



Cite this: *Phys. Chem. Chem. Phys.*,
2026, **28**, 24410

Benchmark *ab initio* mapping of the full reaction landscape of the $\text{Cl}(^2\text{P}_{3/2}) + \text{C}_2\text{H}_5\text{OH}$ system

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A detailed exploration of the potential energy surface (PES) of the $\text{Cl}(^2\text{P}_{3/2}) + \text{C}_2\text{H}_5\text{OH}$ reaction is carried out using modern quantum chemical computations, extending beyond the H-abstraction pathway to include additional channels such as OH abstraction and substitution processes involving the exchange of a single atom (H) as well as entire functional groups (OH, CH_3 , and CH_2OH) considering the possibility of Walden and front-side mechanisms. Beyond the reactants, all relevant stationary points are identified along the different reaction pathways, including transition states, post-reaction complexes, and the corresponding products, along with additional conformers associated with each species. The most accurate geometries are obtained at the CCSD(T)-F12b/aug-cc-pVDZ theoretical level, followed by single-point CCSD(T)-F12b/aug-cc-pVTZ and CCSD(T)-F12b/aug-cc-pVQZ energy computations. The resulting quadruple-zeta energies are refined by including five additional contributions, namely post-CCSD(T) correlation corrections ($\delta[\text{T}]$ and $\delta[\text{Q}]\text{]}$), core-correlation, scalar relativistic effects, and spin-orbit coupling, yielding benchmark classical energies, from which adiabatic energies are derived by incorporating zero-point energy corrections. Comparison of our theoretical adiabatic reaction enthalpies with experimental values derived from the ATcT database for ten product channels reveals outstanding agreement, demonstrating the high accuracy of the present calculations.

Received 12th May 2026,
Accepted 13th September 2026

DOI: 10.1039/d6cp01759b

rsc.li/pccp

1. Introduction

Alcohols constitute an important member of the family of oxygenated volatile organic compounds (OVOCs) that are present in the atmosphere due to both biogenic and anthropogenic emissions. Ethanol, in particular, is released into the atmosphere from emissions originating from living and decaying vegetation and biomass burning, as well as from human activities such as its use as an industrial solvent and its increasing application as a biofuel and fuel additive.^{1–5} In the atmosphere, ethanol undergoes oxidation processes leading to the formation of aldehydes, ketones, and other oxygenated products, thereby contributing, *via* complex reaction pathways, to the formation of secondary pollutants including tropospheric ozone. This oxidation is initiated by reactive oxidants, including chlorine (Cl) radicals, which are formed through the photolysis of chlorine-containing species and heterogeneous reactions involving sea-salt aerosols.^{6–10} Around the early 2000s, several researchers investigated the title reaction from a kinetic perspective,^{11–13} others focused on its dynamics,¹⁴ while some works complemented experimental investigations with theoretical calculations aimed at characterizing

stationary points and their structures on the underlying potential energy surface (PES), with their attention predominantly restricted to the hydrogen (H) abstraction pathway.^{15,16} However, the $\text{Cl} + \text{C}_2\text{H}_5\text{OH}$ system is not limited to the H-abstraction processes, and at sufficiently high energies, alternative reaction pathways may become accessible, including abstraction of the hydroxyl (OH) group as well as substitution reactions, in which either single atom (H) or functional groups (OH, CH_3 , CH_2OH) can be exchanged. To explore additional reaction pathways beyond H abstraction, modern computational chemistry provides a powerful framework, and therefore the present study aims to obtain a detailed and high-level *ab initio* characterization of the key stationary points and energetics of the system by employing state-of-the-art quantum chemical methods, including geometry optimizations and energy computations utilizing the gold-standard CCSD(T) method and its F12 variant in conjunction with correlation-consistent basis sets. Previous studies on the $\text{Cl} + \text{C}_2\text{H}_5\text{OH}$ reaction provide a solid foundation for the present work,^{15,16} and, in addition, earlier investigations in our research group on reactions of the Cl atom with smaller organic molecules, in which not only H abstraction but also higher-energy pathways were identified, offer valuable guidance for revealing the stationary points associated with all relevant reaction channels of the title system.^{17–19} The results obtained in the present work provide a comprehensive description of the stationary point structures and the topology of the PES across all possible reaction channels,

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and establish a reliable basis for future PES developments, thereby enabling subsequent investigations of the reaction dynamics.

II. Computational details

The stationary points are initially identified using the second-order Møller-Plesset perturbation theory (MP2)²⁰ with the augmented correlation-consistent polarized-valence-double-zeta (aug-cc-pVDZ)²¹ basis set, followed by geometry optimizations with the explicitly-correlated coupled-cluster singles, doubles and perturbative triples method (CCSD(T)-F12b)²² utilizing the same basis set, with harmonic frequency computations performed at the corresponding levels of theory to confirm the nature of the stationary points. To enhance basis set convergence, energies are further refined at the most accurate geometries using the CCSD(T)-F12b method in conjunction with the larger aug-cc-pVTZ²¹ and aug-cc-pVQZ²² basis sets. To approach chemical accuracy, additional single-point computations are performed, including the effects of post-CCSD(T) correlation, core electron correlation, scalar relativistic effects, and spin-orbit coupling. The post-CCSD(T) correlation correction is determined using the CCSD(T),²³ CCSDT,²⁴ and CCSDT(Q)²⁵ methods in combination with the cc-pVDZ basis set, according to the following equations:

$$\delta[\text{T}] = \Delta E(\text{CCSDT/cc-pVDZ}) - \Delta E(\text{CCSD(T)/cc-pVDZ}) \quad (1)$$

and

$$\delta[(\text{Q})] = \Delta E(\text{CCSDT(Q)/cc-pVDZ}) - \Delta E(\text{CCSDT/cc-pVDZ}) \quad (2)$$

To account for core electron effects, all-electron (AE) calculations are carried out, in which not only the valence electrons, as in the frozen-core (FC) approach, but also the 1s² electrons of the carbon and oxygen atoms and the 2s²2p⁶ electrons of the chlorine atom are correlated, and the corresponding correction is then derived as the difference between the AE and FC energies computed at the CCSD(T)-F12b/cc-pCVTZ-F12²⁶ level of theory, according to the following expression:

$$\begin{aligned} \Delta_{\text{core}} = & \Delta E(\text{AE-CCSD(T)-F12b/cc-pCVTZ-F12}) \\ & - \Delta E(\text{FC-CCSD(T)-F12b/cc-pCVTZ-F12}) \end{aligned} \quad (3)$$

The scalar relativistic effect is determined as the difference between second-order Douglas-Kroll (DK)²⁷ relativistic AE energies and the corresponding non-relativistic AE values, as given by the following formula:^{23,28}

$$\begin{aligned} \Delta_{\text{rel}} = & \Delta E(\text{DK-AE-CCSD(T)/aug-cc-pwCVTZ-DK}) \\ & - \Delta E(\text{AE-CCSD(T)/aug-cc-pwCVTZ}) \end{aligned} \quad (4)$$

The spin-orbit (SO) contribution is obtained based on the Breit-Pauli Hamiltonian within the interacting-states approach,²⁹ using the Davidson-corrected³⁰ multi-reference configuration interaction³¹ (MRCI+Q) method with the aug-cc-pwCVTZ basis set in the AE treatment. Note that the Davidson correction (+Q) is only applied to the diagonal elements of the SO matrix. In the MRCI computations, 3 doublet states are considered and an active

space comprising 27 valence electrons distributed among 14 spatial orbitals is employed, while the 1s-like core molecular orbital of the chlorine atom is kept frozen. The SO correction is calculated as the difference between the relativistic spin-orbit (SO1) and non-relativistic (non-SO1) ground states as follows:

$$\begin{aligned} \Delta_{\text{SO}} = & \text{SO1}(\text{MRCI+Q/aug-cc-pwCVTZ}) \\ & - \text{non-SO1}(\text{MRCI+Q/aug-cc-pwCVTZ}) \end{aligned} \quad (5)$$

The benchmark classical energies are constructed by combining the most accurate single-point energies with the computed correction terms, as given by the following expression:

$$\begin{aligned} \Delta E_{\text{Classical}} = & \Delta E(\text{CCSD(T)-F12b/aug-cc-pVQZ}) \\ & + \delta[\text{T}] + \delta[(\text{Q})] + \Delta_{\text{core}} + \Delta_{\text{rel}} + \Delta_{\text{SO}} \end{aligned} \quad (6)$$

