


 Cite this: *Phys. Chem. Chem. Phys.*, 2024, 26, 16048

# 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  $\alpha$ -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  $\alpha$ -nucleophile  $\text{HOO}^-$  with methyl halides have been thoroughly investigated experimentally and theoretically; however, these investigations have mainly focused on identifying and characterizing the  $\alpha$ -effect of  $\text{HOO}^-$ . 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.

 Received 11th March 2024,  
 Accepted 6th May 2024

DOI: 10.1039/d4cp01071j

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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.<sup>1-10</sup> In step with the progress of computational chemistry and experimental methodology,<sup>11-16</sup> 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.<sup>17-21</sup>

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  $\text{HO}^-$ .<sup>22-38</sup> 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.<sup>22</sup> 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.<sup>39-41</sup> Over the years, the primary focus has been on the dynamical characterization of the  $\text{HO}^- + \text{CH}_3\text{I}$  reaction.<sup>42-48</sup> 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.<sup>10,14,49</sup> 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.<sup>50-52</sup> 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.<sup>53,54</sup> 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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† Electronic supplementary information (ESI) available: Benchmark Cartesian coordinates ( $\text{\AA}$ ) and energies ( $E_{\text{h}}$ ) of the stationary points. See DOI: <https://doi.org/10.1039/d4cp01071j>



in order to analyze the dynamics of the reaction in a more detailed manner.<sup>55</sup> 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.<sup>56,57</sup>

Besides considering di- or polyatomic 'normal' nucleophiles (e.g., HO<sup>-</sup>, CN<sup>-</sup>, NH<sub>2</sub><sup>-</sup>, PH<sub>2</sub><sup>-</sup> etc.),<sup>10,24,58-63</sup> a significant emphasis has been placed on  $\alpha$ -nucleophiles (e.g., HOO<sup>-</sup>, ClO<sup>-</sup>, BrO<sup>-</sup>, CH<sub>3</sub>OO<sup>-</sup>, HOHN<sup>-</sup>, NH<sub>2</sub>O<sup>-</sup>, etc.) participating in S<sub>N</sub>2 reactions.<sup>8,9,64-71</sup> In the case of these  $\alpha$ -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.<sup>72</sup> This phenomenon is known as the  $\alpha$ -effect.<sup>73</sup> While the existence of the  $\alpha$ -effect was beyond doubt in solution, the situation was not as clearly defined in the gas phase.<sup>72,74,75</sup> By comparing the branching ratios for the reactions of HO<sup>-</sup> and HOO<sup>-</sup> with methyl formate, DePuy and co-workers concluded that HOO<sup>-</sup> does not show the  $\alpha$ -effect in the gas phase.<sup>76</sup> In addition, Villiano *et al.* unveiled that a noticeable  $\alpha$ -effect cannot be observed for the HOO<sup>-</sup>/ClO<sup>-</sup>/BrO<sup>-</sup> + CH<sub>3</sub>R (R = CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>, etc.) systems, as well.<sup>65</sup> In contrast, the opposite of these findings has been confirmed, and several studies have verified that the  $\alpha$ -effect stems from the intrinsic properties of  $\alpha$ -nucleophiles validating the manifestation of this phenomenon in the gas phase.<sup>77-85</sup> However, the identification of these intrinsic properties of  $\alpha$ -nucleophiles remained disputed.<sup>86-93</sup> Recently, Hamlin *et al.* reported an extensive theoretical survey on the origin of the  $\alpha$ -effect in the gas phase.<sup>71</sup> 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  $\alpha$ -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  $\alpha$ -nucleophiles compared to their 'normal' counterparts.

