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Benchmark *ab initio* characterization of the complex potential energy surfaces of the $\text{HOO}^- + \text{CH}_3\text{Y}$ [Y = F, Cl, Br, I] reactions†

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The α -effect is a well-known phenomenon in organic chemistry, and is related to the enhanced reactivity of nucleophiles involving one or more lone-pair electrons adjacent to the nucleophilic center. The gas-phase bimolecular nucleophilic substitution ($\text{S}_{\text{N}}2$) reactions of α -nucleophile HOO^- with methyl halides have been thoroughly investigated experimentally and theoretically; however, these investigations have mainly focused on identifying and characterizing the α -effect of HOO^- . Here, we perform the first comprehensive high-level *ab initio* mapping for the $\text{HOO}^- + \text{CH}_3\text{Y}$ [Y = F, Cl, Br and I] reactions utilizing the modern explicitly-correlated CCSD(T)-F12b method with the aug-cc-pVnZ [$n = 2-4$] basis sets. The present *ab initio* characterization considers five distinct product channels of $\text{S}_{\text{N}}2$: ($\text{CH}_3\text{OOH} + \text{Y}^-$), proton abstraction ($\text{CH}_2\text{Y}^- + \text{H}_2\text{O}_2$), peroxide ion substitution ($\text{CH}_3\text{OO}^- + \text{HY}$), $\text{S}_{\text{N}}2$ -induced elimination ($\text{CH}_2\text{O} + \text{HY} + \text{HO}^-$) and $\text{S}_{\text{N}}2$ -induced rearrangement ($\text{CH}_2(\text{OH})\text{O}^- + \text{HY}$). Moreover, besides the traditional back-side attack Walden inversion, the pathways of front-side attack, double inversion and halogen-bond complex formation have also been explored for $\text{S}_{\text{N}}2$. With regard to the Walden inversion of $\text{HOO}^- + \text{CH}_3\text{Cl}$, the previously unaddressed discrepancies concerning the geometry of the corresponding transition state are clarified. For the $\text{HOO}^- + \text{CH}_3\text{F}$ reaction, the recently identified $\text{S}_{\text{N}}2$ -induced elimination is found to be more exothermic than the $\text{S}_{\text{N}}2$ channel, submerged by $\sim 36 \text{ kcal mol}^{-1}$. The accuracy of our high-level *ab initio* calculations performed in the present study is validated by the fact that our new benchmark 0 K reaction enthalpies show excellent agreement with the experimental data in nearly all cases.

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1. Introduction

Theoretical and experimental investigations of the gas-phase bimolecular nucleophilic substitution ($\text{S}_{\text{N}}2$) reactions have gained increasing prominence since the 1970s.¹⁻¹⁰ In step with the progress of computational chemistry and experimental methodology,¹¹⁻¹⁶ the initially conceived simple picture of the elemental $\text{S}_{\text{N}}2$ reactions has been found to be incomplete, as it became apparent that along with the traditional Walden inversion and front-side attack, several alternative mechanisms may also occur depending on the reactants and the reaction conditions.¹⁷⁻²¹

Transcending the conventional reactions between halide ions and methyl halides, our understanding of $\text{S}_{\text{N}}2$ was also

reshaped by the examination of reactions involving HO^- .²²⁻³⁸ In 2002, Sun *et al.* investigated the $\text{HO}^- + \text{CH}_3\text{F}$ $\text{S}_{\text{N}}2$ reaction by performing direct dynamics simulations and revealed that the reaction avoids the region of the deep H-bonded $\text{CH}_3\text{OH} \cdots \text{F}^-$ minimum in the exit channel.²² Since then, other theoretical studies have uncovered a novel oxide ion substitution for the $\text{HO}^- + \text{CH}_3\text{F}$ reaction utilizing quasi-classical trajectory (QCT), as well as, direct dynamics calculations.³⁹⁻⁴¹ Over the years, the primary focus has been on the dynamical characterization of the $\text{HO}^- + \text{CH}_3\text{I}$ reaction.⁴²⁻⁴⁸ Wester and co-workers examined several $\text{S}_{\text{N}}2$ reactions experimentally, including $\text{HO}^- + \text{CH}_3\text{I}$, with the crossed-beam ion-imaging technique.^{10,14,49} Direct dynamics simulations were also performed by Hase and co-workers, paving the way for comprehensive experimental-theoretical studies of the $\text{HO}^- + \text{CH}_3\text{I}$ reaction.⁵⁰⁻⁵² Furthermore, the present authors developed several global analytical *ab initio* potential energy surfaces (PESs) for $\text{HO}^- + \text{CH}_3\text{I}$ at seven different levels of theory using the in-house ROBOSURFER program package.^{53,54} Afterwards, on the final PES, which was confirmed to be the most suitable for further investigations, more than half a million trajectories were computed, comparing the results with the results of revised crossed-beam experiments

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in order to analyze the dynamics of the reaction in a more detailed manner.⁵⁵ Recently, the mode specificity in the dynamics of the reaction was also studied at several collision energies by exciting certain vibrational modes of the reactants.^{56,57}

Besides considering di- or polyatomic ‘normal’ nucleophiles (e.g., HO⁻, CN⁻, NH₂⁻, PH₂⁻ etc.),^{10,24,58–63} a significant emphasis has been placed on α -nucleophiles (e.g., HOO⁻, ClO⁻, BrO⁻, CH₃OO⁻, HOHN⁻, NH₂O⁻, etc.) participating in S_N2 reactions.^{8,9,64–71} In the case of these α -nucleophiles, one or more lone-pair electrons are located on the atom adjacent to the nucleophilic center, inducing enhanced reactivity compared to that expected from the Brønsted-type correlation.⁷² This phenomenon is known as the α -effect.⁷³ While the existence of the α -effect was beyond doubt in solution, the situation was not as clearly defined in the gas phase.^{72,74,75} By comparing the branching ratios for the reactions of HO⁻ and HOO⁻ with methyl formate, DePuy and co-workers concluded that HOO⁻ does not show the α -effect in the gas phase.⁷⁶ In addition, Villiano *et al.* unveiled that a noticeable α -effect cannot be observed for the HOO⁻/ClO⁻/BrO⁻ + CH₃R (R = CH₃, CH₃CH₂, etc.) systems, as well.⁶⁵ In contrast, the opposite of these findings has been confirmed, and several studies have verified that the α -effect stems from the intrinsic properties of α -nucleophiles validating the manifestation of this phenomenon in the gas phase.^{77–85} However, the identification of these intrinsic properties of α -nucleophiles remained disputed.^{86–93} Recently, Hamlin *et al.* reported an extensive theoretical survey on the origin of the α -effect in the gas phase.⁷¹ They employed the activation strain model of reactivity in combination with Kohn–Sham molecular orbital theory and arrived at the conclusion that the adjacent atom of α -nucleophiles induces a reduction in Pauli repulsion between the reactants by polarizing orbital density away from the nucleophilic center. As a result, an enhancement of the reactivity can be obtained for α -nucleophiles compared to their ‘normal’ counterparts.

