Supporting Information for

Unraveling the Dissociation Pathways of Acetic Acid upon Electron Transfer in Potassium Collisions: Experimental and Theoretical Studies

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This Supporting Information includes:

- relative energies associated to the conformational change from HAc⁻ to HAc⁻(c) at ωB97X/6-311++G(3df,3pd) level, charges and spin densities from the natural population analysis at ωB97X/6-311++G(3df,3pd) level for all stationary points found in the energy profiles of Scheme 1 and Scheme 2,

- a detailed discussion of the mechanism associated to the direct OH fragmentation and formation of OH• along with the relative energies of the process at ωB97X/6-311++G(3df,3pd) level of calculation and charge and spin density from natural population analysis also at ωB97X/6-311++G(3df,3pd) level to describe this mechanism about formation of OH•,

- relative energies at ωB97X/6-311++G(3df,3pd) level for each stationary point of the analyzed pathways in Scheme 1 and Scheme 2 to release OH⁻ formation, relative energies of all the stationary points found in the two mechanisms associated to the production of OH⁻ at different levels of calculation: LC-ωPBE/6-311++G(3df,3pd), BHandHLYP/6-311++G(3df,3pd), M06HF/6-311++G(3df,3pd), MP2/6-

311++G(3df,3pd) and CCSD(T)/6-311++G(3df,3pd)//BHandHLYP/6-311++G(3df,3pd), and Cartesian coordinates of the optimized structures for the stationary points of the proposed mechanisms.

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asymptote. Zero point correction and thermal corrections to Gibbs Free energy are also included. Energies in eV.

Table S7. Relative energies at BHandHLYP/6-311++(3df,3pd) level for each stationary point of the analyzed pathways in Scheme 1 and Scheme 2 to release OH^- considering HAc^- as asymptote. Zero point correction and thermal corrections to Gibbs Free energy are also included. Energies in eV.

Table S8. Relative energies at M06HF/6-311++(3df,3pd) level for each stationary point of the analyzed pathways in Scheme 1 and Scheme 2 to release OH^- considering HAc^- as asymptote. Zero point correction and thermal corrections to Gibbs Free energy are also included. Energies in eV.

Table S9. Relative energies at MP2/6-311++(3df,3pd) level for each stationary point of the analyzed pathways in Scheme 1 and Scheme 2 to release OH^- considering HAc^- as asymptote. Zero point correction and thermal corrections to Gibbs Free energy are also included. Energies in eV.

Table S10. Relative energies at CCSD(T)/6-311++G(3df,3pd)//BHandHLYP/6-311++G(3df,3pd) level for each stationary point of the analyzed pathways in Scheme 1 and Scheme 2 to release OH^- considering HAc^- as asymptote. Zero point correction and thermal corrections to Gibbs Free energy are also included. Energies in eV.

Table S11. Cartesian coordinates of the following optimized stationary points at ωB97X/6-311++G(3df,3pd) level: HAc^-, $TS_{HAc/diol}$, $diol^-$, $TS_{diol/P\bullet}$, $P^\bullet\cdots OH^-$, $TS_{HAc/I1}$, I1, $TS_{I1/I2}$, I2, $TS_{I2/diol}$.

Table S1. Relative energies of the anionized acetic acid with respect to HAc⁻ structure at ωB97X/6-311++G(3df,3pd) level. Zero point correction and thermal corrections to Gibbs free energy are included. Energies in eV.

System	ΔE	ΔE_{ZPE}	ΔG^o_{298K}
HAc⁻	0.00	0.00	0.00
TS$_{HAc/HAc-(c)}$	0.32	0.25	0.26
HAc⁻(c)	-0.12	-0.12	-0.12
diol⁻	1.13	1.10	1.10

Table S2. Charge (spin density) from natural population analysis at ωB97X/6-311++G(3df,3pd) level for all stationary points found in the energy profiles of Scheme 1 and Scheme 2.

System	Fragment		
	OH	CO	CH$_3$
HAc⁻	-0.38(0.16)	0.18(0.01)	-0.81(0.83)
TS$_{HAc/diol}$[a]	-1.01(0.92)	0.51(0.07)	-0.50/(0.01)
diol⁻[a]	-0.27(0.03)	-0.36(084)	-037(0.13)
TS$_{diol/P•}$[a]	-0.32(0.81)	-0.27(0.20)	-0.41(0.00)
P•···OH⁻[a]	-0.69(0.42)	0.01(0.63)	-0.32(-0.06)
TS$_{HAc/I1}$	-0.96(0.97)	0.06(0.00)	-0.10(0.02)
I1	-0.89(0.98)	0.01(0.00)	-0.12(0.02)
TS$_{I1/I2}$[a]	-0.76(0.99)	0.41(0.00)	-065(0.00)
I2[a]	-0.86(0.97)	0.38(0.00)	-0.51(0.03)
TS$_{I2/diol}$[a]	-0.94(0.93)	0.39(0.02)	-0.45(0.06)

[a]CO includes the H transferred from CH_3, whereas such H is not included in CH_3.

