

Supporting information

Reactivity of Oxidants towards Phenyl and Benzyl Substituted 5-Selanylpentanoic Acids: Radiolytic and Theoretical Insights

Beena G. Singh,^{1,2*} Kavanal P. Prasanthkumar,³ Francesca Mangiavacchi,^{4,5} Francesca Marini,⁴ Claudio Santi^{4*}

¹ Radiation & Photochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai – 4000851; beenam@barc.gov.in (ORCID: 0000-0002-1679-5456)

² Homi Bhabha National Institute, Anushaktinagar, Mumbai – 400 094

³ Post Graduate and Research Department of Chemistry, Maharaja's College, Ernakulam, Kerala 682011, India; prasanthkumarkp@gmail.com (ORCID: 0000-0001-6769-6485)

⁴ Group of Catalysis, Synthesis and Organic Green Chemistry, Department of Pharmaceutical Sciences, University of Perugia, Via del Liceo 1, 06123 Perugia Italy. F.Mar. Francesca.marini@unipg.it (ORCID: 0000-0003-0747-5060); C.S. claudio.santi@unipg.it (ORCID: 0000-0002-7698-8970)

⁵ Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 13, Sesto Fiorentino, I-50019 Florence, Italy; F.manfrancesca.mangiavacchi@unifi.it (ORCID: 0000-0001-5344-2310)

*Correspondence: B.G.S: beenam@barc.gov.in; C.S. claudio.santi@unipg.it

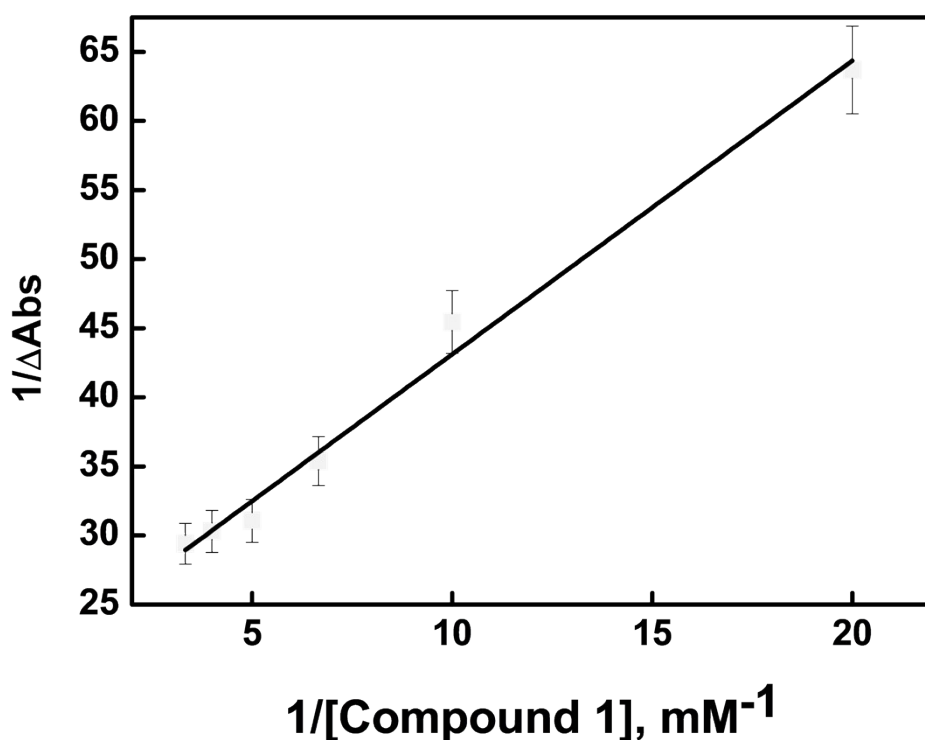


Figure S1: Double reciprocal plot of absorbance at 630 nm against varying concentration of compound 1 (50-300 μM). The plot was fitted in accordance to equation (4).

