZ structure.

Fig. 4 Structures of the minima and transition states corresponding to the OH\textsuperscript{−} + CH\textsubscript{3}CH\textsubscript{2}Y [Y = F, Cl, Br, I] E2 reactions showing the relevant bond lengths (Å) and angles (degree) obtained at the CCSD(T)-F12b/aug-cc-pVTZ level of theory.
Table 1 Benchmarks classical and adiabatic energies (kcal mol⁻¹) of the stationary points relative to the reactants for the OH⁻ + CH₃CH₂Y [Y = F, Cl, Br, I] S₂,2 and E2 reactions

| OH⁻ + CH₃CH₂Y | MP2 | CCSD(T)-F12b |
|---------------|-----|--------------|
|               | DZ 6 | DZ 6 | TZ 6 | QZ 6 | ΔZPE | Adiabatic c |
| PreMIN        | -16.63 | -16.54 | -16.41 | -16.21 | 0.73 | -15.48 |
| syn-E2 PostMIN | -40.86 | -40.60 | -40.40 | -40.29 | -0.79 | -41.09 |
| syn-E2 PostMIN | -40.75 | -40.29 | -40.14 | -40.08 | -0.96 | -41.04 |
| syn-E2 PostMIN | -50.56 | -50.31 | -50.19 | -50.02 | 1.34 | -50.68 |
| DITS          | -2.52 | -0.66 | -0.83 | -0.59 | 0.64 | 0.05  |
| FSSTs         | 40.73 | 43.05 | 42.93 | 43.41 | -0.05 | 43.36 |
| DITS          | 24.19 | 20.93 | 22.18 | 22.43 | -1.30 | 21.13 |

0.164 Å relative to the corresponding bond lengths in PreMIN for Y = F, Cl, Br, I, respectively. Considering the lengths of the H···Y hydrogen bond and the dissociation energy of the leaving Y⁻ at S₂,2 PostHMIN, the trend is similar to the OH⁻ + CH₃Y reactions: as the H···Y⁻ bond decreases the dissociation energy increases, resulting in Dₑ (D₀) values of 30.8 (31.6) kcal mol⁻¹ for Y = F. For Y = Cl the classical energies of PreMIN and S₂,2 PostMIN are deeper by 0.3 and 16.4 kcal mol⁻¹ relative to the classical energies of the relevant stationary points for the F⁻ + CH₃CH₂Cl reaction. Regarding the point-group symmetries of PreMIN, WaldenTS, S₂,2 PostHMIN and S₂,2 PostMIN, all structures have Cₛ symmetry. In contrast to the above-described back-side attack mechanism, the front-side attack proceeds via high classical (adiabatic) barriers of 43.4 (43.4), 28.9 (28.8), 22.4 (22.9) and 16.5 (17.0) kcal mol⁻¹, for Y = F, Cl, Br and I, respectively, as Fig. 1 shows. In the entrance channel a front-side complex is found for Y = Cl, Br, I. In the case of F⁻ + CH₃I, an important front-side complex formation was exposed, thus, it is worth noting that in the title reaction for Y = FFSMIN is below PreMIN by 2.8 (2.8) kcal mol⁻¹. In FSMIN the arrangement of O···YC is almost collinear, and in the cases of Y = Br and I, the OH group rotates out of the Cₛ symmetry plane by ~88°, leading to a C₁ symmetry structure. In all cases, FSSTs has C₁ point-group symmetry. For the F⁻ + CH₃CH₂Cl reaction, a front-side transition state with 29.6 kcal mol⁻¹ classical height was found, similar to OH⁻ + CH₃CH₂Cl, where a slightly deeper classical energy, 28.9 kcal mol⁻¹, emerges. At higher energies, besides the front-side attack, double inversion can also occur, resulting in a lower-energy retention pathway. Double inversion begins with a proton-abstraction induced inversion via DITS followed by a second inversion through WaldenTS resulting in retention of the initial configuration. That the trend between the barrier heights of the double inversion and the weights of the halogen is inversely proportional: 22.4 (21.1), 7.4 (6.7) and 4.8 (4.3) kcal mol⁻¹, for Y = F, Cl and Br, respectively. For Y = I, similar to OH⁻ + CH₃I, double inversion becomes a barrier-less pathway through a slightly submerged DITS with an energy of ~0.3 (−0.6) kcal mol⁻¹.

