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SUPPLEMENTARY MATERIAL

Directionality and the Role of Polarization in Electric Field Effects on Radical Stability

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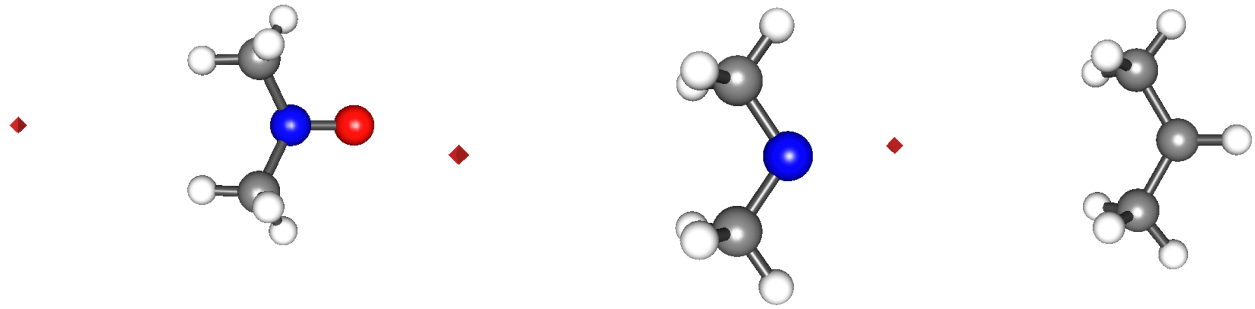
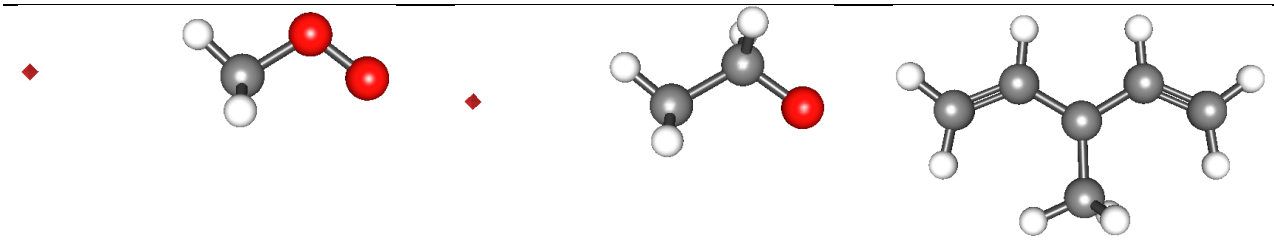
Effect of point charges on relative radical energies

This data is shown in Figure 1 of the manuscript. The point charge is placed at 6Å distance from the formal radical centre in $CH_3OO•$ and $C_2H_5O•$, at 5Å from the N–O bond middle in $(CH_3)_2NO•$ and at 5Å from the formal radical centre in all other species:



$(CH_3)_2NO•$ **$(CH_3)_2N•$** **$(CH_3)_2CH•$**



$CH_3OO•$ **$CH_3CH_2O•$** **$(CH_2{=}CH)_2C•CH_3$**

Table S1. Computed radical energies and their components in the presence of a charge relative to no charge (M06-2X/6-31+G(d) electronic energies, kJ mol^{-1}).

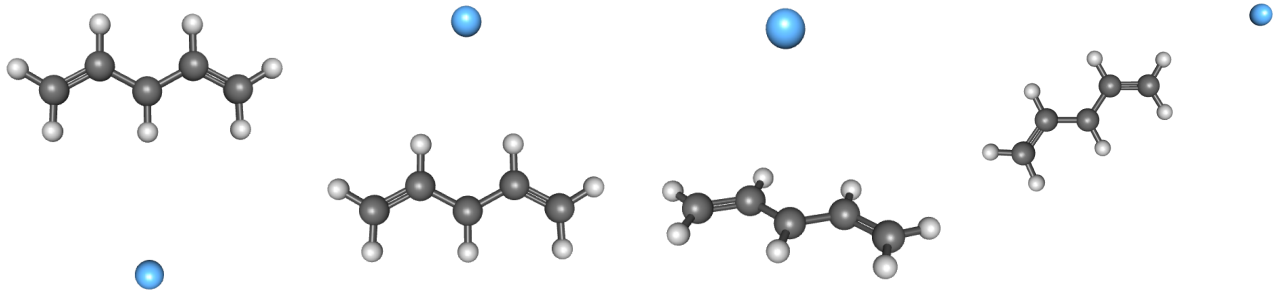
Species	Exchange	Hartree	Correlation	Total
		(–1) point charge		
$Me_2NO•$	-4.77	44.92	1.55	41.70
$Me_2N•$	-2.55	27.36	0.65	25.45
$Me_2CH•$	-8.32	16.39	1.26	9.33
$MeOO•$	-2.02	44.13	4.25	46.36
$EtO•$	2.39	22.48	1.70	26.58
diallyl•	-26.82	45.23	3.63	22.04
		(+1) point charge		
$Me_2NO•$	-1.35	-19.76	-1.42	-22.53
$Me_2N•$	-11.78	2.07	1.13	-8.58
$Me_2CH•$	-3.38	9.89	0.12	6.63
$MeOO•$	-10.15	-15.65	-2.47	-28.26
$EtO•$	-18.13	16.79	1.19	-0.14
diallyl•	-5.13	13.78	1.52	10.17