Regarding S_N2 reactions involving HOO⁻, several theoretical investigations have concentrated on the stationary-point and dynamical characterization, as well.^{74,88,94–97} In the course of the aforementioned α -effect examinations, the stationary points of the corresponding Walden-inversion pathways were determined for several S_N2 reactions of HOO⁻ at various levels of theory. The HOO⁻⋯CH₃Y → [HOO⋯CH₃⋯Y]⁻ → CH₃OOH⋯Y⁻ path was explored by Evanseck *et al.* for Y = Cl at the level of HF/6-31+G(d).⁷⁴ Later, in the theoretical surveys of Ren *et al.*, the geometries of the [HOO⋯CH₃⋯Y]⁻ transition states were optimized in the case of Y = F and Cl at the MP2/6-31+G(d) level of theory, and the corresponding energies were determined with the G2(+) method.^{78,79} Associated with the microsolvated variants of the HOO⁻ + CH₃Cl S_N2 reaction, the unsolvated Walden-inversion pathways were also characterized in the studies of Thomsen *et al.*⁸⁸ and Hu *et al.*⁹⁷ utilizing the MP2/6-311++G(d,p) level of theory in combination with G3 and CCSD(T)/aug-cc-pVTZ energy calculations, respectively. The most thorough *ab initio* mapping was achieved by Wu *et al.* in the case of the HOO⁻(H₂O)_n + CH₃Y [Y = F, Cl, Br, I; n = 0, 1, 2]

S_N2 reactions, whereby they identified two H-bonded stationary points in the entrance channel, as well.⁹⁶ The dynamics of the HOO⁻(H₂O)_n + CH₃Cl reactions, where n = 0 or 1, was also examined with direct dynamics simulations.^{94,95} It is noteworthy that, based on the earlier work of Anick *et al.*,⁹⁸ the only stable structure for the singly hydrated hydroperoxide ion is HO⁻(HOH), which indicates that in the S_N2 reaction with CH₃Cl, two distinct pathways may be possible, leading to the CH₃OOH + Cl⁻ + H₂O and CH₃OH + Cl⁻ + H₂O₂ products. Recently, dynamics simulations performed by Zhao *et al.*⁹⁵ have substantiated that both reaction routes are viable, indicating the fact that a single solvent water molecule can induce a new nucleophile in S_N2 reactions, which opens the door for an alternative pathway. Moreover, for the unsolvated HOO⁻ + CH₃Cl reaction, similar to the case of ClO⁻ + CH₃Cl,^{65,69} a novel non-S_N2 pathway generating the CH₂O + HCl + HO⁻ products was also unveiled. Besides the dynamical description, the PES of the considered product channels of the HOO⁻ + CH₃Cl reaction was mapped at the MP2/6-31+G(d,p) level of theory.⁹⁵

In the present work, based on the prominent attention paid to the S_N2 reactions involving hydroperoxide ions, we perform a comprehensive benchmark *ab initio* characterization of HOO⁻ + CH₃Y [Y = F, Cl, Br and I] using the explicitly-correlated CCSD(T)-F12b method with the aug-cc-pVnZ [n = 2 (D), 3 (T) and 4 (Q)] basis sets. Besides the traditional Walden-inversion path, we analyze the halogen-bonded complex mechanism⁴⁸ and the possible S_N2 retention routes of front-side attack and double inversion.¹⁹ We identify the stationary points of the proton-abstraction channel, as well; furthermore, relying on the previous study of Xie and co-workers,⁹⁵ our high-level stationary-point mapping also considers other possible pathways. Detailed insights into the applied *ab initio* methods can be found in Section II. In the subsequent Section III, a comprehensive description and discussion of the results are presented, followed by a brief summary of the work in Section IV.

II. Computational details

The stationary points of the title reactions are searched and preoptimized using the second-order Møller–Plesset perturbation theory (MP2)⁹⁹ with the augmented correlation-consistent polarized-valence-double- ζ (aug-cc-pVDZ) basis set.¹⁰⁰ The exploration of the stationary points was conducted based on previous studies and chemical intuition;^{24,38,95} nevertheless, it is important to note that automated methods and approaches for identifying reaction pathways and stationary points in chemical reactions are becoming more and more prevalent.^{101–103} Thereafter, in order to attain more accurate geometries, energies and harmonic frequencies for the stationary points, the explicitly-correlated coupled-cluster singles, doubles, and perturbative triples (CCSD(T)-F12b) method^{104–106} is utilized with the aug-cc-pVDZ and aug-cc-pVTZ basis sets.¹⁰⁰ To achieve a more in-depth mapping, intrinsic reaction coordinate (IRC) computations are also carried out from the saddle points at the MP2/aug-cc-pVDZ level of theory. In order to avoid any spurious stationary point, it is