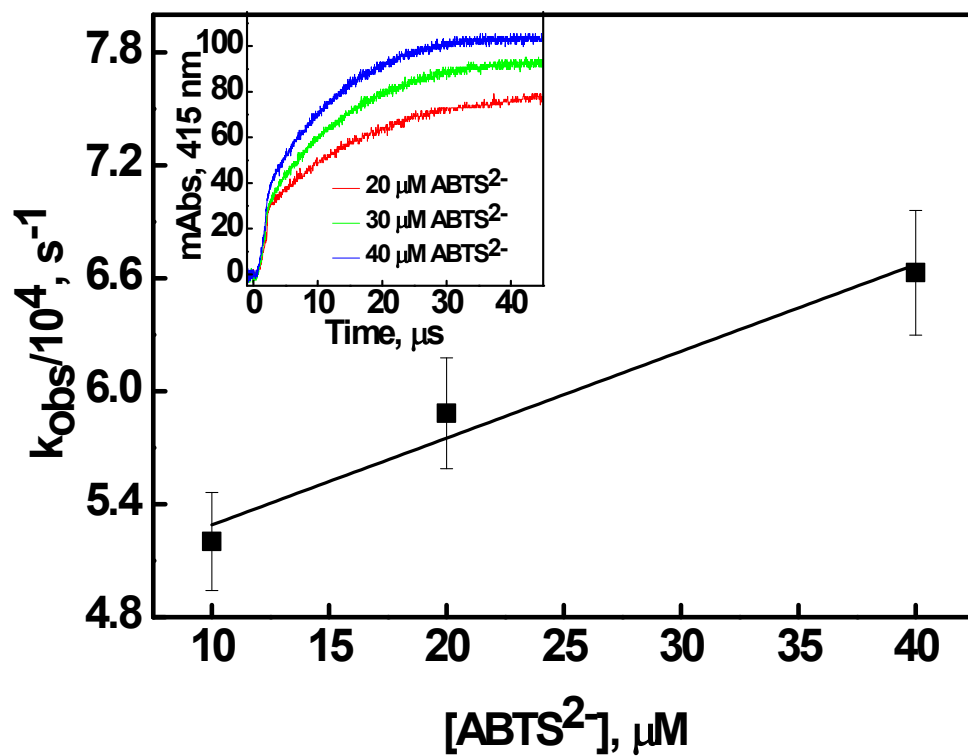


Figure S2: Plot showing the observed rate (k_{obs}) for the electron transfer between $ABTS^{2-}$ and the oxidizing transient derived from product of hydroxyl radical reaction with Compound **1**. Inset shows the absorbance–time plot at 415 nm obtained on pulse irradiating N_2O -saturated aqueous solutions at pH 7, containing 1 mM of compound **1** and 10–40 μM $ABTS^{2-}$.

