I. Introduction

Moving beyond the reactions of atoms with alkanes,\textsuperscript{1-16} the reactions of the OH radical with methane (CH\textsubscript{4}) and ethane (C\textsubscript{2}H\textsubscript{6}) have been thoroughly investigated by theory and experiment to uncover the fundamental rules of polyatomic chemical reactivity.\textsuperscript{16-39} The main product channel of the OH + CH\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} reactions results in H\textsubscript{2}O+CH\textsubscript{3}/C\textsubscript{2}H\textsubscript{5} via hydrogen-abstraction (HA). In the early years the kinetics of the OH + CH\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} reactions were investigated using experimental techniques as well as transition-state theory.\textsuperscript{17,18,28,30,31} The stationary points along the HA pathway were characterized by various \textit{ab initio} and density functional methods reporting pre- and post-reaction complexes separated by a transition state for each reaction.\textsuperscript{19,22,23,27,28,13,15,38} In the case of the OH + CH\textsubscript{4} system, the CH\textsubscript{4} \cdot OH and H\textsubscript{2}O \cdot CH\textsubscript{3} complexes were also studied by different experimental techniques using stimulated Raman, infrared and electronic excitation,\textsuperscript{24,36,37} photoelectron–photofragment coincidence,\textsuperscript{34} and infrared spectroscopy in helium nanodroplets.\textsuperscript{26,32} Furthermore, detailed reactive scattering experiments were performed for the different isotope-variants of the OH + CH\textsubscript{4} \rightarrow H\textsubscript{2}O + CH\textsubscript{3} reaction by Liu and co-workers.\textsuperscript{29}

For the OH + C\textsubscript{2}H\textsubscript{6} system, the nascent H\textsubscript{2}O vibrational distributions were measured by infrared chemiluminescence.\textsuperscript{21} In order to simulate some of the above-mentioned experiments the development of a full-dimensional potential energy surface (PES) is necessary. Following the early work of Espinosa-Garcia and co-workers,\textsuperscript{22} Li and Guo\textsuperscript{38} developed such a PES for the OH + CH\textsubscript{4} reaction and investigated its dynamics using quasi-classical trajectory and reduced-dimensional quantum methods.\textsuperscript{39}

In this study we focus on the high-level \textit{ab initio} characterization of the PES of the OH + CH\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} reactions providing benchmark structures and energies for the stationary points, thereby complementing our recent work on atom (F, Cl, Br, I) + CH\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} systems.\textsuperscript{13-15} Several aspects of the present study move beyond the previous work: (1) unlike most of the early work except ref. 38, we use the explicitly correlated CCSD(T)-F12 method\textsuperscript{40} to obtain structures, frequencies, and energies; (2) basis sets as large as aug-cc-pV5Z (OH + CH\textsubscript{4}) and aug-cc-pVQZ (OH + C\textsubscript{2}H\textsubscript{6}) are employed; (3) post-CCSD(T) correlation effects are considered up to the CCSDT(Q) level of theory; (4) the correlation energy contribution of the core electrons is taken into account; (5) scalar relativistic corrections are determined; and (6) spin–orbit effects are computed. Furthermore, besides the above-mentioned quantitative advances, we investigate several new alternative reaction pathways for the OH + CH\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} systems, namely hydrogen-substitution and methyl-substitution forming H + CH\textsubscript{3}OH/C\textsubscript{2}H\textsubscript{5}OH and CH\textsubscript{3} + CH\textsubscript{2}OH products, respectively. Knowing the energetics of the above
channels is essential to develop global PESs for the title reactions and to advance our knowledge on complex reaction mechanisms of multi-channel reactions.

In Section II we describe the computational details of the composite approach used to determine the best technically feasible stationary-point properties. The results are presented and discussed in Section III. The paper ends with summary and conclusions in Section IV.

II. Computational details

Stationary-point search is performed on the basis of previous studies and chemical intuition using the second-order Moller–Plesset perturbation theory (MP2) with the aug-cc-pVDZ basis set. The obtained minima and saddle points are further optimized with the explicitly-correlated coupled-cluster singles, doubles, and perturbative triples (CCSD(T)-F12b) method using the aug-cc-pVDZ and aug-cc-pVTZ basis sets. Harmonic vibrational frequencies are computed for each stationary point using the MP2/aug-cc-pVDZ, CCSD(T)-F12b/aug-cc-pVDZ, and CCSD(T)-F12b/aug-cc-pVTZ (except for some of the OH + C₂H₆ stationary points) levels of theory.

