DFT study of the oxidation reaction of various primary alcohols in presence of 4-BenzoyloxyTEMPO⁺ cation and NaCO₃⁻ anion

Computational details

All calculations employed the following protocol: rB3LYP/6-311+G(d,p)/SCRF=(cpcm,solvent=water)/ temperature=298.15.
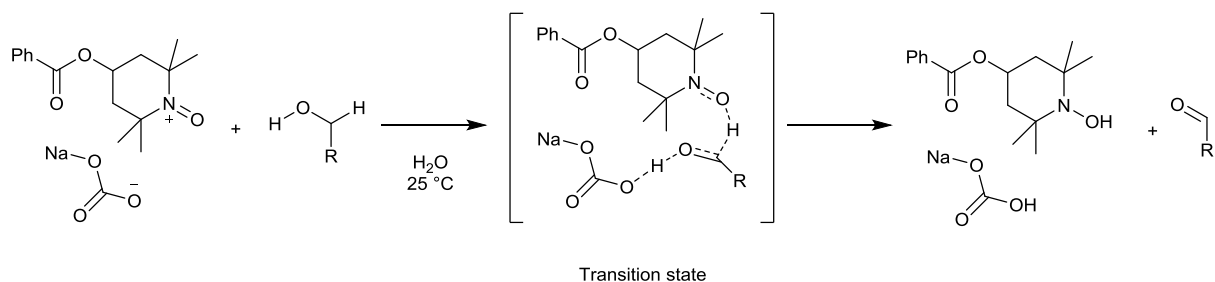
The B3LYP functional is a hybrid of exact (Hartree-Fock) exchange with local and gradient-corrected exchange and correlation terms, as first suggested by Becke.[1] In B3LYP,[2] the exchange is provided by Becke 88 exchange functional[3] and the correlation is provided by the correlation functional of Lee, Yang and Parr (LYP),[4] with some local correlation expression of Vosko, Wilk, and Nusair.[5] 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.[6] The split-valence triple ζ 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 73 atoms, and an associated maximum of 1071 basis functions.

All geometries were fully optimized without any symmetry or geometry constrains. 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. In one case (benzylalcohol), this was augmented by an intrinsic reaction coordinate (IRC) calculation,[7] which also confirmed the identity of the reaction. Free energies were calculated within the harmonic approximation for vibrational frequencies. Only the most stable conformational isomers are reported for all intermediates.

All calculations were performed using the Gaussian09 suite of codes.[8]

Computed free enthalpies reaction path between oxidised 4B-TEMPO⁺ cation, NaCO₃⁻ anion and various primary alcohols

Computed free enthalpies reaction path between oxidised 4B-TEMPO$^+$ cation, NaCO$_3^-$ anion and various primary alcohols

Transition state

Thermodynamics of the reaction between oxidised 4B-TEMPO$^+$ cation, NaCO$_3^-$ anion and various primary alcohols was examined using DFT. The key hydride transfer step was also calculated and was found to occur via a cyclic transition state. For α-D-glucose, the oxidation to glucono-δ-lactone was found to be kinetically and thermodynamically favoured compared to the formation of the aldehyde. For D-sorbitol, which features two stereochemically different primary alcohols, only one set of calculation was performed.

Table S1. Summary of DFT calculation results in terms of the approximate activation barrier for the two-electron transfer process converting a primary alcohol to an aldehyde and the overall thermodynamics of the reaction between 4B-TEMPO$^+$ cation, NaCO$_3^-$ anion and a primary alcohol.

	System	Transition state $\Delta(\Delta G^{TS}_{298.15K})$ (kJ mol^{-1})	Free enthalpies of formation $\Delta(\Delta G_{298.15K})$ (kJ mol^{-1})
(i)	α-D-glucose	19.0	-271.6
(ii)	D-sorbitol	11.2	-221.8
(iii)	1,3-propanediol	18.5	-225.2
(iv)	methanol	15.2	-199.2
(v)	ethanol	20.3	-230.8
(vi)	propan-1-ol	19.9	-229.0
(vii)	butan-1-ol	20.1	-231.4
(viii)	pentan-1-ol	18.8	-230.8
(ix)	hexan-1-ol	19.0	-230.8
(x)	4-pyridine-methanol	13.6	-226.4
(xi)	3-pyridine-methanol	14.4	-233.1
(xii)	1,4-benzenedimethanol	9.4	-243.1
(xiii)	benzylalcohol	13.1	-241.4

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

System	G (Hartree)
[4B-TEMPO$^+$][NaCO$_3^-$]	-1329.535876
4B-TEMPOH	-903.893483
NaHCO$_3$	-426.918515
α-D-glucose	-687.258413
TS$_{(i)}$	-2016.787043
glucono-δ-lactone	-686.085721
D-sorbitol	-688.451248
TS$_{(ii)}$	-2017.98286
aldehyde$_{(ii)}$	-687.259617
1,3-propanediol	-269.584476
TS$_{(iii)}$	-1599.113323
β-hydroxypropionaldehyde	-268.394131
methanol	-115.742804
TS$_{(iv)}$	-1445.272891
formaldehyde	-114.542556
ethanol	-155.046871
TS$_{(v)}$	-1484.57499
acetaldehyde	-153.858659
propan-1-ol	-194.345048
TS$_{(vi)}$	-1523.87334
propanal	-193.156152
butan-1-ol	-233.643376
TS$_{(vii)}$	-1563.171613
butanal	-232.455382
pentan-1-ol	-272.941932
TS$_{(viii)}$	-1602.470647
pentanal	-271.753712
hexan-1-ol	-312.240396
TS$_{(ix)}$	-1641.769034
hexanal	-311.052167
4-pyridine-methanol	-362.837382
TS$_{(x)}$	-1692.368094
pyridine-4-aldehyde	-361.647486
3-pyridine-methanol	-362.83647
TS$_{(xi)}$	-1692.366875
pyridine-3-aldehyde	-361.649129
1,4-benzenedimethanol	-461.32215
TS$_{(xii)}$	-1790.854441
p-(hydroxymethyl)benzaldehyde	-460.138628
benzylalcohol	-346.781922
TS$_{(xiii)}$	-1676.312829
benzaldehyde	-345.59773

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