Table S2. Absolute electronic energies of radicals species with and without the point charge, computed at M06-2X/6-31+G(d) and HF/6-31+G(d) levels of theory, in Hartrees.

Species	Charge	Hartree-Fock	Exchange	Hartree	Correlation	M06-2X
Me_2NO•	0	-208.46578	-27.29616	-181.16962	-1.15642	-209.62220
	+1	-208.48107	-27.29434	-181.18673	-1.15701	-209.63809
	–1	-208.45774	-27.29565	-181.16209	-1.15588	-209.61362
Me_2N•	0	-133.63058	-19.08949	-114.54108	-0.80316	-134.43373
	+1	-133.64002	-19.08852	-114.55150	-0.80340	-134.44343
	–1	-133.62688	-19.08501	-114.54187	-0.80359	-134.43046
Me_2CH•	0	-117.63758	-18.03653	-99.60105	-0.76531	-118.40289
	+1	-117.64065	-18.03336	-99.60729	-0.76579	-118.40644
	–1	-117.64006	-18.03524	-99.60481	-0.76536	-118.40541
MeOO•	0	-189.20705	-22.61142	-166.59563	-0.92610	-190.13316
	+1	-189.22309	-22.61065	-166.61244	-0.92772	-190.15081
	–1	-189.19723	-22.60755	-166.58967	-0.92516	-190.12239
EtO•	0	-153.46425	-20.36049	-133.10376	-0.82974	-154.29399
	+1	-153.47373	-20.36140	-133.11232	-0.83039	-154.30411
	–1	-153.46374	-20.35359	-133.11015	-0.83019	-154.29394
$(CH_2=CH)_2C$•Me	0	-232.40878	-34.33970	-198.06909	-1.45851	-233.86729
	+1	-232.41580	-34.32948	-198.08632	-1.45989	-233.87569
	–1	-232.41208	-34.33774	-198.07434	-1.45909	-233.87117

Directionality of the point charge effect on radical stability

This data is shown in Figure 2 of the manuscript. The point charge is placed at 5Å distance from the closest carbon atom in $(CH_2=CH)_2CH•$ radical in four different geometric configurations:



I **II** **III** **IV**

Table S3. Computed radical energies and their components in the presence of a charge relative to no charge (M06-2X/6-31+G(d) electronic energies, kJ mol^{-1}).

Configuration	Exchange	Hartree	Correlation	Total
		(–1) point charge		
I	-11.96	25.55	0.52	14.11
II	-13.32	35.67	0.68	23.03
III	-13.30	6.83	-0.02	-6.49
IV	-13.05	21.98	1.95	10.88
		(+1) point charge		
I	-3.63	2.43	0.46	-0.74
II	-9.93	10.41	1.35	1.83
III	-8.00	24.88	0.61	17.49
IV	-18.23	19.97	1.59	3.33

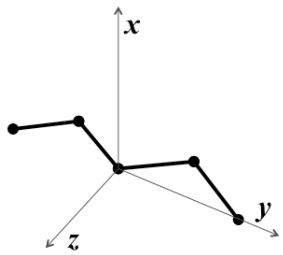
Table S4. Absolute electronic energies of diallyl radical with and without the point charge, computed at M06-2X/6-31+G(d) and HF/6-31+G(d) levels of theory, in Hartrees.

Configuration	Charge	Hartree-Fock	Exchange	Hartree	Correlation	M06-2X
no charge	0	-193.37546	-28.42445	-164.95101	-1.19433	-194.56980
I	–1	-193.38064	-28.41989	-164.96075	-1.19453	-194.57517
	+1	-193.37501	-28.42307	-164.95194	-1.19451	-194.56951
II	–1	-193.38398	-28.41938	-164.96460	-1.19459	-194.57857
	+1	-193.37565	-28.42067	-164.95498	-1.19485	-194.57050
III	–1	-193.37300	-28.41939	-164.95361	-1.19433	-194.56733
	+1	-193.38189	-28.42140	-164.96049	-1.19457	-194.57646
IV	–1	-193.37886	-28.41948	-164.95939	-1.19508	-194.57394
	+1	-193.37612	-28.41751	-164.95862	-1.19494	-194.57106

Polarizabilities of R• and RH

This data is shown in Scheme 4 of the manuscript.