In order to achieve sub-chemical accuracy we perform the following single-point energy computations at the best geometries obtained at the CCSD(T)-F12b/aug-cc-pVTZ level:

1. CCSD(T)-F12b computations are carried out using the aug-cc-pVQZ and, in the case of the OH + CH₄ system, the aug-cc-pV5Z basis sets.
2. CCSD(T), CCSDT, and CCSDT(Q) methods are used with the cc-pVDZ and, in the case of the OH + CH₄ system, the aug-cc-pVTZ basis sets.
3. All-electron (AE) and frozen-core (FC) computations are performed at the CCSD(T)-F12b/cc-pCVTZ-F12 level of theory.
4. Second-order Douglas–Kroll (DK) relativistic energies are computed at the AE-CCSD(T)-F12b/cc-pCVTZ-F12 level of theory.
5. Spin–orbit (SO) corrections are determined using the Breit–Pauli Hamiltonian in the interacting-states approach using the Davidson-corrected multi-reference configuration interaction (MRCI-Q) method with the aug-cc-pVDZ and aug-cc-pVTZ basis sets. The MRCI computations utilize an active space of 15/21 electrons in 8/11 spatial orbitals keeping all the 4/6 core electrons frozen for OH + CH₂/C₂H₆. Two doubly-degenerate electronic states are determined, non-SO₁ and non-SO₂, resulting in a 4 × 4 SO matrix, whose eigenvalues correspond to the two-fold ground (SO₁) and excited (SO₂) spin–orbit states.

The benchmark classical relative energies are calculated by the following composite energy expression:

\[ \delta[\text{CCSDT}] = \text{CCSDT}/(\text{aug-cc-pVDZ} - \text{CCSD(T)}/(\text{aug-cc-pVDZ}), \]
\[ \delta[\text{CCSDT}[Q]] = \text{CCSDT}[Q]/(\text{aug-cc-pVDZ} - \text{CCSD(T)}/(\text{aug-cc-pVDZ}), \]
\[ A_{\text{core}} = \text{AE-CCSD(T)-F12b/cc-pCVTZ-F12} - \text{FC-CCSD(T)-F12b/cc-pCVTZ-F12} \]
\[ A_{\text{rel}} = D_{\text{K}} - A_{\text{AE-CCSD(T)-F12b/cc-pCVTZ-F12}} - \text{AE-CCSD(T)-F12b/cc-pCVTZ-F12} \]
\[ A_{\text{SO}} = \text{SO}_1(\text{MRCI+Q/aug-cc-pVTZ}) - \text{non-SO}_1(\text{MRCI+Q/aug-cc-pVTZ}). \]

including the terms defined in eqn (1)–(6) and the zero-point energy correction \( A_{\text{ZPE}} \) determined at the CCSD(T)-F12b/aug-cc-pVTZ level, except for some of the OH + C₂H₆ stationary points, where the frequency computations are performed without symmetry at the CCSD(T)-F12b/aug-cc-pVDZ level.

For open-shell systems the MP2 method is used in a restricted formalism (RMP2), unless otherwise noted, whereas all the CCSD(T)-F12b computations utilize the unrestricted CCSD(T)-F12b method based on restricted open-shell Hartree–Fock (ROHF) orbitals. For the determination of the post-CCSD(T) correlation effects we use unrestricted Hartree–Fock (UHF) reference and the unrestricted CCSD(T), UCCSDT, and UCCSDT(Q) methods. Note that, for the sake of simplicity, we usually omit the reference function as well as the R (restricted) and U (unrestricted) abbreviations in the notations.

All the MP2, CCSD(T)-F12b, MRCI, and SO computations are carried out with the MOLPRO program package, whereas the CCSD(T), CCSDT, and CCSDT(Q) energies are obtained with MRCI interfaced to MOLPRO.

III. Results and discussion

The topology of the PESs with the benchmark classical and adiabatic energies of the OH + CH₄ and OH + C₂H₆ reactions are shown in Fig. 1 and 2, respectively, and the corresponding stationary-point geometries showing the most important structural parameters at different levels of theory are given in Fig. 3 and 4. The HA pathways are exothermic with benchmark classical(adiabatic) \( \Delta E(H\Delta E) \) values of −13.07(−14.37) / −16.70(−18.19) kcal mol⁻¹ for the OH(2Π₁₂) + CH₄/C₂H₆ → H₂O + CH₄/C₂H₆ reactions. The HA barrier is significantly higher for OH + CH₄, i.e., 6.30/4.78 kcal mol⁻¹ than in the case of OH + C₂H₆, 3.69/2.18 kcal mol⁻¹. The structures of the hydrogen-abstraction transition-states (HA TSs) are reactant-like in both cases as the reactive C–H bonds are only stretched by 0.118/0.087 Å relative to the corresponding bond lengths in
The OH + CH₄ reaction has lower and more reactant-like barrier as the CH₃ fragment.