Besides the S₂,2 reaction, elimination can also occur by two different mechanisms: anti-E2 and syn-E2, where the simultaneously breaking C-Y and C-H bonds are in anti and syn arrangements, respectively. In the entrance channel for both E2 mechanisms the same complex (PreMIN) is found as in the back-side attack substitution, as shown in Fig. 2. All stationary points of E2 are submerged: the global minimum is anti-E2 PostMIN for anti-E2, and syn-E2 PostMIN1 for syn-E2. Anti-E2 TS is below syn-E2 TS by 9.2 (8.8), 10.3 (9.6), and 10.3 (9.3) kcal mol⁻¹ for Y = Cl, Br and I, respectively. These latter energy differences are in agreement with the case of F⁻ + CH₃CH₂Cl, where a value of 10.6 (10.3) kcal mol⁻¹ was obtained. For the OH⁻ + CH₃CH₄F reaction anti-E2 TS and syn-E2 TS cannot be found. Compared to the back-side attack substitution, the WaldenTS is below anti-E2 TS by 0.6 (Cl), 1.7 (Br) and 2.2 (I) kcal mol⁻¹ without taking the ZPE corrections into consideration, as seen in Fig. 2. However, the picture changes with ZPE corrections, the anti-E2 TSs get energetically more favored, thus the adiabatic barrier heights of anti-E2 TSs are below WaldenTSs by 2.8, 1.3 and 0.3 kcal mol⁻¹, for Y = Cl, Br and I respectively. This peculiarity is not unique: the same can be observed for the F⁻ + CH₃CH₂Cl reaction, indicating that the
Kinetic control predicts a higher reactivity for E2 reaction than for back-side attack SN2. Both anti-E2 TS and syn-E2 TS have C1 symmetry; in syn-E2 TS the breaking C–H bond is lengthened by 0.122 (Cl), 0.123 (Br) and 0.109 (I) Å, however, the O–H bond of the H2O fragment is shortened by 0.121 (Cl), 0.153 (Br) and 0.169 (I) Å relative to the corresponding bond lengths in anti-E2 TS, as shown in Fig. 4. For syn-E2, in the product channel two ion-dipole complexes are revealed (syn-E2 postMIN1 and syn-E2 postMIN2), which can lead to Y−···HOH + CH3H4 and afterwards to the final products. It should be noted that for the Cl−···HF + CH3H4 products of the F− + CH3Cl reaction, the Dv (Dg) dissociation energy is 23.4 (22.2) kcal mol−1,25,43 while in the case of OH− + CH3Cl, Dv (Dg) values of 14.9 (13.7) kcal mol−1 can be determined for Cl−···HOH, as seen in Fig. 2. Nevertheless, in the exit channel, the Dv (Dg) dissociation energy for the three-body breakup of the Cl−···CH3H4···HF complex for the F− + CH3Cl reaction is around 15.4 (13.1) kcal mol−1,25,43 while in OH− + CH3Cl for anti-E2 PostMIN it is 20.4 (17.9) kcal mol−1. This trend breaks for the F− + CH3Cl reaction: the Dv dissociation energies of CH3H4···HF are 24.7 and 16.5 kcal mol−1, while for the OH− + CH3OH reaction the corresponding Dv values are 10.7 and 15.4 kcal mol−1, in order. Concerning the structures of the stationary points: syn-E2 PostMIN2 complexes have Cs symmetry, as seen in Fig. 4, whereas for syn-E2 PostMIN1 and anti-E2 PostMIN no plane symmetry is detected.

