Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information (SI)

Insights on the kinetics and mechanisms of the peroxyl radical scavenging capacity of Caftaric acid: the important role of the acid-base equilibrium

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Table S1: The Cartesian coordinates and energies of TS of the reaction between compound CA with HOO• following the FHT mechanism in studied solvents

Name				**TS-CA-O6-H-OOH-FHT-G**
Cartesian Coordinates				Frequency and Energy
C	-3.35949000	-2.01131000	-0.54602700	Zero-point correction= 0.263013 (Hartree/Particle)
C	-2.43323100	-1.00553600	-0.18852900	Thermal correction to Energy= 0.286839
C	-2.88998600	0.11863300	0.48757600	Thermal correction to Enthalpy= 0.287783
C	-4.24212600	0.24117400	0.82727000	Thermal correction to Gibbs Free Energy= 0.203251
C	-5.15181600	-0.79253200	0.45415100	Sum of electronic and zero-point Energies= -1330.167969
C	-4.70293100	-1.91390600	-0.23651700	Sum of electronic and thermal Energies= -1330.144143
O	-4.73626200	1.27214800	1.47937400	Sum of electronic and thermal Enthalpies= -1330.143198
O	-6.44645300	-0.64439200	0.74886500	Sum of electronic and thermal Free Energies= -1330.227731
C	-1.03267600	-1.19529500	-0.55570800	
C	-0.00946100	-0.37186900	-0.29216700	
C	1.33474500	-0.74436100	-0.75220500	
O	2.25834200	0.21279000	-0.37952200	
O	1.65287400	-1.72320200	-1.36135800	
O	5.50241100	1.40510100	-0.93143800	
C	3.62046200	-0.02936500	-0.76006300	
C	4.35045000	-0.88797000	0.29800600	
O	5.50552900	-1.44448000	-0.22567400	
C	4.31251500	1.31681500	-0.97129800	
O	3.52120100	2.36171500	-1.22288900	
O	5.73015600	-0.02136700	2.05533900	
C	4.64380600	-0.08517000	1.57445400	
O	3.59013700	0.55319800	2.11712700	
H	-3.00027400	-2.88516700	-1.07812900	
H	-2.23101000	0.92748500	0.77864800	
H	-5.40955500	-2.68671000	-0.51035600	
H	-5.19046900	1.99397500	0.72088400	
H	-6.53542000	0.13866600	1.31544500	
H	-0.79786800	-2.10583800	-1.10273900	
H	-0.11174400	0.56136400	0.24685200	
H	3.64796200	-0.58786700	-1.69848500	
H	3.66985500	-1.70779100	0.55570000	
H	6.22581100	-0.81253100	-0.09605800	
H	2.59642900	2.10082900	-1.12713000	
H	2.79646900	0.43669100	1.57912900	
H	-6.11358300	1.04121600	-1.48168400	
O	-5.76679700	2.42066800	-0.28748200	
O	-5.33465700	1.57655100	-1.25931000	
Name				**TS-CA-O7-H-OOH-FHT-G**
Cartesian Coordinates				Frequency and Energy
C	3.31551200	1.90162600	-0.38172800	Zero-point correction= 0.262955 (Hartree/Particle)
C	2.37495000	0.88470800	-0.10680200	Thermal correction to Energy= 0.286756
C	2.79260500	-0.29918300	0.50843600	Thermal correction to Enthalpy= 0.287700
C	4.12282500	-0.45757100	0.85139500	Thermal correction to Gibbs Free Energy= 0.204376
C	5.07552400	0.56990100	0.57904900	Sum of electronic and zero-point Energies= -1330.167961
C	4.64364100	1.74736100	-0.05585000	Sum of electronic and thermal Energies= -1330.144160
O	4.54920100	-1.60202300	1.41045500	Sum of electronic and thermal Enthalpies= -1330.143216
O	6.31829000	0.36252300	0.94733200	Sum of electronic and thermal Free Energies= -1330.226541
C	0.98514800	1.12118600	-0.48202900	
C	-0.05686100	0.30526900	-0.26920500	
C	-1.39111600	0.72492200	-0.72258300	