The benchmark adiabatic energies are obtained by adding zero-point energy (ZPE) corrections, derived from harmonic frequency computations at the CCSD(T)-F12b/aug-cc-pVDZ level of theory, to the benchmark classical energies, as described by the following equation:

$$\Delta E_{\text{Adiabatic}} = \Delta E_{\text{Classical}} + \Delta \text{ZPE} \quad (7)$$

Apart from the CCSD(T), CCSDT, and CCSDT(Q) computations, which are carried out using the MRCC^{32,33} code interfaced to MOLPRO, all other computations are performed with the MOLPRO program package.³⁴ For the AE and F12 coupled-cluster calculations, ROHF orbitals are used as the reference, whereas UHF orbitals are employed for the MP2 and post-CCSD(T) correction calculations. Default convergence criteria are used for the HF computations and geometry optimizations and the CCSD(T)-F12b method utilizes the standard preset auxiliary basis sets as defined in MOLPRO 2015.1.³⁴

III. Results and discussion

The left panel of Fig. 1 shows the schematic potential energy profiles of four distinct H-abstraction pathways of the Cl(²P_{3/2}) + C₂H₅OH reaction, including both classical and adiabatic energies, considering only the lowest-energy conformers of the transition states (TSs) and post-reaction minima (PMs). H abstraction can proceed from different sites of the ethanol molecule, namely from the hydroxyl (OH) group, the methylene (CH₂) group, and two nonequivalent positions of the methyl (CH₃) group corresponding to H atoms in *trans* and same-side orientations relative to the OH group, consistent with the C_s point-group symmetry of ethanol. The most favorable pathway corresponds to H abstraction from the CH₂ group of ethanol, proceeding *via* a very low barrier with classical(adiabatic) barrier height of −7.72(−11.01) kcal mol^{−1}. The reaction is further driven thermodynamically by its exothermic character, as both syn and anti conformers of the CH₃CHOH + HCl product pair lie lower in energy than the reactants. The anti-CH₃CHOH + HCl products are stabilized by 4.38(8.80) kcal mol^{−1}, while the syn-CH₃CHOH + HCl products lie 4.06(8.51) kcal mol^{−1} below the reactants. In addition, a post-reaction minimum (H abs H6 PM)

Hydrogen abstraction

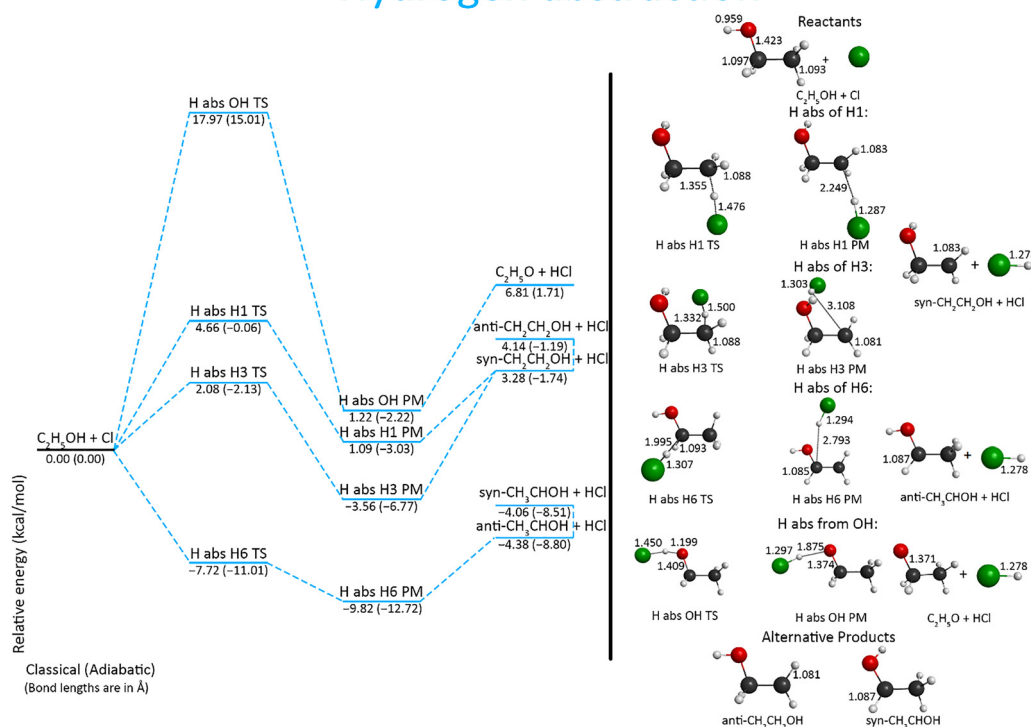


Fig. 1 Schematic potential energy surface for the hydrogen-abstraction pathways of the $Cl(^2P_{3/2}) + C_2H_5OH$ reaction shown in the left panel, while the right panel presents the CCSD(T)-F12b/aug-cc-pVDZ structures of the corresponding transition states (TSs) and minima, including reactants, post-reaction complexes (PMs), and products, with key bond lengths indicated. For the transition states and post-reaction complexes, only the lowest-energy conformers are depicted.

is located along the exit channel, connecting the transition state to the products on the PES, with classical(adiabatic) energy of $-9.82(-12.72)$ kcal mol $^{-1}$. H abstraction from the CH_3 group can occur at two different positions of the ethanol molecule, however, both pathways lead to the same product channel, which appears endothermic classically, while inclusion of zero-point energy corrections renders the process slightly exothermic. In contrast to abstraction from the CH_2 group, the resulting $CH_2CH_2OH + HCl$ products exhibit a reversed conformational stability order, with syn and anti conformers having relative classical(adiabatic) energies of $3.28(-1.74)$ and $4.14(-1.19)$ kcal mol $^{-1}$, respectively. Among the two methyl-H abstraction pathways, the channel involving H removal from the same-side position relative to the OH group is energetically more favorable than that from the *trans* position. This preference is reflected in both the transition states and the post-reaction complexes. The corresponding barrier heights are $2.08(-2.13)$ kcal mol $^{-1}$ for the same-side H abstraction (H abs H3 TS) and $4.66(-0.06)$ kcal mol $^{-1}$ for the *trans* (H abs H1 TS) pathway. A similar trend is observed for the post-reaction minima, which lie at $-3.56(-6.77)$ kcal mol $^{-1}$ and $1.09(-3.03)$ kcal mol $^{-1}$ relative to the reactants for the same-side (H abs H3 PM) and *trans* (H abs H1 PM) pathways, respectively. Among the H-abstraction pathways, the highest barrier is associated with H removal from the alcoholic OH group (H abs OH TS), with relative classical(adiabatic) energy of $17.97(15.01)$ kcal mol $^{-1}$ with respect to the reactants. The corresponding post-reaction minimum (H abs OH PM) lies at

$1.22(-2.22)$ kcal mol $^{-1}$ relative to the reactants, whereas the $C_2H_5O + HCl$ products are located at $6.81(1.71)$ kcal mol $^{-1}$. The right panel of Fig. 1 displays the CCSD(T)-F12b/aug-cc-pVDZ optimized geometries of the stationary points depicted in the energy profiles, with the most relevant forming and breaking bond lengths highlighted. Among the four H abstraction pathways, three correspond to H removal from a carbon center of the ethanol molecule. Inspection of the transition-state geometries reveals that H abstraction from the CH_3 group proceeds through two distinct transition states (H abs H3 TS and H abs H1 TS), exhibiting nearly identical C-H bond elongations of 1.332 and 1.355 Å, respectively. The forming H-Cl distances are likewise similar, 1.500 and 1.476 Å, indicating a close structural resemblance between the two transition states. In contrast, H abstraction from the CH_2 group leads to a markedly different transition-state geometry. In the H abs H6 TS, the breaking C-H bond is significantly more elongated, while the forming H-Cl bond is notably shorter compared to the methyl-H abstraction cases. The transition state is shifted toward the products along the reaction coordinate, as reflected by the bond lengths of the reactants and products, where the C-H bond length in ethanol is 1.097 Å, whereas the H-Cl bond length in the HCl molecule is 1.278 Å. Furthermore, a clear structural difference is observed in the orientation of the hydroxyl group. For the transition states associated with methyl-H-abstraction (H abs H3 TS and H abs H1 TS), the H atom of the OH group is oriented nearly

perpendicular to the OCC plane. In contrast, in the H abs H6 TS corresponding to methylene-H abstraction, the H of the OH group lies approximately in the OCC plane. Such a difference in orientation may contribute to the significantly more favorable kinetics of H abstraction from the CH₂ group. The fourth H abstraction pathway involves H removal from the hydroxyl group, where in the corresponding transition state, the forming H–Cl bond distance is 1.450 Å, while the breaking O–H bond is significantly elongated from 0.959 Å in the reactant to 1.199 Å. For the post-reaction minima, a general trend can be observed across all abstraction pathways, where the forming H–Cl bond distances approach closely the equilibrium bond length of the HCl product. Among the carbon-centered abstraction cases, the smallest difference between the H–Cl bond lengths in the post-reaction minimum and in the product is found for H abs H1 PM, amounting to only 0.009 Å, with the departing H atom remaining relatively close to the carbon atom at a C–H distance of 2.249 Å. By contrast, in the other carbon-centered post-reaction minima, the H atom is located significantly farther from the carbon center. The corresponding C–H distances increase to 2.793 Å for H abs H6 PM and 3.108 Å for H abs H3 PM, respectively. For the carbon-centered H-abstraction pathways, both syn and anti conformers of the products have been identified. In the case of CH₂–H abstraction, the two conformers differ primarily in the spatial orientation of the hydroxyl group. In contrast, for CH₃–H abstraction, the structural differences extend beyond the hydroxyl group, as the orientation of the remaining CH₂ fragment also varies between the conformers. An additional degree of structural variation may contribute to the observed difference in conformational stability, where the syn conformer is thermodynamically favored for CH₃–H

abstraction, whereas the stability order is reversed for CH₂–H abstraction, with the anti conformer being lower in energy.