Regarding S<sub>N</sub>2 reactions involving HOO<sup>-</sup>, several theoretical investigations have concentrated on the stationary-point and dynamical characterization, as well.<sup>74,88,94-97</sup> In the course of the aforementioned  $\alpha$ -effect examinations, the stationary points of the corresponding Walden-inversion pathways were determined for several S<sub>N</sub>2 reactions of HOO<sup>-</sup> at various levels of theory. The HOO<sup>-</sup>···CH<sub>3</sub>Y → [HOO···CH<sub>3</sub>···Y]<sup>-</sup> → CH<sub>3</sub>OOH···Y<sup>-</sup> path was explored by Evanseck *et al.* for Y = Cl at the level of HF/6-31+G(d).<sup>74</sup> Later, in the theoretical surveys of Ren *et al.*, the geometries of the [HOO···CH<sub>3</sub>···Y]<sup>-</sup> 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.<sup>78,79</sup> Associated with the microsolvated variants of the HOO<sup>-</sup> + CH<sub>3</sub>Cl S<sub>N</sub>2 reaction, the unsolvated Walden-inversion pathways were also characterized in the studies of Thomsen *et al.*<sup>88</sup> and Hu *et al.*<sup>97</sup> 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<sup>-</sup>(H<sub>2</sub>O)<sub>n</sub> + CH<sub>3</sub>Y [Y = F, Cl, Br, I; n = 0, 1, 2]

S<sub>N</sub>2 reactions, whereby they identified two H-bonded stationary points in the entrance channel, as well.<sup>96</sup> The dynamics of the HOO<sup>-</sup>(H<sub>2</sub>O)<sub>n</sub> + CH<sub>3</sub>Cl reactions, where n = 0 or 1, was also examined with direct dynamics simulations.<sup>94,95</sup> It is noteworthy that, based on the earlier work of Anick *et al.*,<sup>98</sup> the only stable structure for the singly hydrated hydroperoxide ion is HO<sup>-</sup>(HOH), which indicates that in the S<sub>N</sub>2 reaction with CH<sub>3</sub>Cl, two distinct pathways may be possible, leading to the CH<sub>3</sub>OOH + Cl<sup>-</sup> + H<sub>2</sub>O and CH<sub>3</sub>OH + Cl<sup>-</sup> + H<sub>2</sub>O<sub>2</sub> products. Recently, dynamics simulations performed by Zhao *et al.*<sup>95</sup> have substantiated that both reaction routes are viable, indicating the fact that a single solvent water molecule can induce a new nucleophile in S<sub>N</sub>2 reactions, which opens the door for an alternative pathway. Moreover, for the unsolvated HOO<sup>-</sup> + CH<sub>3</sub>Cl reaction, similar to the case of ClO<sup>-</sup> + CH<sub>3</sub>Cl,<sup>65,69</sup> a novel non-S<sub>N</sub>2 pathway generating the CH<sub>2</sub>O + HCl + HO<sup>-</sup> products was also unveiled. Besides the dynamical description, the PES of the considered product channels of the HOO<sup>-</sup> + CH<sub>3</sub>Cl reaction was mapped at the MP2/6-31+G(d,p) level of theory.<sup>95</sup>

In the present work, based on the prominent attention paid to the S<sub>N</sub>2 reactions involving hydroperoxide ions, we perform a comprehensive benchmark *ab initio* characterization of HOO<sup>-</sup> + CH<sub>3</sub>Y [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 mechanism<sup>48</sup> and the possible S<sub>N</sub>2 retention routes of front-side attack and double inversion.<sup>19</sup> We identify the stationary points of the proton-abstraction channel, as well; furthermore, relying on the previous study of Xie and co-workers,<sup>95</sup> 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)<sup>99</sup> with the augmented correlation-consistent polarized-valence-double- $\zeta$  (aug-cc-pVDZ) basis set.<sup>100</sup> The exploration of the stationary points was conducted based on previous studies and chemical intuition;<sup>24,38,95</sup> 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.<sup>101-103</sup> 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<sup>104-106</sup> is utilized with the aug-cc-pVDZ and aug-cc-pVTZ basis sets.<sup>100</sup> 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