The pathway resulting in H + CH₃OH products via a Walden-inversion reaction we have found a front-side (FS) attack retention pathway via a higher barrier with classical(adiabatic) height of 54.13(52.48) kcal mol⁻¹. At the HS W TS the forming O–C and breaking C–H bonds are nearly collinear (168.3°) and the H₂C–C unit is almost planar, whereas at the HS FS TS the O–C–H angle is 58.2° along the reaction coordinate and the H₂C–CH₃ unit is ethane-like retaining its retains configuration. Similar HS FS TS was found for the X + C₂H₆ [X = F, Cl, Br, I] reactions, comparing the barrier heights against the X = Cl case has similar, though slightly larger, value of 59.14(54.97) kcal mol⁻¹. For the OH + C₂H₆ reaction we have found weakly-bound H···C₂H₅OH complexes in the exit channels of the HS inversion and retention pathways with small D_v values of 0.26 and 0.32 kcal mol⁻¹, respectively. However, these shallow HS product-channel wells may not support a bound vibrational state, because the ZPE-corrected energies of the HS W PostMIN and HS FS PostMIN complexes are slightly above the vibrationally ground-state product asymptote by 0.05 and 0.04 kcal mol⁻¹ (Fig. 2).

Unlike for OH + CH₄, for the OH + C₂H₆ reaction a third product channel is possible resulting in CH₃OH + CH₃ via methyl substitution (MS). As Fig. 2 shows, MS is slightly exothermic ΔE(ΔH₀) = −0.94(−2.20) kcal mol⁻¹ and goes over a classical (adiabatic) Walden-inversion barrier of 39.89(39.60) kcal mol⁻¹ height. Thus, similarly to the halogen + C₂H₆ reactions, MS is both thermodynamically and kinetically favored over HS. At the central MS W TS the O–C–C atoms are nearly collinear and the forming O–C and breaking C–C bonds are stretched by 0.407 and 0.413 Å, respectively, relative to their corresponding equilibrium.

CH₄/C₂H₆, whereas the forming O–H bonds are stretched by 0.363/0.428 Å relative to the H₂O product as shown in Fig. 3 and 4. Thus, the exothermic HA processes feature early barriers in accord with the Hammond postulate and the more exothermic HA processes feature early barriers in accord with the ratio of the intermolecular C···H distances of 2.383/2.312 Å. The greater stability of the latter can be explained by the fact that the C₂H₅ unit has a higher barrier with classical(adiabatic) height of 44.30(43.53) kcal mol⁻¹ as shown in Fig. 1. The HS W TS has C₄v symmetry with nearly collinear O–C–H arrangement, where the O–C and C–H distances are 1.717 and 1.415 Å, respectively, stretched by 0.297 and 0.327 Å relative the corresponding bonds in CH₃OH and CH₄ (Fig. 3); thus, HS has a central or slightly-late barrier. The HS pathway of the OH + CH₄ reaction is revealed for the first time in the present study, but for atom + methane reactions HS is not unprecedented. For the O(3P) + CH₄ reactions HS was investigated both experimentally and theoretically. For Cl + CH₄ we found a Walden-inversion barrier height of 42.08(38.84) kcal mol⁻¹ which is similar to that of OH + CH₄. Besides Walden inversion, for the O(3P) and Cl + CH₄ reactions front-side attack TSs with C₄v and C₃v symmetry, respectively, were reported. In the case of OH + CH₄ we do not find front-side attack TS; however, reaction dynamics simulations may reveal retention trajectories as we found that the retention pathways of the Cl + CH₄ → H + CH₃Cl reaction avoid the high-energy C₄v TS.

In the case of the OH + C₂H₆ reaction HS pathways leading to H + CH₃OH also exist as shown in Fig. 2. The endothermicity of the HS channel, ΔE(ΔH₀) = 9.10(7.12) kcal mol⁻¹, is less than that of the OH + CH₄ reaction, ΔE(ΔH₀) = 14.33(13.19) kcal mol⁻¹, whereas the Walden-inversion classical(adiabatic) barrier heights of the two systems are similar, i.e., 43.32(41.73) kcal mol⁻¹ for OH + C₂H₆ and 44.30(43.53) kcal mol⁻¹ for OH + CH₄. Furthermore, these HS barrier heights are also very similar to that of the Cl + C₂H₆ system, 41.60(37.66) kcal mol⁻¹. For the OH + C₂H₆ reaction we have found a front-side attack TS; however, reaction dynamics simulations may reveal retention trajectories as we found that the retention pathways of the Cl + CH₄ → H + CH₃Cl reaction avoid the high-energy C₄v TS.
values in the product and reactant (Fig. 4). For the halogen + C$_2$H$_6$ systems we reported a higher-energy front-side attack MS pathway as well,$^{14}$ however, for OH + C$_2$H$_6$ MS FS TS is not found, though its existence cannot be ruled out. Nevertheless, we have found a H$_3$C/C1/C1/C1/CH$_3$OH complex in the product channel of MS with $D_e$($D_0$) values of 0.69(0.38) kcal mol$^{-1}$. The stability trend, $D_e = \{2.4, 0.7, 0.3\}$ kcal mol$^{-1}$, of the $\{HA, MS, HS\}$ PostMIN complexes, $\{HOH/C1/C1/C1/C2H5, H_3C/C1/C1/C1/CH3OH, H/C1/C1/C1/C2H5OH\}$, reflects the facts that HA PostMIN is stabilized by dipole–dipole interaction and CH$_3$ is more polarizable than the H atom.