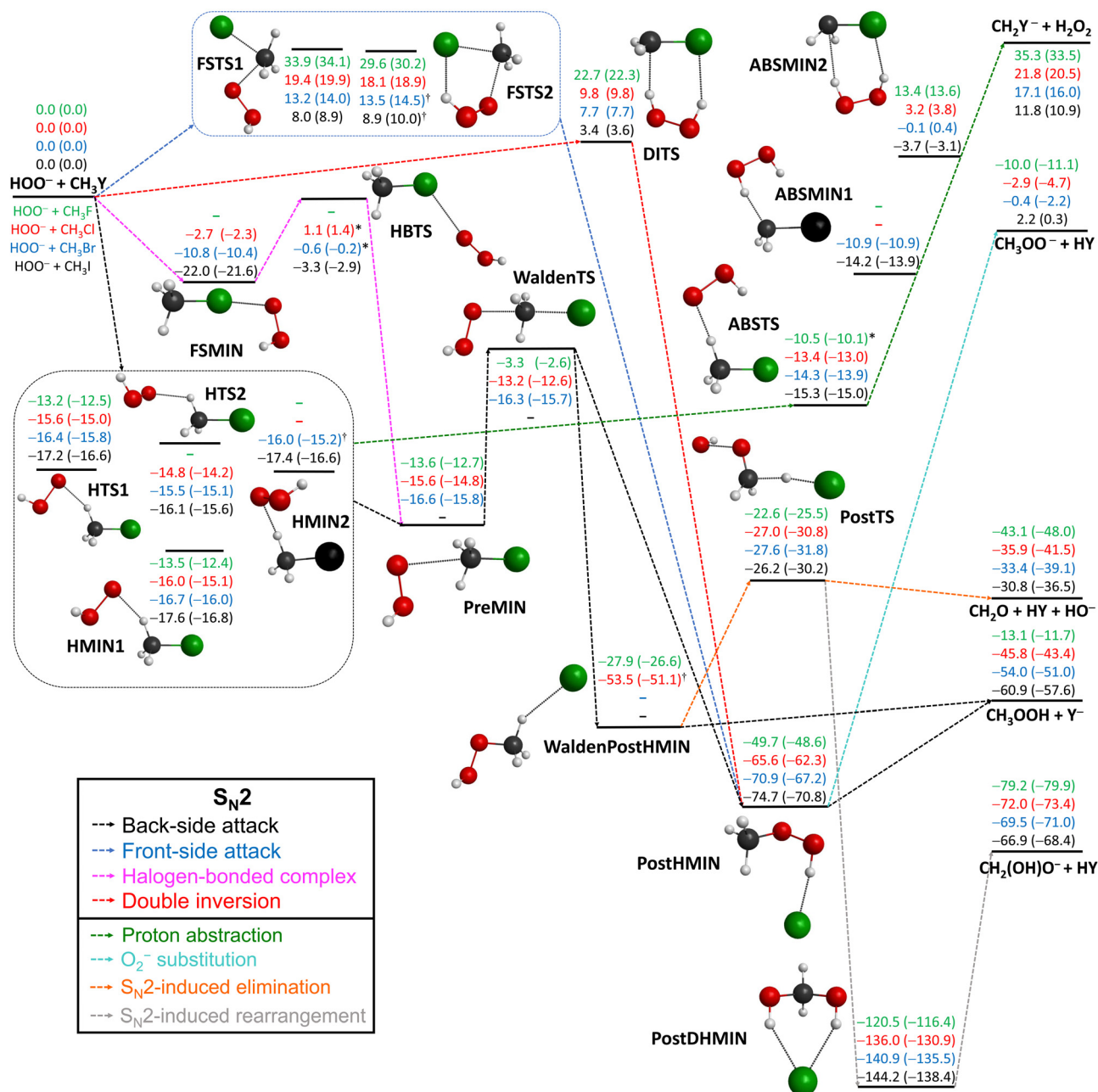


Fig. 1 Schematic representation of the complex potential energy surfaces of the $HOO^- + CH_3Y$ [$Y = F, Cl, Br, I$] reactions presenting the classical (adiabatic) CCSD(T)-F12b/aug-cc-pVQZ (+ ΔZPE [CCSD(T)-F12b/aug-cc-pVTZ]) relative energies (kcal mol⁻¹) of the stationary points along the possible reaction routes. [†]MP2/aug-cc-pVDZ structure; *CCSD(T)-F12b/aug-cc-pVDZ structure.

important to note that for all geometry optimizations, the default (3×10^{-4}) required accuracy of the optimized gradient is changed to 10^{-5} in atomic units. Small-core relativistic effective core potentials (ECPs)¹⁰⁷ are employed for Br and I, and the aug-cc-pVnZ-PP [$n = 2-4$] basis sets are applied to replace the inner-core $1s^2 2s^2 2p^6$ (Br) and $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ (I) electrons. For the stationary points identified in the present work, the computed T_1 -diagnostic values are below 0.02 in every case, except for FSTS and FSTS2 (see Fig. 1), where the values are between 0.02 and 0.04, validating that the multi-reference character is

not a probable issue for the $HOO^- + CH_3Y$ [$Y = F, Cl, Br$ and I] systems. The benchmark classical (adiabatic) relative energies are computed for the CCSD(T)-F12b/aug-cc-pVTZ] structures as follows:

$$\Delta E[\text{CCSD(T)-F12b/aug-cc-pVQZ}] (+\Delta ZPE[\text{CCSD(T)-F12b/aug-cc-pVTZ}]), \quad (1)$$

where ΔZPE is the harmonic zero-point energy correction. The *ab initio* calculations are performed with the MOLPRO program package.¹⁰⁸

Table 1 Benchmark classical and adiabatic energies (kcal mol⁻¹) of the stationary points relative to the reactants for the possible pathways of the HOO⁻ + CH₃Y [Y = F, Cl, Br, I] reactions

HOO ⁻ + CH ₃ F	MP2	CCSD(T)-F12b			ΔZPE^e	Adiabatic ^f
	DZ ^a	DZ ^b	TZ ^c	QZ ^d		
HMIN1	-14.41	-13.95	-13.69	-13.47	1.09	-12.38
HTS1	-14.00	-13.49	-13.32	-13.15	0.67	-12.49
PreMIN	-14.45	-14.01	-13.80	-13.59	0.84	-12.74
WaldenTS	-6.77	-3.37	-3.44	-3.27	0.66	-2.61
FSTS1	29.87	33.40	33.50	33.87	0.25	34.12
FSTS2	25.76	29.26	29.28	29.64	0.59	30.23
DITS	21.68	21.81	22.37	22.72	-0.37	22.35
PostHMIN	-53.64	-50.43	-49.99	-49.74	1.11	-48.63
WaldenPostHMIN	-32.77	-28.62	-28.08	-27.91	1.26	-26.65
ABSTS	-11.38	-11.00	-10.71 ^g	-10.52 ^g	0.44 ^g	-10.08 ^g
ABSMIN2	12.34	12.43	13.00	13.37	0.28	13.65
PostTS	-28.42	-23.65	-22.93	-22.62	-2.89	-25.51
PostDHMIN	-127.02	-121.31	-120.63	-120.45	4.07	-116.38
HOO ⁻ + CH ₃ Cl	MP2 ^a	DZ ^b	TZ ^c	QZ ^d	ΔZPE^e	Adiabatic ^f
HMIN1	-17.02	-16.26	-16.14	-15.97	0.89	-15.08
HTS1	-16.57	-15.78	-15.74	-15.62	0.62	-15.00
HTS2	-15.45	-15.04	-14.98	-14.82	0.59	-14.23
FSMIN	-1.81	-3.25	-2.87	-2.73	0.47	-2.27
HBTS	1.54	0.80	1.06 ^g	1.14 ^g	0.26 ^g	1.40 ^g
PreMIN	-16.35	-15.73	-15.72	-15.57	0.79	-14.78
WaldenTS	-14.39	-13.03	-13.33	-13.24	0.62	-12.62
FSTS1	18.84	19.20	19.19	19.40	0.48	19.88
FSTS2	18.12	17.44	17.80	18.07	0.85	18.93
DITS	9.64	9.13	9.61	9.82	-0.02	9.81
PostHMIN	-68.49	-65.91	-65.58	-65.61	3.26	-62.34
WaldenPostHMIN	-57.10	-53.75 ^h	-53.44 ^h	-53.55 ^h	2.48 ^h	-51.07 ^h
ABSTS	-14.49	-13.79	-13.59	-13.43	0.45	-12.98
ABSMIN2	3.08	2.71	3.03	3.23	0.52	3.75
PostTS	-38.33	-27.93	-27.17	-27.01	-3.75	-30.76
PostDHMIN	-141.29	-136.29	-135.89	-136.00	5.14	-130.86
HOO ⁻ + CH ₃ Br	MP2 ^a	DZ ^b	TZ ^c	QZ ^d	ΔZPE^e	Adiabatic ^f
HMIN1	-17.61	-17.21	-16.92	-16.74	0.74	-15.99
HMIN2	-17.22	-16.57 ^h	-16.18 ^h	-15.97 ^h	0.82 ^h	-15.15 ^h
HTS1	-17.13	-16.72	-16.49	-16.35	0.54	-15.81
HTS2	-15.90	-15.92	-15.71	-15.53	0.42	-15.11
FSMIN	-10.48	-11.07	-10.89	-10.76	0.37	-10.39
HBTS	-0.36	-0.67	-0.70 ^g	-0.62 ^g	0.39 ^g	-0.23 ^g
PreMIN	-16.87	-16.88	-16.73	-16.57	0.79	-15.77
WaldenTS	-16.35	-16.41	-16.45	-16.32	0.62	-15.70
FSTS1	14.09	12.96	12.98	13.17	0.78	13.95
FSTS2	14.10	13.18 ^h	13.29 ^h	13.55 ^h	0.95 ^h	14.50 ^h
DITS	7.23	6.88	7.42	7.69	0.05	7.73
PostHMIN	-72.09	-71.45	-70.85	-70.93	3.71	-67.22
ABSTS	-15.27	-14.80	-14.48	-14.30	0.41	-13.89
ABSMIN1	-11.03	-11.55	-11.18	-10.89	0.00	-10.90
ABSMIN2	0.38	-0.79	-0.37	-0.12	0.57	0.45
PostTS	-40.96	-28.82	-27.82	-27.63	-4.16	-31.80
PostDHMIN	-144.57	-141.54	-140.79	-140.94	5.48	-135.46
HOO ⁻ + CH ₃ I	MP2 ^a	DZ ^b	TZ ^c	QZ ^d	ΔZPE^e	Adiabatic ^f
HMIN1	-18.52	-18.05	-17.75	-17.57	0.72	-16.84
HMIN2	-18.45	-17.96	-17.60	-17.40	0.79	-16.61
HTS1	-18.02	-17.56	-17.31	-17.17	0.53	-16.64
HTS2	-16.44	-16.51	-16.27	-16.10	0.54	-15.56
FSMIN	-22.36	-22.28	-22.11	-22.03	0.44	-21.59
HBTS	-2.65	-3.19	-3.37	-3.30	0.40	-2.90
FSTS1	9.16	7.85	7.91	8.04	0.87	8.91
FSTS2	10.01	8.46 ^h	8.67 ^h	8.93 ^h	1.08 ^h	10.01 ^h
DITS	3.40	2.68	3.11	3.36	0.19	3.55