In the following paragraphs we describe the most intuitive reaction pathway leading to the formation of OH but as a neutral species (OH$^\bullet$). This pathway comes from the direct fragmentation of OH and the calculated energy profile is shown in Scheme 3, whereas relative energies including zero point corrections and entropic effects are depicted in Table S3. The computed mechanism involves two elementary steps. The first step corresponds to the OH fragmentation to form H_2O via H transfer from CH_3. In the second and final step one H of H_2O is transferred to the C atom of $COCH_2$ to form the final products [CHOCH$_2$]$^-$ and OH$^-$.

Table S3. Relative energies at ωB97X/6-311++G(3df,3pd) level of calculation for each stationary point of the pathways to release OH$^-$ considering HAc$^-$ as asymptote. Inclusion of zero point correction and thermal corrections to Gibbs Free energy are also included. Energies in eV.

System	Energy		
	ΔE	ΔE_{ZPE}	ΔG^{o}_{298K}
HAc$^-$	0.00	0.00	0.00
TS$_{HAc/I3}$	1.51	1.31	1.26
I3	0.42	0.26	0.20
TS$_{I3/P-}$	1.74	1.53	1.51
P$^-\cdots$OH$^\bullet$	1.47	1.28	1.24

The first step produces a H_2O molecule and the [CH$_3$CO]$^-$ species, such system being slightly less stable (0.2 eV) than the initial anionized acetic acid although the barrier to overcome the TS$_{HAc/I3}$ is not really very high, 1.3 eV, which is within our energy window of work (~3 eV) (see Table S3). Such energy cost is mainly due to the OH cleavage and geometric and electronic reorganizations. The resulting species of this step is a system consisting in H_2O and the [CH$_3$CO]$^-$ species and natural population analysis in Table S4 shows the electronic reorganization mentioned above. Indeed, in the anionized acetic acid the charge and spin was mainly localized at CH_3 group, whereas in the resulting product, charge is also distributed

along CO and the spin density is now localized at CO. Such NPA analysis also shows the neutral nature of the formed H_2O.

Table S4. Charge (spin density) from natural population analysis at ωB97X/6-311++G(3df,3pd) level of calculation for all stationary points of Table S3.

System	Fragment		
	OH	CO	CH$_3$
HAc$^-$	-0.38(0.16)	0.18(0.01)	-0.81(0.83)
TS$_{HAc/I3}$	-0.92(0.01)	-0.01(0.90)	-0.07(0.09)
I3[a]	-0.03(0.01)	-0.42(0.96)	-0.55(0.03)
TS$_{I3/P-}$[b]	-0.24(0.76)	-0.36(0.22)	-0.40(0.01)
P-···OH$^{\bullet}$[b]	-0.11(0.99)	-0.50(0.00)	-0.39(0.00)

[a]OH includes the H transferred from CH$_3$, whereas H is not included in CH$_3$.

[b]CO includes the H transferred from H_2O, whereas one H is not included in CH$_3$.

In the second and last step the OH$^{\bullet}$ is produced via H transfer from H_2O to [CH$_2$CO]$^-$ species. This last product is 1.0 eV less stable than its precursor and remains 1.2 eV above the asymptote (HAc$^-$. Also, an energy barrier of 1.3 eV has also to be overcome in the transition state TS$_{I3/P-}$. Natural population analysis confirms the radical nature of the released OH being the computed spin density 0.99 and the anionic nature the CH$_2$COH fragment being the computed charge -0.89 in this fragment.

Table S5. Relative energies at ωB97X/6-311++G(3df,3pd) level for each stationary point of the analyzed pathways in Scheme 1 and Scheme 2 to release OH⁻ considering HAc⁻ as asymptote. Zero point correction and thermal corrections to Gibbs Free energy are also included. Energies in eV.

System	Energy		
	ΔE	ΔE_{ZPE}	ΔG^{o}_{298K}
HAc⁻	0.00	0.00	0.00
$TS_{HAc/diol}$	3.05	2.86	2.88
diol⁻	1.13	1.10	1.10
$TS_{diol/P}$•	3.29	2.99	2.94
P•···OH⁻	3.26	2.98	2.92
$TS_{HAc/I1}$	0.81	0.51	0.46
I1	0.77	0.47	0.39
$TS_{I1/I2}$	3.20	2.72	2.67
I2	2.00	1.68	1.65
$TS_{I2/diol}$	2.04	1.72	1.71

Table S6. Relative energies at LC-ωPBE/6-311++(3df,3pd) level for each stationary point of the analyzed pathways in Scheme 1 and Scheme 2 to release OH⁻ considering HAc⁻ as asymptote. Zero point correction and thermal corrections to Gibbs Free energy are also included. Energies in eV.