The left panel of Fig. 2 presents the schematic potential energy profiles of the H-substitution pathways in the Cl(²P_{3/2}) + C₂H₅OH reaction, including both classical and adiabatic energies, with only the lowest-energy conformers of the transition states and post-reaction minima depicted. H substitution occurs at two distinct sites of the ethanol molecule, involving the hydroxyl (OH) group as well as the methyl (CH₃) group, the latter proceeding *via* two different mechanistic pathways, namely Walden inversion and front-side mechanism, where in the former the departing H atom leaves opposite to the attacking Cl atom, while in the latter both the attack of Cl and the departure of H take place on the same side. The transition states associated with all three substitution pathways lie significantly above the reactants in energy. The lowest barrier corresponds to the Walden-inversion mechanism, with a classical(adiabatic) barrier height of 42.96(38.96) kcal mol^{−1}, followed by the front-side pathway, which is higher in energy by 15.18(14.94) kcal mol^{−1}. The most kinetically hindered route is H substitution at the OH group, exceeding the front-side barrier by an additional 9.41(8.35) kcal mol^{−1}, corresponding to an energy of 67.55(62.25) kcal mol^{−1} above the reactants classically(adiabatically). Progressing along the reaction coordinate from the transition state toward the post-reaction complex, the potential energy decreases by 6.90(7.22) kcal mol^{−1} in the case of H substitution at the OH group of the ethanol molecule. A much more pronounced stabilization is observed for substitution at the CH₃ group. For the Walden-inversion pathway, the post-reaction complex lies at 22.02(16.97) kcal mol^{−1} relative to the reactants, corresponding to a decrease in energy of

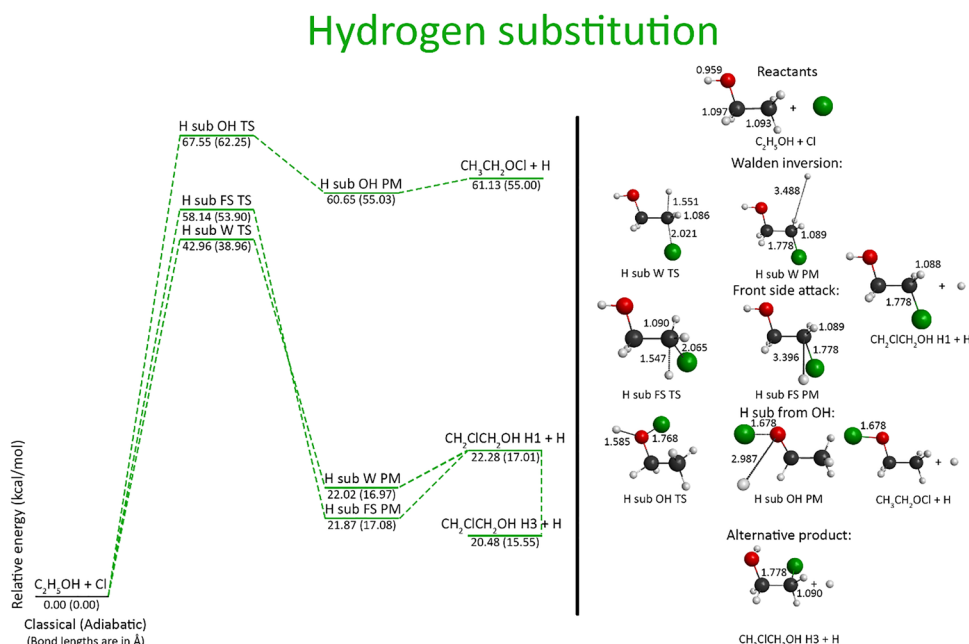


Fig. 2 Schematic potential energy surface for the hydrogen-substitution pathways of the Cl(²P_{3/2}) + C₂H₅OH reaction shown in the left panel, while the right panel presents the CCSD(T)-F12b/aug-cc-pVDZ structures of the corresponding transition states (TSs) and minima, including reactants, post-reaction complexes (PMs), and products, with key bond lengths indicated. For the transition states and post-reaction complexes, only the lowest-energy conformers are depicted.

20.94(21.99) kcal mol⁻¹ from the transition state, whereas in the front-side mechanism, the post-reaction complex is located at 21.87(17.08) kcal mol⁻¹ relative to the reactants, reflecting a substantially larger decrease in energy of 36.27(36.82) kcal mol⁻¹ along the reaction coordinate. H-substitution pathways, involving both oxygen- and carbon-centered processes, are endothermic, with the latter exhibiting a significantly lower degree of endothermicity. In the carbon-centered case, the CH₂ClCH₂OH H1 + H products lie at 22.28(17.01) kcal mol⁻¹ above the reactant, with the initially formed CH₂ClCH₂OH H1 conformer can undergo conformational relaxation to the more stable CH₂ClCH₂OH H3 structure, which is lower in energy by 1.80(1.46) kcal mol⁻¹ classically(adiabatically). In contrast, oxygen-centered H substitution is substantially more thermodynamically disfavored, with the CH₃CH₂OCl + H products lying 61.13(55.00) kcal mol⁻¹ above the reactants. The right panel of Fig. 2 illustrates the CCSD(T)-F12b/aug-cc-pVDZ optimized structures of the stationary points associated with the H-substitution pathways, with the key forming and breaking bond lengths indicated. Examination of the transition-state geometries reveals that for carbon-centered H substitution, the breaking C–H bond lengths are nearly identical for the two mechanisms, differing by only 0.004 Å. In contrast, oxygen-centered substitution is characterized by a significantly greater elongation of the breaking O–H bond, which increases from 0.959 Å in the reactant to 1.585 Å in the transition state. A comparison of the transition-state geometries for the Walden-inversion and front-side mechanisms of H substitution at the CH₃ group reveals that the position of the Cl atom relative to the carbon center differs only slightly, with C–Cl distances of 2.021 and 2.065 Å for the Walden-inversion and front-side pathways, respectively. Observation of the post-reaction complexes identified along the exit channel reveals that the departing H atom is located farthest from its original bonding center in the carbon-centered Walden-inversion pathway among the H-substitution pathways, with a C–H distance of 3.448 Å. In the front-side mechanism, the

C–H bond is slightly less elongated, corresponding to a distance of 3.396 Å. Finally, oxygen-centered H substitution exhibits the smallest extent of bond elongation, with the breaking O–H bond reaching a distance of 2.987 Å in the post-reaction complex. Inspection of the product structures reveals that the newly forming C–Cl bond distances are already established in the corresponding post-reaction complexes. Furthermore, in the carbon-centered H-substitution pathway, the initially formed CH₂ClCH₂OH H1 product can stabilize in a lower-energy conformation through internal rotation of the CH₂Cl group by approximately 60°, accompanied by a reorientation of the hydroxyl-H, which moves away from the CCO plane and approaches the Cl atom of the CH₂Cl group.