The above-discussed stationary-point properties correspond to our new benchmark values obtained by the composite ab initio approach described in Section II. Now let us discuss the accuracy of the computed results. The most important structural parameters of the stationary points obtained by the MP2/aug-cc-pVDZ, CCSD(T)-F12b/aug-cc-pVDZ, and CCSD(T)-F12b/aug-cc-pVTZ levels of theory are shown in Fig. 3 and 4. As seen, the MP2 and CCSD(T)-F12b results may differ by about 0.01 Å, whereas the CCSD(T)-F12b/aug-cc-pVTZ levels of theory are shown in Fig. 3 and 4. As seen, the MP2 and CCSD(T)-F12b results may differ by about 0.01 Å, whereas the CCSD(T)-F12b/aug-cc-pVTZ result is basis converged within 0.1 kcal mol$^{-1}$. This finding for OH + CH$_4$ is useful for the larger OH + C$_2$H$_6$ system, where we do not perform the CCSD(T)-F12b/aug-cc-pVQZ computations. For OH + C$_2$H$_6$, the aug-cc-pVDZ and aug-cc-pVTZ levels of theory are converged with average absolute deviations of 0.27 and 0.04 kcal mol$^{-1}$, respectively, with respect to the CCSD(T)-F12b/aug-cc-pVQZ results.

The large-basis CCSD(T)-F12b computations provide a very good estimate of the complete-basis-set limit of the CCSD(T) relative energies. If one aims to approach the “exact” energies additional small corrections, such as post-CCSD(T) and core electron correlation as well as scalar and SO relativistic effects should be considered. Furthermore, to get experimentally observable quantities the ZPE corrections have to be taken into account. These so-called auxiliary corrections are given in Tables 3 and 4 for the OH + CH$_4$ and OH + C$_2$H$_6$ systems, respectively. For OH + CH$_4$ we have determined the $\delta[CCSDT]$
and \( \delta^{[\text{CCSDT(Q)}]} \) corrections with the cc-pVDZ and aug-cc-pVDZ basis sets. As Table 3 shows even the small cc-pVDZ basis provides good estimates for these post-CCSD(T) correlation effects suggesting that it is sufficient to perform only the CCSDT(Q)/cc-pVDZ computations for the larger OH + \( \text{C}_2\text{H}_6 \) system. In the case of the products and HA PostMIN of the \( \text{OH} + \text{CH}_4 \) reaction the \( \delta^{[\text{CCSDT}]} \) and \( \delta^{[\text{CCSDT(Q)}]} \) absolute corrections are between 0–0.2 kcal mol\(^{-1}\) and partially cancel each other. However, for the HA TS and HS W TS the aug-cc-pVDZ(cc-pVDZ) corrections add up to \( -0.35 (-0.26) \) and \( -0.61 (-0.61) \) kcal mol\(^{-1}\), respectively, showing the good performance of the smaller basis set. For the \( \text{OH} + \text{C}_2\text{H}_6 \) system most of the post-CCSD(T) corrections have the same negative sign, except the HS products and PostMINs (Table 4). The largest cumulative post-CCSD(T) corrections are found for the TSs, namely \( -0.25, -0.67, -0.88, \) and \( -0.91 \) kcal mol\(^{-1}\), for HA TS, HS W TS, HS FS TS, and MS W TS, respectively, which are clearly not negligible if sub-chemical accuracy is desired.

For both reactions the core correlation corrections are in the range from \( -0.11 \) to \( +0.39 \) kcal mol\(^{-1}\), whereas the scalar
Table 1 Energies (kcal mol⁻¹) of the stationary points and product channels of the OH + CH₄ reaction relative to the reactants at different levels of theory

