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On the Importance of Time Scale and Local Environment in Electron-Driven Proton Transfer. The Anion of Acetoacetic Acid

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Supporting Information Available

We constructed a linear synchronous path connecting $G_{M^-_{dbs}}$ with $G_{M^-_{VB}}$. By using the same set of geometric variables β_k (inter-atomic distances, angles and dihedral angles, $k = 1, \ldots, 3N-6$), we define a set of $\lambda - 1$ ($NB : \lambda = 20$) intermediate structures:

$$\beta_k^m = \beta_k^i + m\delta_k \qquad m = 1 \ldots, \lambda - 1 \tag{S1a}$$

$$\delta_k = \frac{\beta_k^f - \beta_k^i}{\lambda}, \tag{S1b}$$

where β_k^f and β_k^i are the values of the k^{th} variable for the final (**VB**) and initial (**DB**) structure, respectively.

Table S1: The absolute electronic energies and zero-point corrections (in hartrees) of *keto* **K1** structure of neutral acetoacetic acid calculated at different levels of theory.

Optimal geometry	Level of theory	Description	Absolute value
MP2/ADZ	MP2/ADZ	Energy	-380.773165687
MP2/ADZ	MP2/ADZ	ZPE	0.099681
CCSD/ADZ	CCSD/ADZ	Energy	-380.8099873
CCSD/ADZ+DF	CCSD/ADZ+DF	Energy	-380.8100437
CCSD/ADZ+DF	CCSD/ADZ+DF	ZPE	0.099638
CCSD/ADZ	CCSD(T)/ADZ	Energy	-380.8556121
CCSD/ADZ+DF	CCSD(T)/ADZ+DF	Energy	-380.85610522

