



Correction: Understanding MAOS through computational chemistry

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Correction for 'Understanding MAOS through computational chemistry' by P. Prieto *et al.*, *Chem. Soc. Rev.*, 2017, 46, 431–451.

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The authors regret that in the final version of the article some relevant and important research findings were omitted.

At the end of section 2.2 **Activation energy**, the following results should be included:

Keglevich and colleagues¹ have studied experimentally and computationally the esterification,² thioesterification³ and amidation⁴ of phosphinic acids and phospholene oxides. Reactions did not occur under conventional heating, while under microwave irradiation partial or complete conversion was observed. Computational calculations, free energy of activation and enthalpy justify this result. For example, for the reaction of 1-hydroxy-3-methyl-3-phospholene 1-oxide with butanol, thiobutanol and hexylamine, the computed thermodynamic data calculated at the B3LYP/6-31G(d,p) level of theory are listed in Table 1. Esterification is a slightly endothermic process with a medium energy TS, thioesterification is strongly endothermic with a high energy TS and finally, amidation is strongly endothermic with a medium energy TS. These results show that each of the three reactions follow a different mechanism.⁵

Table 1 Computed enthalpies, Gibbs free enthalpies and entropies for the esterification, thioesterification and amidation of 1-hydroxy-3-methyl-1-phospholene 1-oxide, computed at the B3LYP/6-31G(d,p) level of theory⁵

Reaction	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
Esterification	6.14	0.8	−11.3
Thioesterification	50.64	47.9	−5.8
Amidation	41.77	35.2	−13.9

The authors proposed that the enhancement observed under microwave irradiation could be attributed to a statistically occurred local overheating and that the role of microwave irradiation is to enhance reactions with high enthalpy of activation. They also consider that the reversibility of the reactions is avoided due to the hydrophobic nature of the final products.

In order to prove the occurrence of the local overheating described, they developed a mathematical model based on a statistical distribution of local overheating in the mixture. Based on the Arrhenius equation, the rate enhancements (k_{rel}') were calculated according to the equation:⁶

$$k_{\text{rel}}' = (V_{\text{bulk}} \cdot k_{\text{bulk}} + \sum V_{\text{OH}}^n \cdot k_{\text{OH}}^n) / k_{\text{bulk}}$$

where V_{bulk} and k_{bulk} are the volume and temperature of the bulk of the mixture and V_{OH} and k_{OH} are the volume and temperature of the individual overheated segments. The good agreement between the calculated and experimental overheating supports the model proposed. For example, for the esterification of hydroxy-3-phospholene oxides the exponential model predicts an overheating in the range of 5–60 °C, and the overheated segment is 40%.

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

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