The left panel of Fig. 3 shows the schematic potential energy profiles of the OH-abstraction and OH-substitution pathways of the Cl(²P_{3/2}) + C₂H₅OH reaction, including both classical and adiabatic energies, with only the lowest-energy conformers of the transition states and post-reaction minima depicted, where the OH-abstraction pathway is traced along the magenta curve and the OH-substitution pathway is indicated in purple. Both reaction pathways are associated with substantial energy barriers, amounting to 38.27(36.42) kcal mol⁻¹ for OH-substitution (OH sub TS) and 46.97(42.99) kcal mol⁻¹ for OH-abstraction (OH abs TS), indicating a reversal of the kinetic preference: abstraction is favored over substitution for single H removal, whereas for the OH group, substitution becomes the less hindered pathway. Both reaction pathways are endothermic, with the relative energy of the C₂H₅Cl + OH products formed *via* OH-substitution being 11.97(8.90) kcal mol⁻¹, while the C₂H₅ + HOCl products of OH-abstraction lie significantly higher, at 42.01(37.31) kcal mol⁻¹ above the reactants classically(adiabatically). It is also worth noting that, along the exit channel of OH-abstraction, a post-reaction complex is identified that connects the transition state to the products, lying only 1.09(0.38) kcal mol⁻¹ below the product energy classically(adiabatically). The right panel of Fig. 3 presents the CCSD(T)-F12b/aug-cc-pVDZ optimized geometries of the stationary points

OH abstraction and substitution

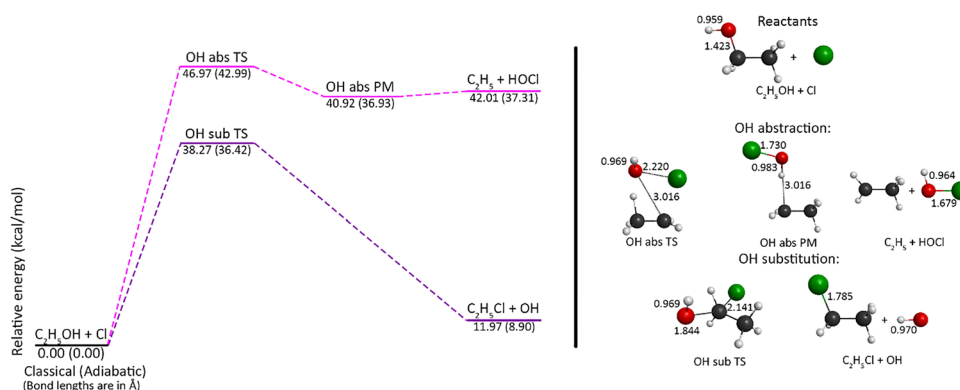


Fig. 3 Schematic potential energy surface for the OH-abstraction and substitution pathways of the Cl(²P_{3/2}) + C₂H₅OH reaction shown in the left panel, while the right panel presents the CCSD(T)-F12b/aug-cc-pVDZ structures of the corresponding transition states (TSs) and minima, including reactants, post-reaction complexes (PMs), and products, with key bond lengths indicated. For the transition states and post-reaction complexes, only the lowest-energy conformers are depicted.

corresponding to the OH-abstraction and OH-substitution pathways, with the most relevant forming and breaking bond lengths highlighted. Comparison of the transition-state geometries reveals that the forming bond distances differ only marginally between the two pathways, with the Cl–O bond in OH-abstraction and the Cl–C bond in OH-substitution differing by merely 0.079 Å. In contrast, a pronounced difference is observed for the breaking bonds: while in OH-substitution the O–C distance increases to 1.844 Å, in OH-abstraction the same bond is significantly more elongated, reaching 3.016 Å, corresponding to an approximately 2.2-fold increase relative to its equilibrium value in ethanol. In the post-reaction complex of the OH-abstraction pathway, the forming HOCl molecule undergoes a significant spatial reorientation relative to the transition state, with the oxygen atom of HOCl positioned 3.016 Å from the carbon atom, resulting in an O··C–C angle of approximately 90°. Comparison of the transition-state geometries with the corresponding reactant and product structures reveals similar characteristics for the two pathways. In the case of OH-abstraction, the reaction exhibits a late-barrier character, as the transition-state geometry more closely resembles the products: the O–C bond is significantly elongated relative to its equilibrium value in ethanol, while the forming Cl–O bond remains closer to its value in the HOCl product. Similarly to OH abstraction, a late-barrier character can also be assigned to OH substitution, as the O–C bond is more significantly elongated in the transition state relative to its equilibrium value in ethanol than the forming Cl–C bond is to its corresponding value in the products.

The left panel of Fig. 4 presents the schematic potential energy profiles of the methyl (CH_3) and hydroxymethyl (CH_2OH) substitution pathways of the $\text{Cl}(^2\text{P}_{3/2}) + \text{C}_2\text{H}_5\text{OH}$ reaction, including

both classical and adiabatic energies, with the lowest-energy conformers of the transition states and post-reaction minima shown, where the CH_3 pathway is depicted in red, whereas the CH_2OH pathway is shown in orange. In analogy with H substitution, the CH_3 and CH_2OH group-substitution pathways can be distinguished as proceeding *via* Walden-inversion and front-side mechanisms as well. The lowest barrier among the substitution pathways is found for the Walden-type CH_2OH substitution, with the corresponding transition state located at 28.84(27.65) kcal mol^{−1} relative to the reactants classically(adiabatically). A considerably higher barrier is obtained for the front-side mechanism of the same pathway, exceeding the Walden barrier by 15.56(15.07) kcal mol^{−1}. In the case of CH_3 substitution, only the Walden-type transition state is identified, with a barrier of 34.74(32.16) kcal mol^{−1}, lying between the two CH_2OH substitution channels. Progressing along the reaction coordinate, the relative energies of the post-reaction minima reveal a reversal in the ordering of the two mechanisms for CH_2OH substitution compared to the transition states. While the front-side post-complex lies at 1.28(−0.58) kcal mol^{−1}, the corresponding Walden-type minimum is located higher in energy at 4.36(1.96) kcal mol^{−1} above the reactants classically(adiabatically). In analogy with the transition-state energetics, the post-reaction minimum corresponding to CH_3 substitution is positioned between the Walden and front-side CH_2OH substitution complexes, whereas the intermediate is found along the front-side pathway. Both product channels are endothermic, with the $\text{CH}_3\text{Cl} + \text{CH}_2\text{OH}$ products formed *via* CH_2OH substitution lying at 6.28(3.30) kcal mol^{−1} classically(adiabatically), slightly below the $\text{CH}_3 + \text{CH}_2\text{ClOH}$ products of CH_3 substitution by 1.27(0.01) kcal mol^{−1}. The right panel of Fig. 4 illustrates the CCSD(T)-F12b/aug-cc-pVDZ

Methyl and hydroxymethyl substitution

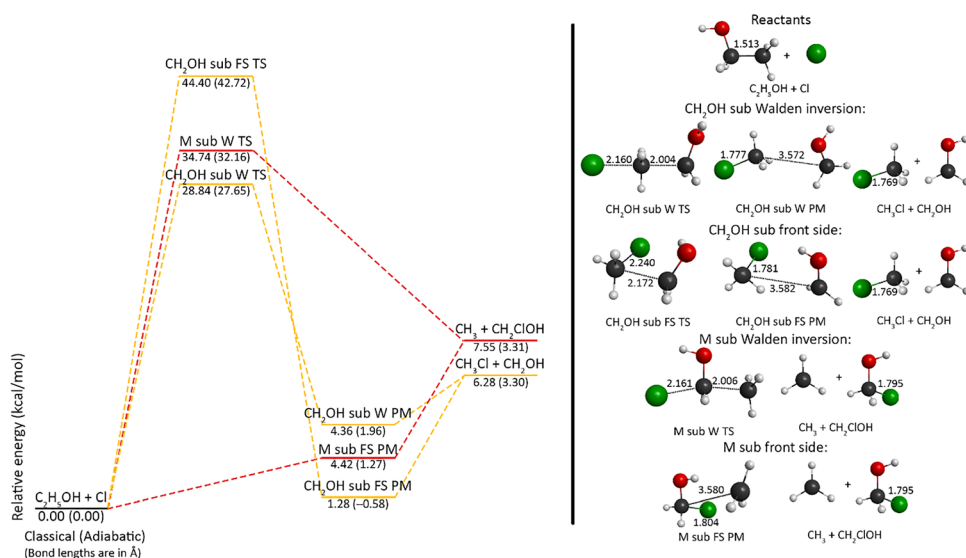


Fig. 4 Schematic potential energy surface for the methyl- and hydroxymethyl-substitution pathways of the $\text{Cl}(^2\text{P}_{3/2}) + \text{C}_2\text{H}_5\text{OH}$ reaction shown in the left panel, while the right panel presents the CCSD(T)-F12b/aug-cc-pVDZ structures of the corresponding transition states (TSs) and minima, including reactants, post-reaction complexes (PMs), and products, with key bond lengths indicated. For the transition states and post-reaction complexes, only the lowest-energy conformers are depicted.