System	Energy		
	ΔE	ΔE_{ZPE}	ΔG^o_{298K}
HAc⁻	0.00	0.00	0.00
TS$_{HAc/diol}$	2.98	2.79	2.81
diol⁻	1.11	1.08	1.09
TS$_{diol/P}$•	3.55	3.25	3.20
P•···OH⁻	3.19	3.05	3.00
TS$_{HAc/ I1}$	0.81	0.49	0.44
I1	0.78	0.47	0.40
TS$_{I1/I2}$	3.13	2.66	2.60
I2	2.02	1.69	1.65
TS$_{I2/diol}$	2.05	1.71	1.72

Table S7. Relative energies at BHandHLYP/6-311++(3df,3pd) level for each stationary point of the analyzed pathways in Scheme 1 and Scheme 2 to release OH⁻ considering HAc⁻ as asymptote. Zero point correction and thermal corrections to Gibbs Free energy are also included. Energies in eV.

System	Energy		
	ΔE	ΔE_{ZPE}	ΔG^{o}_{298K}
HAc⁻	0.00	0.00	0.00
TS$_{HAc/diol}$	3.23	2.98	2.99
diol⁻	1.13	1.10	1.11
TS$_{diol/P}$•	3.49	3.22	3.17
P•···OH⁻	3.31	3.07	3.02
TS$_{HAc/ I1}$	1.10	0.78	0.73
I1	1.05	0.74	0.68
TS$_{I1/I2}$	3.61	3.14	3.10
I2	2.22	1.90	1.87
TS$_{I2/diol}$	2.26	1.93	1.92

Table S8. Relative energies at M06HF/6-311++(3df,3pd) level for each stationary point of the analyzed pathways in Scheme 1 and Scheme 2 to release OH⁻ considering HAc⁻ as asymptote. Zero point correction and thermal corrections to Gibbs Free energy are also included. Energies in eV.

System	Energy		
	ΔE	ΔE_{ZPE}	ΔG^o_{298K}
HAc⁻	0.00	0.00	0.00
TS$_{HAc/diol}$	3.01	2.77	2.78
diol⁻	0.91	0.88	0.88
TS$_{diol/P}$•	3.71	3.43	3.40
P•···OH⁻	3.41	3.18	3.14
TS$_{HAc/ I1}$	1.29	0.98	0.96
I1	1.10	0.80	0.74
TS$_{I1/I2}$	3.36	2.89	2.85
I2	2.08	1.75	1.72
TS$_{I2/diol}$	2.23	1.90	1.89

Table S9. Relative energies at MP2/6-311++(3df,3pd) level for each stationary point of the analyzed pathways in Scheme 1 and Scheme 2 to release OH⁻ considering HAc⁻ as asymptote. Zero point correction and thermal corrections to Gibbs Free energy are also included. Energies in eV.

System	Energy		
	ΔE	ΔE_{ZPE}	$\Delta G^o{}_{298K}$
HAc⁻	0.00	0.00	0.00
TS$_{HAc/diol}$	3.04	2.86	2.88
diol⁻	1.14	1.10	1.10
TS$_{diol/P}$•	4.01	3.75	3.71
P•···OH⁻	3.68	3.45	3.40
TS$_{HAc/ I1}$	0.97	0.67	0.65
I1	0.87	0.55	0.42
TS$_{I1/I2}$	3.14	2.67	2.57
I2	2.02	1.67	1.58
TS$_{I2/diol}$	2.10	1.78	1.77

Table S10. Relative energies at CCSD(T)/6-311++G(3df,3pd)//BHandHLYP/6-311++G(3df,3pd) level for each stationary point of the analyzed pathways in Scheme 1 and Scheme 2 to release OH⁻ considering HAc⁻ as asymptote. Zero point correction and thermal corrections to Gibbs Free energy are also included. Energies in eV.

System	Energy		
	ΔE	ΔE_{ZPE}	ΔG^{o}_{298K}
HAc⁻	0.00	0.00	0.00
TS$_{HAc/diol}$	2.95	2.71	2.72
diol⁻	1.13	1.10	1.11
TS$_{diol/P}$•	3.44	3.17	3.12
P•···OH⁻	3.39	3.15	3.10
TS$_{HAc/I1}$	1.03	0.72	0.66
I1	0.99	0.68	0.62
TS$_{I1/I2}$	3.34	2.87	2.84
I2	2.16	1.84	1.81
TS$_{I2/diol}$	2.18	1.86	1.84

Table S11. Cartesian coordinates of the following optimized stationary points at ωB97X/6-311++G(3df,3pd) level: HAc⁻, TS$_{HAc/diol}$, diol⁻, TS$_{diol/P•}$, P•···OH⁻, TS$_{HAc/I1}$, I1, TS$_{I1/I2}$, I2, TS$_{I2/diol}$.

