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# Reply to the 'Comment on "Theoretical study of the NO<sub>3</sub> radical reaction with CH<sub>2</sub>ClBr, CH<sub>2</sub>ICl, CH<sub>2</sub>BrI, CHCl<sub>2</sub>Br, and CHClBr<sub>2</sub>"' by C. J. Nielsen and Y. Tang, *Phys. Chem. Chem. Phys.*, 2022, 24, DOI: 10.1039/D2CP03013F

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In this Reply, we answer the main argument raised in the Comment about the energy of the NO<sub>3</sub> radical and its influence in the reaction profiles of the reaction of the NO<sub>3</sub> radical with CH<sub>2</sub>ClBr, CH<sub>2</sub>ICl, CH<sub>2</sub>BrI, CHCl<sub>2</sub>Br, and CHClBr<sub>2</sub> by C. J. Nielsen and Y. Tang. The optimized geometry of the NO<sub>3</sub> radical has been obtained using 49 DFT functionals: 26 functionals predict a minimum with D<sub>3h</sub> symmetry and 23 with C<sub>2v</sub> symmetry. The former functionals have been used to calculate the thermodynamic values of three reactions (X + HNO<sub>3</sub> → XH + NO<sub>3</sub>, X = OH, CH<sub>3</sub> and CCl<sub>3</sub>) and compared with experimental data. Those functionals with smaller errors have been used to recalculate the barriers of the reaction of NO<sub>3</sub> with CH<sub>2</sub>ClBr, CH<sub>2</sub>ICl, CH<sub>2</sub>BrI, CHCl<sub>2</sub>Br, and CHClBr<sub>2</sub>. The results show differences of 10.5 kJ mol<sup>-1</sup> when compared to those obtained with the M08HX functional.

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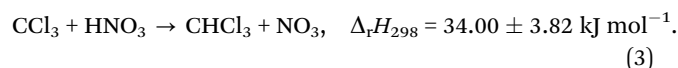
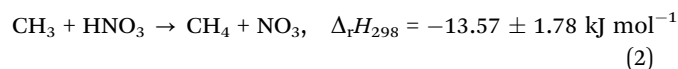
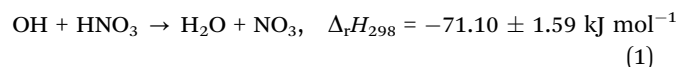
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The molecular symmetry of the ground state of the NO<sub>3</sub> radical has been difficult to determine by experiment<sup>1</sup> and theoretical calculation.<sup>2–4</sup> However, the latest experimental results indicate that it has D<sub>3h</sub> symmetry<sup>5</sup> with an NO distance of 1.240 Å<sup>6</sup> (the bond distance of 1.238 Å mentioned by Nielsen and Tang does not appear in Kawaguchi *et al.*<sup>7</sup>). Our calculations with the M08-HX DFT functional provide a C<sub>2v</sub> symmetry minimum, while the D<sub>3h</sub> geometry corresponds to a second-order saddle point with a relative energy of 9.6 kJ mol<sup>-1</sup>.<sup>8</sup>

We have examined the performance of 49 functionals (using in all cases the 6-311+G(2df,2p) basis set): for 26<sup>9</sup> of them the D<sub>3h</sub> geometry is predicted to be the minimum, while for 23<sup>10</sup> the D<sub>3h</sub> geometry exhibits two degenerate imaginary frequencies. In order to check the reliability for studying proton transfer reactions of those DFT functionals that predict NO<sub>3</sub> to be a minimum with D<sub>3h</sub> symmetry, we examined the enthalpy of three reactions for which experimental data is available (eqn (1)–(3)). The first reaction was already proposed in the Comment by Nielsen and Tang, but we think that the second and third are probably more appropriate in the present

case since they involve CH groups as the hydrogen donor, as in the reactions studied in our paper.<sup>8</sup> The heats of formation of all the molecules were obtained from the NIST database,<sup>11</sup> apart from the NO<sub>3</sub> (ΔH<sub>f</sub><sup>0</sup> = 73.72 ± 1.38 kJ mol<sup>-1</sup>)<sup>12</sup> and OH (ΔH<sub>f</sub><sup>0</sup> = 37.3 ± 0.7 kJ mol<sup>-1</sup>)<sup>13</sup> radicals.