optimized geometries of the stationary points along the CH₃ and CH₂OH substitution pathways, with key forming and breaking bond lengths highlighted. Comparison of the forming and breaking bond lengths in the Walden-type transition states for CH₃ and CH₂OH substitution reveals a remarkable structural similarity. The forming Cl–C bond distances are 2.161 and 2.160 Å, respectively, differing by only 0.001 Å, while the breaking C–C bonds measure 2.006 and 2.004 Å, corresponding to a difference of merely 0.002 Å. In the front-side transition state for CH₂OH substitution, both the forming and breaking bond distances are slightly longer, with the Cl–C bond being 2.240 Å and the C–C bond extending to 2.172 Å. Such elongation can be attributed to increased steric hindrance, as the attacking Cl atom approaches above the C–C bond in close proximity to the O atom of the OH group. Examination of the post-reaction complexes shows that the steric effects observed in the transition states are no longer present, as the forming and breaking bond distances become nearly identical within 0.01 Å, independent of the substitution site (CH₃ or CH₂OH) and the reaction mechanism (Walden or front-side). Finally, comparison of the product structures with the corresponding transition states indicates that both group-substitution pathways proceed *via* late-barrier mechanisms, as evidenced by the more pronounced elongation of the C–C bond relative to its equilibrium value in ethanol, compared to the smaller deviation of the forming Cl–C bond from its product value, together with the product-like orientation of the OH group already present in the transition-state geometries.

To obtain an overall picture of the topology of the PES of the Cl(²P_{3/2}) + C₂H₅OH system, one-dimensional potential energy scans of the entrance channel are performed for six different reactant orientations at the CCSD(T)-F12b/aug-cc-pVDZ level of theory by varying a selected intermolecular atom–atom

distance, as illustrated in Fig. 5. The six orientations can be classified into three groups according to the direction of the Cl-atom approach. The first group corresponds to approaches along the C–C bond axis, either from the CH₃ or the CH₂OH side of the ethanol molecule. The corresponding potential energy profiles are very similar, exhibiting shallow minima slightly deeper than 1 kcal mol^{−1}. The minimum is located at a C···Cl distance of approximately 3.3 Å for the CH₃-side approach, whereas it shifts to a slightly larger separation when Cl approaches from the CH₂OH side, which can be attributed to the larger steric demand of the CH₂OH group. The second group comprises three orientations in which the Cl atom approaches one of the non-equivalent hydrogen atoms of the carbon backbone along the corresponding C–H bond. Among these, the approach toward the hydrogen atom of the CH₂ group results in the deepest minimum, with a well depth of approximately 1.5 kcal mol^{−1} located at an H···Cl distance of about 2.0 Å. In contrast, the two approaches toward the non-equivalent hydrogen atoms of the CH₃ group produce very similar potential energy curves, both exhibiting minima at H···Cl distances of approximately 2.8 Å with well depths slightly below 1 kcal mol^{−1}. The remaining orientation involves the hydroxyl group. The approach toward the oxygen atom from the methyl side of the ethanol molecule gives rise to the deepest potential well among all orientations considered, with a depth of approximately 2.8 kcal mol^{−1} located at an O···Cl distance of about 3.0 Å.

The computed electronic structure data are summarized in Table 1 for the saddle points and in Table 2 for the minima, including post-reaction complexes and products, with all identified conformers taken into account. *T*₁-diagnostic³⁵ values

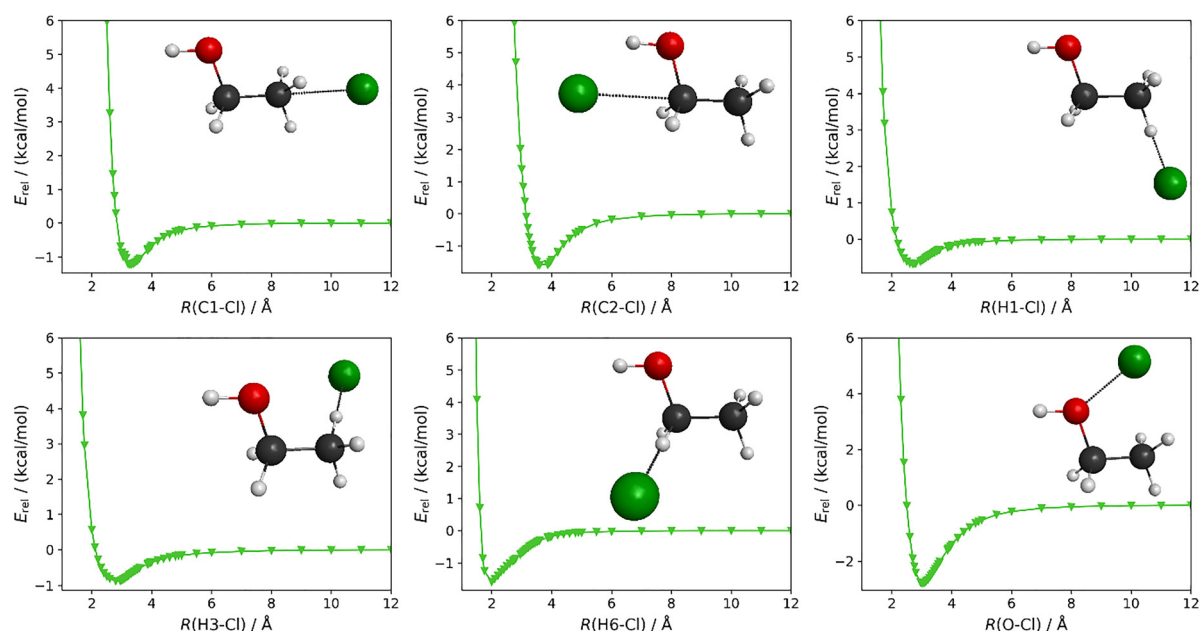


Fig. 5 One-dimensional potential energy curves for the entrance channel of the Cl(²P_{3/2}) + C₂H₅OH system, obtained by varying the intermolecular distance (dotted bond) between the reactants for six different orientations at the CCSD(T)-F12b/aug-cc-pVDZ level of theory, with the ethanol molecule kept at its equilibrium geometry.

Table 1 Relative energies (in kcal mol^{−1}) of the transition states identified in the Cl(²P_{3/2}) + C₂H₅OH system with respect to the reactants, together with the corresponding correction terms, computed at different levels of theory

Stationary point	MP2	CCSD(T)-F12b			$\delta[T]^e$	$\delta[(Q)]^f$	Δ_{core}^g	Δ_{rel}^h	Δ_{SO}^i	$E_{\text{Classical}}^j$	Δ_{ZPE}^k	$E_{\text{Adiabatic}}^l$
	DZ ^a	DZ ^b	TZ ^c	QZ ^d								
H abs H1 TS	5.29	3.55	4.16	4.10	−0.17	−0.17	−0.02	0.10	0.82	4.66	−4.72	−0.06
H abs H1 TS 2	5.30	3.56	4.18	4.11	−0.17	−0.17	−0.02	0.10	0.82	4.67	−4.64	0.03
H abs H1 TS 3	5.71	4.23	4.89	4.82	−0.14	−0.15	−0.03	0.11	0.82	5.43	−4.97	0.46
H abs H3 TS	2.70	0.93	1.61	1.53	−0.15	−0.16	−0.06	0.10	0.82	2.08	−4.21	−2.13
H abs H3 TS 2	3.10	0.62	1.63	1.59	−0.10	−0.06	−0.05	0.24	0.83	2.45	−4.42	−1.97
H abs H3 TS 3	4.86	3.17	3.83	3.76	−0.13	−0.14	−0.06	0.11	0.82	4.36	−4.67	−0.31
H abs H3 TS 4	5.74	3.96	4.63	4.57	−0.14	−0.14	−0.05	0.10	0.82	5.16	−4.66	0.50
H abs H6 TS	−6.66	−9.33	−8.34	−8.41	−0.12	−0.09	−0.16	0.23	0.83	−7.72	−3.29	−11.01
H abs H6 TS 2	−6.07	−8.86	−7.90	−7.96	−0.13	−0.10	−0.16	0.24	0.83	−7.28	−3.22	−10.50
H abs H6 TS 3	−3.38	−6.09	−5.10	−5.14	−0.12	−0.08	−0.15	0.24	0.83	−4.42	−3.95	−8.37
H abs H6 TS 4	−2.03	−4.67	−3.64	−3.68	−0.11	−0.06	−0.16	0.25	0.83	−2.93	−4.48	−7.41
H abs OH TS	17.79	16.11	17.66	17.54	−0.19	−0.21	−0.11	0.11	0.83	17.97	−2.96	15.01
OH abs TS	55.39	46.96	48.01	48.04	−1.03	−0.92	0.15	−0.10	0.83	46.97	−3.98	42.99
OH abs TS 2	85.54	77.63	78.43	78.20	−0.54	−0.25	0.22	−0.01	0.83	78.45	−4.64	73.81
H sub W TS	43.54	41.83	42.42	42.35	−0.23	−0.29	0.22	0.09	0.82	42.96	−4.00	38.96
H sub W TS 2	43.85	41.83	42.35	42.28	−0.26	−0.30	0.23	0.08	0.82	42.85	−3.99	38.86
H sub FS TS	60.34	57.11	57.81	57.77	−0.34	−0.32	0.19	0.02	0.82	58.14	−4.24	53.90
H sub OH TS	74.47	66.07	67.32	67.38	−0.26	−0.52	0.20	−0.07	0.82	67.55	−5.30	62.25
OH sub TS	46.56	38.21	38.37	38.47	−0.78	−0.50	0.32	−0.07	0.83	38.27	−1.85	36.42
M sub W TS	38.17	34.17	34.36	34.30	−0.45	−0.35	0.36	0.07	0.81	34.74	−2.58	32.16
CH ₂ OH sub W TS	32.91	28.58	28.48	28.38	−0.43	−0.33	0.34	0.07	0.81	28.84	−1.19	27.65
CH ₂ OH sub FS TS	51.33	44.05	44.45	44.41	−0.70	−0.49	0.29	0.07	0.82	44.40	−1.68	42.72
CH ₂ OH sub FS TS 2	59.02	51.06	51.67	51.66	−0.69	−0.42	0.32	0.04	0.82	51.73	−1.63	50.10