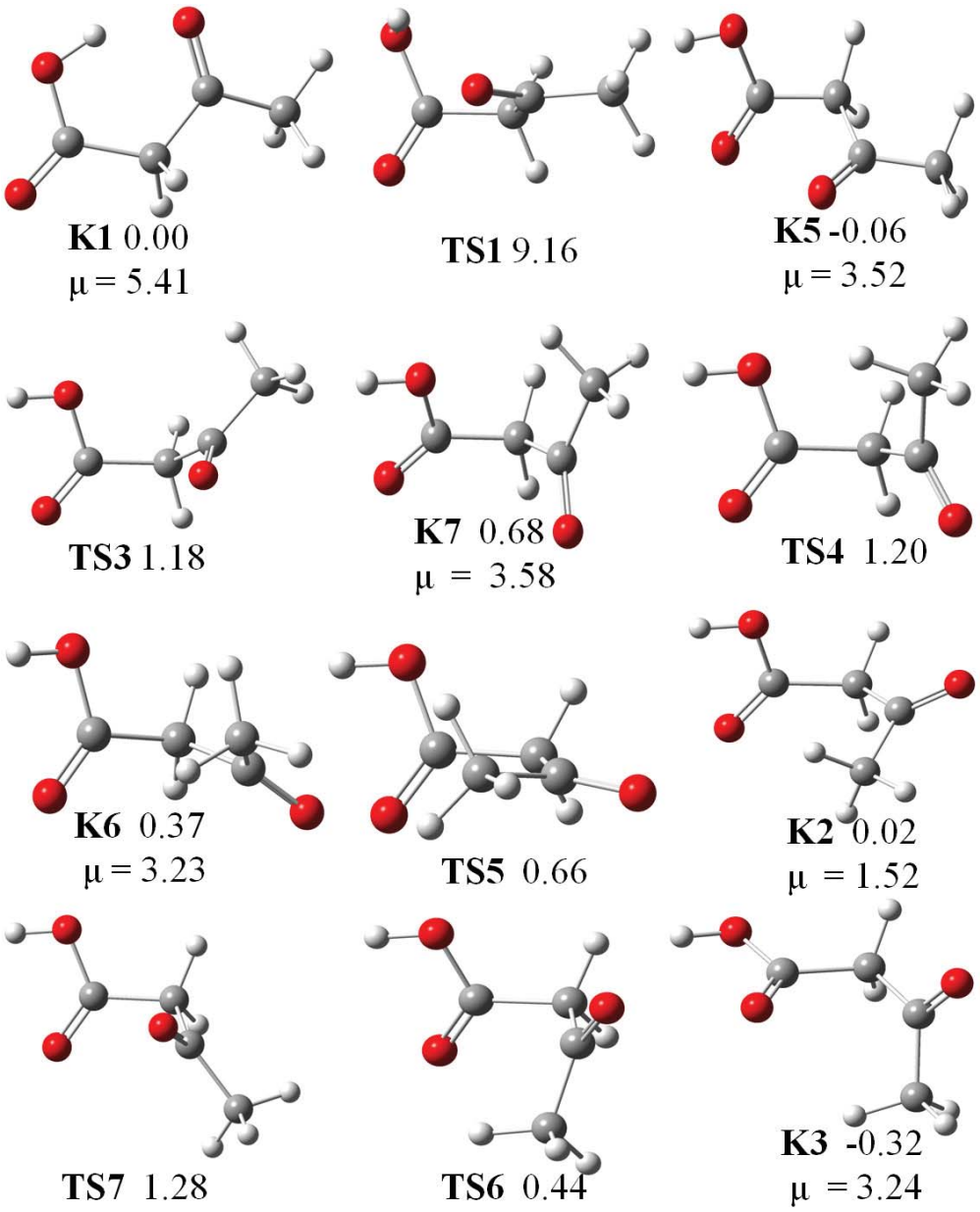


Figure S1: The low-lying conformers of the neutral *keto* structures of AA with interconnecting barriers separating them. The relative energies (in kcal/mol) were obtained at the CCSD(T)/ADZ level of theory and corrected for the MP2/ADZ zero-point vibration energies. The dipole moments, μ, determined at the CCSD level are in Debyes.

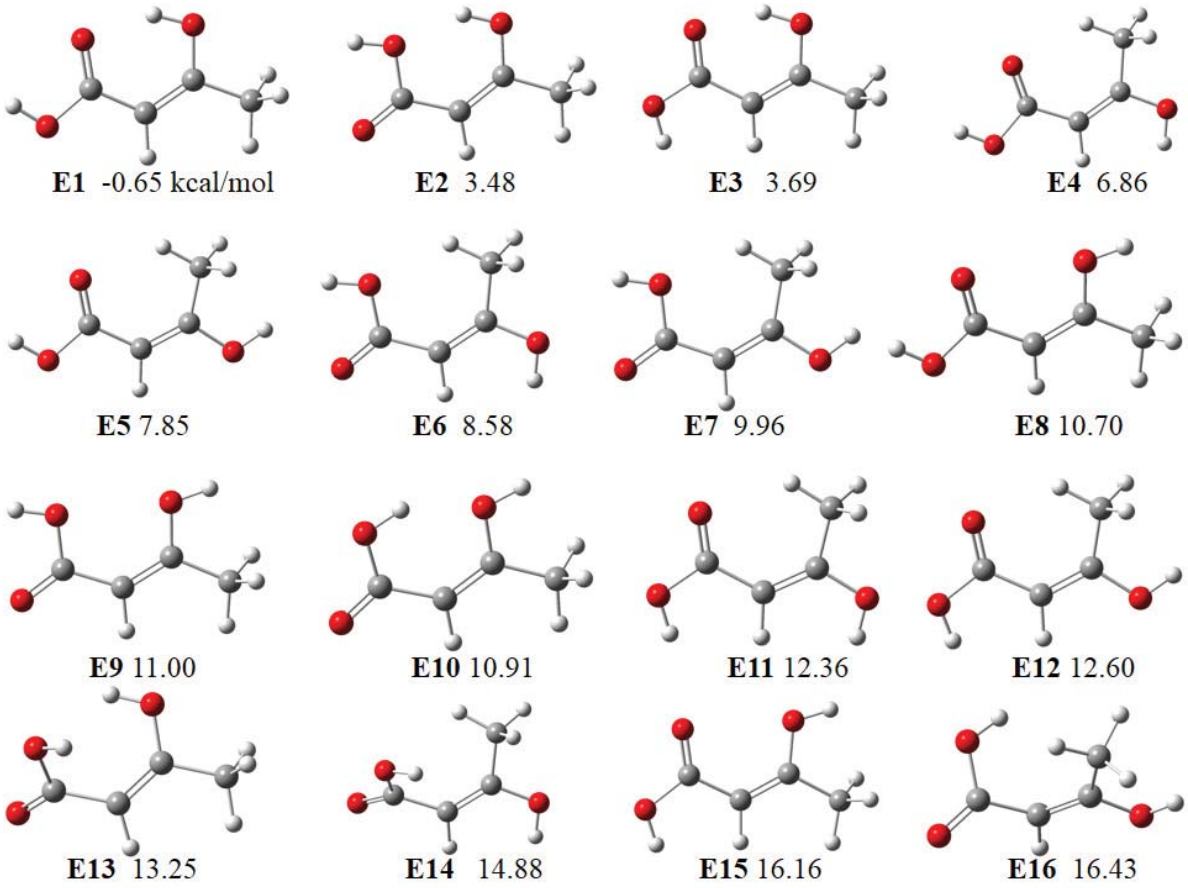


Figure S2: The low-lying conformers of the neutral *enol* structures of AA. The relative energies (in kcal/mol, *with respect to* **K1**) were obtained at the CCSD/ADZ level of theory and corrected for the MP2/ADZ zero-point vibration energies.