**Table 1** Benchmark classical and adiabatic energies (kcal mol<sup>-1</sup>) of the stationary points relative to the reactants for the possible pathways of the HOO<sup>-</sup> + CH<sub>3</sub>Y [Y = F, Cl, Br, I] reactions

HOO <sup>-</sup> + CH <sub>3</sub> F	MP2	CCSD(T)-F12b			$\Delta ZPE^e$	Adiabatic <sup>f</sup>
	DZ <sup>a</sup>	DZ <sup>b</sup>	TZ <sup>c</sup>	QZ <sup>d</sup>		
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 <sup>g</sup>	-10.52 <sup>g</sup>	0.44 <sup>g</sup>	-10.08 <sup>g</sup>
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 <sup>-</sup> + CH <sub>3</sub> Cl	MP2 <sup>a</sup>	DZ <sup>b</sup>	TZ <sup>c</sup>	QZ <sup>d</sup>	$\Delta ZPE^e$	Adiabatic <sup>f</sup>
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 <sup>g</sup>	1.14 <sup>g</sup>	0.26 <sup>g</sup>	1.40 <sup>g</sup>
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 <sup>h</sup>	-53.44 <sup>h</sup>	-53.55 <sup>h</sup>	2.48 <sup>h</sup>	-51.07 <sup>h</sup>
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 <sup>-</sup> + CH <sub>3</sub> Br	MP2 <sup>a</sup>	DZ <sup>b</sup>	TZ <sup>c</sup>	QZ <sup>d</sup>	$\Delta ZPE^e$	Adiabatic <sup>f</sup>
HMIN1	-17.61	-17.21	-16.92	-16.74	0.74	-15.99
HMIN2	-17.22	-16.57 <sup>h</sup>	-16.18 <sup>h</sup>	-15.97 <sup>h</sup>	0.82 <sup>h</sup>	-15.15 <sup>h</sup>
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 <sup>g</sup>	-0.62 <sup>g</sup>	0.39 <sup>g</sup>	-0.23 <sup>g</sup>
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 <sup>h</sup>	13.29 <sup>h</sup>	13.55 <sup>h</sup>	0.95 <sup>h</sup>	14.50 <sup>h</sup>
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 <sup>-</sup> + CH <sub>3</sub> I	MP2 <sup>a</sup>	DZ <sup>b</sup>	TZ <sup>c</sup>	QZ <sup>d</sup>	$\Delta ZPE^e$	Adiabatic <sup>f</sup>
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 <sup>h</sup>	8.67 <sup>h</sup>	8.93 <sup>h</sup>	1.08 <sup>h</sup>	10.01 <sup>h</sup>
DITS	3.40	2.68	3.11	3.36	0.19	3.55



Table 1 (continued)

HOO <sup>-</sup> + CH <sub>3</sub> I	MP2 <sup>a</sup>	DZ <sup>b</sup>	TZ <sup>c</sup>	QZ <sup>d</sup>	ΔZPE <sup>e</sup>	Adiabatic <sup>f</sup>
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