Table 1 (continued)

HOO ⁻ + CH ₃ I	MP2 ^a	DZ ^b	TZ ^c	QZ ^d	ΔZPE ^e	Adiabatic ^f
PostHMIN	-75.63	-75.15	-74.52	-74.74	3.94	-70.80
ABSTS	-16.32	-15.83	-15.48	-15.30	0.28	-15.02
ABSMIN1	-14.52	-14.76	-14.42	-14.15	0.28	-13.88
ABSMIN2	-2.98	-4.37	-3.97	-3.75	0.66	-3.09
PostTS	-36.02	-27.58	-26.36	-26.15	-4.08	-30.23
PostDHMIN	-147.56	-144.70	-143.92	-144.19	5.79	-138.40

^a MP2/aug-cc-pVDZ. ^b CCSD(T)-F12b/aug-cc-pVDZ. ^c CCSD(T)-F12b/aug-cc-pVTZ. ^d CCSD(T)-F12b/aug-cc-pVQZ at CCSD(T)-F12b/aug-cc-pVTZ geometry. ^e ΔZPE(CCSD(T)-F12b/aug-cc-pVTZ). ^f QZ + ΔZPE. ^g CCSD(T)-F12b/aug-cc-pVDZ geometry and frequencies. ^h MP2/aug-cc-pVDZ geometry and frequencies.

III. Results and discussion

The complex PESs of the HOO⁻ + CH₃Y [Y = F, Cl, Br and I] reactions showing the benchmark classical (adiabatic) relative energies of the stationary points along the considered pathways are presented in Fig. 1. The *ab initio* energies determined at the MP2/aug-cc-pVDZ and CCSD(T)-F12b/aug-cc-pVnZ [*n* = 2, 3 and 4] levels of theory are summarized in Tables 1 and 2. Taking a cue from previous studies on the HOO⁻/ClO⁻ + CH₃Cl and HO⁻ + CH₃F reactions,^{40,65,69,95} in addition to the typical S_N2 (CH₃OOH + Y⁻) and proton-abstraction (CH₂Y⁻ + H₂O₂) routes, alternative channels of peroxide ion substitution (CH₃OO⁻ + HY), S_N2-induced elimination (CH₂O + HY + HO⁻) and S_N2-induced rearrangement (CH₂(OH)O⁻ + HY) are also analyzed. It should be noted that in the case of the HOO⁻ + CH₃Cl reaction, the dynamical characterization reported by Xie and co-workers did not reveal the existence of the corresponding peroxide ion substitution, S_N2-induced rearrangement and proton abstraction, presumably, due to the fact that overall 1154 trajectories were run at one sole collision energy of 0.9 kcal mol⁻¹.⁹⁵ However, the pathways of peroxide ion substitution and S_N2-induced rearrangement were also considered in the course of their stationary-point survey.

As seen in Fig. 1, in the entrance channel of the back-side attack Walden inversion, several H-bonded stationary points can be found for HOO⁻ + CH₃Y: HMIN1 [Y = F, Cl, Br and I], HTS1 [Y = F, Cl, Br and I], HMIN2 [Y = Br and I] and HTS2 [Y = Cl, Br and I]. The energetics of these minima and transition states are similar, and the differences in the relative energies are within ~1.5 kcal mol⁻¹. Moreover, the typical PreMIN ion-dipole complex does not demonstrate notable distinctions, as well. On the other hand, for the alternative pre-reaction halogen-bonded complex pathway, a different situation can be found. In line with HO⁻ + CH₃Y,^{24,38} FSMIN is situated above HMIN1 by 13.2 (12.8) and 6.0 (5.6) kcal mol⁻¹ for Y = Cl and Br, in order; while for Y = I, FSMIN is below HMIN1 by 4.5 (4.7) kcal mol⁻¹. Note that the back-side attack Walden-inversion mechanism is submerged except for Y = F, where HBTS is positioned above the reactant asymptote by 1.1 (1.4) kcal mol⁻¹. With the atomic number of Y, the barrier height of HBTS is increasing: 3.9 (3.7), 10.1 (10.2) and 18.7 (18.7) kcal mol⁻¹ relative to the corresponding FSMIN, for Y = F, Cl, Br and I, respectively. The deep well of the FSMIN complex at Y = I points out the common occurrence of the front-side complex formation mechanism in

S_N2 reactions involving CH₃I.^{48,60,109} The energy profile of the conventional stationary points of the Walden-inversion pathway (PreMIN → WaldenTS → WaldenPostMIN/PostHMIN) is also profoundly comparable with that of the HO⁻ case.^{24,38} For instance, the classical (adiabatic) barrier heights of WaldenTS are 10.3 (10.1), 2.3 (2.2) and 0.2 (0.1) kcal mol⁻¹ for Y = F, Cl and Br, respectively, while in the case of HO⁻ at the same level of theory, these values are 11.2 (11.4), 2.4 (2.4) and 0.2 (0.1) kcal mol⁻¹, in the same order. The global minimum of S_N2 is also located at PostHMIN, although, compared to HO⁻ + CH₃Y, higher classical energies of -49.7, -65.6, -70.9 and -74.7 kcal mol⁻¹ can be determined for HOO⁻ in the case of Y = F, Cl, Br and I, respectively. In tandem with this, a notable disparity emerges in the reaction enthalpies of the S_N2 channels: HOO⁻ + CH₃Y happens to be more endothermic by exactly 6.1 kcal mol⁻¹ in all cases. As a result, in the case of the S_N2 reactions of HOO⁻, larger dissociation energies can be observed for the leaving Y⁻ at PostHMIN, indicating a more significant post-reaction hydrogen-bonded complex formation. Here, one may highlight the relevance of peroxide ion substitution, as well, because the formation of the CH₃OO⁻ + HY products is also more exothermic than that of the HO⁻ cases, predicting a substantially increased probability for peroxide ion substitution, especially for HOO⁻ + CH₃F.⁴⁰ WaldenPostHMIN also plays a significant role, as Zhao *et al.*⁹⁵ uncovered, and the reaction can proceed through this minimum towards PostTS, leading to the unusual CH₂O + HY + HO⁻ products. In the case of Y = Cl, WaldenPostHMIN could not be identified at the CCSD(T)-F12b/aug-cc-pVnZ [*n* = 2, 3] levels of theory. It is noteworthy that for Y = F, the novel mechanism of S_N2-induced elimination is exceedingly more exothermic than S_N2, submerged by 29.9 (36.3) kcal mol⁻¹. The global minimum of the PES is situated at the double H-bonded PostDHMIN complex, and the most exothermic process corresponds to the S_N2-induced rearrangement channel, but it is supposedly an improbable reaction route considering the multiple bond-breaking and -forming processes involved. Concerning the S_N2 pathways that result in the retention of the initial CH₃Y configuration, two different transition states (FSTS1 and FSTS2) can be identified for front-side attacks. According to the study of Ma *et al.*,¹¹⁰ double inversion may not be an IRC path through a DITS-like transition state; despite that, theoretical investigations underscored its crucial character in the mechanism.^{111,112} Similarly to the HO⁻ case, the transition state of double inversion has lower energy than that of front-side attack; however, no submerged DITS can be obtained.^{24,38} The most endothermic channel is proton abstraction with reaction enthalpies

