

## SUPPORTING INFORMATION for

### ***Mechanistic Aspects of C-H Hydrogen Abstraction Processes with the Tetrachloro-Phthalimido-N-Oxyl (Cl<sub>4</sub>PINO) Catalyst: Electrochemical Radicalisation of Alcohols***

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## DFT Calculations

### ***Computational details***

All calculations employed the following protocol: rB3LYP/6-311+G(d,p)/SCRF=(cpcm,solvent=acetonitrile)/ temperature=298.15.

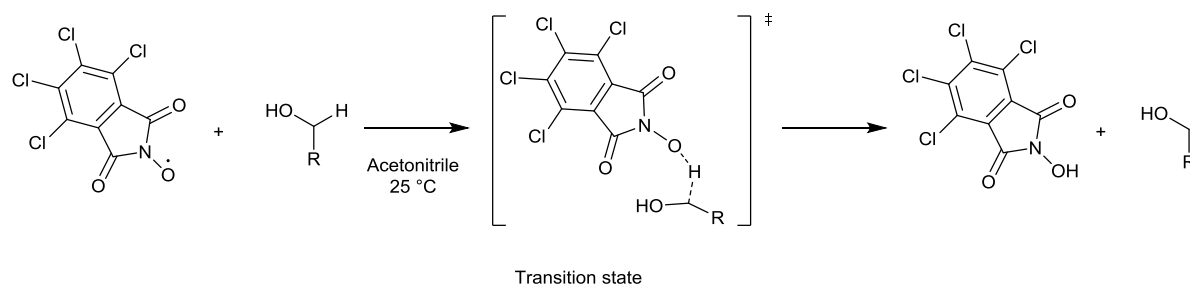
The B3LYP functional is a hybrid of exact (Hartree-Fock) exchange with local and gradient-corrected exchange and correlation terms, as first suggested by Becke.<sup>1</sup> In B3LYP,<sup>2</sup> the exchange is provided by Becke 88 exchange functional<sup>3</sup> and the correlation is provided by the correlation functional of Lee, Yang and Parr (LYP),<sup>4</sup> with some local correlation expression of Vosko, Wilk, and Nusair.<sup>5</sup> The calculations were all carried out using a self-consistent-reaction-cavity continuum solvation model to account for the reactions conditions (in water). Implementation of the self-consistent-reaction-cavity continuum solvation model has recently been enhanced to allow efficient evaluation of first and second energy derivatives, following an earlier suggestion of the method.<sup>6</sup> The split-valence triple  $\zeta$  with polarization and diffuse functions 6-311+G(d,p) basis set was selected to account for potential ions and nonbonding interactions, while allowing the models to scale up to the maximum size of 43 atoms.

All geometries were fully optimized without any symmetry or geometry constraints. In addition, frequency calculations were carried out to check their nature: all stationary points as minima and

characterised by no imaginary mode, whereas transition states were characterized by precisely one imaginary mode corresponding to the intended reaction. Free energies were calculated within the harmonic approximation for vibrational frequencies. Only the most stable conformational isomers are reported for all structures.

All calculations were performed using the Gaussian09 suite of codes.<sup>8</sup> The authors would like to acknowledge the use of the High Performance Computing (HPC) facilities (Balena cluster) at the University of Bath, in carrying out this work.

***Computed free enthalpies for the reaction between tetrachloro-phthalimido-N-oxyl (Cl<sub>4</sub>PINO) radical and various alcohols***



**Figure S1. Reaction between Cl<sub>4</sub>PINO radical and various alcohols via C-H hydrogen abstraction transition state**

The kinetics of the reaction between Cl<sub>4</sub>PINO radical and various primary alcohols was examined using DFT by modelling of the hydrogen abstraction transition states and computation of the related activation barriers. Full coordinates for all stationary points, together with computed free enthalpies and vibrational frequency data, are also available via the corresponding Gaussian 09 output files, stored in the digital repository (DOI: 10.6084/m9.figshare.5131723): <https://figshare.com/s/20230ca9daea0ff4d0fa>

**Table S1.** DFT computed free enthalpy differences for the activation barrier of the hydrogen abstraction process converting a primary alcohol to radical alcohol and for the overall thermodynamics of the reaction between Cl<sub>4</sub>PINO radical and an alcohol (reference: sum of free enthalpies: alcohol + Cl<sub>4</sub>PINO·).

	<i>Alcohol</i>	<i>Hydrogen abstraction activation barrier <math>\Delta(\Delta G_{298.15K}^{TS})(\text{kJ mol}^{-1})</math></i>	<i>Free enthalpy of formation of the alcohol radical <math>\Delta G_{298.15K}(\text{kJ mol}^{-1})</math></i>
(i)	Ethanol	+92.5	+50.1
(ii)	Octan-1-ol	+90.7	+51.2
(iii)	2-Phenylethanol	+96.1	+51.4
(iv)	iso-Propanol	+84.6	+43.0
(v)	Pentan-3-ol	+85.6	+41.8
(vi)	1-Phenylethanol	+77.5	-9.1
(vii)	2-Nitroethanol	+107.8	+34.0
(viii)	Cyclohexanol	+88.3	+43.8
(ix)	Cyclopentanol	+85.9	+42.7
(x)	Benzyl alcohol	+78.4	+0.6

**Table S2.** List of all computed structures and their computed free enthalpies.

<i>System</i>	<i>G (Hartree)</i>
Cl <sub>4</sub> PINO·	-2426.224061
Cl <sub>4</sub> PINOH	-2426.85005
Ethanol	-155.046766
TS <sub>(i)</sub>	-2581.235592
Ethanol radical	-154.401684
Octan-1-ol	-390.837035
TS <sub>(ii)</sub>	-2817.026537
Octan-1-ol radical	-390.191562
2-Phenylethanol	-386.082422
TS <sub>(iii)</sub>	-2812.269882
2-Phenylethanol radical	-385.436832
iso-Propanol	-194.350374
TS <sub>(iv)</sub>	-2620.542207
iso-Propanol radical	-193.707993
Pentan-3-ol	-272.94319
TS <sub>(v)</sub>	-2699.134638
Pentan-3-ol radical	-272.301271
1-Phenylethanol	-386.084137

TS <sub>(vi)</sub>	-2812.278665
1-Phenylethanol radical	-385.461629
2-Nitroethanol	-359.614363
TS <sub>(vii)</sub>	-2785.797363
2-Nitroethanol radical	-358.975421
Cyclohexanol	-311.051047
TS <sub>(v)</sub>	-2737.241465
Cyclohexanol radical	-310.408366
Cyclopentanol	-271.746055
TS <sub>(vi)</sub>	-2697.937409
Cyclopentanol radical	-271.103803
Benzyl alcohol	-346.782136
TS <sub>(vii)</sub>	-2772.976332
Benzyl alcohol radical	-346.155925

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