^a MP2/aug-cc-pVDZ relative energies based on MP2/aug-cc-pVDZ structures. ^b CCSD(T)-F12b/aug-cc-pVDZ relative energies based on CCSD(T)-F12b/aug-cc-pVDZ structures. ^c CCSD(T)-F12b/aug-cc-pVTZ relative energies based on CCSD(T)-F12b/aug-cc-pVDZ structures. ^d CCSD(T)-F12b/aug-cc-pVQZ relative energies based on CCSD(T)-F12b/aug-cc-pVDZ structures. ^e CCSDT – CCSD(T) energies computed with the cc-pVDZ basis set at CCSD(T)-F12b/aug-cc-pVDZ structures. ^f CCSDT(Q) – CCSDT energies computed with the cc-pVDZ basis set at CCSD(T)-F12b/aug-cc-pVDZ structures. ^g Core-correlation correction determined as the difference of AE-CCSD(T)-F12b/cc-pCVTZ-F12 and FC-CCSD(T)-F12b/cc-pCVTZ-F12 relative energies at CCSD(T)-F12b/aug-cc-pVDZ structures. ^h Scalar relativistic correction determined as the difference between the DK-AE-CCSD(T)/aug-cc-pwCVTZ-DK and non-relativistic AE-CCSD(T)/aug-cc-pwCVTZ relative energies at CCSD(T)-F12b/aug-cc-pVDZ structures. ⁱ Spin-orbit correction determined as the energy difference between SO and non-SO ground-state utilizing MRCI+Q/aug-cc-pwCVTZ computations at CCSD(T)-F12b/aug-cc-pVDZ structures. ^j Benchmark classical relative energy determined as CCSD(T)-F12b/aug-cc-pVQZ + $\delta[T]$ + $\delta[(Q)]$ + Δ_{core} + Δ_{rel} + Δ_{SO} . ^k Δ_{ZPE} computed at the CCSD(T)-F12b/aug-cc-pVDZ level of theory. ^l Benchmark adiabatic relative energy determined as sum of $\Delta E_{\text{Classical}}$ and Δ_{ZPE} .

(<0.020) indicate that all the minima and H-abstraction TSs, except H abs OH TS (0.023), are well described by single-reference methods. The other TSs have T_1 values usually between 0.02 and 0.03, with three outliers, *i.e.*, OH abs TS (0.042), OH abs TS 2 (0.041), and OH sub TS (0.052). Nevertheless, we expect reasonable accuracy for these high-energy TSs as well, especially with the post-(T) correlation corrections. Comparison of the MP2 and coupled-cluster results reveals that the former approach systematically overestimates the relative energies of the transition states, a tendency that becomes particularly pronounced for higher-energy saddle points, as exemplified by the OH abs TS 2 stationary point, where the difference between the MP2/aug-cc-pVDZ and CCSD(T)-F12b/aug-cc-pVDZ levels reaches nearly 8 kcal mol^{−1}, in accordance with the large T_1 value. For minima, the same trend is not observed consistently, although MP2 still tends to overestimate the relative energies compared to the coupled-cluster results in most cases. For instance, for the H abs OH PM 2 post-reaction complex, the MP2/aug-cc-pVDZ method yields a relative energy higher by 6.74 kcal mol^{−1}, while for the HOCl + C₂H₅ products, the discrepancy between the two methods amounts to 7.07 kcal mol^{−1}, again with MP2 predicting higher energies. Opposite behavior can also be identified in certain cases for minima, where the MP2 method gives lower relative energies than the

coupled-cluster approach. Such a deviation is observed, for example, for the H sub W PM post-reaction complex, where the CCSD(T)-F12b/aug-cc-pVDZ level provides a relative energy higher by 1.56 kcal mol^{−1}. A similar tendency is observed for all H-substitution products in which H replacement occurs at the carbon backbone of the ethanol molecule, with MP2 consistently underestimating the relative energies compared to the coupled-cluster results. A clear basis-set convergence is observed for the CCSD(T)-F12b energies when comparing results obtained with multiple basis sets, as the differences between the double- and triple-zeta descriptions exceed 1 kcal mol^{−1} in several cases, whereas the transition from triple- to quadruple-zeta results in only minor changes, typically within 0.1 kcal mol^{−1}, except for a few cases, with the largest differences being the OH abs TS2 transition state (0.23 kcal mol^{−1}) and the CH₃Cl + CH₂OH products of the CH₂OH substitution pathway (0.20 kcal mol^{−1}). Examination of the post-CCSD(T) correlation corrections reveals that for most minima and for transition states associated with H abstraction from the carbon backbone of ethanol, both $\delta[T]$ and $\delta[(Q)]$ remain below 0.20 kcal mol^{−1}, whereas for other transition states the corrections generally exceed 0.25 kcal mol^{−1} in absolute value, with the largest contributions observed for the OH abs TS, where $\delta[T]$ and $\delta[(Q)]$ reach −1.03 and −0.92 kcal mol^{−1}, respectively.

Table 2 Relative energies (in kcal mol^{−1}) of the minima identified in the Cl(²P_{3/2}) + C₂H₅OH system with respect to the reactants, including post-reaction complexes and products, together with the corresponding correction terms, computed at different levels of theory