Table 2 The best available experimental and our benchmark *ab initio* 0 K reaction enthalpies (kcal mol⁻¹) of several product channels for the HOO⁻ + CH₃Y [Y = F, Cl, Br, I] reactions

HOO ⁻ + CH ₃ F	MP2	CCSD(T)-F12b			ΔZPE ^e	Adiabatic ^f	Experiment ^g
	DZ ^a	DZ ^b	TZ ^c	QZ ^d			
CH ₃ OOH + F ⁻	-18.24	-13.38	-13.06	-13.13	1.46	-11.67	-11.82 ± 0.14
CH ₂ F ⁻ + H ₂ O ₂	34.54	34.87	35.22	35.32	-1.84	33.48	—
CH ₃ OO ⁻ + HF	-11.24	-10.28	-10.08	-10.02	-1.11	-11.12	-11.00 ± 0.15
CH ₂ O + HF + HO ⁻	-51.98	-43.50	-42.94	-43.06	-4.92	-47.98	-47.99 ± 0.10
CH ₂ (OH)O ⁻ + HF	-85.40	-79.85	-79.22	-79.15	-0.70	-79.85	—
HOO ⁻ + CH ₃ Cl	MP2 ^a	DZ ^b	TZ ^c	QZ ^d	ΔZPE ^e	Adiabatic ^f	Experiment ^g
CH ₃ OOH + Cl ⁻	-48.79	-45.72	-45.61	-45.83	2.44	-43.39	-43.07 ± 0.14
CH ₂ Cl ⁻ + H ₂ O ₂	22.01	21.82	21.80	21.81	-1.33	20.48	21.64 ± 0.49
CH ₃ OO ⁻ + HCl	-3.64	-3.44	-3.10	-2.89	-1.77	-4.66	-4.31 ± 0.14
CH ₂ O + HCl + HO ⁻	-44.38	-36.66	-35.97	-35.93	-5.58	-41.51	-41.30 ± 0.09
CH ₂ (OH)O ⁻ + HCl	-77.81	-73.01	-72.24	-72.02	-1.36	-73.39	—
HOO ⁻ + CH ₃ Br	MP2 ^a	DZ ^b	TZ ^c	QZ ^d	ΔZPE ^e	Adiabatic ^f	Experiment ^g
CH ₃ OOH + Br ⁻	-54.91	-54.21	-53.65	-53.98	2.85	-51.14	-50.60 ± 0.14
CH ₂ Br ⁻ + H ₂ O ₂	18.32	16.94	17.14	17.15	-1.17	15.98	—
CH ₃ OO ⁻ + HBr	-0.72	-1.04	-0.51	-0.37	-1.86	-2.23	-1.85 ± 0.14
CH ₂ O + HBr + HO ⁻	-41.46	-34.26	-33.37	-33.41	-5.68	-39.08	-38.84 ± 0.10
CH ₂ (OH)O ⁻ + HBr	-74.89	-70.61	-69.65	-69.50	-1.46	-70.96	—
HOO ⁻ + CH ₃ I	MP2 ^a	DZ ^b	TZ ^c	QZ ^d	ΔZPE ^e	Adiabatic ^f	Experiment ^g
CH ₃ OOH + I ⁻	-61.29	-60.78	-60.32	-60.89	3.25	-57.64	-56.97 ± 0.14
CH ₂ I ⁻ + H ₂ O ₂	13.49	11.84	11.92	11.84	-0.95	10.89	—
CH ₃ OO ⁻ + HI	2.44	1.68	2.14	2.24	-1.93	0.32	0.83 ± 0.14
CH ₂ O + HI + HO ⁻	-38.30	-31.54	-30.72	-30.80	-5.74	-36.54	-36.16 ± 0.10
CH ₂ (OH)O ⁻ + HI	-71.72	-67.89	-67.00	-66.89	-1.52	-68.41	—

^a MP2/aug-cc-pVDZ. ^b CCSD(T)-F12b/aug-cc-pVDZ. ^c CCSD(T)-F12b/aug-cc-pVTZ. ^d CCSD(T)-F12b/aug-cc-pVQZ at CCSD(T)-F12b/aug-cc-pVTZ geometry. ^e ΔZPE(CCSD(T)-F12b/aug-cc-pVTZ). ^f QZ + ΔZPE. ^g Data obtained from the latest version (1.130) of the Active Thermochemical Tables (ATcT).^{113,114} The uncertainties are derived using the Gaussian error-propagation law on the uncertainties of each 0 K enthalpy of formation provided in ATcT.

of 33.5 (F), 20.5 (Cl), 16.0 (Br) and 10.9 (I) kcal mol⁻¹. The entrance channel of proton abstraction is found to be the same as that for S_N2 and is supported by IRC calculations, in which three stationary points (two minima and one transition state) are explored along the pathway: ABSTS [Y = F, Cl, Br and I], ABSMIN1 [Y = Br and I], and ABSMIN2 [Y = F, Cl, Br and I].

The structures of the stationary points featuring the selected bond lengths and angles are shown in Fig. 2. The associated stationary points in the reactant channels (HMIN1/HTS1 and HMIN2/HTS2) demonstrate slight differences in their geometries, and the most pronounced disparity is discerned in the orientation of the corresponding HOO⁻ group. Regarding WaldenTS, two distinct structures are characterized depending on Y: the dihedral angle of O–O···C–H is ~180° (*trans* arrangement) at Y = F, whereas a value of ~0° (*cis* arrangement) is obtained at Y = Cl and Br, as seen in Fig. 2. According to earlier investigations on S_N2 reactions, similar discrepancies observed at CH₃F are not uncommon;²⁴ for instance, in the case of HO⁻ + CH₃Y,³⁸ for Y = Cl, Br and I FSTS has C_s symmetry, while for Y = F, the symmetry is broken. It should be noted that previous studies on the HOO⁻ + CH₃Cl S_N2 reaction reported a *trans* alignment for the O–O···C–H torsion angle of WaldenTS computed at the MP2/6-311++G(d,p) level of theory.^{96,97} The geometries of PreMIN and WaldenTS defined in the early work of