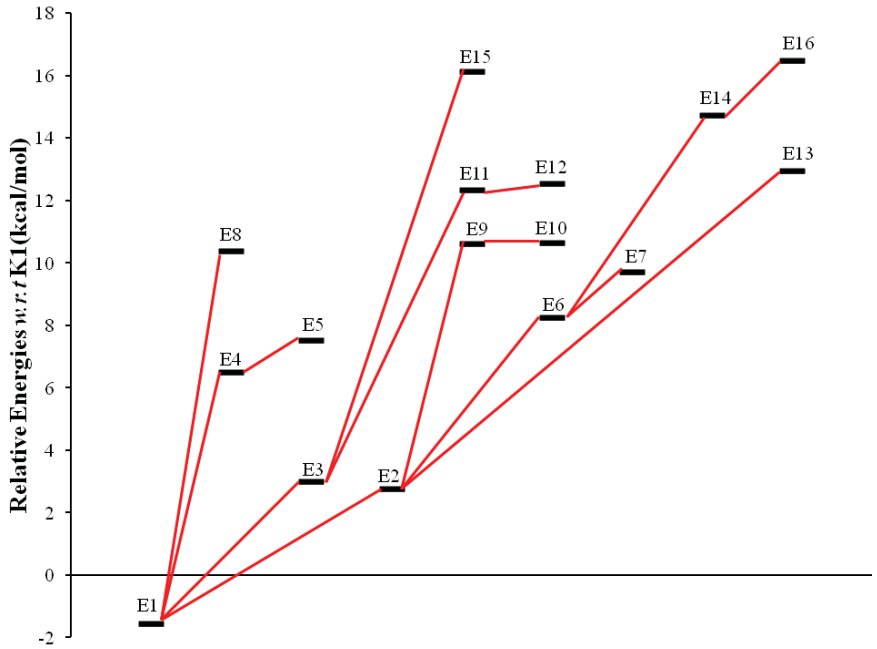


Figure S3: Energy profile interconnecting minima of *enol* structures of AA. The energies (in kcal/mol) are the CCSD/ADZ optimal energies.

Table S2: The Relative Electronic Energies (kcal/mol) of *keto* conformers of neutral acetoacetic acid calculated at different levels of theory followed by their dipole moments (D) calculated at the CCSD/ADZ level of theory. Single point CCSD(T) energy calculation at the CCSD optimal geometries.

	ADZ					
Str.	E_{elect}^{MP2}	E_{elec}^{MP2} $+E_{0,vib}^{MP2}$	E_{elec}^{CCSD}	$E_{elec}^{CCSD(T)}$	$E_{elec}^{CCSD(T)}$ $+E_{0,vib}^{MP2}$	μ^{CCSD}
K1	0.00	0.00	0.00	0.00	0.00	5.41
K2	0.03	-0.17	-0.04	0.23	0.03	1.52
K3	0.04	-0.29	-0.41	0.01	-0.32	3.24
K4	0.10	0.04	—	—	—	—
K5	0.24	-0.10	-0.13	0.28	-0.06	3.52
K6	0.43	0.20	0.36	0.60	0.37	3.23
K7	0.74	0.54	0.55	0.88	0.68	3.58

Table S3: The dipole moments of the neutral AA at HF, MP2 and CCSD levels of theory at the three representative geometries; (i) optimal geometry of **K1**, (G_M), (ii) optimal geometry of DB, ($G_{M^-_{dbs}}$), (iii) optimal geometry of VB, ($G_{M^-_{VB}}$).

	Dipole moments, μ		
Neutral@Geometry	HF	MP2	CCSD
N	5.63	5.42	5.41
$N^{(MP2)}$	6.15	5.42	5.54
$N@G_M$	6.01	5.31	5.41
DBA	5.71	5.59	5.57
$DBA^{(MP2)}$	6.32	5.59	5.70
$N@G_{M^-_{dbs}}$	6.18	5.47	5.57
VBA	11.09	9.69	10.00
$VBA^{(MP2)}$	10.72	9.69	9.85
$N@G_{M^-_{VB}}$	10.87	9.84	10.00

Table S4: Incremental electronic binding energies (in meV) of the dipole-bound anionic state at G_M, $G_{M^-_{dbs}}$ and $G_{M^-_{VB}}$ geometries using the CCSD/ADZ+DF optimal geometries.