Table S5. Exact SCF polarizabilities (in $Bohr^3$), calculated at M06-2X/maug-cc-pVTZ//M06-2X/6-31+G(d) level of theory.

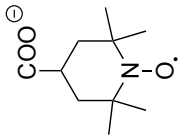
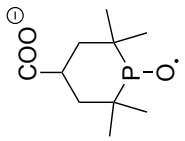
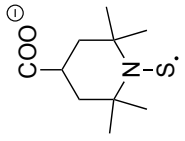
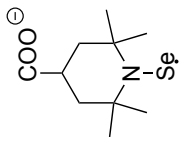
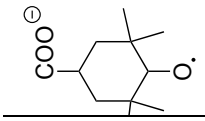


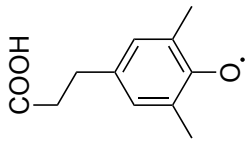
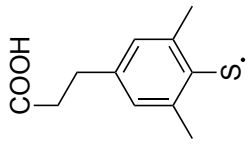
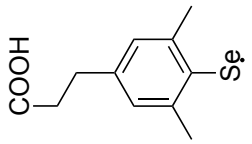
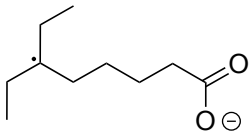
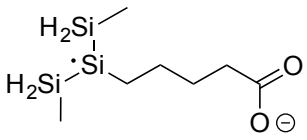
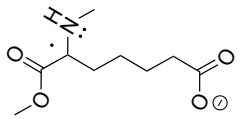
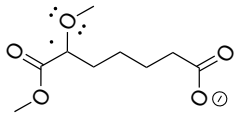
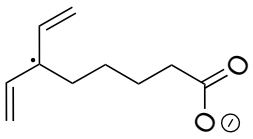
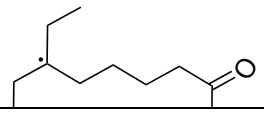
Species	x	y	z
$(CH_2{=}CH)_2CH$•	41.827	**131.910**	54.031
$(CH_2{=}CH)_2CH_2$	49.622	**79.397**	59.770
$(C_2H_5)_2CH$•	55.133	**75.539**	61.001
$(C_2H_5)_2CH_2$	56.675	**75.151**	60.498
Twisted $(CH_2{=}CH)_2CH$•	49.824	**72.801**	66.514

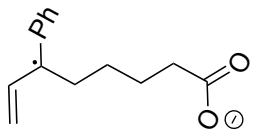
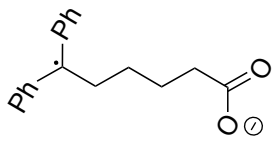
Effect of remote charged groups on the bond strengths

This data is shown in Figure 3 of the manuscript is a reproduction of the results, published in Ref. 7 of the manuscript. For the Cartesian coordinates of these species, please see Supporting Information of that paper.

Table S6. Absolute electronic energies of R•, X• and RX species (in Hartrees), corresponding energies of the homolytic R–X bond dissociation and 'switches' on them by deprotonation of the remote carboxylic group (in kJ mol^{-1}), as well as distances between the charge (in Å) and the radical and Mulliken spin densities (μ) on the formal radical centres (all at the M06-2X/6-31+G(d) level of theory).

R• [a]	Species	*r*, Å	μ	E_e	BDE	ΔBDE
	X = •CH_3			-39.80808		
	(-H)R•	6.218	0.488	-671.47594		
	(-H)R–X			-711.36547	213.863	
	(H)R•		0.513	-672.01816		
	(H)R–X			-711.91503	233.129	19.266
	(-H)R•	6.075	0.263	-958.10922		
	(-H)R–X			-998.00953	242.168	
	(H)R•		0.290	-958.64919		
	(H)R–X			-998.55854	265.887	23.719
	(-H)R•	6.095	0.619	-994.46921		
	(-H)R–X			-1034.36569	232.085	
	(H)R•		0.663	-995.01106		
	(H)R–X			-1034.91416	249.480	17.395
	(-H)R•	6.246	0.729	-2997.59523		
	(-H)R–X			-3037.48783	221.902	
	(H)R•		0.811	-2998.13834		
	(H)R–X			-3038.03642	236.303	14.401
	(-H)R•	5.760	0.866	-655.42917		
	(-H)R–X			-695.37536	362.607	
	(H)R•		0.878	-655.97667		