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

### III. Results and discussion

The complex PESs of the HOO<sup>-</sup> + CH<sub>3</sub>Y [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<sup>-</sup>/ClO<sup>-</sup> + CH<sub>3</sub>Cl and HO<sup>-</sup> + CH<sub>3</sub>F reactions,<sup>40,65,69,95</sup> in addition to the typical S<sub>N</sub>2 (CH<sub>3</sub>OOH + Y<sup>-</sup>) and proton-abstraction (CH<sub>2</sub>Y<sup>-</sup> + H<sub>2</sub>O<sub>2</sub>) routes, alternative channels of peroxide ion substitution (CH<sub>3</sub>OO<sup>-</sup> + HY), S<sub>N</sub>2-induced elimination (CH<sub>2</sub>O + HY + HO<sup>-</sup>) and S<sub>N</sub>2-induced rearrangement (CH<sub>2</sub>(OH)O<sup>-</sup> + HY) are also analyzed. It should be noted that in the case of the HOO<sup>-</sup> + CH<sub>3</sub>Cl reaction, the dynamical characterization reported by Xie and co-workers did not reveal the existence of the corresponding peroxide ion substitution, S<sub>N</sub>2-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<sup>-1</sup>.<sup>95</sup> However, the pathways of peroxide ion substitution and S<sub>N</sub>2-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<sup>-</sup> + CH<sub>3</sub>Y: 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<sup>-1</sup>. 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<sup>-</sup> + CH<sub>3</sub>Y,<sup>24,38</sup> FSMIN is situated above HMIN1 by 13.2 (12.8) and 6.0 (5.6) kcal mol<sup>-1</sup> for Y = Cl and Br, in order; while for Y = I, FSMIN is below HMIN1 by 4.5 (4.7) kcal mol<sup>-1</sup>. 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<sup>-1</sup>. 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<sup>-1</sup> 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<sub>N</sub>2 reactions involving CH<sub>3</sub>I.<sup>48,60,109</sup> 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<sup>-</sup> case.<sup>24,38</sup> 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<sup>-1</sup> for Y = F, Cl and Br, respectively, while in the case of HO<sup>-</sup> at the same level of theory, these values are 11.2 (11.4), 2.4 (2.4) and 0.2 (0.1) kcal mol<sup>-1</sup>, in the same order. The global minimum of S<sub>N</sub>2 is also located at PostHMIN, although, compared to HO<sup>-</sup> + CH<sub>3</sub>Y, higher classical energies of -49.7, -65.6, -70.9 and -74.7 kcal mol<sup>-1</sup> can be determined for HOO<sup>-</sup> 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<sub>N</sub>2 channels: HOO<sup>-</sup> + CH<sub>3</sub>Y happens to be more endothermic by exactly 6.1 kcal mol<sup>-1</sup> in all cases. As a result, in the case of the S<sub>N</sub>2 reactions of HOO<sup>-</sup>, larger dissociation energies can be observed for the leaving Y<sup>-</sup> 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 CH<sub>3</sub>OO<sup>-</sup> + HY products is also more exothermic than that of the HO<sup>-</sup> cases, predicting a substantially increased probability for peroxide ion substitution, especially for HOO<sup>-</sup> + CH<sub>3</sub>F.<sup>40</sup> WaldenPostHMIN also plays a significant role, as Zhao *et al.*<sup>95</sup> uncovered, and the reaction can proceed through this minimum towards PostTS, leading to the unusual CH<sub>2</sub>O + HY + HO<sup>-</sup> 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<sub>N</sub>2-induced elimination is exceedingly more exothermic than S<sub>N</sub>2, submerged by 29.9 (36.3) kcal mol<sup>-1</sup>. The global minimum of the PES is situated at the double H-bonded PostDHMIN complex, and the most exothermic process corresponds to the S<sub>N</sub>2-induced rearrangement channel, but it is supposedly an improbable reaction route considering the multiple bond-breaking and -forming processes involved. Concerning the S<sub>N</sub>2 pathways that result in the retention of the initial CH<sub>3</sub>Y configuration, two different transition states (FSTS1 and FSTS2) can be identified for front-side attacks. According to the study of Ma *et al.*,<sup>110</sup> 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.<sup>111,112</sup> Similarly to the HO<sup>-</sup> case, the transition state of double inversion has lower energy than that of front-side attack; however, no submerged DITS can be obtained.<sup>24,38</sup> 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<sup>-1</sup>) of several product channels for the HOO<sup>-</sup> + CH<sub>3</sub>Y [Y = F, Cl, Br, I] reactions