Evanseck *et al.* are discrepant from our benchmark results due to their implemented symmetry-constrained geometry optimizations.⁷⁴ Moreover, Ren *et al.* revealed two different transition states for Walden inversion with a *trans* alignment of the corresponding O–O···C–H torsion angle for both cases.⁷⁸ Nevertheless, in other investigations, the geometry of the uncovered WaldenTS of HOO⁻ + CH₃Cl is in accordance with that presented in this benchmark work.^{79,88,95} It should also be highlighted that Wu *et al.* identified PreMIN and WaldenTS for Y = I at the MP2/6-311++G(d,p) level of theory,⁹⁶ although, in the course of the present study, WaldenTS cannot be found for Y = I at the MP2/aug-cc-pVDZ and CCSD(T)-F12b/aug-cc-pVnZ [*n* = 2, 3] levels of theory. Hence, the issues regarding these stationary points underline the relevance of employing higher-level *ab initio* methods for theoretical investigations. Concerning PostHMIN, alternative conformational isomers cannot be determined in contrast to the HO⁻ + CH₃F reaction.⁴⁰ As shown in Fig. 2, the transition states of the front-side attack mechanism differ from each other in the orientation of the HOO⁻ group, and owing to the additional Y···HO bond, FSTS2 is below FSTS1 in the case of Y = F and Cl. It is noteworthy that all the stationary-point characterizations can be performed without imposing symmetry restrictions, except for ABSMIN1, which has C_s symmetry. There are cases, where a C_s symmetry

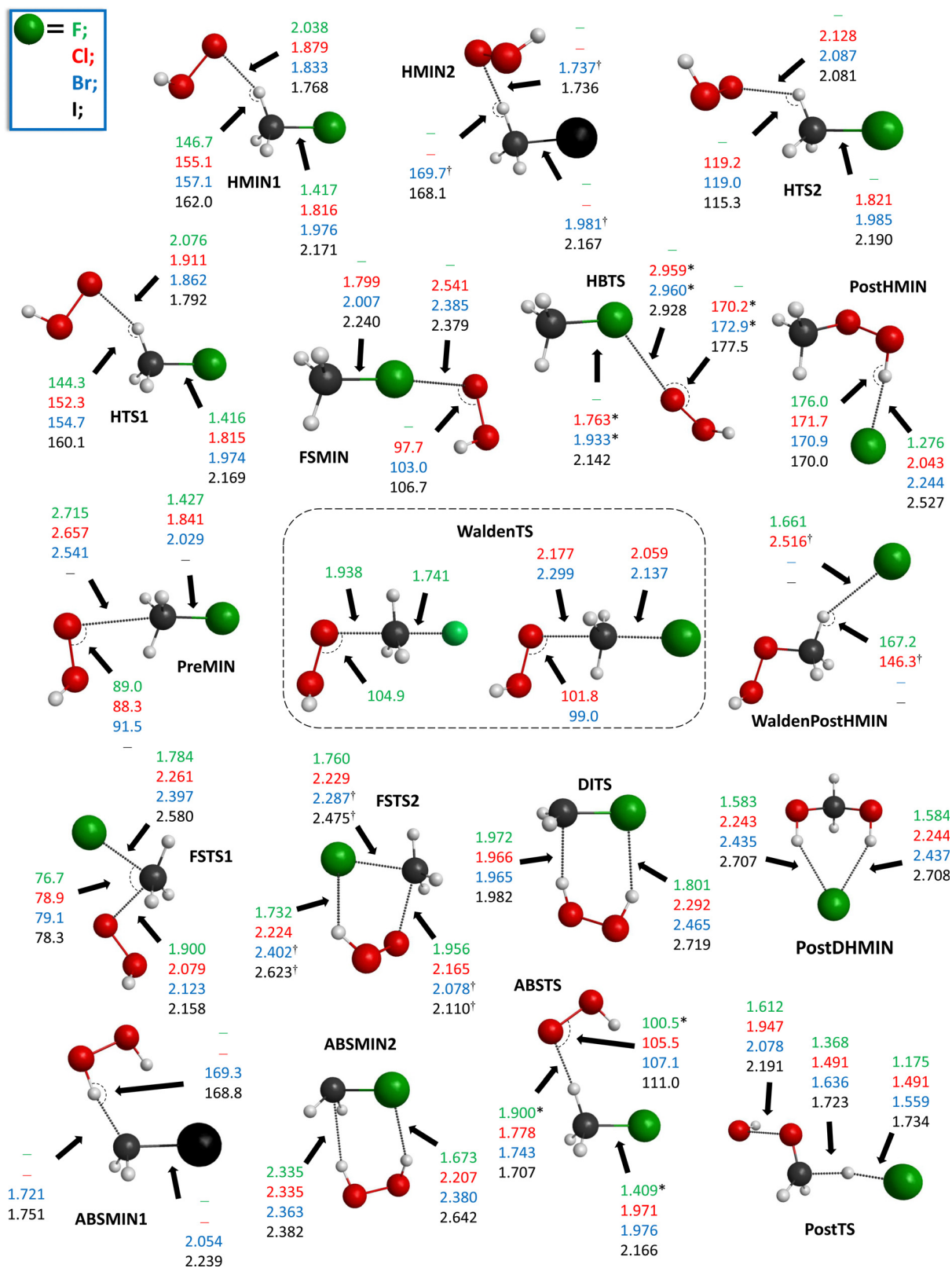


Fig. 2 Structures of the stationary points of the $\text{HOO}^- + \text{CH}_3\text{Y}$ [$\text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$] reactions showing the most important bond lengths (Å) and angles (°) obtained at the CCSD(T)-F12b/aug-cc-pVTZ level of theory. [†] MP2/aug-cc-pVDZ structure; *CCSD(T)-F12b/aug-cc-pVDZ structure. Note that for $\text{Y} = \text{F}$ at WaldenTS, a distinct structure can be identified compared to the case of $\text{Y} = \text{Cl}$ and Br .

would also be expected (e.g., HTS1, ABSTS); however, the corresponding geometry optimizations do not converge. The most accurate, CCSD(T)-F12b/aug-cc-pVTZ Cartesian coordinates of the stationary points, as well as of reactants and products, are provided in the ESI.†

The calculated classical and adiabatic *ab initio* relative energies of the products and the available “experimental” reaction enthalpies obtained from the active thermochemical tables (ATcT)^{113,114} are given in Table 2. The benchmark structures of the reactants and products are shown in Fig. 3. The reaction enthalpies of S_N2 and proton abstraction decrease with increasing atomic weight of Y, whereas for the other pathways, a reverse tendency is revealed. Alongside the proton-abstraction channels for Y = F, Cl, Br and I, peroxide ion substitution is also an endothermic pathway in the case of Y = I. It is notable that for Y = F, the difference between the reaction enthalpies of S_N2 and peroxide ion substitution is only 0.5 kcal mol⁻¹. In most instances, our benchmark results are in satisfactory agreement with the experimental data, except for the $\text{CH}_2\text{Cl}^- + \text{H}_2\text{O}_2$ products, where a difference of 1.2 kcal mol⁻¹ emerges. However, it should be noted that the derived uncertainty of the experimental reaction enthalpy is remarkably substantial (± 0.5 kcal mol⁻¹). Similarly, for the $\text{F}^- + \text{CH}_3\text{Cl} \rightarrow \text{CH}_2\text{Cl}^- + \text{HF}$ proton-abstraction channel, a large deviation (0.9 kcal mol⁻¹) can also be observed between the experimental and our calculated benchmark reaction enthalpy with a significant uncertainty (0.5 kcal mol⁻¹) of the experimental value.¹¹² Thus, these cases may highlight the inaccuracy of the available 0 K enthalpy of formation for CH_2Cl^- in the ATcT. In the case of the $\text{HOO}^- + \text{CH}_3\text{Y}$ [Y = F and Cl] S_N2 reactions, the reaction energies of -13.0 (F) and -45.3 (Cl) kcal mol⁻¹, obtained by Wu *et al.* utilizing CCSD(T)/aug-cc-pVTZ(-PP) energy calculations at the MP2/6-311++G(d,p) geometries,⁹⁶ in kcal mol⁻¹ are in conformity with our benchmark values of -13.0 (F) and -45.8 (Cl) kcal mol⁻¹. Although, for Y = Br and I, their S_N2 reaction energies of -50.9 and -56.4 kcal mol⁻¹ are higher than our results by 3.1 and 4.5 kcal mol⁻¹, respectively. The classical