	(H)R–X			-695.92665	372.559	9.953
	(H)R•		0.368	-652.40396		
	(H)R–X			-692.31783	277.787	
	(-H)R•	7.991	0.340	-651.86161		
	(-H)R–X			-691.76629	253.630	24.157
	(H)R•		0.700	-975.37041		
	(H)R–X			-1015.28707	285.082	
	(-H)R•	8.431	0.615	-974.82706		
	(-H)R–X			-1014.73739	268.475	16.607
	(H)R•		1.090	-2978.50319		
	(H)R–X			-3018.40909	256.835	
	(-H)R•	8.609	1.092	-2977.95678		
	(H-)R–X			-3017.85952	248.516	8.319
	(-H)R•	6.462	0.988	-542.12517		
	(-H)R–X			-582.08012	385.613	
	(H)R•		0.963	-542.68050		
	(H)R–X			-582.63602	387.111	1.499
	(-H)R•	6.820	1.057	-1296.24736		
	(-H)R–X			-1336.18984	352.852	
	(H)R•		1.055	-1296.79988		
	(H)R–X			-1336.74343	355.684	2.833
	X = H•			-0.49667		
	(-H)R•	6.426	0.562	-707.39776		
	(-H)R–X			-708.02374	339.494	
	(H)R•		0.590	-707.95040		
	(H)R–X			-708.57983	348.586	9.091
	(-H)R•	6.418	0.721	-727.24180		
	(-H)R–X			-727.87790	366.081	
	(H)R•		0.741	-727.79155		
	(H)R–X			-728.42929	370.408	4.327
	(-H)R•	6.532	0.669	-539.69956		
	(-H)R–X			-540.33037	352.188	
	(H)R•		0.668	-540.25313		
	(H)R–X			-540.88628	358.326	6.138
Same species in C_S symmetry	(-H)R•	6.457	0.670	-539.70656		
	(-H)R–X			-540.32480	319.198	
	(H)R•		0.671	-540.26094		
	(H)R–X			-540.88061	322.952	3.754
	(-H)R•	6.487	1.016	-542.12393		
	(-H)R–X			-542.78289	426.108	
	(H)R•		1.032	-542.68014		

	(H)R–X			-543.33923	426.440	0.332
Same species in C_S	(-H)R•	6.462	0.988	-542.12517		
symmetry	(-H)R–X			-542.78437	426.750	
	(H)R•		0.963	-542.68050		
	(H)R–X			-543.34070	429.360	2.609
	(-H)R•	6.466	0.735	-693.30260		
	(-H)R–X			-693.93307	351.312	
	(H)R•		0.738	-693.85597		
	(H)R–X			-694.48893	357.838	6.526
	(-H)R•	6.471	0.676	-846.89609		
	(-H)R–X			-847.53399	370.803	
	(H)R•		0.697	-847.44936		
	(H)R–X			-848.08874	374.701	3.897

[a] (-H) prefix corresponds to deprotonated COOH group, (H) – to the protonated one.

Effect of the remote point charge on the kinetics of identity reactions

This data is shown in Figure 4 of the manuscript. The switches on the absolute energies of the pre-complexes and transition states, and on the forward reaction barriers by the –1 point charges were computed at M06-2X/aug-cc-pVTZ level of theory. Additionally, these switches were also computed in the gas and solvent phases at M06-2X/aug-cc-pVTZ and G3(MP2,CC)(+) levels of theory in the presence of F^- anion instead of a point charge for benchmarking purposes.

Table S7. Switches on the energies of the pre-complexes and transition states and corresponding absolute barriers for H• transfer identity reactions, induced by a remote negative point charge (M06-2X/aug-cc-pVTZ, kJ mol^{-1}).