O	-2.33556600	-0.22783500	-0.39808500
O	-1.68206600	1.73580100	-1.29066200
O	-5.59855300	-1.33120400	-1.01817400
C	-3.69034800	0.05761700	-0.77743100
C	-4.41249800	0.88615100	0.30979500
O	-5.55182300	1.48534700	-0.20064800
C	-4.40715500	-1.26469500	-1.04872800
O	-3.63467500	-2.31348800	-1.34054100
O	-5.82348300	-0.02515200	2.01930000
C	-4.73230900	0.03751300	1.54993500
O	-3.69534900	-0.64309900	2.07402300
H	2.97760300	2.81329600	-0.86025600
H	2.10476200	-1.10463900	0.73310700
H	5.37905800	2.51464400	-0.26212500
H	5.46748400	-1.47577200	1.69450800
H	6.81087600	-0.33623800	0.20066200
H	0.77605500	2.06293100	-0.98424300
H	0.02150600	-0.65345900	0.22740800
H	-3.69900000	0.65495400	-1.69203700
H	-3.71918200	1.68178900	0.60644800
H	-6.28411100	0.86056400	-0.10852600
H	-2.70584500	-2.07460300	-1.22934600
H	-2.89481000	-0.51861300	1.54847200
H	5.31749400	-1.95191600	-1.11169900
O	6.96633900	-1.24268000	-0.64025500
O	5.82876200	-1.16841100	-1.37373100

Name			**TS-CA-C2-OOH-RAF-G**
Cartesian Coordinates			Frequency and Energy
C	2.83249000	0.28373300	0.01817300
C	3.94405200	1.01329500	0.48834800
C	5.22242700	0.64479600	0.13564400
C	5.43828800	-0.47085400	-0.68933500
C	4.35113500	-1.20934400	-1.14399500
C	3.06420900	-0.84034000	-0.79483400
C	1.51343200	0.70328100	0.39430400
C	0.34114400	0.16872600	-0.11563800
O	6.69007200	-0.83384800	-1.03003000
O	6.36261600	1.29015200	0.52943300
H	3.78682200	1.87732600	1.12712600
H	4.54318700	-2.07945500	-1.75896500
H	2.23044800	-1.44992400	-1.11920400
H	1.41776200	1.45084400	1.17521700
H	7.31491400	-0.22801900	-0.61257600
O	0.04644700	-1.50707200	0.70865400
H	6.15918500	2.00562600	1.13728600
C	-0.91891800	0.82873700	0.27417400
O	-1.97574800	0.33509200	-0.40069200
O	-1.04318700	1.69316000	1.11226800
C	-3.26891400	0.61104900	0.14088700
C	-4.15385000	-0.58239100	-0.18293700
C	-3.83288200	1.91442700	-0.43595800
H	-3.19046400	0.70268800	1.22814300
O	-4.38213800	-0.77230400	-1.55344800
C	-3.45778500	-1.83075100	0.36495800

Zero-point correction= 0.269146 (Hartree/Particle)
Thermal correction to Energy= 0.292116
Thermal correction to Enthalpy= 0.293060
Thermal correction to Gibbs Free Energy= 0.214073
Sum of electronic and zero-point Energies= -1330.178198
Sum of electronic and thermal Energies= -1330.155229
Sum of electronic and thermal Enthalpies= -1330.154284
Sum of electronic and thermal Free Energies= -1330.233271

H	-5.09556300	-0.46657400	0.36821900
O	-4.82493400	1.93341000	-1.11425200
O	-3.16294300	3.01261000	-0.12575800
H	-4.84537500	0.00631700	-1.89119100
O	-3.00272400	-1.84805200	1.47847100
O	-3.41055800	-2.86314700	-0.45240200
H	-3.78388600	-2.59515200	-1.30865800
H	-2.40804300	2.80257000	0.45685500
H	0.32039700	-0.33892800	-1.07191900
O	-0.25667600	-1.38557300	2.03384400
H	-1.22018900	-1.52892700	2.05823000