Stationary point	MP2	CCSD(T)-F12b			$\delta[\text{T}]^e$	$\delta[(\text{Q})]^f$	Δ_{core}^g	Δ_{rel}^h	Δ_{SO}^i	$E_{\text{Classical}}^j$	Δ_{ZPE}^k	$E_{\text{Adiabatic}}^l$
	DZ ^a	DZ ^b	TZ ^c	QZ ^d								
H abs H1 PM	1.73	−0.73	0.29	0.24	−0.11	−0.07	−0.03	0.23	0.83	1.09	−4.12	−3.03
H abs H1 PM 2	2.33	0.45	1.47	1.44	−0.09	−0.07	−0.01	0.23	0.83	2.33	−4.08	−1.75
H abs H3 PM	−3.63	−5.41	−4.31	−4.39	−0.09	−0.09	−0.07	0.25	0.83	−3.56	−3.21	−6.77
H abs H3 PM 2	−3.32	−5.11	−4.05	−4.14	−0.08	−0.08	−0.06	0.26	0.83	−3.27	−3.33	−6.60
H abs H3 PM 3	−2.56	−4.31	−3.22	−3.30	−0.07	−0.08	−0.07	0.26	0.83	−2.43	−3.59	−6.02
H abs H3 PM 4	−2.49	−4.27	−3.15	−3.23	−0.07	−0.07	−0.08	0.26	0.83	−2.36	−3.56	−5.92
H abs H3 PM 5	−0.02	−2.36	−1.31	−1.34	−0.10	−0.08	−0.05	0.23	0.83	−0.51	−3.59	−4.10
H abs H6 PM	−8.78	−11.49	−10.46	−10.54	−0.12	−0.08	−0.17	0.26	0.83	−9.82	−2.90	−12.72
H abs H6 PM 2	−8.45	−10.90	−9.90	−9.96	−0.12	−0.09	−0.16	0.23	0.83	−9.27	−3.08	−12.35
H abs OH PM	3.12	−0.74	0.41	0.44	−0.18	0.05	−0.06	0.14	0.83	1.22	−3.44	−2.22
H abs OH PM 2	6.08	−0.66	0.50	0.53	−0.19	0.04	−0.06	0.14	0.83	1.29	−2.86	−1.57
OH abs PM	45.93	39.08	40.34	40.30	−0.12	−0.20	0.06	0.05	0.83	40.92	−3.99	36.93
H sub W PM	18.00	19.56	21.09	21.04	0.08	−0.16	0.00	0.23	0.83	22.02	−5.05	16.97
H sub FS PM	17.89	19.63	20.96	20.90	0.08	−0.16	0.00	0.22	0.83	21.87	−4.79	17.08
H sub FS PM 2	18.02	19.39	21.09	21.02	0.08	−0.16	0.00	0.22	0.83	21.99	−4.92	17.07
H sub OH PM	60.13	58.10	59.88	59.93	0.08	−0.35	0.12	0.04	0.83	60.65	−5.62	55.03
H sub OH PM 2	60.28	58.32	60.06	60.08	0.08	−0.34	0.12	0.04	0.83	60.81	−5.86	54.95
H sub OH PM 3	60.78	58.72	60.51	60.54	0.07	−0.35	0.11	0.04	0.83	61.24	−5.49	55.75
H sub OH PM 4	60.95	58.74	60.53	60.54	0.07	−0.35	0.11	0.04	0.83	61.24	−5.76	55.48
M sub FS PM	5.95	2.53	3.52	3.48	−0.08	−0.09	0.11	0.17	0.83	4.42	−3.15	1.27
M sub FS PM 2	6.12	2.67	3.64	3.59	−0.07	−0.09	0.12	0.17	0.83	4.55	−3.24	1.31
M sub FS PM 3	7.09	3.78	4.81	4.74	−0.07	−0.08	0.11	0.17	0.83	5.70	−3.38	2.32
M sub FS PM 4	7.78	3.77	4.80	4.74	−0.07	−0.08	0.11	0.17	0.83	5.70	−3.38	2.32
M sub FS PM 5	7.82	2.53	3.52	3.48	−0.08	−0.09	0.11	0.17	0.83	4.42	−3.21	1.21
M sub FS PM 6	8.10	3.77	4.80	4.74	−0.07	−0.08	0.11	0.17	0.83	5.70	−3.35	2.35
CH ₂ OH sub W PM	7.61	2.90	3.59	3.47	−0.13	−0.07	0.03	0.23	0.83	4.36	−2.40	1.96
CH ₂ OH sub W PM 2	7.78	−0.10	0.72	0.63	−0.13	−0.09	−0.01	0.22	0.83	1.45	−2.01	−0.56
CH ₂ OH sub W PM 3	7.79	−0.27	0.55	0.47	−0.14	−0.09	−0.01	0.22	0.83	1.28	−1.82	−0.54
CH ₂ OH sub FS PM	4.58	−0.27	0.55	0.47	−0.14	−0.09	−0.01	0.22	0.83	1.28	−1.86	−0.58
CH ₂ OH sub FS PM 2	6.74	2.14	2.98	2.87	−0.14	−0.08	0.01	0.23	0.83	3.72	−2.16	1.56
CH ₂ OH sub FS PM 3	7.83	2.14	2.98	2.88	−0.13	−0.08	0.01	0.23	0.83	3.74	−2.29	1.45
HCl + anti-CH ₂ CH ₂ OH	5.28	2.51	3.31	3.21	−0.08	−0.04	−0.01	0.23	0.83	4.14	−5.33	−1.19
HCl + anti-CH ₃ CHOH	−2.32	−5.76	−5.06	−5.18	−0.12	−0.05	−0.10	0.24	0.83	−4.38	−4.42	−8.80
HCl + syn-CH ₂ CH ₂ OH	4.49	1.70	2.47	2.37	−0.09	−0.05	−0.01	0.23	0.83	3.28	−5.02	−1.74
HCl + syn-CH ₃ CHOH	−1.63	−5.40	−4.74	−4.85	−0.12	−0.06	−0.10	0.24	0.83	−4.06	−4.45	−8.51
HCl + C ₂ H ₅ O	12.71	5.08	5.94	5.96	−0.17	0.07	0.00	0.12	0.83	6.81	−5.10	1.71
HOCl + C ₂ H ₅	47.54	40.47	41.49	41.34	−0.12	−0.18	0.08	0.06	0.83	42.01	−4.70	37.31
H + CH ₂ ClCH ₂ OH H1	18.21	19.88	21.38	21.30	0.08	−0.16	0.00	0.23	0.83	22.28	−5.27	17.01
H + anti-CH ₂ ClCH ₂ OH H3	18.99	20.54	22.08	22.03	0.08	−0.16	−0.01	0.22	0.83	22.99	−5.26	17.73
H + syn-CH ₂ ClCH ₂ OH H3	17.06	18.12	19.61	19.54	0.07	−0.17	−0.01	0.22	0.83	20.48	−4.93	15.55
H + CH ₃ CHClOH	10.77	12.97	14.47	14.43	0.09	−0.18	−0.03	0.17	0.83	15.31	−5.49	9.82
H + CH ₃ CH ₂ OCl	60.50	58.69	60.37	60.40	0.08	−0.35	0.13	0.04	0.83	61.13	−6.13	55.00
OH + C ₂ H ₅ Cl	14.75	10.55	11.30	11.22	−0.03	0.04	0.02	0.08	0.64	11.97	−3.07	8.90
CH ₃ + CH ₂ ClOH	9.50	5.89	6.71	6.56	−0.06	−0.07	0.12	0.17	0.83	7.55	−4.24	3.31
CH ₃ Cl + CH ₂ OH	10.16	4.97	5.59	5.39	−0.12	−0.06	0.02	0.22	0.83	6.28	−2.98	3.30

^a MP2/aug-cc-pVDZ relative energies based on MP2/aug-cc-pVDZ structures. ^b CCSD(T)-F12b/aug-cc-pVDZ relative energies based on CCSD(T)-F12b/aug-cc-pVDZ structures. ^c CCSD(T)-F12b/aug-cc-pVTZ relative energies based on CCSD(T)-F12b/aug-cc-pVDZ structures. ^d CCSD(T)-F12b/aug-cc-pVQZ relative energies based on CCSD(T)-F12b/aug-cc-pVDZ structures. ^e CCSDT – CCSD(T) energies computed with the cc-pVDZ basis set at CCSD(T)-F12b/aug-cc-pVDZ structures. ^f CCSDT(Q) – CCSDT energies computed with the cc-pVDZ basis set at CCSD(T)-F12b/aug-cc-pVDZ structures. ^g Core-correlation correction determined as the difference of AE-CCSD(T)-F12b/cc-pCVTZ-F12 and FC-CCSD(T)-F12b/cc-pCVTZ-F12 relative energies at CCSD(T)-F12b/aug-cc-pVDZ structures. ^h Scalar relativistic correction determined as the difference between the DK-AE-CCSD(T)-F12b/aug-cc-pwCVTZ-DK and non-relativistic AE-CCSD(T)-F12b/aug-cc-pwCVTZ relative energies at CCSD(T)-F12b/aug-cc-pVDZ structures. ⁱ Spin-orbit correction determined as the energy difference between SO and non-SO ground-state utilizing MRCI+Q/aug-cc-pwCVTZ computations at CCSD(T)-F12b/aug-cc-pVDZ structures. ^j Benchmark classical relative energy determined as CCSD(T)-F12b/aug-cc-pVQZ + $\delta[T]$ + $\delta[(Q)]$ + Δ_{core} + Δ_{rel} + Δ_{SO} . ^k Δ_{ZPE} computed at the CCSD(T)-F12b/aug-cc-pVDZ level of theory. ^l Benchmark adiabatic relative energy determined as the sum of $\Delta E_{\text{Classical}}$ and Δ_{ZPE} .