X•		Switches on the species [a]					Absolute barriers [b]			
		Exch.	Correl.	Hartree	M06-2X		Exch.	Correl.	Hartree	M06-2X
•CH_3	PC	-3.806	0.048	8.433	4.674	(0)	76.304	-51.716	50.609	75.197
	TS	-10.862	1.174	17.783	8.095	(-1)	83.361	-52.843	41.258	71.776
•OH	PC	-30.491	5.625	26.892	2.026	(0)	156.184	-101.283	-0.628	54.273
	TS	3.584	-4.058	12.059	11.585	(-1)	122.108	-91.600	14.205	44.713
•SH	PC	1.147	7.492	3.946	12.585	(0)	79.839	-40.375	-2.072	37.392
	TS	-3.671	-1.064	14.993	10.258	(-1)	84.657	-31.819	-13.119	39.719
•NH_2	PC	12.954	16.196	-2.671	26.479	(0)	136.170	-84.871	0.756	52.055
	TS	2.409	-0.425	30.823	32.807	(-1)	146.715	-68.250	-32.738	45.727
•PH_2	PC	11.354	7.370	0.823	19.547	(0)	71.187	-44.422	9.777	36.542
	TS	-14.991	0.785	37.602	23.396	(-1)	97.532	-37.836	-27.002	32.693
•PH_4	PC	-6.848	5.154	12.910	11.216	(0)	94.808	-62.829	-0.698	31.281
	TS	-31.849	13.203	41.695	23.050	(-1)	119.809	-70.878	-29.484	19.447

[a] 'PC' stands for 'pre-complex'; [b] (0) refers to the absence of any charge, (–1) – presence of a point charge. 'Exch' stands for exchange, 'Correl' – for correlation energy component.

Table S8. Switches on the energies of the pre-complexes and transition states and corresponding absolute barriers for H• transfer identity reactions, induced by a remote fluorine anion (M06-2X/aug-cc-pVTZ and G3(MP2,CC)(+), kJ mol^{-1}).The gas-phase values are electronic energies; numbers in solution are based on G3(MP2,CC)(+) gas-phase data, corrected for solvation free energies at 25 °C, in kJ mol^{-1}. Solvation energies are computed using CPCM model with UAKS radii, scaled by 1.3, for toluene, and using PCM model with UAKS radii, scaled by 1.2, for water, all at the B3LYP/6-31+G(d) level.

X•		Switches on the species [a]					Absolute barriers [b]			
		M06-2X [c]	G3(MP2,CC)(+)				M06-2X [c]	G3(MP2,CC)(+)		
		gas	gas	water	toluene		gas	gas	water	toluene
•CH_3	PC	5.317	5.827	4.799	6.598	(0)	72.128	78.599	72.281	73.369
	TS	8.977	9.680	4.720	8.150	(F^-)	68.468	74.745	72.360	71.817
•OH	PC	-3.547	-1.920	-11.944	-16.504	(0)	62.731	70.313	78.890	74.329
	TS	11.927	11.089	5.291	10.563	(F^-)	47.257	57.304	61.655	47.262
•SH	PC	13.992	13.234	-44.738	-32.186	(0)	44.240	42.222	51.469	46.866

	TS	12.703	9.462	1.238	7.765	(F^-)	45.529	45.994	5.493	6.916
•NH_2	PC	29.740	21.041	-6.179	-7.601	(0)	55.795	63.652	66.330	62.815
	TS	38.655	35.613	-1.229	15.130	(F^-)	46.880	49.079	61.380	40.084
•PH_2	PC	22.945	20.757	-33.449	-14.621	(0)	35.294	38.480	38.438	37.977
	TS	26.939	25.855	-4.879	5.414	(F^-)	31.300	33.382	9.868	17.943
•PH_4	PC	10.929	14.578	-23.645	-9.336	(0)	27.647	36.538	39.132	37.668
	TS	21.009	29.280	-22.918	-5.471	(F^-)	17.566	21.836	38.405	33.802

[a] 'PC' stands for 'pre-complex'; [b] (0) refers to the absence of any charge, (F^-) – presence of a fluorine anion; [c] With 6-31+G(d) basis set.

Table S9. Absolute electronic energies and their components, as well as solvation free energies for the transition states and pre-complexes (in Hartrees) of the H• transfer identity reactions between XH and X• with and without the negative point charge or the fluorine anion.