Name			**TS-CA-O6-H-OOH-FHT-P**
Cartesian Coordinates			Frequency and Energy
C	-3.43759200	-1.98485900	-0.86366200
C	-2.49257600	-1.07865400	-0.33017700
C	-2.93061600	-0.08013800	0.53015600
C	-4.28849600	0.02518900	0.85583300
C	-5.21936800	-0.90172300	0.30177100
C	-4.78343700	-1.90452500	-0.55868700
O	-4.77028200	0.94139700	1.67676800
O	-6.50996500	-0.79013300	0.61900300
C	-1.09353000	-1.23642100	-0.71529700
C	-0.07249400	-0.43882300	-0.37028800
C	1.27179200	-0.75721500	-0.85483800
O	2.18612200	0.17044600	-0.38136800
O	1.61276500	-1.66561100	-1.55684300
O	5.39074900	1.48305400	-0.87104400
C	3.55077300	-0.01376900	-0.75818800
C	4.30287700	-0.87425800	0.28375100
O	5.49484600	-1.36265900	-0.22985900
C	4.19885700	1.35832900	-0.91559300
O	3.38839800	2.39095000	-1.11707400
O	5.60249400	-0.00589700	2.10909700
C	4.53167300	-0.10063100	1.59030900
O	3.44845700	0.48324400	2.12484600
H	-3.09056300	-2.76480600	-1.53279300
H	-2.25019200	0.63961900	0.97084200
H	-5.50036100	-2.60372900	-0.97062700
H	-4.84141500	1.91168400	1.12983500
H	-6.59853100	-0.07767100	1.27316500
H	-0.87190800	-2.09061400	-1.35116000
H	-0.18165700	0.44156000	0.25071900
H	3.61056200	-0.53142800	-1.71853100
H	3.66109300	-1.73288100	0.50992400
H	6.14476900	-0.64678500	-0.20752600
H	2.46318700	2.11031000	-1.05454900
H	2.65846300	0.33256900	1.58527400
H	-5.52956400	1.90146500	-1.34441700
O	-5.01275900	2.77439100	0.21814900
O	-4.68140200	2.08695500	-0.90438300

Zero-point correction= 0.262854 (Hartree/Particle)
Thermal correction to Energy= 0.286524
Thermal correction to Enthalpy= 0.287468
Thermal correction to Gibbs Free Energy= 0.205364
Sum of electronic and zero-point Energies= -1330.209110
Sum of electronic and thermal Energies= -1330.185441
Sum of electronic and thermal Enthalpies= -1330.184496
Sum of electronic and thermal Free Energies= -1330.266601

Name			**TS-CA-O7-H-OOH-FHT-P**
Cartesian Coordinates			Frequency and Energy
C	-3.33835300	-1.55120500	0.82725000
C	-2.35980600	-0.61423300	0.42877600

Zero-point correction= 0.262600 (Hartree/Particle)
Thermal correction to Energy= 0.286434

C	-2.72091200	0.71691300	0.19267100	Thermal correction to Enthalpy= 0.287379
C	-4.03852200	1.10548300	0.35070800	Thermal correction to Gibbs Free Energy= 0.204836
C	-5.02812700	0.16151000	0.75195200	Sum of electronic and zero-point Energies= -1330.209055
C	-4.65171500	-1.17285200	0.98802000	Sum of electronic and thermal Energies= -1330.185220
O	-4.40512800	2.37452500	0.12505400	Sum of electronic and thermal Enthalpies= -1330.184276
O	-6.25934900	0.60957100	0.90323400	Sum of electronic and thermal Free Energies= -1330.266818
C	-0.98689700	-1.08763500	0.28007200	
C	0.08046400	-0.34506300	-0.04822600	
C	1.39336500	-0.99042300	-0.15348100	
O	2.36901200	-0.05266100	-0.44057700	
O	1.66038400	-2.14967200	-0.01899500	
O	5.63340900	0.41381500	-1.59488700	
C	3.70607600	-0.53596000	-0.58359700	
C	4.43306900	-0.57866300	0.78030400	
O	5.56909100	-1.37170600	0.72129500	
C	4.43586500	0.36188000	-1.57814600	
O	3.68735400	1.05928300	-2.42560700	
O	5.85471100	1.15379100	1.64507900	
C	4.76174500	0.83177600	1.28960600	
O	3.74182700	1.70321600	1.30928100	
H	-3.04224300	-2.57838300	1.00514100	
H	-1.99553100	1.46010000	-0.11499300	
H	-5.41535900	-1.88015700	1.28969500	
H	-5.34669400	2.45749800	0.34404000	
H	-6.88411400	0.25208800	0.06071600	
H	-0.82942300	-2.14864700	0.45958800	
H	0.03404200	0.71971400	-0.23944000	
H	3.69835000	-1.55256200	-0.98471200	
H	3.74096700	-1.04034400	1.49308900	
H	6.27439900	-0.85334500	0.31007200	
H	2.74780500	0.94203900	-2.22111100	
H	2.92403500	1.30521500	0.97737200	
H	-5.85241700	0.14785700	-2.30326400	
O	-7.26560300	-0.08120200	-1.11338700	
O	-6.11900300	-0.54208600	-1.67047200	