| Stationary points | MP2 [aVDZ] | CCSD(T)-F12b [aVDZ] | CCSD(T)-F12b [aVTZ] | CCSD(T)-F12b [aVQZ] | CCSD(T)-F12b [aVSZ] | ΔV [kcal mol⁻¹] | Classical [kcal mol⁻¹] | ΔZPE [kcal mol⁻¹] | Adiabatic [kcal mol⁻¹] |
|-------------------|------------|----------------------|----------------------|----------------------|----------------------|----------------|----------------------|-----------------|------------------|
| HA TS             | 8.50       | 6.08                 | 6.27                 | 6.30                 | 6.38                 | -0.08         | 6.30                 | -1.52           | 4.78             |
| HA PostMIN        | -18.22     | -15.15               | -14.99               | -15.00               | -14.96               | +0.16         | -14.80               | -0.22           | -15.02           |
| HS W TS           | 41.07      | 44.52                | 44.40                | 44.38                | 44.42                | -0.12         | 44.30                | -0.77           | 43.53            |
| CH₂OH + H₂H     | 7.62       | 13.39                | 14.00                | 13.95                | 13.98                | +0.35         | 14.33                | -0.14           | 13.19            |
| CH₃ + H₂O        | -16.28     | -13.19               | -13.15               | 13.23                | -13.23               | +0.18         | -13.07               | -1.30           | -14.37           |

[a] MP2/aug-cc-pVDZ relative energies obtained at MP2/aug-cc-pVDZ geometries. [b] CCSD(T)-F12b/aug-cc-pVQZ relative energies obtained at CCSD(T)-F12b/aug-cc-pVTZ geometries. [c] CCSD(T)-F12b/aug-cc-pVQZ relative energies obtained at CCSD(T)-F12b/aug-cc-pVTZ geometries. [d] CCSD(T)-F12b/aug-cc-pVTZ relative energies obtained at CCSD(T)-F12b/aug-cc-pVTZ geometries. [e] CCSD(T)-F12b/aug-cc-pVTZ relative energies obtained at CCSD(T)-F12b/aug-cc-pVTZ geometries. [f] Benchmark classical relative energy obtained at CCSD(T)-F12b/aVQZ + ΔV. [g] Benchmark adiabatic relative energy obtained as classical + ΔZPE.

Table 2 Energies (kcal mol⁻¹) of the stationary points and product channels of the OH + C₂H₆ reaction relative to the reactants at different levels of theory

| Stationary points | MP2 [aVDZ] | CCSD(T)-F12b [aVDZ] | CCSD(T)-F12b [aVTZ] | CCSD(T)-F12b [aVQZ] | CCSD(T)-F12b [aVSZ] | ΔV [kcal mol⁻¹] | Classical [kcal mol⁻¹] | ΔZPE [kcal mol⁻¹] | Adiabatic [kcal mol⁻¹] |
|-------------------|------------|----------------------|----------------------|----------------------|----------------------|----------------|----------------------|-----------------|------------------|
| HA TS             | 6.21       | 3.45                 | 3.65                 | 3.70                 | -0.01                | 3.69          | -1.51                | 2.18            |
| HA PostMIN        | -21.78     | -19.28               | -19.07               | -19.09               | +0.03                | -19.06        | -0.48                | -19.54          |
| HS W TS           | 39.89      | 43.57                | 43.49                | 43.51                | -0.19                | 43.32         | -1.59                | 41.73           |
| HS W PostMIN      | 2.11       | 7.96                 | 8.62                 | 8.63                 | +0.21                | 8.84          | -1.67                | 7.17            |
| HS FS TS          | 55.68      | 54.33                | 54.47                | 54.53                | -0.40                | 54.13         | -1.65                | 52.48           |
| HS FS PostMIN     | 2.00       | 7.90                 | 8.56                 | 8.57                 | +0.21                | 8.78          | -1.62                | 7.16            |
| MS W TS           | 44.80      | 40.29                | 40.21                | 40.21                | -0.32                | 39.89         | -0.29                | 39.60           |
| MS W PostMIN      | -3.14      | -2.02                | -1.85                | -1.89                | +0.26                | -1.63         | -0.95                | -2.58           |
| CH₂OH + CH₃ + H₂  | 2.29       | 8.29                 | 8.91                 | 8.89                 | +0.21                | 9.10          | -1.98                | 7.12            |
| CH₃ + H₂O + H₂O   | -2.24      | -1.16                | -1.61                | -1.21                | +0.27                | -0.94         | -1.26                | -2.20           |
| CH₃ + H₂O         | -18.96     | -16.64               | -16.61               | -16.75               | +0.05                | -16.70        | -1.49                | -18.19          |

[a] MP2/aug-cc-pVDZ relative energies obtained at MP2/aug-cc-pVDZ geometries. [b] CCSD(T)-F12b/aug-cc-pVQZ relative energies obtained at CCSD(T)-F12b/aug-cc-pVTZ geometries. [c] CCSD(T)-F12b/aug-cc-pVQZ relative energies obtained at CCSD(T)-F12b/aug-cc-pVTZ geometries. [d] CCSD(T)-F12b/aug-cc-pVTZ relative energies obtained at CCSD(T)-F12b/aug-cc-pVTZ geometries. [e] CCSD(T)-F12b/aug-cc-pVTZ relative energies obtained at CCSD(T)-F12b/aug-cc-pVTZ geometries. [f] Benchmark classical relative energy obtained as classical + ΔZPE. [g] Benchmark adiabatic relative energy obtained as classical + ΔZPE.