X• [a]		Point charge			Fluorine anion			
		HF/aug-cc-pVTZ		M06-2X/ aug-cc-pVTZ		G3(MP2,CC)(+)	(C)PCM-UAKS B3LYP/6-31+G*	
		E_e	Exchange	E_e	E_e	E_e	$\Delta\Delta G^{298}$, kcal mol^{-1}	
							toluene	water
F^-					-99.81104	-99.76426	-97.77	-54.55
•CH_3	PC(0)	-79.79025	-12.81617	-80.32858	-80.29279	-80.25330	3.59	2.15
	TS(0)	-79.74191	-12.78711	-80.29994	-80.26532	-80.22336	2.08	0.90
	PC(–)	-79.79201	-12.81472	-80.33036	-180.10585	-180.01977	-92.04	-50.69
	TS(–)	-79.74454	-12.78297	-80.30302	-180.07977	-179.99130	-92.61	-51.39
•OH	PC(0)	-151.48803	-17.50766	-152.17294	-152.09289	-152.03809	-8.44	-3.13
	TS(0)	-151.42878	-17.44817	-152.15227	-152.06899	-152.01130	-6.39	-2.17
	PC(–)	-151.48666	-17.49604	-152.17371	-251.90258	-251.80161	-101.92	-52.30
	TS(–)	-151.43474	-17.44953	-152.15668	-251.88458	-251.77978	-100.88	-54.70
•SH	PC(0)	-796.81608	-51.09574	-798.13223	-798.03977	-797.27266	-1.06	-0.73
	TS(0)	-796.78646	-51.06533	-798.11799	-798.02292	-797.25658	1.15	0.38
	PC(–)	-796.81802	-51.09618	-798.13702	-897.85614	-897.04196	-83.08	-42.53
	TS(–)	-796.79077	-51.06393	-798.12189	-897.83880	-897.02444	-92.76	-51.87
•NH_2	PC(0)	-111.80924	-14.95534	-112.42827	-112.36818	-112.32951	-7.75	-2.61
	TS(0)	-111.75709	-14.90347	-112.40844	-112.34693	-112.30527	-7.11	-2.81
	PC(–)	-111.81316	-14.96027	-112.43835	-212.19055	-212.10178	-97.12	-48.42
	TS(–)	-111.76974	-14.90439	-112.42094	-212.17269	-212.08309	-94.18	-50.57
•PH_2	PC(0)	-684.37280	-47.01190	-685.62214	-685.53892	-684.79621	3.55	1.71
	TS(0)	-684.34196	-46.98479	-685.60823	-685.52547	-684.78155	3.54	1.59
	PC(–)	-684.37744	-47.01623	-685.62959	-785.35869	-784.56837	-79.37	-42.49
	TS(–)	-684.35058	-46.97908	-685.61714	-785.34677	-784.55565	-84.99	-46.18
•PH_4	PC(0)	-686.53207	-48.44220	-687.86667	-687.77312	-687.06555	2.51	0.35
	TS(0)	-686.49622	-48.40609	-687.85474	-687.76259	-687.05164	3.13	0.62
	PC(–)	-686.53438	-48.43959	-687.87093	-787.58833	-786.83536	-84.23	-46.59
	TS(–)	-686.49998	-48.39396	-687.86352	-787.58163	-786.82705	-80.27	-43.73

[a] 'PC' stands for 'pre-complex', 'TS' – transition state, (0) refers to the absence of any charge, (–) – presence of a negative charge or fluorine anion.

Switching of the model enzyme kinetics

This data is shown in Figure 5 of the manuscript.

Table S10. Shown are components and net values for the absolute barriers, switches on the barriers and switches on the reactant pre-compexes (PC) and transition states (TS), induced by remote point charge(s). All values are electronic energies in kJ mol^{-1}, calculated using M06-2X and UHF methods with an aug-cc-pVTZ basis set. [a]

S-m [b]		Absolute barriers [c]				Switches on the barriers [c]				Switches on the species				
		Ex.	Corr.	Hart.	Net	Ex.	Corr.	Hart.	Net		Ex.	Corr.	Hart.	Net
(0)	fwd	175.874	15.830	-64.978	126.726									
	rev	176.485	7.633	-44.240	139.879									
(–1)	fwd	210.888	2.119	-92.097	120.909	-35.014	13.711	27.119	5.817	PC	9.394	-1.685	-4.450	3.260
	rev	194.849	-3.801	-62.301	128.747	-18.363	11.434	18.061	11.132	TS	-25.619	12.027	22.669	9.077
										PR	-7.256	0.593	4.608	-2.055
(–2)	fwd	242.292	-13.568	-117.769	110.955	-66.418	29.398	52.791	15.771	PC	13.532	-2.555	4.430	15.407
	rev	208.424	-17.119	-76.660	114.646	-31.939	24.752	32.420	25.233	TS	-52.886	26.843	57.220	31.178
										PR	-20.947	2.091	24.800	5.945
(G)	fwd	248.906	-17.327	-134.374	97.205	-73.032	33.156	69.396	29.521	PC	10.511	-1.667	120.339	129.184
	rev	226.510	-22.389	-102.500	101.620	-50.024	30.022	58.261	38.259	TS	-62.521	31.490	189.735	158.704
										PR	-12.497	1.467	131.475	120.446
(D)	fwd	124.104	33.981	-25.901	132.185	51.770	-18.152	-39.077	-5.459	PC	-39.092	4.319	161.012	126.239
	rev	153.364	22.707	-20.987	155.084	23.122	-15.074	-23.253	-15.205	TS	12.679	-13.833	121.935	120.781
										PR	-10.443	1.241	145.188	135.986
(E)	fwd	131.665	30.121	-94.922	66.865	44.209	-14.291	29.943	59.861	PC	-43.525	8.274	519.027	483.775
	rev	109.213	30.732	-20.214	119.730	67.273	-23.099	-24.025	20.149	TS	0.684	-6.017	548.970	543.637
										PR	-66.589	17.081	572.996	523.488