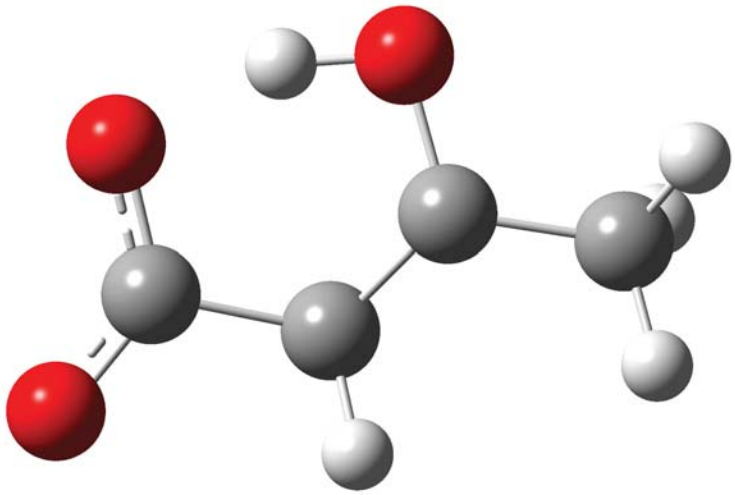
Method	EBE		
	G_M	$G_{M^-_{dbs}}$	$G_{M^-_{VB}}$
$KT(EA)$	21.59	24.33	113.30
ΔE^{SCF}_{bind}	2.47	2.56	14.38
$\Delta E^{MP2-disp}_{bind}$	24.32	26.69	172.36
$\Delta E^{MP2-no-disp}_{bind}$	-15.57	-17.27	-82.32
ΔE^{CCSD}_{bind}	19.52	20.27	-20.87
ΔE^{T}_{bind}	-0.15	-0.04	0.19
Total	52.19	56.55	197.04

Table S5: The contributions from the Amber force field. The energies of **K1**, **K3** and **K5** (kcal/mol).

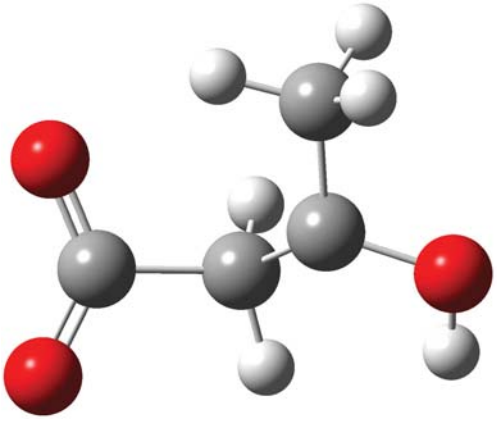
FF-comp	Amber		
	K1	K3	K5
Bond Stretching	1.3976	0.8843	0.954
Angle Bending	3.5055	1.8546	1.6753
Improper Torsion	0.0419	0.0074	0.0009
Torsional Angle	1.955	0.7796	1.4466
Van der Waals	2.2484	1.1863	1.769
Charge-Charge	-18.9634	-22.9145	-18.3529
Total	-18.9634	-18.202	-12.5068

Table S6: The Relative Electronic Energies (kcal/mol) of valence anions of acetoacetic acid calculated at different levels of theory. The absolute MP2 electronic energy of **VB1** is -380.7835041 Hartrees and the zero point vibration energy is 0.096712 Hartrees. **VB1** is equivalent to **VB** in the main text.

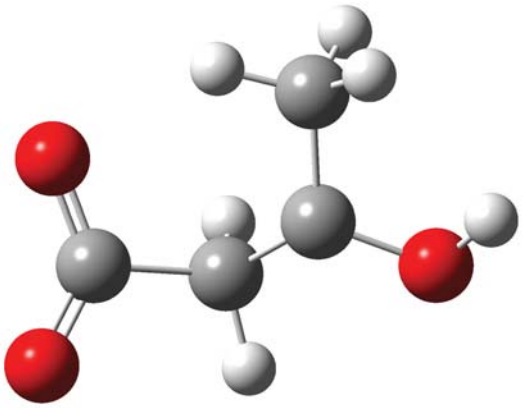
	ADZ + DF			
Str.	E_{elec}^{B3LYP}	E_{elec}^{B3LYP} $+E_{0,vib}^{B3LYP}$	E_{elect}^{MP2}	E_{elec}^{MP2} $+E_{0,vib}^{MP2}$
VB1	0.00	0.00	0.00	0.00
VB2	13.56	13.50	12.65	12.56
VB3	15.33	15.14	15.84	15.68



(a) VB1 -8.35, 2.29, 0.23, 178.2°



(b) VB2 4.21, 2.96, -0.33, −62.8°



(c) VB3 7.33, 2.97, -0.42, −59.8°

Figure S4: The relative energies (in kcal/mol, with respect to **K1**), the VDEs and AEAs (in eV) and the C1-C2-C3-C4 dihedral angle (in °) for valence-bound anionic structures considered in this study, all characterized at MP2/ADZ level of theory. **VB1** is equivalent to **VB** in the main text.