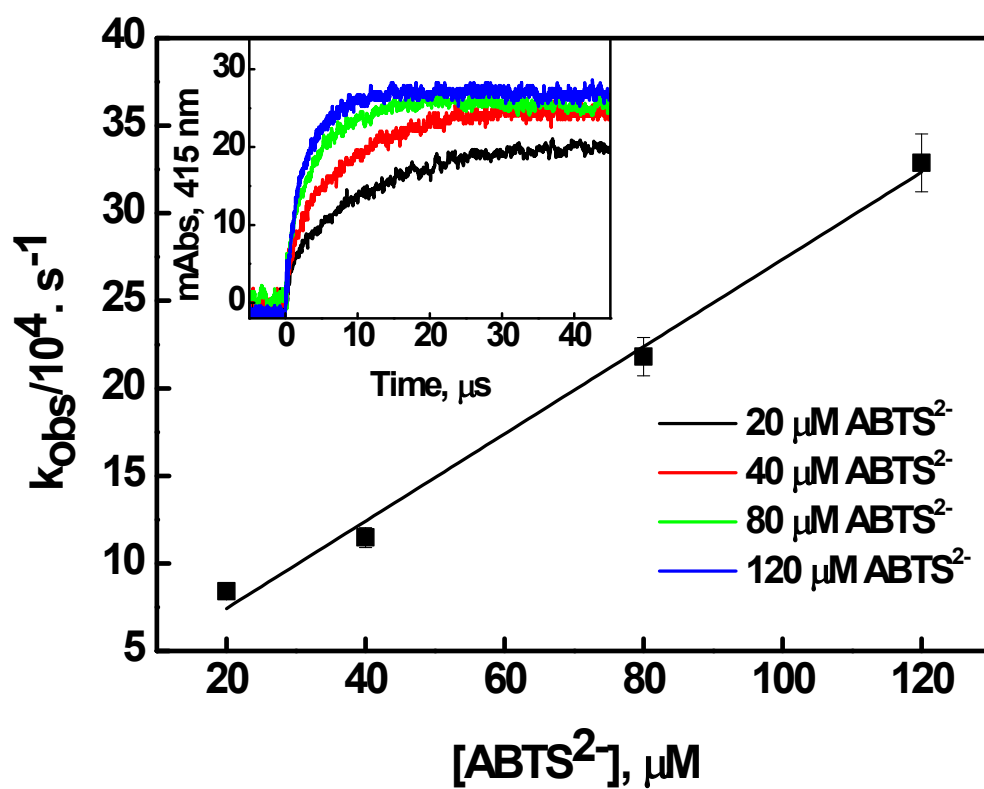


Figure S3: Plot showing the observed rate (k_{obs}) for the electron transfer between ABTS^{2-} and the oxidizing transient derived from product of hydroxyl radical reaction with Compound **2**. Inset shows the absorbance –time plot at 415 nm obtained on pulse irradiating N_2O -saturated aqueous solutions at pH 7, containing 1 mM Compound **2** and 20-120 μM ABTS^{2-} .