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

<sup>a</sup> MP2/aug-cc-pVDZ. <sup>b</sup> CCSD(T)-F12b/aug-cc-pVDZ. <sup>c</sup> CCSD(T)-F12b/aug-cc-pVTZ. <sup>d</sup> CCSD(T)-F12b/aug-cc-pVQZ at CCSD(T)-F12b/aug-cc-pVTZ geometry. <sup>e</sup> ΔZPE(CCSD(T)-F12b/aug-cc-pVTZ). <sup>f</sup> QZ + ΔZPE. <sup>g</sup> Data obtained from the latest version (1.130) of the Active Thermochemical Tables (ATcT).<sup>113,114</sup> 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<sup>-1</sup>. The entrance channel of proton abstraction is found to be the same as that for S<sub>N</sub>2 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<sup>-</sup> 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<sub>N</sub>2 reactions, similar discrepancies observed at CH<sub>3</sub>F are not uncommon;<sup>24</sup> for instance, in the case of HO<sup>-</sup> + CH<sub>3</sub>Y,<sup>38</sup> for Y = Cl, Br and I FSTS has C<sub>s</sub> symmetry, while for Y = F, the symmetry is broken. It should be noted that previous studies on the HOO<sup>-</sup> + CH<sub>3</sub>Cl S<sub>N</sub>2 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.<sup>96,97</sup> 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.<sup>74</sup> 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.<sup>78</sup> Nevertheless, in other investigations, the geometry of the uncovered WaldenTS of HOO<sup>-</sup> + CH<sub>3</sub>Cl is in accordance with that presented in this benchmark work.<sup>79,88,95</sup> 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,<sup>96</sup> 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<sup>-</sup> + CH<sub>3</sub>F reaction.<sup>40</sup> As shown in Fig. 2, the transition states of the front-side attack mechanism differ from each other in the orientation of the HOO<sup>-</sup> 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<sub>s</sub> symmetry. There are cases, where a C<sub>s</sub> symmetry