[a] 'Ex.' Stands for exchange, 'Corr.' – correlation and 'Hart.' – Hartree components of the net energy; [b] (0) refers to the absence of any charge, (–1) – in the presence of one negative point charge X=–1, (–2) – in the presence of a doubly negative point charge x=–2, (G) – in the presence of both X=–1 and Y=+1 point charges (*i.e.* electrostatic gradient), (D) – when charges are reversed compared to (G), (E) – in the model resembling enzyme active site; [c] 'fwd' refers to a forward activation barrier, 'rev' – a reverse one.

Appendix 1

Cartesian coordinates of the optimised geometries for all species in this study. XX denotes a point charge.

Me_2NO•

11

0 2

O	-0.199259	-1.306719	0.000000
N	-0.237113	-0.033114	0.000000
C	0.050601	0.652857	1.250578
C	0.050601	0.652857	-1.250578
H	-0.374419	1.659281	1.225710
H	1.135403	0.720000	1.410142
H	-0.398285	0.073457	2.057301
H	1.135404	0.720000	-1.410142
H	-0.374419	1.659281	-1.225710
H	-0.398285	0.073457	-2.057301
XX	-0.385659	4.964679	-0.000000

Me_2N•

10

0 2

N	0.000006	-0.640737	-0.000030
C	-1.187395	0.173045	-0.000081
C	1.187385	0.173045	0.000031
H	-1.212262	0.833744	-0.882433
H	-1.216205	0.826466	0.887582
H	-2.079707	-0.455909	-0.004374
H	1.214819	0.828941	-0.885827
H	2.079711	-0.455915	0.001375
H	1.213663	0.831289	0.884190
XX	-0.000043	4.359234	0.017119

Me_2CH•

11

0 2

C	1.290808	-0.200491	0.004950
C	-0.000005	0.543825	-0.058451
C	-1.290798	-0.200508	0.004931
H	2.146818	0.442129	-0.219750
H	1.298530	-1.039127	-0.703853
H	1.463533	-0.637677	1.003075
H	-0.000026	1.612367	0.132334
H	-1.297844	-1.040241	-0.702560
H	-2.146699	0.441673	-0.221451
H	-1.464342	-0.636076	1.003624
XX	0.027616	-4.324289	1.082033

MeOO•

7

0 2

C	1.085383	-0.181467	0.000012
O	-0.157976	0.539894	-0.000002
O	-1.172823	-0.276539	-0.000005
H	1.865959	0.579270	0.002664
H	1.135219	-0.796611	-0.899928
H	1.132924	-0.800697	0.897251
XX	4.822069	-0.024145	0.005118

EtO•

9

0 2

C	0.000000	-0.258432	-1.290011
C	0.000000	0.522639	0.015492
O	0.000000	-0.251730	1.151128
H	0.000000	0.419479	-2.149780
H	-0.886608	-0.895574	-1.349863
H	0.886608	-0.895574	-1.349863
H	0.872602	1.197396	0.093239
H	-0.872602	1.197396	0.093239
XX	0.000000	-0.268228	-4.848848

diallyl•

16

0 2

C	2.461020	0.222770	0.000630
C	1.208360	0.746970	-0.000220
C	-0.007440	-0.002820	-0.000630
C	-1.242750	0.705060	-0.000510
C	-2.498730	0.180600	0.000730
H	3.334400	0.865330	0.001000
H	2.639910	-0.848060	0.001080
H	1.105730	1.832040	-0.000420
C	0.057830	-1.501210	-0.000380
H	-1.157200	1.791980	-0.001180
H	-2.692440	-0.886570	0.001830
H	-3.365830	0.831360	0.000830
H	0.602870	-1.866120	-0.879730
H	-0.930510	-1.961810	-0.005900
H	0.593330	-1.866350	0.884770
XX	0.210125	-4.998085	0.000203