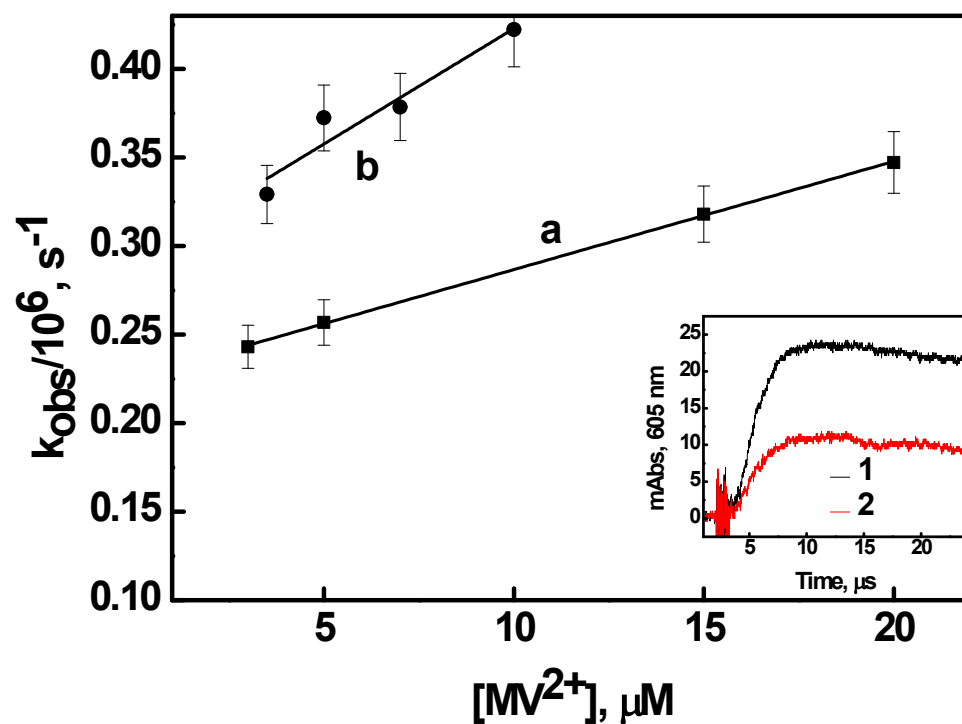


Figure S4: Plot showing the observed rate (k_{obs}) for the electron transfer between MV^{2+} and the reducing transient derived from product of hydroxyl radical reaction with (a) Compound 1 and (b) Compound 2, respectively. Inset shows the absorbance –time plot at 605 nm obtained on pulse irradiating N_2O -saturated aqueous solutions at pH 7, containing 1 mM Compounds 1/2 and $5 \mu M$ MV^{2+} .

Cartesian coordinates and excerpt of thermochemical parameters of compound (1), radical cation (1•), sigma dimer (D₁) and pi-dimer (D₁').

Compound (1)

Charge = -1, Multiplicity = 1

6	3.916590000	1.760365000	0.184393000
6	2.643343000	1.215764000	0.033464000
6	2.484004000	-0.167615000	0.022216000
6	3.597642000	-0.998056000	0.159738000
6	4.862162000	-0.444587000	0.308496000
6	5.027807000	0.937980000	0.322213000
1	4.033074000	2.835951000	0.193315000
1	1.794606000	1.875482000	-0.072674000
1	3.474192000	-2.073502000	0.150009000
1	5.719176000	-1.096312000	0.413961000
1	6.013211000	1.367573000	0.439052000
6	-0.409408000	0.532449000	-0.323014000
6	-1.843258000	0.047631000	-0.473756000
1	-0.289876000	1.128344000	0.578792000
1	-0.096355000	1.107946000	-1.191140000
6	-2.799340000	1.228605000	-0.635401000
1	-1.926322000	-0.606538000	-1.344947000
1	-2.126122000	-0.539280000	0.403690000
1	-2.711334000	1.891812000	0.226784000
1	-2.513582000	1.804339000	-1.518104000
34	0.778581000	-1.025998000	-0.176699000
6	-4.248594000	0.768424000	-0.785632000
1	-4.897016000	1.636184000	-0.928174000
1	-4.352596000	0.123565000	-1.657789000
6	-4.759699000	0.027819000	0.445808000
8	-5.330003000	-1.085049000	0.277892000
8	-4.597536000	0.582009000	1.567587000

Zero-point correction= 0.219157 (Hartree/Particle)

Thermal correction to Energy= 0.233403

Thermal correction to Enthalpy= 0.234347

Thermal correction to Gibbs Free Energy= 0.173076

Sum of electronic and zero-point Energies= -2978.965122

Sum of electronic and thermal Energies= -2978.950876

Sum of electronic and thermal Enthalpies= -2978.949932

Sum of electronic and thermal Free Energies= -2979.011202

Monomer radical cation (1•)

Charge = 0, Multiplicity = 2

6	3.927294000	1.735559000	0.215634000
6	2.645581000	1.236990000	0.067902000

6	2.466132000	-0.151843000	0.022928000
6	3.554938000	-1.031664000	0.122156000
6	4.829034000	-0.512819000	0.266759000
6	5.014717000	0.866976000	0.314496000
1	4.083209000	2.804262000	0.254224000
1	1.806958000	1.912620000	-0.008532000
1	3.392045000	-2.100299000	0.084140000
1	5.675690000	-1.180024000	0.342081000
1	6.011462000	1.269572000	0.429078000
6	-0.423326000	0.546400000	-0.319210000
6	-1.845522000	0.037423000	-0.484550000
1	-0.291986000	1.128634000	0.591636000
1	-0.078889000	1.115254000	-1.181793000
6	-2.802278000	1.219540000	-0.633630000
1	-1.913925000	-0.602284000	-1.366220000
1	-2.124970000	-0.560557000	0.385168000
1	-2.715440000	1.872179000	0.236317000
1	-2.517700000	1.804282000	-1.510382000
34	0.795860000	-0.965905000	-0.166355000
6	-4.248002000	0.751599000	-0.786579000
1	-4.899785000	1.617836000	-0.921727000
1	-4.349577000	0.113724000	-1.663953000
6	-4.755024000	-0.000561000	0.440216000
8	-5.335559000	-1.106062000	0.261738000
8	-4.579137000	0.538560000	1.566926000