Name	**TS-CA-C2-OOH-RAF-FHT-P**
Cartesian Coordinates	Frequency and Energy

C	2.85782100	0.23624600	0.00028500	Zero-point correction= 0.268487 (Hartree/Particle)
C	3.96662400	0.85677800	0.61498800	Thermal correction to Energy= 0.291433
C	5.24957200	0.53618900	0.23200000	Thermal correction to Enthalpy= 0.292377
C	5.47026100	-0.41529100	-0.77786700	Thermal correction to Gibbs Free Energy= 0.214072
C	4.38574400	-1.03560500	-1.39103800	Sum of electronic and zero-point Energies= -1330.214062
C	3.09513500	-0.71703200	-1.00841900	Sum of electronic and thermal Energies= -1330.191115
C	1.54217300	0.61058500	0.43164500	Sum of electronic and thermal Enthalpies= -1330.190171
C	0.35626500	0.08335600	-0.05373700	Sum of electronic and thermal Free Energies= -1330.268476
O	6.72496100	-0.73031700	-1.15217600	
O	6.38229100	1.07835200	0.76155200	
H	3.80609400	1.59164000	1.39800300	
H	4.57756900	-1.77021200	-2.16383300	
H	2.26651900	-1.21870800	-1.49242700	
H	1.47172300	1.32506600	1.24623800	
H	7.35094000	-0.22033900	-0.62003700	
O	0.03536400	-1.55474500	0.86643100	
H	6.17000200	1.68979400	1.47638900	

C	-0.89142900	0.77298000	0.32857800
O	-1.95317100	0.29460800	-0.34480600
O	-0.99729600	1.65541700	1.15160100
C	-3.25562900	0.63375100	0.14365700
C	-4.18279500	-0.51090300	-0.23641800
C	-3.73444400	1.96470800	-0.44812000
H	-3.22794400	0.72494100	1.23362900
O	-4.34619600	-0.67119500	-1.62117600
C	-3.59004200	-1.80736600	0.31417100
H	-5.14374000	-0.35766700	0.27013400
O	-4.71704000	2.04621400	-1.13672600
O	-3.00642000	3.02546300	-0.13965900
H	-4.83686100	0.08907600	-1.96046000
O	-3.15347100	-1.88077900	1.43502600
O	-3.60812400	-2.83785000	-0.50671400
H	-3.95861300	-2.54654600	-1.36687900
H	-2.27821700	2.77974300	0.46460100
H	0.31648000	-0.44796200	-0.99611300
O	-0.45074900	-1.35076600	2.13400500
H	-1.41068400	-1.48441600	2.03353900