Besides SN2 and E2, five other product channels are investigated for the OH− + CH3CH2Y [Y = F, Cl, Br and I] reactions: H2O+H3C–CHY, H−+H3C–CHYOH, H−+HOH2−C−CH2Y, OHY−+CH3H2, and HOY + CH3CH2, as seen in Table 2 and Fig. 5. In all cases, the most endothermic pathway is the HOY + CH3CH2. For Y = F, Cl, Br and I, in most cases, the H2O+H3C–CHY, H−+H3C–CHYOH, H−+HOH2−C−CH2Y and endothermic, and the endothermicity is increasing in the same order. All the reaction enthalpies decrease from Y = F to I, except for H−+HOH2−C−CH2Y, where the trend is reversed. Moreover, it should also be mentioned that, except for SN2, MP2 provides notably larger values of reaction enthalpies, than CCSD(T)-F12b. If one compares the benchmark 0 K reaction enthalpies in the present study with the available “experimental” reaction enthalpies obtained from the Active Thermochemical Tables (ATcT),53,54 an excellent agreement can be observed, except for the H−+HOH2−C−CH2Y products, where a difference of ~2 kcal mol−1 can be evinced. Note that the decreasing trend for the experimental reaction enthalpies of H−+HOH2−C−CH2Y breaks at Y = I, querying the accuracy of either the experimental or the benchmark ab initio energies. It should be emphasized that the sum of the post-CCSD(T) and
core-correlation effects of the $S_{N2}$ channels was substantial for the $\text{OH}^- + \text{CH}_3\text{Y}$ [$\text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$] reactions: a sum of 0.40 (Cl), 0.68 (Br) and 1.07 (I) kcal mol$^{-1}$ was revealed. Therefore, to resolve this latter issue of the $\text{H}^- + \text{HOH}_2\text{C}-\text{CH}_3\text{Y}$ channel,
more accurate benchmark reaction enthalpies should be determined, considering post-CCSD(T) correlations, core-correlation corrections, as well as relativistic effects besides Br and I and anharmonic ZPE corrections. However, these auxiliary correction computations are out of the scope of the present work, because previous studies on SN2 reactions showed that the chemical accuracy for most of the benchmark energies is not significantly affected by these corrections.38–57

For a detailed evaluation of the accuracy of our benchmark energies, the basis-set convergence of the CCSD(T)-F12b relative energies can be analyzed. As shown in Fig. 6, the deviations of the corresponding basis sets are within ±0.65 kcal mol⁻¹ for the stationary points, excluding FSMIN in \( \text{OH}^- + \text{CH}_2\text{CH}_2\text{Cl} \), where the aug-cc-pVDZ (DZ) basis set gives a 0.79 kcal mol⁻¹ deviation from aug-cc-pVQZ (QZ). Concerning the product channels, at the \( \text{H}^- + \text{H}_2\text{C}\text{CH} = \text{OH} \) and \( \text{H}^- + \text{HOH}_2\text{C}\text{CH}_2\text{Y} \) pathways, a large difference of almost 2 kcal mol⁻¹ can be obtained between DZ and QZ reaction enthalpies, however, due to the fast basis-set convergence of the F12 methods, aug-cc-pVTZ (TZ) provides a more reduced deviation of roughly 0.4 kcal mol⁻¹ from QZ, as seen in Fig. 7. For the reaction enthalpies of E2, the basis-set convergence is not that smooth, especially for \( \text{OH}^- + \text{CH}_3\text{CH}_2\text{I} \), the difference between the TZ and QZ enthalpies is 0.89 kcal mol⁻¹. In \( \text{OH}^- + \text{CH}_3\text{Y} \) \( [\text{Y} = \text{Cl}, \text{Br}, \text{I}] \), a similar situation occurs, and the largest deviations in the TZ and QZ data appear for the reaction enthalpies.38 For PreMIN, FSMIN, anti-E2 PostMIN, syn-E2 PostMIN1, syn-E2 PostMIN2, WaldenTS, FSTS, and DTIS, in most cases, the ZPE effects are within ±1 kcal mol⁻¹, as Table 1 shows. More significant ZPE corrections can be recognized for Sn2 PostMIN and Sn2 PostHMIN, in the range of 1.3–4.2 kcal mol⁻¹. For anti-E2 TS and syn-E2 TS the ΔZPEs are between −1.8 and −3.1 kcal mol⁻¹, decreasing the barrier heights of the anti-E2 TS below WaldenTS, as discussed earlier. In respect of the product channels, as seen in Table 2, only Sn2 channels have positive ZPE corrections, from about 2.2 to 3.8 kcal mol⁻¹, all other product channels have negative and usually substantial ΔZPEs.