The average calculated errors of the energies obtained in these three reactions, for the 26 functionals under consideration, range between +19 and -69 kJ mol<sup>-1</sup>. Only five functionals show an average unsigned error below 8 kJ mol<sup>-1</sup> (approx. 2 kcal mol<sup>-1</sup>): B3PW91 (3.8 kJ mol<sup>-1</sup>), X3LYP (4.6 kJ mol<sup>-1</sup>), B3LYP (5.1 kJ mol<sup>-1</sup>), and B971 and B972 (8.0 kJ mol<sup>-1</sup>).

We therefore used these five functionals to recalculate the proton transfer barrier and the corresponding relative energy of the exit channel, for the five reactions in our study. The average values are listed in Table 1, together with the energies computed using the M08HX functional. The TS of the proton transfer computed at M08HX is between 8.8 and 11.9 kJ mol<sup>-1</sup> (average 10.5 kJ mol<sup>-1</sup>) lower than the average of the five

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**Table 1** Proton transfer barrier and relative energy ( $\text{kJ mol}^{-1}$ ) of the exit channel at M08HX level and average of the selected five DFT functionals, in parenthesis

	$\text{CH}_2\text{ClBr:NO}_3$	$\text{CH}_2\text{ClI:NO}_3$	$\text{CH}_2\text{BrI:NO}_3$	$\text{CHCl}_2\text{Br:NO}_3$	$\text{CHClBr}_2:\text{NO}_3$
TS-H transfer	16.7 ( $28.1 \pm 2.3$ )	14.7 ( $23.5 \pm 2.6$ )	13.3 ( $22.4 \pm 2.7$ )	13.7 ( $25.6 \pm 2.6$ )	11.7 ( $23.2 \pm 2.7$ )
Exit channel	-58.2 ( $-20.4 \pm 1.6$ )	-57.1 ( $-21.9 \pm 1.4$ )	-53.6 ( $-19.8 \pm 1.2$ )	-74.0 ( $-38.9 \pm 1.6$ )	-73.4 ( $-21.9 \pm 1.4$ )

selected DFT methods. The effect is larger in the evaluation of the proton transfer exit channel, where the differences in the overall reaction energy predicted by M08HX are 37.8, 35.2, 35.1, and 51.5  $\text{kJ mol}^{-1}$  for the four reactions (with three of these giving errors that closely match the 37  $\text{kJ mol}^{-1}$  difference anticipated in the Comment).

These results partially agree with the comments of Nielsen and Tang, although the difference in the barrier heights between M08HX and the five chosen DFT methods is significantly smaller than the  $\sim 37 \text{ kJ mol}^{-1}$  that they anticipated. Importantly, the main conclusion of our paper is unchanged: the oxidations of  $\text{CH}_2\text{ClBr}$ ,  $\text{CH}_2\text{ClI}$ ,  $\text{CH}_2\text{BrI}$ ,  $\text{CHCl}_2\text{Br}$ , and  $\text{CHClBr}_2$  by  $\text{NO}_3$  are not competitive with other removal processes.

## Conflicts of interest

The authors declare that they have no conflicts of interest.

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- The 26 DFT functionals that predict  $\text{NO}_3$  radical have  $D_{3h}$  geometry in the minimum are: B3LYP, B3PW91, B971, B972, B97D3, B97D, BLYP, BP86, BPW91, BVP86, LSDA, M06-L, M11L, MPWB95, MPWLYP, MPWPW91, N12, O3LYP, OLYP, OPBE, PBEPBE, PW91PW91, SVWN5, TPSSH, TPSSTPSS and X3LYP.
- The 23 DFT functionals that show two imaginary frequencies for the  $\text{NO}_3$  radical with  $D_{3h}$  geometry are: APFD, BMK, CAM-B3LYP, HSEH1PBE, LC-BLYP, M05-2X, M05, M06-2X, M06-HF, M06, M08-HX, M11, MN15, MPW1LYP, MPW1PW91, N12SX, PBE1PBE, PW6B95D3, PW6B95, SOG-GA11X, wB97, wB97XD, and wB97X.
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