Name	**TS-CA-DIANION-O6-H-OOH-FHT-W**
Cartesian Coordinates	Frequency and Energy

C	-3.39641000	-2.02823300	-0.54187600
C	-2.45402600	-1.06125000	-0.11852600
C	-2.90388300	0.05568400	0.57169900
C	-4.26782500	0.21677600	0.84381500
C	-5.19761600	-0.76452300	0.39272800
C	-4.74837200	-1.88639300	-0.29927100
O	-4.73910900	1.25749800	1.52534500
O	-6.50431500	-0.60488300	0.63627400
C	-1.04330600	-1.28786800	-0.43475000
C	-0.03876500	-0.42478100	-0.24248200
C	1.33282100	-0.80197500	-0.62347300
O	2.18840200	0.20794900	-0.41093400
O	1.67379100	-1.87565500	-1.07805300
O	5.47982500	1.31336100	-1.08119700
C	3.56573800	-0.01453600	-0.73347800
C	4.25649300	-0.78878900	0.40335100
O	5.28234200	-1.60963200	-0.11931100
C	4.22538200	1.33762000	-1.05966600
O	3.49240800	2.31745000	-1.31485500
O	5.97861200	-0.07279400	1.88079600
C	4.80416700	0.14613400	1.49771400
O	4.02436100	1.02880400	1.92260500
H	-3.04062200	-2.90253400	-1.07605500
H	-2.22556300	0.82281700	0.92760700
H	-5.46488500	-2.62734400	-0.63169200
H	-5.12330500	1.99297100	0.80543300
H	-6.63633200	0.20134200	1.16119400
H	-0.81138900	-2.25256600	-0.88005700
H	-0.17311200	0.56557400	0.17508800
H	3.62407300	-0.62868800	-1.63578600
H	3.49646800	-1.41997700	0.87895200
H	6.07197700	-1.38119900	0.39752900

Zero-point correction= 0.235181 (Hartree/Particle)
Thermal correction to Energy= 0.257720
Thermal correction to Enthalpy= 0.258664
Thermal correction to Gibbs Free Energy= 0.179486
Sum of electronic and zero-point Energies= -1329.359143
Sum of electronic and thermal Energies= -1329.336604
Sum of electronic and thermal Enthalpies= -1329.335660
Sum of electronic and thermal Free Energies= -1329.414838

O	-5.46589300	2.59514100	-0.29944200
O	-5.19173700	1.64690800	-1.22942300
H	-4.27317700	1.80923100	-1.51135300

Name	**TS-CA-DIANION-O7-H-OOH-FHT-W**
Cartesian Coordinates	Frequency and Energy

C	3.28810100	-1.92781000	0.04615800
C	2.32399900	-0.99080700	-0.38968000
C	2.73005300	0.26787000	-0.83789000
C	4.07646800	0.59242500	-0.84612500
C	5.04851200	-0.34632800	-0.39712400
C	4.62686600	-1.60803000	0.05511200
O	4.46774100	1.80647100	-1.27748600
O	6.33166600	-0.00086100	-0.44127100
C	0.91696500	-1.38976500	-0.34864400
C	-0.13335500	-0.58993800	-0.56862400
C	-1.50227400	-1.12875000	-0.46944500
O	-2.41294900	-0.15740400	-0.62376200
O	-1.79791900	-2.28962200	-0.27936700
O	-5.25843400	-1.28693900	1.22891500
C	-3.77849700	-0.52550400	-0.44268400
C	-4.63557400	0.65956100	-0.92972200
O	-5.98968700	0.26167700	-1.00120900
C	-4.09331700	-0.85162600	1.03313700
O	-3.21935700	-0.63332200	1.89419400
O	-3.45105500	2.62713900	-0.28144600
C	-4.42558200	1.88364100	-0.01038300
O	-5.22296600	2.02156100	0.94660100
H	2.95842500	-2.90378700	0.38310200
H	2.01909200	1.00569300	-1.19005400
H	5.37849500	-2.31127500	0.39356900
H	6.54312000	0.66446900	0.39684100
H	0.72925800	-2.43075900	-0.09739200
H	-0.04428300	0.46511400	-0.79673100
H	-4.01293700	-1.39638300	-1.05792900
H	-4.31532200	0.91752900	-1.93998400
H	-6.20008300	-0.17058900	-0.15733400
O	6.42526300	1.36796900	1.50841300
O	5.10557700	1.23124500	1.77809600
H	5.43653200	1.85476800	-1.27085700
H	5.03047100	0.45227400	2.35882200

Zero-point correction= 0.235167 (Hartree/Particle)
Thermal correction to Energy= 0.257883
Thermal correction to Enthalpy= 0.258827
Thermal correction to Gibbs Free Energy= 0.178793
Sum of electronic and zero-point Energies= -1329.360734
Sum of electronic and thermal Energies= -1329.338018
Sum of electronic and thermal Enthalpies= -1329.337074
Sum of electronic and thermal Free Energies= -1329.417108