Table 3 Auxiliary corrections (kcal mol⁻¹) for the relative energies of the stationary points and product channels of the OH + CH₄ reaction

| Stationary points | δCCSD(T)[a] | δCCSD(T)[b] | Δcore | Δrel | ΔSO | ΔZPE[a] |
|-------------------|-------------|-------------|-------|------|-----|--------|
| HA TS             | -0.11       | -0.12       | 0.06  | 0.02 | 0.18 | 1.05   |
| HA PostMIN        | 0.00        | 0.04        | -0.13 | -0.15| 0.12 | 0.19   |
| HS W TS           | -0.26       | -0.18       | -0.35 | -0.43| 0.25 | 0.05   |
| CH₂OH + H₂H      | 0.09        | 0.18        | -0.20 | -0.19| 0.02 | 0.15   |
| CH₃ + H₂O        | 0.01        | 0.05        | -0.13 | -0.14| 0.04 | 0.12   |

[a] CCSD(T) obtained with the cc-pVDZ (VDZ) and aug-cc-pVDZ (aVDZ) basis sets at CCSD(T)-F12b/aug-cc-pVTZ geometries. [b] CCSD(T) = CCSD obtained with the cc-pVDZ (VDZ) and aug-cc-pVDZ (aVDZ) basis sets at CCSD(T)-F12/aug-cc-pVTZ geometries. [c] Benchmark relative energy obtained as the difference between all-electron and frozen-core CCSD(T)-F12b/cc-pVTZ-F12 relative energies at CCSD(T)-F12b/aug-cc-pVTZ geometries. [d] Core-correlation correction obtained as the difference between the SO and non-SO ground-state MRCHI+ and MRCHI relative energies at CCSD(T)-F12b/aug-cc-pVTZ geometries. [e] SO interaction almost fully quenches at all the stationary points, while lowers the reactant asymptote, thereby increasing the all the relative energies by 0.19 kcal mol⁻¹, as seen in Tables 3 and 4.
pVdz and aug-cc-pVtz basis sets, which result in almost the same corrections of 0.18 (once 0.17) and 0.19 kcal mol$^{-1}$, respectively. These values are in good agreement with the experimental data of 0.20 kcal mol$^{-1}$ deduced from the measured SO splitting ($\varepsilon = 0.40$ kcal mol$^{-1}$) of the OH radical as $\omega/2$. To get deeper insight, we have computed SO and non-SO potential energy curves along the intermolecular coordinates of the CH$_2$OH and CH$_2$OH$\cdot$OH systems while the OH approaches the CH$_4$ and C$_2$H$_6$ molecules from different directions as shown in Fig. 5 and 6. The ground electronic state of the OH radical is the 2-fold degenerate $^2\Pi$, which splits to a 2-fold SO ground ($^2\Pi_{1/2}$) and a 2-fold SO excited state ($^2\Pi_{3/2}$). As OH approaches CH$_4$ the two doublet SO non-SO state remains quasi-degenerate and the SO ground and excited states are below and above the non-SO states by $\omega/2$ as shown in Fig. 5. There is a van der Waals well in the entrance channel whose depth is 0.5 and 0.7 kcal mol$^{-1}$ with HCH$_3$$\cdot$OH and H$_2$CH$\cdot$OH C$_{3v}$ orientations, respectively. The well depths and positions are not affected by the SO interaction, because the wells are at C\cdot\cdot\cdotO distances of 3–4 Å, whereas the SO correction is almost constant until the C\cdot\cdot\cdotO distance decreases to about 2 Å, where the difference between the SO and non-SO ground state energies rapidly drops to zero (see insets in Fig. 5). This fast quenching of SO interaction occurs at high relative energies above 100 kcal mol$^{-1}$, where the quasi-degeneracy of the non-SO states starts lifting. Interestingly, in the case of the halogen (X) + CH$_4$ reactions, the HCH$_3$$\cdot$X minimum is the deeper with depth of 0.6(0.9) kcal mol$^{-1}$ and the H$_2$CH$\cdot$X well is the shallower, 0.3(0.3) kcal mol$^{-1}$, with/without SO correction.\textsuperscript{13,58} In the case of the H$_2$CH$_2$OH$\cdot$OH (C$_{3v}$) and H$_2$CH$_2$CH$\cdot$OH (C$_6$) arrangements in the entrance well of OH + C$_2$H$_6$ reaction, the conclusions are qualitatively the same as for OH + CH$_4$, i.e., the former minimum is 0.6 kcal mol$^{-1}$ deep, whereas the latter is deeper, 0.7 kcal mol$^{-1}$, and these are not affected by the SO interactions. If OH approaches C$_2$H$_6$ perpendicularly to the C–C bond, the well is the deepest, 0.8 kcal mol$^{-1}$, and slightly affected by the SO interaction as the quenching and the departure of the two non-SO states occur in the 2.5–3.5 Å range of the C\cdot\cdot\cdotO distance as seen in Fig. 6. For the X + C$_2$H$_4$ systems, the H$_2$CH$_2$X$\cdot$X (C$_6$) minimum was found to be the deepest, slightly below the perpendicular well, and the H$_2$CH$_3$CH$\cdot$X (C$_6$) arrangement gave the shallowest minimum.\textsuperscript{14} These entrance-channel wells may play an important role in the dynamics of the title reactions at low collision energies, especially for OH + C$_2$H$_6$, which has a low barrier for HA.

