## CORRECTION

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# Correction: The reaction of acetonitrile with hydrogen peroxide in alkaline medium: a DFT mechanistic study of green production of amides

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Correction for 'The reaction of acetonitrile with hydrogen peroxide in alkaline medium: a DFT mechanistic study of green production of amides' by Girolamo Casella *et al.*, *Phys. Chem. Chem. Phys.*, 2023, https://doi.org/10.1039/d3cp02024j.

The original manuscript contains an error in the calculation of the $\Delta G^{\#}_{\text{TS4}}$ = +21.58 kcal mol$^{-1}$ of Scheme 4. The value was erroneously calculated by switching the 6-311+G(d,p) electronic energies of the optimized structures of **OC1** and **TS4** in the equation:

$$G(\text{6-311+G(d,p)}) = E(\text{6-311+G(d,p)}) - E(\text{6-31G(d,p)}) + G(\text{6-31G(d,p)}),$$

Moreover, the optimized geometries leading to **TS4** were proposed with the wrong configuration with respect to the path leading to the needed *trans-syn*-PAIA species. Indeed, according to the substitution mechanism in **TS4**, the hydrogen on the nitrogen should be in *trans* position, hence the starting intermediate should be the *trans-anti*-EtIm. These wrong coordinates were also reported in the original ESI, which has now been replaced with a corrected version. A check of the $\Delta G^{\#}_{\text{TS4}}$ values obtained from the right structures lead to a $\Delta G^{\#}_{\text{TS4}}$ = +62.49 kcal mol$^{-1}$, a very high activation energy while, as stated earlier, the $\Delta G^{\#}_{\text{TS4}}$ = +21.58 kcal mol$^{-1}$ reported in the original Scheme 4 resulted from an error in the calculation of the value, which by pure chance resulted in an acceptable result. Inspection of all data in Scheme 4 confirmed all the data reported, hence only the $\Delta G^{\#}_{\text{TS4}}$ = +62.49 kcal mol$^{-1}$ result changed after the check. According to the computational protocol used [optimization and thermochemistry, *i.e.*, M06-L/6-31G(d,p) and electronic correction to $\Delta G$s by single point calculation M06-L/6-311+G(d,p)] we deemed that the search of the **TS4** transition state was dependent on quite sizeable basis set effects on the optimization and thermochemistry as well.

In this respect, the whole mechanism with the right configurations (see the revised ESI to the original paper) has been re-investigated by using two different protocols with an extended basis set over the original 6-31G(d,p): (i) M06-L/6-311+G(d,p); (ii) M06-L/cc-PVTZ, with no further single point calculation. Hence all the Gibbs free energies given have been calculated as $G = E + G_{\text{corr}}$, where $E$ = electronic energy and $G_{\text{corr}}$ = thermal free energy correction.

Results are given in Schemes S1(a, b) and S2(a, b) in the revised ESI accompanying the original article. Inspection of all the Schemes indicated that the wrong $\Delta G^{\#}_{\text{TS4}}$ = +21.58 kcal mol$^{-1}$ 4 (instead of a $\Delta G^{\#}_{\text{TS4}}$ = +62.49 kcal mol$^{-1}$) reported in the original Scheme 4, is similar to the values obtained with the new protocols. In this respect, the correctness of the proposed mechanism remains substantially unchanged and the mistake is ascribable to the wrong configurations considered for **OC1** and **TS4**. The reaction is driven by the regiocontrolled reaction of formation of the *trans-syn*-PAIA which still remains the rate determining step of the reaction, according to the corresponding activation energies in substantial agreement with the experimental constant rate obtained.

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Moreover, path $a'$ has been revised by also considering its contribution to the formation of the *trans-syn*-PAIA, even if is almost negligible compared to the contribution of the $a''$ one, hence the latter remains the preferred one as reported in Fig. 2 of the original work.

The use of larger basis set lead to an inversion between path **c** and the **PXO** mechanism concerning the fastest step of the reaction. Indeed, the small free energy difference (0.85 kcal mol$^{-1}$) favouring the **c** mechanism in the original work is switched in favour of the **PXO** mechanism, which should better agree with the high reactivity of the peroxide group.

The Royal Society of Chemistry apologises for these errors and any consequent inconvenience to authors and readers.

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