Name	**TS-CA-DIANION-C2-OOH-RAF-FHT-W**
Cartesian Coordinates	Frequency and Energy

C	2.79177900	0.22241800	0.11780500
C	3.89185000	0.44605500	0.97146200
C	5.18161800	0.38014000	0.48902200
C	5.40956900	0.08360000	-0.86391200
C	4.33328200	-0.14870500	-1.71553300
C	3.03757300	-0.08098700	-1.23510300
C	1.46956000	0.31980500	0.67150500
C	0.29229100	0.14038900	-0.03013700
O	6.67423300	0.01693900	-1.35349600
O	6.30218400	0.58679900	1.24566200
H	3.72817500	0.67630200	2.01963100
H	4.53523400	-0.38103100	-2.75434500

Zero-point correction= 0.240811 (Hartree/Particle)
Thermal correction to Energy= 0.263363
Thermal correction to Enthalpy= 0.264307
Thermal correction to Gibbs Free Energy= 0.186144
Sum of electronic and zero-point Energies= -1329.364802
Sum of electronic and thermal Energies= -1329.342250
Sum of electronic and thermal Enthalpies= -1329.341306
Sum of electronic and thermal Free Energies= -1329.419469

H	2.21431700	-0.26907300	-1.91286400
H	1.39731500	0.50605400	1.73873800
H	7.30508800	0.21529500	-0.64667600
O	-0.05817800	-1.76921800	-0.07984500
H	6.06024300	0.79790600	2.15683400
C	-0.98027500	0.48862000	0.64668300
O	-1.99027900	0.55434400	-0.22630100
O	-1.09909900	0.65470400	1.84030700
C	-3.32573200	0.71384300	0.27786500
C	-4.16633200	-0.45478200	-0.23038100
C	-3.86754100	2.09635100	-0.13721900
H	-3.30435600	0.68705700	1.36784300
O	-4.50554000	-0.31644300	-1.59715900
C	-3.39556700	-1.76707500	-0.00629300
H	-5.07164400	-0.50215400	0.38468600
O	-5.11092100	2.17107900	-0.29976700
O	-3.04001400	3.02532700	-0.23879000
H	-5.05300400	0.47902500	-1.65658600
O	-2.93354400	-1.91448700	1.16470600
O	-3.27847000	-2.57238900	-0.94471500
H	0.27164400	0.16647900	-1.11231800
O	-0.31200700	-2.28604500	1.16798100
H	-1.30239100	-2.21876600	1.25182400

Name			**TS-CA-TRIANION-O6-H-OOH-FHT-W**
Cartesian Coordinates			Frequency and Energy
C	3.15854300	-2.03241300	-0.61841700
C	2.26765500	-0.96558000	-0.33755200
C	2.81538100	0.29690300	-0.12460100
C	4.19725300	0.54191600	-0.20264700
C	5.10906200	-0.55460600	-0.50608100
C	4.51641800	-1.83651000	-0.69570000
O	4.64290700	1.77247400	-0.06614900
O	6.37227700	-0.37123200	-0.61633300
C	0.83531200	-1.27375100	-0.31114500
C	-0.22036400	-0.46491500	-0.15327300
C	-1.59701400	-1.05267200	-0.20907300
O	-2.52115700	-0.11402300	-0.13488700
O	-1.79952800	-2.24072300	-0.35906200
O	-5.61369500	-1.00587800	1.47040300
C	-3.90333300	-0.51591700	-0.09407600
C	-4.72491000	0.47662100	-0.94597800
O	-6.06521400	0.00751600	-0.97622400
C	-4.37858400	-0.77121100	1.37947900
O	-3.51213900	-0.81406600	2.25956100
O	-5.26913700	2.33044000	0.47642100
C	-4.62909700	1.98735000	-0.53478800
O	-3.93986300	2.69914800	-1.30665100
H	2.74232200	-3.02268300	-0.77918100
H	2.17733200	1.14626800	0.09446200
H	5.19380700	-2.65467700	-0.91843000
H	5.67029600	1.89803100	0.29246100
H	0.58939500	-2.32446000	-0.45570100
H	-0.15289900	0.60656000	-0.00514900
H	-3.98422800	-1.48946800	-0.58506900

