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Comment on “Theoretical study of the NO₃ radical reaction with CH₂ClBr, CH₂ICl, CH₂BrI, CHCl₂Br, and CHClBr₂” by I. Alkorta, J. M. C. Plane, J. Elguero, J. Z. Dávalos, A. U. Acuña and A. Saiz-Lopez, *Phys. Chem. Chem. Phys.* 2022, 24, 14365

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This comment addresses a systematic error in the potential energy surfaces of the title reactions presented in the original article by Alkorta *et al.* The NO₃ radical has *D*_{3h} symmetry in the electronic ground state while the M08HX functional employed in the original article predicts an incorrect *C*_{2v} geometry and energy. By combining thermodynamic data for the OH + HNO₃ → H₂O + NO₃ reaction with spectroscopic data and results from M08HX calculations on HNO₃, H₂O and the OH radical, the ground state NO₃ radical energy is estimated to be 37 kJ mol^{−1} lower than reported for the *C*_{2v} geometry.

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The authors of the title paper¹ presented theoretical results based on Kohn-Sham density functional theory² calculations employing the M08HX functional³ and single point couple cluster calculations.

The NO₃ radical presents a computational challenge. The electronic ground state has *D*_{3h} symmetry (\tilde{X}^2A_2');^{4,5} the experimental NO distance is 1.238 Å (*r*₀-structure),⁶ and the fundamental modes of vibration (in cm^{−1}) are 1050 A₁', 762.3 A₂', 1492.4 E' and 360 E'.⁷

It is not possible to calculate the electronic structure of the NO₃ radical correctly using any standard size extensive UHF wave function based method that is also applicable to larger systems.⁸ HF calculations locate 3 distinct minimum energy structures: one of *D*_{3h} symmetry, and two of *C*_{2v} symmetry having lower energies and respectively 2 short and 1 long NO distance (2s,1), and 1 short and 2 long NO distances (2l,s).⁸ In contrast, MP2 calculations place the *D*_{3h} structure lower in energy than the two *C*_{2v} structures; even CCSD(T) cannot completely overcome the symmetry breaking of the reference function and still three solutions with slightly different energies are found.⁸

There is a plethora of functionals developed for use in Kohn-Sham density functional theory calculations. Most of

the commonly used “pure” functionals locate a single minimum energy structure of *D*_{3h} symmetry. Many hybrid functionals also predict the *D*_{3h} symmetry structure as the global energy minimum, but there are also many showing symmetry breaking – the M08HX hybrid meta-GGA exchange–correlation functional being among those locating the *D*_{3h}-structure as a saddle point.

An early study on the performance of DFT for symmetry breaking problems concluded that the exchange functional appears to be more important than the correlation functional in providing resistance to symmetry breaking, and that hybrid functionals mixing in large fractions of Hartree–Fock exchange exhibit symmetry breaking.⁹

The NO₃ radical structures and the vibrational frequencies, obtained in M08HX/6-311+G(2df,2p) calculations, deviate substantially from the experimental data. The title study does not report the NO₃ radical structure explicitly. However, the vibrational frequencies (in cm^{−1}) reported in Table S10 – 1705 A₁, 1162 A₁, 544 A₁, 770 B₂ and 520 B₂ – indicate that the *C*_{2v}^{2s,1} structure, having NO-distances of 1.2471 and 1.1805 Å, is selected.

While the calculated electronic energy differences between the two local *C*_{2v} minimum energy structures and the *D*_{3h} saddle point structure are <10 kJ mol^{−1} at the M08HX/6-311+G(2df,2p) level (*C*_{2v}^{2s,1}: −280.17982, *C*_{2v}^{2l,s}: −280.18006 and *D*_{3h}: −280.17641 Hartree), the error in the calculated energy of the NO₃ radical may well be quite different from the above variance.

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Assuming that the quantum chemistry method harmonises with the thermochemistry data for HNO_3 , H_2O and OH , one may estimate the error in the calculated ground state NO_3 radical energy by combining the theoretical method results for the $\text{OH} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO}_3$ reaction, the standard enthalpies of formation from the NIST-JANAF Thermochemical Tables for OH ($38.99 \pm 1.21 \text{ kJ mol}^{-1}$), H_2O ($-241.826 \pm 0.042 \text{ kJ mol}^{-1}$) and HNO_3 ($-134.31 \pm 0.42 \text{ kJ mol}^{-1}$),¹⁰ the newest NO_3 photodissociation results ($73.72 \pm 1.38 \text{ kJ mol}^{-1}$),¹¹ and the experimental fundamental modes of vibration for NO_3 .⁷

The abovementioned experimental enthalpies of formation give $\Delta_r H_{298} = -72.79 \pm 1.88 \text{ kJ mol}^{-1}$ for the $\text{OH} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO}_3$ reaction, which, combined with the M08HX/6-311+G(2df,2p) electronic energies and calculated thermal corrections to the Enthalpies (HNO_3 : -280.836573 , 0.03187 ; H_2O : -76.42803 , 0.02551 ; OH : -75.72716 , 0.01197) results in a ground state electronic energy of the NO_3 radical of -280.19415 ± 0.00072 Hartree at the UM08HX/6-311+G(2df,2p) level of theory, which is 37 kJ mol^{-1} lower than the incorrect $C_{2v}^{21,s}$ energy used in the title study.

The electronic energy profiles presented in Fig. 5 in the title study are obviously not correct. The NO_3 radical H-abstraction reaction occurs on a path starting with a ground state NO_3 radical having D_{3h} -symmetry, proceeding *via* a saddle point in which the NO_3 radical distorts towards a $(2s,1)$ -like structure, and terminating with HNO_3 . The saddle point region of the potential energy surface and the product region can presumably be characterized reasonably well in M08HX calculations. The path connecting the electronic ground state of the NO_3 radical and the C_{2v} -like distorted pre-reaction NO_3 radical cannot. The pre-reaction complexes presented in the title study are, at least in part, artefacts of the methodology employed. Further, the barriers to the reactions are most likely not around 13 kJ mol^{-1} but rather around 50 kJ mol^{-1} above the entrance energy of the reactants. This does not change the main conclusion of the title study: the atmospheric chemical lifetimes of

the alkyl halides investigated are not substantially affected by nitrate radical reactions.

Conflicts of interest

There are no conflicts to declare.

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