The ZPE effects on the relative energies are always negative and in the most cases the absolute corrections are in the range of 1–2 kcal mol$^{-1}$ as shown in Tables 1 and 2. The mean absolute deviation of the MP2 ZPE corrections from the CCSD(T)-F12b results is about 0.2 kcal mol$^{-1}$, whereas the CCSD(T)-F12b/aug-cc-pVdz data are converged within 0.1 kcal mol$^{-1}$ as Tables 3 and 4 show. These ZPE effects are clearly not negligible if we aim to compute chemically accurate, measurable adiabatic relative energies.

For the reaction enerthals comparison between the present computed adiabatic relative energies and the “experimental” data deduced from 0 K enthalpies of formation taken from the Active Thermochemical Tables (ATcT)\textsuperscript{61} is possible. Note that ATcT collects the best measured and computed thermochemical data, thereby providing the best available predictions for enthalpies of formation and their uncertainties of several chemical species. We call these ATcT data as “experimental” even if they rely on both theory and experiment. As Table 5 shows the agreement between the present \textit{ab initio} 0 K reaction enthalpies and experiment is excellent; the mean absolute deviation between theory and experiment is only 0.07 kcal mol$^{-1}$ and, in most cases, the theoretical predictions are within the error bars of the experiment. This comparison demonstrates that one needs to consider the auxiliary corrections (post-CCSD(T), core, scalar relativistic, SO) to achieve this outstanding accuracy, because the cumulative effect of these corrections averaged for the five reaction channels is 0.21 kcal mol$^{-1}$, which is

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**Table 4** Auxiliary corrections (kcal mol$^{-1}$) for the relative energies of the stationary points and product channels of the OH + C$_2$H$_6$ reaction

| Stationary points | $\delta$[CCSD(T)] | $\delta$[CCSDT(F12)] | $A_{\text{core}}$ | $A_{\text{rel}}$ | $A_{\text{ZPE}}$ | $D_{\text{SO}}$ | Product Channel |
|-------------------|------------------|-------------------|------------------|------------------|----------------|-----------------|----------------|
| HA TS             | -0.11            | -0.14             | 0.03             | 0.02             | 0.18           | 0.19            | -2.08           |
| HA PostMIN        | -0.04            | -0.13             | -0.11            | 0.12             | 0.18           | 0.19            | -0.08           |
| HS W TS           | -0.27            | -0.40             | 0.24             | 0.05             | 0.18           | 0.19            | -1.55           |
| HS W PostMIN      | 0.10             | -0.20             | -0.02            | 0.14             | 0.18           | 0.19            | -1.82           |
| HS FS TS          | -0.38            | -0.50             | 0.26             | 0.03             | 0.18           | 0.19            | -1.82           |
| MS W TS           | -0.48            | -0.43             | 0.39             | 0.01             | 0.18           | 0.19            | -1.80           |
| MS W PostMIN      | 0.02             | 0.12              | 0.09             | 0.18             | 0.18           | 0.19            | -0.84           |
| C$_2$H$_5$OH + H  | 0.10             | 0.20              | 0.12             | 0.12             | 0.20           | 0.19            | -0.15           |
| CH$_3$OH + CH$_3$ | 0.02             | -0.11             | 0.09             | 0.18             | 0.18           | 0.19            | -1.51           |
significantly larger than the above-mentioned mean deviation between theory and experiment. Furthermore, the excellent agreement for these measurable quantities confirms the accuracy of the present theoretical predictions for the experimentally hardly accessible properties, such as barrier heights.