The magnitudes of these post-(T) corrections correlate well with the above-mentioned T_1 values. Analysis of the core-correlation corrections shows that the largest contribution is obtained for M sub W TS, amounting to 0.36 kcal mol^{−1}, whereas for all other stationary points the corrections are smaller and in some cases vanish entirely, with no change in the relative energy upon inclusion of core correlation, for example as observed for

the H-substitution post-reaction complexes (H sub W PM, H sub FS PM, and H sub FS PM2). Scalar relativistic corrections are found to be comparable in magnitude to the core-correlation contributions, although their maximum value is smaller, reaching 0.26 kcal mol^{−1}, which is observed for four post-reaction complexes (H abs H3 PM2, H abs H3 PM3, H abs H3 PM4, and H abs H6 PM), and, with the exception of four

transition states (OH abs TS, OH abs TS 2, H sub OH TS, and OH sub TS), the scalar relativistic contributions are positive in all cases. The spin-orbit coupling splits the non-relativistic ground state of the Cl atom into a lower-energy ($^2P_{3/2}$) and a higher-energy ($^2P_{1/2}$) level, leading to a lowering of the reactant energy and, consequently, an increase of all relative energies by 0.81–0.83 kcal mol^{−1}. An exception is found for the OH + C₂H₅Cl product channel, where the spin-orbit correction amounts to only 0.64 kcal mol^{−1}. The deviation arises from the formation of the OH radical, for which the non-relativistic $^2\Pi$ state also splits into $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ components, resulting in additional stabilization of the products. The corresponding energy reduction is about 0.20 kcal mol^{−1} experimentally, in good agreement with the present results, as reflected by the difference between the Cl-based correction (0.81–0.83 kcal mol^{−1}) and the value obtained for the OH-containing product channel (0.64 kcal mol^{−1}). Examination of the zero-point energy corrections shows that the corrections are negative, thereby reducing the classical energies of the corresponding stationary points. The resulting adiabatic energies, obtained as the sum of the benchmark classical energies and the zero-point energy corrections, can be directly compared to experimental reaction enthalpies evaluated from the heats of formation reported in the ATcT database.³⁶ The ATcT values are referred to as “experimental”, although it is important to note that they are derived from weighted averages of numerous experimental and theoretical data. Table 3 presents a comparison between our high-accuracy results and the reaction enthalpies derived from the ATcT database for ten different product channels. A clear and excellent agreement is observed between the theoretical results obtained in the present work and the experimental data, with half of the values coinciding within the ATcT uncertainty limits, while the remaining cases show only minor deviations, the largest being 0.31 kcal mol^{−1} for the CH₃ + CH₂ClOH product channel. Consequently, the outstanding consistency between the theoretical and experimental results can be attributed to the inclusion of the five different correction terms, whose combined contribution ranges between 0.67 and 0.99 kcal mol^{−1}.

Table 3 Comparison of the benchmark adiabatic 0 K energies (in kcal mol^{−1}) obtained in the present work with reaction enthalpies derived from ATcT formation enthalpies for the different reaction channels of the Cl($^2P_{3/2}$) + C₂H₅OH system

Reaction	Theory ^a	ATcT ^b
Cl + C ₂ H ₅ OH → HCl + anti-CH ₂ CH ₂ OH	−1.19	−1.26 ± 0.23
Cl + C ₂ H ₅ OH → HCl + syn-CH ₂ CH ₂ OH	−1.74	−1.75 ± 0.12
Cl + C ₂ H ₅ OH → HCl + anti-CH ₃ CHOH	−8.80	−8.88 ± 0.12
Cl + C ₂ H ₅ OH → HCl + syn-CH ₃ CHOH	−8.51	−8.55 ± 0.22
Cl + C ₂ H ₅ OH → HCl + C ₂ H ₅ O	1.71	1.66 ± 0.11
Cl + C ₂ H ₅ OH → HOCl + C ₂ H ₅	37.31	37.10 ± 0.07
Cl + C ₂ H ₅ OH → H + syn-CH ₂ ClCH ₂ OH H3	15.55	15.25 ± 0.15
Cl + C ₂ H ₅ OH → OH + C ₂ H ₅ Cl	8.90	9.05 ± 0.08
Cl + C ₂ H ₅ OH → CH ₃ + CH ₂ ClOH	3.31	3.62 ± 0.29
Cl + C ₂ H ₅ OH → CH ₃ Cl + CH ₂ OH	3.30	3.06 ± 0.09

^a Benchmark adiabatic energies determined at 0 K in the present work.

^b Reaction enthalpies calculated from version 1.220 of ATcT³⁶ formation enthalpies at 0 K. The associated uncertainties are derived from the uncertainties of the individual 0 K formation enthalpies reported in ATcT using standard Gaussian error propagation.

IV. Summary and conclusions

By considering all possible product channels, the reaction pathways of the Cl($^2P_{3/2}$) + C₂H₅OH system have been systematically explored using highly-accurate electronic structure computations. In addition to the previously-investigated H-abstraction processes, alternative reaction channels opening at higher energies are identified, including OH-abstraction and substitution pathways involving H, OH, CH₃, and CH₂OH exchange, with Walden-inversion and front-side mechanisms distinguished for the H, CH₃, and CH₂OH substitution channels. The benchmark energies are constructed by combining CCSD(T)-F12b/aug-cc-pVQZ single-point energies, evaluated at CCSD(T)-F12b/aug-cc-pVDZ optimized geometries, with five additional corrections, including post-CCSD(T) correlation contributions ($\delta[T]$ and $\delta[Q]$), core-correlation effects, scalar relativistic contributions, and spin-orbit coupling. H abstraction, whether from the carbon backbone or the OH group of ethanol, is favored over any other pathways both kinetically and thermodynamically when zero-point energy corrections are included. Within the H-abstraction route, both the barrier heights and the product energies indicate that H removal by the Cl atom occurs most readily from the CH₂ group of ethanol, followed by the CH₃ group, while abstraction from the OH group is the least favorable. In terms of thermodynamic preference, group-substitution pathways follow H abstraction, with CH₂OH substitution being the most favorable among them and comparable in stability to H abstraction at the OH site of the ethanol molecule, since classical energies place the CH₃Cl + CH₂OH products slightly below the C₂H₅O + HCl products, whereas inclusion of zero-point energy corrections reverses the ordering. The CH₃ substitution products (CH₃ + CH₂ClOH) are only marginally higher in energy by 1.27(0.01) kcal mol^{−1} than the CH₂OH substitution products classically(adiabatically), while the OH substitution channel forming C₂H₅Cl + OH is considerably less favorable, with its energy exceeding that of the reactants by 11.97(8.90) kcal mol^{−1}. Beyond these pathways, H-substitution reactions occurring at the carbon backbone of ethanol follow in thermodynamic preference, succeeded by the OH abstraction channel yielding C₂H₅ + HOCl, while the least favorable process is the H substitution at the OH group by the Cl atom. From a kinetic perspective, H abstraction is most favorable at the CH₂ site, where a submerged barrier of −7.72(−11.01) kcal mol^{−1} is observed, while H abstraction from the CH₃ group proceeds with relatively low barriers of 2.08(−2.13) and 4.66(−0.06) kcal mol^{−1}, in contrast to the significantly more hindered H removal from the OH group, which involves a barrier of 17.97(15.01) kcal mol^{−1}. Beyond H abstraction, all alternative reaction pathways involve substantially higher barriers, the lowest of which corresponds to the Walden-type CH₂OH substitution, with a transition-state energy of 28.84(27.65) kcal mol^{−1} classically(adiabatically), 10.87(12.64) kcal mol^{−1} higher than that of H abstraction at the OH group of ethanol. It is further observed that for both H and CH₂OH substitution, the Walden mechanism is consistently favored, with the front-side pathways lying approximately

15 kcal mol^{−1} higher in barrier height. The computed adiabatic energies of the products are compared with reaction enthalpies derived from ATcT heats of formation for ten product channels, revealing excellent agreement within the ATcT uncertainty limits for five cases and very good agreement for the remaining channels, with the largest deviation between theoretical and experimental values being only 0.31 kcal mol^{−1}. The geometries of the identified transition states are compared with the corresponding bond lengths in the reactant ethanol and the products, revealing that all transition states in the studied system exhibit a product-like, late-barrier character. Overall, the present work provides a comprehensive characterization of the stationary points of the Cl(²P_{3/2}) + C₂H₅OH reaction, including their structures and energetics across multiple reaction channels, thereby laying the foundation for future dynamical studies, even at hyperthermal collision energies where high-energy pathways may also become accessible.

Conflicts of interest

There are no conflicts of interest to declare.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Supplementary information (SI): Cartesian coordinates (in Å) and energies (in E_h) of the identified stationary points obtained at the CCSD(T)-F12b/aug-cc-pVDZ level of theory for the Cl + C₂H₅OH reaction. See DOI: <https://doi.org/10.1039/d6cp01759b>.

Acknowledgements

We thank the National Research, Development and Innovation Office–NKFIH, K-146759 and the Momentum (Lendület) Program of the Hungarian Academy of Sciences for the financial support.

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