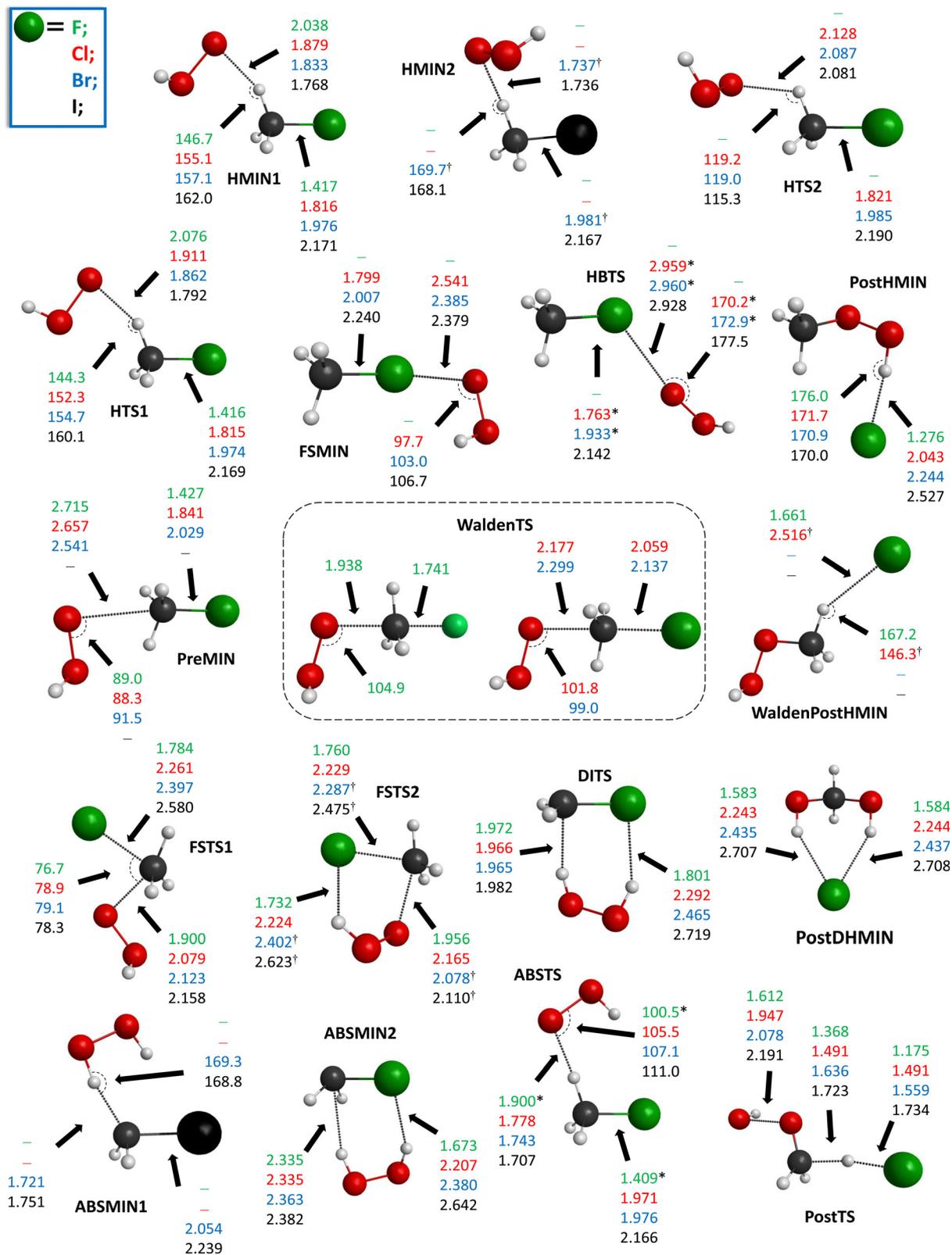


Fig. 2 Structures of the stationary points of the  $\text{HOO}^- + \text{CH}_3\text{Y}$  [ $\text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ] reactions showing the most important bond lengths (Å) and angles (°) obtained at the CCSD(T)-F12b/aug-cc-pVTZ level of theory. <sup>†</sup> MP2/aug-cc-pVDZ 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  $\text{Br}$ .



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)<sup>113,114</sup> 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<sup>-1</sup>. 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<sup>-1</sup> emerges. However, it should be noted that the derived uncertainty of the experimental reaction enthalpy is remarkably substantial ( $\pm 0.5$  kcal mol<sup>-1</sup>). 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<sup>-1</sup>) can also be observed between the experimental and our calculated benchmark reaction enthalpy with a significant uncertainty (0.5 kcal mol<sup>-1</sup>) of the experimental value.<sup>112</sup> Thus, these cases may highlight the inaccuracy of the available 0 K enthalpy of formation for  $\text{CH}_2\text{Cl}^-$  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<sup>-1</sup>, obtained by Wu *et al.* utilizing CCSD(T)/aug-cc-pVTZ(-PP) energy calculations at the MP2/6-311++G(d,p) geometries,<sup>96</sup> in kcal mol<sup>-1</sup> are in conformity with our benchmark values of -13.0 (F) and -45.8 (Cl) kcal mol<sup>-1</sup>. Although, for Y = Br and I, their  $S_N2$  reaction energies of -50.9 and -56.4 kcal mol<sup>-1</sup> are higher than our results by 3.1 and 4.5 kcal mol<sup>-1</sup>, respectively. The classical

energies of the stationary points of the present work can also be compared with the results of Wu *et al.*<sup>96</sup> 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.*,<sup>95</sup> 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<sup>-1</sup> occurs; moreover, an enormous deviation of 13.2 kcal mol<sup>-1</sup> 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.<sup>108</sup> 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  $\pm 0.3$  kcal mol<sup>-1</sup>. 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<sup>-1</sup>, 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.*,<sup>95</sup> 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<sup>-1</sup>. It can be seen that for certain cases, the provided energies differ from the experiment by more than 4 kcal mol<sup>-1</sup>; especially for proton abstraction, an enormous difference of 6.1 kcal mol<sup>-1</sup> occurs, which casts doubt on the reliability of MP2/6-31+G(d,p). The G2+ adiabatic energies of WaldenTS (-13.5 kcal mol<sup>-1</sup>) and the  $S_N2$  products (-43.2 kcal mol<sup>-1</sup>), computed by Ren *et al.* for  $\text{HOO}^- + \text{CH}_3\text{Cl}$ , are also in consonance with the present study.<sup>79</sup>