energies of the stationary points of the present work can also be compared with the results of Wu *et al.*⁹⁶ They characterized five stationary points (HMIN1, HTS2, PreMIN, WaldenTS and PostHMIN) along the back-side attack Walden inversion, mainly, their computed CCSD(T)/aug-cc-pVTZ(-PP) energies are in good agreement with our benchmark data. In an earlier study on $\text{HOO}^- + \text{CH}_3\text{Cl}$ by Zhao *et al.*,⁹⁵ the reported energies of PreMIN and PostHMIN at the MP2/6-31+G(d,p) level of theory are in good agreement with the present benchmark values. For WaldenTS, a difference of more than 2 kcal mol⁻¹ occurs; moreover, an enormous deviation of 13.2 kcal mol⁻¹ is obtained at Walden-PostHMIN, remarkably. Motivated by this discrepancy, we characterized the corresponding stationary points of $\text{HOO}^- + \text{CH}_3\text{Cl}$ at the MP2/6-31+G(d,p) level of theory using the MOLPRO program package.¹⁰⁸ In the course of computations, spherical harmonic basis functions are used; however, it is noteworthy that by employing Cartesian functions, comparable relative energies can be obtained within ± 0.3 kcal mol⁻¹. Our obtained MP2/6-31+G(d,p) classical energies of -14.9 (PreMIN), -10.5 (WaldenTS), -64.6 (PostHMIN), -53.2 (WaldenPostHMIN), -31.5 (PostTS), and -136.5 (PostDHMIN), in kcal mol⁻¹, are in conformity with the benchmark data. While our optimized structures of the stationary points show satisfactory alignment with those determined by Zhao *et al.*,⁹⁵ significant inexplicable disparities are unveiled for the classical energies in a few cases. We also determined the classical (adiabatic) energies of the products at the MP2/6-31+G(d,p) level; $\text{CH}_2\text{Cl}^- + \text{H}_2\text{O}_2$: 29.4 (27.7), $\text{CH}_3\text{OOH} + \text{Cl}^-$ -45.7 (-43.5), $\text{CH}_3\text{OO}^- + \text{HCl}$: -2.1 (-3.7), $\text{CH}_2\text{O} + \text{HCl} + \text{HO}^-$: -40.0 (-45.8) and $\text{CH}_2(\text{OH})\text{O}^- + \text{HCl}$: -75.2 (-76.8), in kcal mol⁻¹. It can be seen that for certain cases, the provided energies differ from the experiment by more than 4 kcal mol⁻¹; especially for proton abstraction, an enormous difference of 6.1 kcal mol⁻¹ occurs, which casts doubt on the reliability of MP2/6-31+G(d,p). The G2+ adiabatic energies of WaldenTS (-13.5 kcal mol⁻¹) and the S_N2 products (-43.2 kcal mol⁻¹), computed by Ren *et al.* for $\text{HOO}^- + \text{CH}_3\text{Cl}$, are also in consonance with the present study.⁷⁹

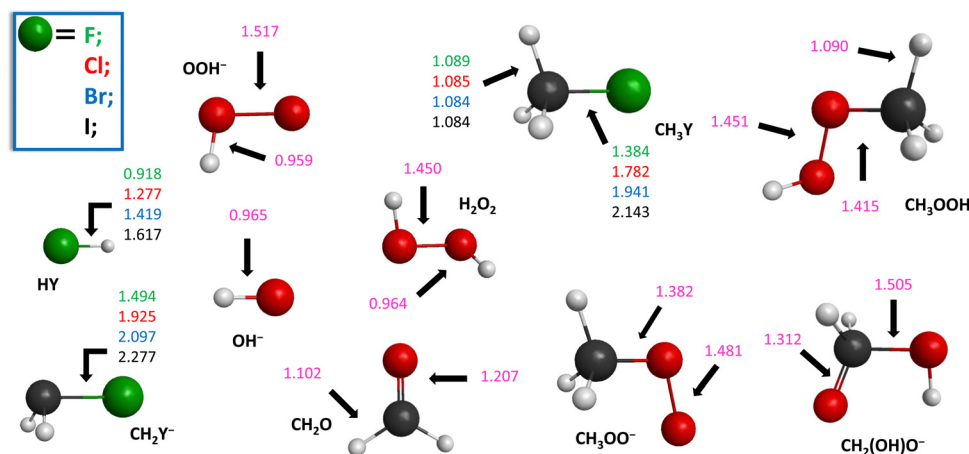


Fig. 3 Structures of the reactants and products of the $\text{HOO}^- + \text{CH}_3\text{Y}$ [Y = F, Cl, Br, I] reactions showing the most important bond lengths (Å) obtained at the CCSD(T)-F12b/aug-cc-pVTZ level of theory.

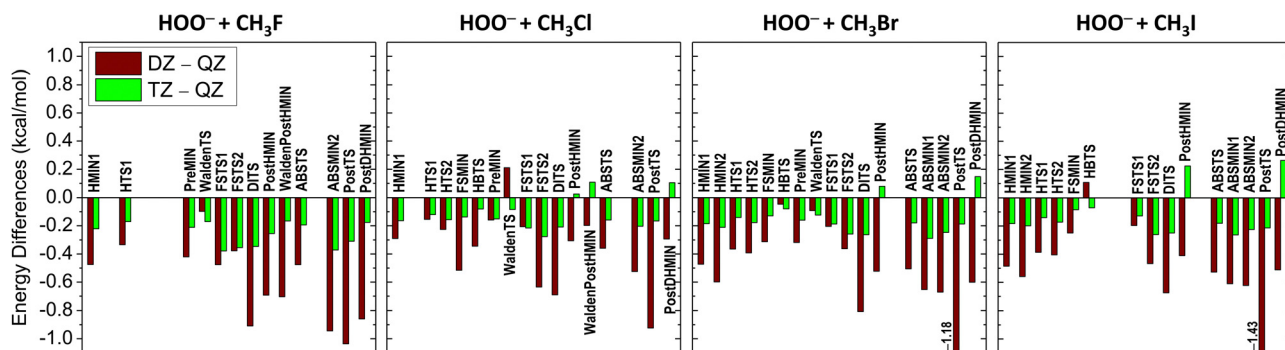


Fig. 4 Convergence of the CCSD(T)-F12b relative energies for the stationary points of the $\text{HOO}^- + \text{CH}_3\text{Y}$ [$\text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$] reactions utilizing the aug-cc-pVDZ (DZ), aug-cc-pVTZ (TZ) and aug-cc-pVQZ (QZ) basis sets.