IV. Summary and conclusions

In this work, we have explored the complex potential energy surfaces of the \( \text{OH}^- + \text{CH}_3\text{CH}_2\text{Y} \) \( [\text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}] \) reactions by characterizing the stationary points of the E2 and Sn2 pathways using the explicitly-correlated CCSD(T)-F12b method. In the case of elimination, anti-E2 and syn-E2 mechanisms have been investigated, as far as for the substitution, besides the traditional back-side attack, front-side attack and double inversion have been studied. We have found that the thermodynamically most favored back-side attack substitution goes through almost the same pathway as in the \( F^- + \text{CH}_3\text{CH}_2\text{Cl} \) reaction.53 Furthermore, in the exit channel, the dissociation energies of the leaving nucleophiles of the hydrogen-bonded \( \text{CH}_2\text{CH}_2\text{OH} \cdot \cdot \cdot \text{Y} \) global minimum follow a similar trend to that for the reactions of \( \text{OH}^- \) with methyl-halides.38 In the entrance channel, a front-side complex formation is unveiled,23,37,52 resulting in a submerged \( \text{HO}^- \cdot \cdot \cdot \text{YCH}_2\text{CH}_3 \) minimum, especially for \( \text{Y} = \text{I} \), where this front-side complex is below the traditional ion-dipole \( \text{HO}^- \cdot \cdot \cdot \text{H}_2\text{CYCH}_3 \) complex. The barrier heights of double inversion are reduced by 22.2 (F), 22.1 (Cl), 18.7 (Br) and 17.6 (I) kcal mol⁻¹ relative to the corresponding barriers of the front-side attack, leading to a barrierless double-inversion pathway for \( \text{OH}^- + \text{CH}_3\text{CH}_2\text{I} \), similar to \( \text{OH}^- + \text{CH}_3\text{Cl} \).38 Regarding the elimination, in all cases, the pathway of the anti-E2 is lower than the syn-E2. As in \( F^- + \text{CH}_3\text{CH}_2\text{Cl} \), at the transition states of the anti-E2 notable ZPE effects occur, causing a less kinetically favorable back-side attack Sn2. It should be also highlighted that all stationary points of the E2 are submerged, as in the back-side attack substitution. Along with the Sn2 and E2, we examined several reaction enthalpies of other product channels, as well. Our benchmark reaction enthalpies are in excellent agreement with those obtained from ATcT,53,54 except for the \( \text{H}^- + \text{HOH}_2\text{C}\text{CH}_2\text{Y} \) channel, addressing, in this case, an uncertainty of either the “experimental” or the ab initio reaction enthalpies. We have also analyzed the basis-set convergence of the CCSD(T)-F12b method and the ZPE effects on the classical energies. Overall, for the first time, we have presented a high-level characterization of the title reactions, extending our knowledge on Sn2 and E2 reactions and motivating future potential energy surface developments, reaction dynamics simulations as well as experiments.

Conflicts of interest

There are no conflicts of interest to declare.
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