Zero-point correction= 0.219212 (Hartree/Particle)

Thermal correction to Energy= 0.233475

Thermal correction to Enthalpy= 0.234419

Thermal correction to Gibbs Free Energy= 0.173595

Sum of electronic and zero-point Energies= -2978.760079

Sum of electronic and thermal Energies= -2978.745815

Sum of electronic and thermal Enthalpies= -2978.744871

Sum of electronic and thermal Free Energies= -2978.805695

Sigma dimer (**D₁**)

Charge = -1, Multiplicity = 2

6	3.817856000	-2.534165000	0.030855000
6	2.431547000	-2.429151000	0.018942000
6	1.810781000	-1.808365000	-1.061784000
6	2.554591000	-1.311935000	-2.129992000
6	3.938648000	-1.427348000	-2.106015000
6	4.571695000	-2.031777000	-1.024380000
1	4.306927000	-3.007790000	0.871154000
1	1.855831000	-2.822055000	0.844431000
1	2.058411000	-0.828902000	-2.961435000
1	4.521273000	-1.035907000	-2.928593000

1	5.649989000	-2.108840000	-1.002792000
6	-0.551215000	-1.690596000	0.759291000
6	-1.968097000	-1.180137000	0.961208000
1	-0.450900000	-2.737547000	1.038431000
1	0.185060000	-1.092703000	1.293629000
6	-2.337271000	-1.183997000	2.443635000
1	-2.052409000	-0.163369000	0.576475000
1	-2.668949000	-1.801975000	0.398897000
1	-2.345684000	-2.207569000	2.821856000
1	-1.578283000	-0.633779000	3.004537000
34	-0.086554000	-1.577068000	-1.144176000
34	0.091521000	1.421649000	-1.317992000
6	-1.807888000	1.649729000	-1.277158000
6	-2.438815000	2.397924000	-0.286882000
6	-2.541968000	1.016881000	-2.277882000
6	-3.825725000	2.494581000	-0.296404000
6	-3.926858000	1.125105000	-2.276451000
6	-4.569998000	1.857582000	-1.283724000
1	-1.870010000	2.894778000	0.485791000
1	-2.037982000	0.435356000	-3.038550000
1	-4.323459000	3.066814000	0.474591000
1	-4.501651000	0.628034000	-3.045778000
1	-5.648852000	1.929370000	-1.277699000
6	0.545727000	1.750094000	0.562321000
1	0.431363000	2.819916000	0.724838000
1	-0.183436000	1.205045000	1.158834000
6	1.970153000	1.285117000	0.815125000
1	2.660087000	1.856602000	0.189315000
1	2.072733000	0.235214000	0.538757000
6	2.340300000	1.450217000	2.287899000
1	1.595458000	0.943181000	2.905484000
1	2.325309000	2.507402000	2.558503000
6	3.719090000	0.854553000	2.580080000
1	3.965792000	0.998291000	3.633757000
1	3.714777000	-0.214659000	2.367617000
6	4.808737000	1.525087000	1.751423000
8	4.954300000	2.771450000	1.888211000
8	5.499182000	0.806712000	0.978374000
6	-3.699054000	-0.527662000	2.675270000
1	-3.944689000	-0.555527000	3.739002000
1	-3.669623000	0.514677000	2.357327000
6	-4.818090000	-1.244442000	1.927670000
8	-4.955738000	-2.481654000	2.135597000
8	-5.545350000	-0.566955000	1.151202000