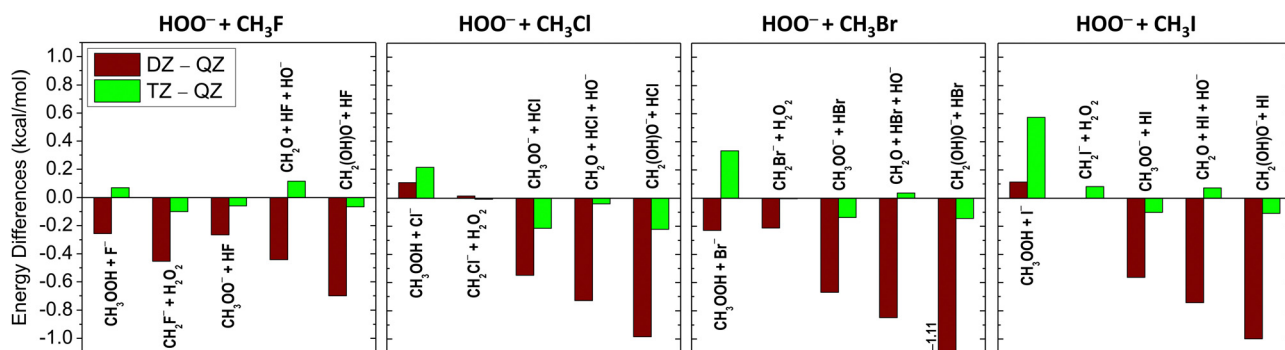


Fig. 5 Convergence of the CCSD(T)-F12b relative energies for the product channels of the $\text{HOO}^- + \text{CH}_3\text{Y}$ [$\text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$] reactions utilizing the aug-cc-pVDZ (DZ), aug-cc-pVTZ (TZ) and aug-cc-pVQZ (QZ) basis sets.

As shown in Fig. 4 and 5, the basis-set convergence of the CCSD(T)-F12b relative energies is also investigated for the title reactions. In most cases, a fast and smooth basis-set convergence can be recognized, except for WaldenTS [$\text{Y} = \text{F}$ and Br], HBTS [$\text{Y} = \text{Br}$], FST1 [$\text{Y} = \text{Cl}$] and $\text{CH}_3\text{OOH} + \text{Y}^-$ [$\text{Y} = \text{Cl}, \text{Br}$ and I], as in these instances the relative energy differences between aug-cc-pVDZ (DZ) and aug-cc-pVQZ (QZ) are smaller than the corresponding values of aug-cc-pVTZ (TZ) and QZ. The largest differences emerge at PostTS [$\text{Y} = \text{Br}$ and I] and $\text{CH}_2(\text{OH})\text{O}^- + \text{HBr}$, where the deviations between the DZ and QZ relative energies are found to be in the range of 1.1–1.4 kcal mol^{-1} . In contrast, the energy differences between TZ and QZ are within $\pm 0.4 \text{ kcal mol}^{-1}$, except at $\text{CH}_3\text{OOH} + \text{I}^-$ ($0.57 \text{ kcal mol}^{-1}$). Regarding the ZPE effects, the most significant contributions appear at the post-reaction stationary points (PostHMIN, WaldenPostHMIN, PostTS and PostDHMIN) and for the products of $\text{CH}_3\text{OOH} + \text{Y}^-$ and $\text{CH}_2\text{O} + \text{HY} + \text{HO}^-$. The vast majority of the stationary points have positive ZPE corrections, whereas, in the case of the reaction channels, positive ZPE effects occur only for the $\text{CH}_3\text{OOH} + \text{Y}^-$ products.

IV. Summary and conclusions

In this study, we have characterized the complex potential energy surfaces of the $\text{HOO}^- + \text{CH}_3\text{Y}$ [$\text{Y} = \text{F}, \text{Cl}, \text{Br}$ and I] reactions using the modern explicitly-correlated CCSD(T)-F12b

method with the aug-cc-pVnZ [$n = 2-4$] basis sets. For $\text{S}_{\text{N}}2$, we have considered the pathways of back-side attack Walden inversion, front-side attack, double inversion¹⁹ and halogen-bonded complex formation.⁴⁸ In most cases, the entrance channel of $\text{HOO}^- + \text{CH}_3\text{Y}$ comprises seven stationary points: two H-bonded, a front-side halogen-bonded and a traditional ion-dipole minima, as well as two H-bonded and front-side halogen-bonded transition states. Similar to the $\text{HO}^- + \text{CH}_3\text{Y}$ $\text{S}_{\text{N}}2$ reactions,^{24,38} no typical transition state has been identified for the Walden inversion in the case of $\text{Y} = \text{I}$, and in light of the discrepancy of the earlier findings, we have clarified the accurate structure of the Walden-inversion transition state for $\text{Y} = \text{Cl}$. In the exit channel of $\text{S}_{\text{N}}2$, two H-bonded minima are situated: $\text{Y}^- \cdots \text{HOOCH}_3$ and $\text{Y}^- \cdots \text{HCH}_2\text{OOH}$. Based on the findings of Xie and co-workers,⁹⁵ the $\text{HOO}^- + \text{CH}_3\text{Cl}$ reaction can proceed through $\text{Cl}^- \cdots \text{HCH}_2\text{OOH}$ towards the $[\text{Cl} \cdots \text{H} \cdots \text{CH}_2\text{O} \cdots \text{OH}]^-$ transition state generating the unusual products of $\text{CH}_2\text{O} + \text{HCl} + \text{HO}^-$. It should be highlighted that for $\text{HOO}^- + \text{CH}_3\text{F}$, the reaction enthalpy of this novel $\text{S}_{\text{N}}2$ -induced elimination is more negative by $36.3 \text{ kcal mol}^{-1}$ than the corresponding $\text{S}_{\text{N}}2$ process. Concerning the retention paths of $\text{S}_{\text{N}}2$, two distinct transition states have been recognized for front-side attacks, and as observed for $\text{HO}^- + \text{CH}_3\text{Y}$, double inversion is a lower-energy process than front-side attack.^{24,38} Building upon the earlier work of Xie and co-workers,⁹⁵ besides $\text{S}_{\text{N}}2$ -induced elimination, we have also investigated other channels such as proton abstraction ($\text{CH}_2\text{Y}^- + \text{H}_2\text{O}_2$), peroxide ion substitution ($\text{CH}_3\text{OO}^- + \text{HY}$) and

S_N2 -induced rearrangement ($\text{CH}_2(\text{OH})\text{O}^- + \text{HY}$). In the case of $\text{Y} = \text{F}, \text{Cl}$ and Br , the peroxide ion substitution has been found to be exothermic with reaction enthalpies of -11.1 (F), -4.7 (Cl) and -2.2 (Br) kcal mol^{-1} . The most exothermic path is S_N2 -induced rearrangement; however, it is presumed to be an improbable reaction channel due to the complex bond-breaking and -forming processes involved. The benchmark reaction enthalpies presented in this work are usually in excellent agreement with those obtained from ATcT.^{113,114} We have also assessed the basis-set convergence of the CCSD(T)-F12b method and the ZPE contributions of the stationary points.

We are confident that the present benchmark characterization of $\text{HOO}^- + \text{CH}_3\text{Y}$ supports further theoretical and experimental investigations regarding reaction dynamics as well as the influence of the α -effect related to HOO^- .

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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