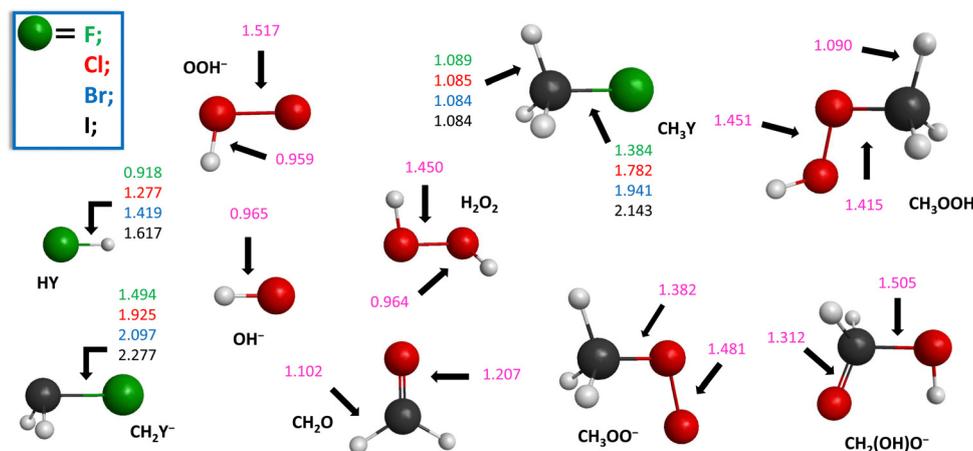


Fig. 3 Structures of the reactants and products of the  $\text{HOO}^- + \text{CH}_3\text{Y}$  [Y = F, Cl, Br, I] reactions showing the most important bond lengths (Å) obtained at the CCSD(T)-F12b/aug-cc-pVTZ level of theory.



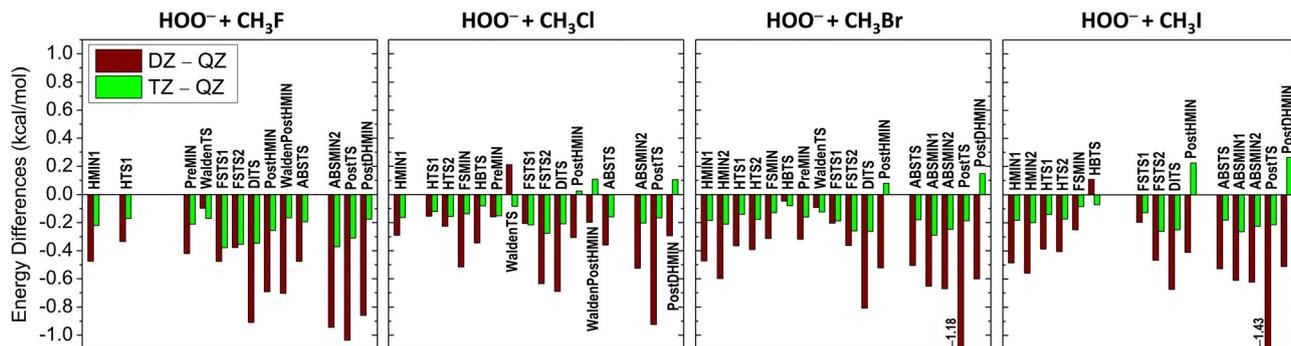


Fig. 4 Convergence of the CCSD(T)-F12b relative energies for the stationary points of the  $\text{HOO}^- + \text{CH}_3\text{Y}$  [ $\text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ] reactions utilizing the aug-cc-pVDZ (DZ), aug-cc-pVTZ (TZ) and aug-cc-pVQZ (QZ) basis sets.