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8
HAc-
C          0.006954000        0.009628000        1.453989000
C          0.051783000        0.069321000       -0.039917000
O          1.014151000        0.346812000       -0.711372000
O         -1.136127000       -0.229052000       -0.594351000
H          0.976831000        0.255190000        1.874402000
H         -0.748144000        0.699770000        1.828840000
H         -0.297716000       -0.986014000        1.774756000
H         -1.021520000       -0.168115000       -1.551758000


8
TSHAc/diol
C         -0.170794000       -0.048200000        0.114040000
C         -0.183032000        0.137455000        1.543368000
H          1.187664000       -0.010341000        0.912868000
H         -0.925973000        0.810752000        1.961822000
H         -0.167528000       -0.828617000        2.045710000
O         -1.132614000        0.142985000       -0.721616000
O          1.025315000       -0.355010000       -0.241616000
H         -0.827766000        0.150976000       -1.669581000


8
diol-
C         -0.507817000        0.104237000        1.548425000
C         -0.213284000        0.003860000        0.254755000
O          0.983761000       -0.177022000       -0.315410000
O         -1.169316000        0.079446000       -0.708448000
H          1.707633000       -0.237971000        0.341537000
H         -1.537515000        0.250107000        1.839868000
H          0.272542000        0.040336000        2.288942000
H         -0.707788000       -0.021455000       -1.546077000


8
TSdiol/P·
C         -0.361148000        0.187892000        1.507023000
C         -0.018230000        0.013012000        0.221615000
O          1.313000000       -0.239273000       -0.063561000
O         -1.797231000       -0.346388000       -1.656575000
H          1.802503000       -0.275222000        0.770925000
H         -1.390515000        0.371052000        1.787189000
H          0.380189000        0.144622000        2.319029000
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H        -1.067353000        0.124843000       -1.110053000


8
P····OH-
C        -0.343480000        0.181953000        1.530396000
C        -0.044070000       -0.056274000        0.239425000
O         1.305131000       -0.269142000       -0.045308000
O        -1.808122000       -0.181649000       -1.817943000
H         1.805901000       -0.203501000        0.780196000
H        -1.366976000        0.357599000        1.840529000
H         0.423977000        0.208961000        2.319651000
H        -1.078147000       -0.118409000       -0.999355000


8
TSHAc/I1
C         0.023727000        0.012255000        1.505410000
C         0.024525000        0.062110000       -0.031328000
O         1.066813000        0.357139000       -0.612186000
O        -1.113417000       -0.223325000       -0.537798000
H         1.009394000        0.262987000        1.896545000
H        -0.719498000        0.711398000        1.892495000
H        -0.265517000       -0.986366000        1.837303000
H        -1.184813000       -0.198660000       -2.003851000


8
I1
C         0.042365000        0.015618000        1.546902000
C        -0.007900000        0.052227000        0.002801000
O         1.036476000        0.349585000       -0.595462000
O        -1.138811000       -0.233327000       -0.476904000
H         1.037833000        0.268922000        1.911623000
H        -0.689857000        0.717823000        1.951070000
H        -0.237520000       -0.980570000        1.896015000
H        -1.206372000       -0.192741000       -2.377454000


8
TSI1/I2
C        -0.064502000        0.098189000        1.714643000
C        -0.265810000       -0.047045000        0.230060000
O         0.969186000        0.071414000       -0.245335000
O        -1.270687000       -0.194341000       -0.454683000
H         1.160502000        0.341562000        0.895914000
H        -0.864814000        0.637840000        2.227660000
H         0.039527000       -0.896680000        2.160489000
H        -0.872185000       -0.014401000       -2.670154000


8
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I2
C        -0.412173000         0.119467000         1.609868000
C        -0.300901000        -0.214040000         0.276955000
O         1.003709000        -0.393464000        -0.223789000
O        -1.203407000        -0.392202000        -0.568533000
H         1.600818000        -0.166345000         0.490114000
H        -1.391670000         0.280464000         2.035466000
H         0.454772000         0.174504000         2.258828000
H        -0.883934000         0.632153000        -2.165315000


8
TSI2/diol
C        -0.428023000         0.147124000         1.532170000
C        -0.239013000        -0.237789000         0.234910000
O         1.065058000        -0.472281000        -0.203068000
O        -1.118503000        -0.413116000        -0.664668000
H         1.648233000        -0.188142000         0.502187000
H        -1.425989000         0.366957000         1.879539000
H         0.394958000         0.193746000         2.236430000
H        -1.035507000         0.584039000        -1.741906000
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