Zero-point correction= 0.223468 (Hartree/Particle)
Thermal correction to Energy= 0.243679
Thermal correction to Enthalpy= 0.244624
Thermal correction to Gibbs Free Energy= 0.169409
Sum of electronic and zero-point Energies= -1328.920258
Sum of electronic and thermal Energies= -1328.900047
Sum of electronic and thermal Enthalpies= -1328.899103
Sum of electronic and thermal Free Energies= -1328.974318

H	-4.33873200	0.41537700	-1.96865300
H	-6.24874600	-0.24960800	-0.04882400
H	6.93332500	0.28451200	0.59762600
O	6.83151600	2.12922600	0.87871000
O	7.21655900	0.90447500	1.36165900

Table S2. The method to calculate rate constant following the conventional transition state theory

The rate constant (*k*) was calculated by using the conventional transition state theory (TST) (at 298.15 K, 1M standard state) according to the equation (1):[1-5]

$$k = \sigma\kappa\frac{k_B T}{h}e^{-(\Delta G^{\neq})/RT} \quad (1)$$

Where: σ is the reaction symmetry number ,[6,7]

κ contains the tunneling corrections calculated using the Eckart barrier,[8]

k_B is the Boltzmann constant,

h is the Planck constant,

$\Delta G^{\neq}$ is the Gibbs free energy of activation.

The Marcus Theory was used to estimate the reaction barriers of SET reactions.[9-12] The free energy of reaction $\Delta G^{\neq}$ for the SET pathway was computed following the equations (2,3).

$$\Delta G_{SET}^{\neq} = \frac{\lambda}{4}\left(1 + \frac{\Delta G_{SET}^{0}}{\lambda}\right)^2 \quad (2)$$

$$\lambda \approx \Delta E_{SET} - \Delta G_{SET}^{0} \quad (3)$$

where ΔG_{SET} is the Gibbs energy of reaction, ΔE_{SET} is the non-adiabatic energy difference between reactants and vertical products for SET.[13,14]

For rate constants that were close to the diffusion limit a correction was applied to yield realistic results[15]. The apparent rate constants (k_{app}) were calculated following the Collins–Kimball theory in the solvents at 298.15K;[16] the steady-state Smoluchowski rate constant (k_D) for an irreversible bimolecular diffusion–controlled reaction was calculated following the literature as corroding to equations (4,5).[15,17]

$$k_{app} = \frac{k_{TST} k_D}{k_{TST} + k_D} \quad (4)$$

$$k_D = 4\pi R_{AB} D_{AB} N_A \quad (5)$$

where R_{AB} is the reaction distance, N_A is the Avogadro constant, and $D_{AB} = D_A + D_B$ (D_{AB} is the mutual diffusion coefficient of the reactants A and B),[16,18] where D_A or D_B is estimated using the Stokes–Einstein formulation (6).[19,20]

$$D_{A\ or\ B} = \frac{k_B T}{6\pi\eta a_{A\ or\ B}} \qquad (6)$$

η is the viscosity of the solvents (i.e. $\eta(H_2O) = 8.91\times10^{-4}$ Pa s, η(pentyl ethanoate) = 8.62×10^{-4} Pa s) and *a* is the radius of the solute.

The kinetic study requires different considerations. In this study, the solvent effects of water and pentyl ethanoate were modelled by the solvation model density (SMD) method [21,22]. Water (dielectric constants, ε = 78.35) and pentyl ethanoate (ε = 4.73) are the *de facto* standard solvents in the literature to mimic the polar and nonpolar environments in the human body [15,23-25]. Thus, these solvents were used to model the physiological environments. The solvent cage effects were included following the corrections proposed by Okuno,[26] adjusted with the free volume theory according to the Benson correction[15,27-29] to reduce over-penalizing entropy losses in solution. For the species that have multiple conformers, all of these were investigated and the conformer with the lowest electronic energy was included in the analysis.[24,25] The hindered internal rotation treatment was also applied to the single bonds to ensure that the obtained conformer has the lowest electronic energy [25,30]. All transition states were characterized by the existence of only one single imaginary frequency. Intrinsic coordinate calculations (IRCs) were performed to ensure that each transition state is connected correctly with the pre-complex and post-complex.

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