Table S7: Cartesian coordinates (in Å) of **K1** neutral, **DB** anion and **VB** anion. Optimal CCSD/ADZ+DF geometries.

				K1 Neutral			
				C	2.516605	-0.648014	-0.164126
				C	1.211565	0.093479	0.037571
				O	1.153675	1.319670	0.001508
				C	-0.021125	-0.764763	0.316302
				C	-1.404072	-0.176482	-0.005698
				O	-1.514892	1.165542	-0.016913
				O	-2.354505	-0.900934	-0.197982
				H	-0.618422	1.551878	0.063044
				H	0.056655	-1.735423	-0.197071
				H	-0.012395	-0.985494	1.401474
				H	2.664376	-1.383781	0.645036
				H	2.464521	-1.209737	-1.113638
				H	3.353198	0.063007	-0.196045
			DB anion				
C	2.528004	-0.637843	-0.134706				
C	1.212397	0.090863	0.024596				
O	1.141073	1.318560	-0.006574				
C	-0.019652	-0.780706	0.265877				
C	-1.405710	-0.177533	-0.005056				
O	-1.503532	1.166336	-0.000845				
O	-2.373320	-0.887120	-0.175374				
H	-0.596109	1.536352	0.061769				
H	0.057258	-1.721840	-0.300587				
H	0.003643	-1.067548	1.336289				
H	2.662289	-1.361688	0.689045				
H	2.509216	-1.215975	-1.075889				
H	3.359697	0.079805	-0.152549				
					VB anion		
				C	2.511211	-0.655154	-0.074065
				C	1.147644	-0.034892	-0.222404
				O	1.132583	1.317090	0.021988
				C	-0.065077	-0.805140	0.256521
				C	-1.433281	-0.102430	0.001885
				O	-1.405513	1.180419	0.029601
				O	-2.430087	-0.838424	-0.166454
				H	0.139806	1.518589	0.058054
				H	-0.089964	-1.811827	-0.193167
				H	0.002606	-0.947620	1.364299
				H	2.818750	-0.697998	0.998761
				H	2.519055	-1.687175	-0.467913
				H	3.270896	-0.060956	-0.612740

Table S8: Cartesian coordinates (in Å) of **E1**, **K3** and **K5** neutrals. Optimal CCSD/ADZ geometries.

E1

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.503238
C	1.137417	0.000000	2.265679
C	1.041627	0.000000	3.722873
O	-0.012773	0.000000	4.365673
O	-1.241577	0.000000	2.023110
O	2.244988	0.000000	4.348049
H	-0.536580	-0.891391	-0.366108
H	1.026462	0.000000	-0.394474
H	-0.536652	0.891348	-0.366108
H	2.120350	0.000000	1.796107
H	-1.145373	0.000000	3.001988
H	2.056589	0.000000	5.299535

K3

C	0.115334	-0.036863	-0.049981
C	-0.069678	-0.033106	1.456198
C	1.193977	0.091214	2.316431
C	1.746135	1.506509	2.303114
O	2.779970	1.635317	3.176253
O	-1.161200	-0.142495	1.990485
O	1.342553	2.421335	1.615833
H	3.079073	2.556773	3.117028
H	0.955520	-0.184095	3.355230
H	1.990554	-0.582892	1.953445
H	0.717346	-0.916439	-0.342873
H	-0.865214	-0.076760	-0.544756
H	0.663200	0.868702	-0.358450

K5

C	0.006954	-0.027579	-0.005948
C	-0.013161	0.017578	1.513017
C	-1.405564	0.042585	2.161775
C	-1.296302	0.097517	3.672557
O	1.003085	0.028471	2.185866
O	-1.109752	1.370181	4.110295
O	-1.360108	-0.861787	4.409858
H	-0.984826	1.315742	5.071003
H	-1.962038	0.915870	1.780826
H	-1.949807	-0.872635	1.878031
H	-0.552318	-0.909758	-0.364205
H	-0.492025	0.869622	-0.413028
H	1.046072	-0.071467	-0.361046

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