IV. Summary and conclusions

The reactions of the OH radical with methane and ethane have become benchmark systems to understand the dynamics and mechanisms of polyatomic reactions. Despite many previous experimental and theoretical studies focusing on the exothermic ($\Delta H_0 = -14.37/-18.19$ kcal mol$^{-1}$) hydrogen-abstraction reaction resulting in H$_2$O + CH$_3$/C$_2$H$_5$ via low adiabatic barriers of 4.78/2.18 kcal mol$^{-1}$, other product channels and their energetic requirements were unknown until the present study. Here, we show that hydrogen-substitution leading to H + CH$_3$OH/C$_2$H$_5$OH is endothermic, $\Delta H_0 = 13.19/7.12$ kcal mol$^{-1}$ and can proceed via a Walden-inversion barrier with adiabatic height of 43.53/41.73 kcal mol$^{-1}$ or for the latter we have also found a front-side attack pathways via an adiabatic barrier of 52.48 kcal mol$^{-1}$. For OH + C$_2$H$_6$ a methyl-substitution channel forming CH$_3$ + H$_2$O + CH$_3$ is also possible, which is exothermic, $\Delta H_0 = -2.20$ kcal mol$^{-1}$, but has a large adiabatic barrier of 39.60 kcal mol$^{-1}$. For the product channel several complexes have been revealed and

Fig. 5  Potential energy curves along the $C_3$ axis of the CH$_4$···OH system obtained at the MRCl+Q/aug-cc-pVDZ level of theory while the structures of the CH$_4$ and OH units are kept frozen at their equilibrium geometries. SO$_1$ and SO$_2$ denote the spin–orbit ground and excited states, whereas non-SO$_1$ and non-SO$_2$ are the non-relativistic ground and excited electronic states, respectively. The insets show the distance dependence of the spin–orbit corrections obtained as difference between the SO$_2$ and non-SO$_2$ energies.

Fig. 6  Potential energy curves along the $C_3$ (left), CH (middle), and CC-perpendicular (right) axes of the C$_2$H$_6$···OH system obtained at the MRCl+Q/aug-cc-pVDZ level of theory while the structures of the C$_2$H$_6$ and OH units are kept frozen at their equilibrium geometries. SO$_1$ and SO$_2$ denote the spin–orbit ground and excited states, whereas non-SO$_1$ and non-SO$_2$ are the non-relativistic ground and excited electronic states, respectively. The insets show the distance dependence of the spin–orbit corrections obtained as difference between the SO$_2$ and non-SO$_2$ energies.
characterized, showing a stability order of HOH⋯C₂H₅, HOH⋯CH₃, H₂C⋯OH, and H⋯C₂H₅OH with Δₑ values of 2.4, 1.7, 0.7, and 0.3 kcal mol⁻¹, respectively. For the first time, we have performed SO computations for the entrance channel, thereby revealing van der Waals wells with depths of 0.5–0.8 kcal mol⁻¹ depending on the relative orientation of the reactants. Unlike for the halogen + CH₄/C₂H₆ systems, the well is the deepest for perpendicular C⋯C⋯OH approach (0.8 kcal mol⁻¹), followed by the H₂CH/H₂CH₂CH⋯OH (0.7 kcal mol⁻¹) and HCH₃/H₂CH₃⋯OH (0.5–0.6 kcal mol⁻¹) arrangements. These pre- and post-reaction wells may play significant roles in the dynamics of the hydrogen-abstraction processes, especially at low collision energies, by steering the reactants in the entrance channels and affecting product rotation in the exit channels, respectively.

The stationary-point properties have been computed using an accurate composite ab initio approach which goes beyond the widely-used standard quantum chemistry. The complete-basis-set limit of CCSD(T) is approached well within 0.1 kcal mol⁻¹ with explicitly-correlated CCSD(T)-F12/aug-cc-pVnZ computations with n = 5 and 4(Q) for OH + CH₄ and OH + C₂H₅, respectively. Post-CCSD(T) correlation (−0.9 to −0.1), core correlation (−0.1 to +0.4), scalar relativistic (+0.0 to +0.2), SO (+0.2), and ZPE (−2 to −1) effects are determined resulting in typical values for the title reactions as indicated in parentheses in kcal mol⁻¹. We conclude that the present theoretical predictions provide sub-chemically accurate relative energies with an estimated uncertainty of around 0.1 kcal mol⁻¹, which is about an order of magnitude better than that of the standard quantum chemistry studies. The outstanding accuracy of the present results can be confirmed by the comparison of the computed reaction enthalpies with the corresponding experimental data showing only 0.07 kcal mol⁻¹ mean absolute deviation.

The new insights into the mechanisms and alternative reaction pathways of the title reactions are essential to develop global PESs for the OH + CH₄/C₂H₅ systems, allowing dynamical investigations over a large collision energy range. Furthermore, the relative energies of the stationary points may guide future experimental investigations showing the thermodynamical and kinetical controls of the different processes. Finally, the present composite approach may be utilized in several similar ab initio investigations if high accuracy is desired.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

We thank the National Research, Development and Innovation Office-NKFIH, K-125317, the Ministry of Human Capacities, Hungary grant 20391-3/2018/FEKUSTRAT, and the Momentum (Lendület) Program of the Hungarian Academy of Sciences for financial support.

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