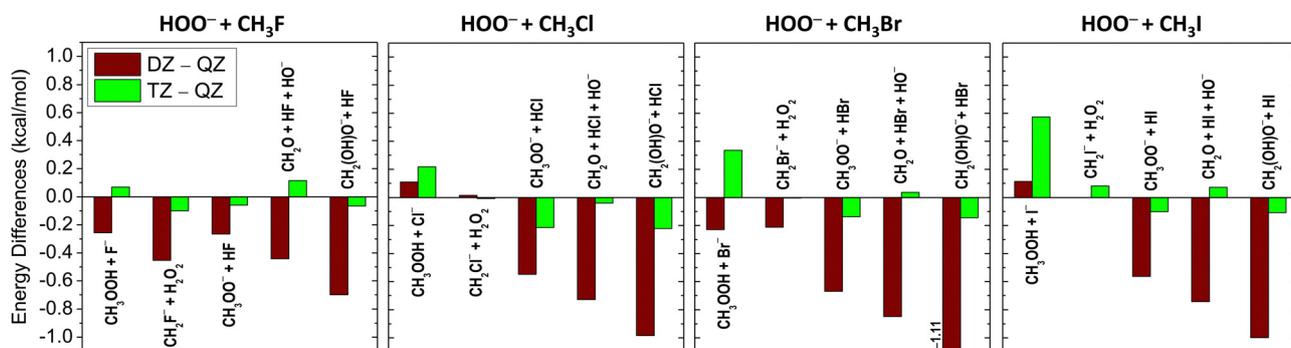


Fig. 5 Convergence of the CCSD(T)-F12b relative energies for the product channels of the  $\text{HOO}^- + \text{CH}_3\text{Y}$  [ $\text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ] reactions utilizing the aug-cc-pVDZ (DZ), aug-cc-pVTZ (TZ) and aug-cc-pVQZ (QZ) basis sets.

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 [ $\text{Y} = \text{Br}$ ], FSTS1 [ $\text{Y} = \text{Cl}$ ] 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<sup>-1</sup>. In contrast, the energy differences between TZ and QZ are within  $\pm 0.4$  kcal mol<sup>-1</sup>, except at  $\text{CH}_3\text{OOH} + \text{I}^-$  (0.57 kcal mol<sup>-1</sup>). 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 inversion<sup>19</sup> and halogen-bonded complex formation.<sup>48</sup> 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,<sup>24,38</sup> 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,<sup>95</sup> 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 kcal mol<sup>-1</sup> 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.<sup>24,38</sup> Building upon the earlier work of Xie and co-workers,<sup>95</sup> 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  $\text{Br}$ , the peroxide ion substitution has been found to be exothermic with reaction enthalpies of  $-11.1$  (F),  $-4.7$  (Cl) and  $-2.2$  (Br)  $\text{kcal mol}^{-1}$ . 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.<sup>113,114</sup> 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  $\alpha$ -effect related to  $\text{HOO}^-$ .

## Conflicts of interest

There are no conflicts of interest to declare.

## Acknowledgements

We acknowledge the financial support of the National Research, Development and Innovation Office-NKFIH, K-125317 and K-146759; project no. TKP2021-NVA-19 provided by the Ministry of Innovation and Technology of Hungary from the National Research, Development and Innovation Fund, financed under the TKP2021-NVA funding scheme; the National Young Talent Scholarship (Grant no. NTP-NFTÖ-22-B-0050 for D. A. T.); and the Momentum (Lendület) Program of the Hungarian Academy of Sciences.

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