Supplementary Information(SI) for

Comment on

"Impact of water on the BrO + HO$_2$ gas-phase reaction: mechanism, kinetics and products" by Tsona et al. PCCP 2019, 21, 20296-20307 by

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(a)Atmospheric Importance and summary of available rate coefficient measurements

The BrO + HO$_2$ reaction is important in the earth's atmosphere as it can lead to enhanced destruction of ozone. This occurs through production of HOBr, which can then undergo photolysis followed by reactions of the radicals produced (OH and Br) with ozone. It is clearly important to establish the mechanism of the BrO + HO$_2$ reaction and determine its rate coefficient at temperatures which are relevant to the troposphere (typically 220-320 K). Experimentally the rate coefficient of this reaction has been measured at different temperatures in this temperature range by a number of research groups (3-14) and they show that the rate coefficient decreases as the temperature increases i.e. a negative temperature dependence is observed. The most recent rate coefficient determinations were made by Ward and Rowley (14). They obtained rate coefficients of (2.55 ± 0.33) x10^{-11}, (2.89 ± 0.31) x10^{-11} and (3.7 ± 1.5) x10^{-11} cm^3. molecule^{-1}s^{-1} at 314.1, 298.1 and 246.1 K respectively.

(b) The characteristics of the electronic structure methods used in this work and refs.(1,2).

(i) DFT calculations with the M06-2X functional

The overall strategy used is to obtain the geometries and harmonic vibrational frequencies of the stationary points of a reaction (reactants, RC,TS,PC and products) on the potential energy surface using DFT calculations with the M06-2X functional, as well as their energies relative to the reactants. As described in ref.(2), the M06-2X functional was chosen because it has been shown to perform well for TS structures and reaction barrier heights in a number of benchmark studies. The M06-2X is a meta exchange-correlation functional and it has been demonstrated that, when a functional of this type is used with codes such as GAUSSIAN, larger integration grids should be used rather than the smaller default grids. Use of default grids can give rise to inaccurate binding energies and geometries, and the inability to locate tansuition states in weakly bound systems (16-19).

(ii) CCSD(T) calculations

CCSD(T)/AVTZ calculations at M06-2X/AVDZ optimised geometries have been performed in refs.(1) and (2). CCSD(T) means coupled cluster (CC) with a full treatment of single (S) and double (D) excitations. An estimate of the connected triples (T) excitations is calculated non-iteratively via many body perturbation theory. The central postulate of CC theory is that the full CI wavefunction can be described by a cluster operator (e^T) acting on a Hartree-Fock (HF) wavefunction. For CCSD calculations the cluster operator only includes single and double excitations. The CCSD(T) method

relies on the HF wavefunction being the dominant determinant (i.e. the method is based on a single determinant being a reasonable approximation to the true wavefunction). One test of multireference character (MR) that is often used is to calculate the T_1 diagnostic of Lee and Taylor. If T_1 is too large (typically > 0.04) then results of CCSD(T) calculations should be treated with caution.

For the CCSD(T)/AVTZ//M06-2X/aug-cc-pVDZ calculations reported by Tsona et al. in ref(1) no T_1 values were reported.

In the work of Chow et al.(2) UCCSD(T)/AVnZ//M06-2X/AVDZ calculations indicate that MR character is only significant for the TS of the triplet surface with a T_1 value of 0.1. For the other stationary points on the singlet and triplet surfaces the T_1 value is much lower than this. Hence for the triplet TS, CASSCF/AVDZ calculations were carried out at the M06-2X/AVDZ geometry.

(iii) CASSCF calculations

In ref.(2) CASSCF/AVDZ calculations were carried out at M06-2X/AVDZ optimised geometries. The complete active space self-consistent field (CASSCF) is a specific type of MCSCF method in which the number of determinants or CSFs used in the expansion of the CI vector are defined by dividing the orbitals into three subspaces. In the first subspace, the *inactive space*, all orbitals are doubly occupied. The second subspace is known as the *active space*, and within this orbital space, a full-CI expansion is considered. The orbitals selected for the active space are those that contribute most to the multireference character of the particular system studied. Finally, the third subspace, known as the *virtual space*, consists of orbitals that are kept unoccupied. This method decreases the number of determinants or CSFs in the CI expansion since it limits the MC wave function within a specific subset of electrons and orbitals rather than treating all electrons in all orbitals as one would do in a traditional MRCI calculation. As such, the CASSCF method cannot be considered merely as a "black box" method, as *a priori* knowledge of the chemical system under study is needed for the proper choice of the active orbitals. A limitation of CASSCF is the number of electrons and orbitals that can be included in the active space, since the CI expansion increases exponentially with respect to the number of electrons and orbitals.

A CASSCF calculation for a given choice of active space and an active electrons will include some non-dynamic electron correlation. A second order perturbation theory calculation (CASPT2 or NEVPT2 (NEVPT stands for N-Electron Valence State Perturbation Theory)) can then be used to calculate the dynamic correlation energy contribution to the total energy.

For the triplet TS, CASSCF/AVDZ calculations were carried out at the M06-2X/AVDZ geometry (2). Inspection of the CI coefficients obtained from these CASSCF calculations, performed with different active electrons and active spaces, show that the MR character is not very large for the triplet TS and in this connection BD methods (see later) are expected to be adequate. For the singlet TS, the CASSCF(2,4)/NEVPT2 results are adequate as the CASSCF(2,4) wavefunction has accounted for the two-configurational open-shell singlet wavefunction. The excellent agreement between the CASSCF/NEVPT2/CBS and BD(TQ)/CBS TS relative energies reinforces this

conclusion. (In CASSCF(2,4) there are 2 active electrons in an active space of 4 orbitals).

(iv) BD Calculations

As outlined above, the CCSD method is based on a HF wavefunction. This may be problematic in some cases. In such cases, before resorting to a multireference approach (e.g. CASSCF), there is a variant of CCSD that has shown larger stability with respect to the choice of the reference function--- the Brueckner doubles (BD) method. In this method, the BD reference function is built such that all the amplitudes for single excitations are zero. Starting from the initial reference (e.g. a HF single determinant), the orbitals are rotated until the above condition is satisfied. BD thus introduces an initial relaxation that is coupled with the CC expansion, which includes only double excitations. In many cases. BD provides a more reliable wavefunction than CCSD.

For the triplet TS, although the CCSD iterations in the UCCSD(T) calculations converged, the computed T_1 diagnostic value was rather large (~ 0.1), suggesting non-negligble multireference (MR) character. In order to circumvent this problem, Brueckner theory was employed, as with Brueckner doubles (BD) the T_1 value is zero. BD(T)/AVQZ and BD(TQ)/AVTZ single energy calculations were carried out. Computed relative BD(T) energies obtained using the AVQZ and AVTZ basis sets were extrapolated to the CBS limit employing the $1/X^3$ formula. The highest level of relative electronic energies obtained in the present study is BD(TQ)/CBS, which combines the BD(T)/CBS value with the (Q) contribution from the {BD(TQ)–BD(T)} relative energies.