Zero-point correction=	0.440636 (Hartree/Particle)
Thermal correction to Energy=	0.470606
Thermal correction to Enthalpy=	0.471550

Thermal correction to Gibbs Free Energy= 0.372365
Sum of electronic and zero-point Energies= -5957.748615
Sum of electronic and thermal Energies= -5957.718645
Sum of electronic and thermal Enthalpies= -5957.717701
Sum of electronic and thermal Free Energies= -5957.816886

Pi dimer (D_1')

Charge = -1, Multiplicity = 2

6	0.231627000	3.420417000	-2.209870000
6	0.392737000	2.041607000	-2.225222000
6	1.086918000	1.419518000	-1.185747000
6	1.620664000	2.165611000	-0.136738000
6	1.456709000	3.545604000	-0.138178000
6	0.762984000	4.174103000	-1.167628000
1	-0.307488000	3.904246000	-3.012704000
1	-0.015559000	1.450478000	-3.034820000
1	2.157190000	1.694511000	0.673518000
1	1.869210000	4.128866000	0.673836000
1	0.636717000	5.248000000	-1.157454000
6	2.267345000	-0.912121000	0.296324000
6	3.755186000	-0.668783000	0.097915000
1	1.845974000	-0.344815000	1.123875000
1	2.051956000	-1.967804000	0.451405000
6	4.515279000	-0.973455000	1.388857000
1	4.117864000	-1.307608000	-0.709449000
1	3.937310000	0.366739000	-0.195733000
1	4.191958000	-0.277950000	2.166278000
1	4.268227000	-1.979723000	1.730796000
34	1.219292000	-0.477488000	-1.295886000
34	-1.268267000	-1.009187000	0.245673000
6	-1.244427000	0.683687000	1.123127000
6	-1.810873000	1.842161000	0.596556000
6	-0.590105000	0.706127000	2.356504000
6	-1.721601000	3.026592000	1.317605000
6	-0.503286000	1.898230000	3.063120000
6	-1.068219000	3.059608000	2.545711000
1	-2.318340000	1.836237000	-0.355613000
1	-0.155988000	-0.200272000	2.758379000
1	-2.160879000	3.927594000	0.911471000
1	0.003976000	1.916692000	4.017894000
1	-1.000588000	3.986994000	3.097677000
6	-2.268872000	-0.707221000	-1.418479000
1	-2.100302000	0.321319000	-1.727327000
1	-1.756387000	-1.368147000	-2.114134000
6	-3.740586000	-1.068870000	-1.293683000
1	-3.826959000	-2.103712000	-0.955081000
1	-4.160487000	-1.026693000	-2.302896000

6	-4.543595000	-0.151002000	-0.378700000
1	-4.489894000	0.872304000	-0.755857000
1	-4.109663000	-0.149309000	0.622889000
6	6.022803000	-0.851301000	1.196521000
1	6.285500000	0.143948000	0.837356000
1	6.532420000	-0.995198000	2.153294000
6	-6.004878000	-0.582430000	-0.301464000
1	-6.566858000	0.120421000	0.319283000
1	-6.457883000	-0.578179000	-1.292894000
6	6.613173000	-1.885330000	0.241276000
8	7.593398000	-1.527885000	-0.469384000
8	6.117884000	-3.044036000	0.237344000
6	-6.202576000	-1.961828000	0.321393000
8	-5.502321000	-2.263929000	1.325172000
8	-7.079500000	-2.713839000	-0.187130000

Zero-point correction= 0.440315 (Hartree/Particle)

Thermal correction to Energy= 0.470157

Thermal correction to Enthalpy= 0.471101

Thermal correction to Gibbs Free Energy= 0.371949

Sum of electronic and zero-point Energies= -5957.751371

Sum of electronic and thermal Energies= -5957.721529

Sum of electronic and thermal Enthalpies= -5957.720585

Sum of electronic and thermal Free Energies= -5957.819737