$(CH_2=CH)_2CH$• I

$(CH_2=CH)_2CH$• II

13
0 2

C	2.456008	0.000000	0.229965
C	1.247954	0.000000	-0.396582
C	0.000000	0.000000	0.272887
H	0.000000	0.000000	1.362589
C	-1.247954	0.000000	-0.396582
H	3.385384	0.000000	-0.327929
H	2.525729	0.000000	1.314323
H	1.223868	0.000000	-1.486649
H	-1.223868	0.000000	-1.486649
C	-2.456008	0.000000	0.229965
H	-2.525729	0.000000	1.314323
H	-3.385384	0.000000	-0.327929
XX	0.000004	0.000000	5.272887

$(CH_2=CH)_2CH•$ III

13
0 2

C	2.456008	0.000000	0.229965
C	1.247954	0.000000	-0.396582
C	0.000000	0.000000	0.272887
H	0.000000	0.000000	1.362589
C	-1.247954	0.000000	-0.396582
H	3.385384	0.000000	-0.327929
H	2.525729	0.000000	1.314323
H	1.223868	0.000000	-1.486649
H	-1.223868	0.000000	-1.486649
C	-2.456008	0.000000	0.229965
H	-2.525729	0.000000	1.314323
H	-3.385384	0.000000	-0.327929
XX	0.000000	5.000000	0.272887

$(CH_2=CH)_2CH_2$

13
0 1

C	-2.10574	-1.34877	0.25760
C	-1.19620	-0.75761	-0.51479
C	0.00000	0.00000	0.00000
H	0.00000	0.00000	1.09601
C	1.29474	-0.57315	-0.51479
H	-2.95013	-1.88487	-0.16491
H	-2.03443	-1.31602	1.34263
H	-1.29643	-0.81581	-1.59945
H	1.40245	-0.61595	-1.59945
C	2.28144	-1.02389	0.25760
H	2.20608	-1.00200	1.34263
H	3.19559	-1.42977	-0.16491
H	-0.07760	1.04788	-0.32584

$(C_2H_5)_2CH_2$

17
0 1

C	-2.54360	0.02995	-0.00573

13
0 2

C	2.456008	0.000000	0.229965
C	1.247954	0.000000	-0.396582
C	0.000000	0.000000	0.272887
H	0.000000	0.000000	1.362589
C	-1.247954	0.000000	-0.396582
H	3.385384	0.000000	-0.327929
H	2.525729	0.000000	1.314323
H	1.223868	0.000000	-1.486649
H	-1.223868	0.000000	-1.486649
C	-2.456008	0.000000	0.229965
H	-2.525729	0.000000	1.314323
H	-3.385384	0.000000	-0.327929
XX	0.000002	0.000000	-4.727113

$(CH_2=CH)_2CH•$ IV

13
0 2

C	2.456008	0.000000	0.229965
C	1.247954	0.000000	-0.396582
C	0.000000	0.000000	0.272887
H	0.000000	0.000000	1.362589
C	-1.247954	0.000000	-0.396582
H	3.385384	0.000000	-0.327929
H	2.525729	0.000000	1.314323
H	1.223868	0.000000	-1.486649
H	-1.223868	0.000000	-1.486649
C	-2.456008	0.000000	0.229965
H	-2.525729	0.000000	1.314323
H	-3.385384	0.000000	-0.327929
XX	7.445705	0.000000	-0.090858

$(C_2H_5)_2CH•$

16
0 2

C	2.50929	0.42406	-0.05230
C	1.27287	-0.18062	-0.71139
C	0.00987	0.10045	0.03021
C	-1.32278	-0.18757	-0.57418
C	-2.48661	0.40267	0.21688
H	3.42274	0.19544	-0.61818
H	2.63758	0.03233	0.96771
H	2.41592	1.51722	0.02062
H	1.41370	-1.27688	-0.81466
H	1.17667	0.18886	-1.74820
H	0.06703	0.23739	1.11579
H	-1.46484	-1.28442	-0.66906
H	-1.34080	0.18856	-1.61296
H	-2.50254	0.00355	1.24197
H	-3.45336	0.17005	-0.25018
H	-2.39432	1.49610	0.28713

Twisted $(CH_2=CH)_2CH•$

12
0 2

C	0.000000	0.000000	0.000000

C	-1.28640	-0.66980	-0.50893
C	-0.00025	-0.01653	-0.01234
C	1.26589	-0.70786	-0.50888
C	2.54336	-0.04579	-0.00575
H	-3.45620	-0.45787	-0.37558
H	-2.56716	1.08015	-0.33364
H	-2.58233	0.02615	1.09405
H	-1.28237	-0.68078	-1.61180
H	-1.29779	-1.72713	-0.19526
H	0.01556	1.04248	-0.32570
H	1.26152	-0.71879	-1.61175
H	1.24577	-1.76503	-0.19513
H	2.59818	1.00321	-0.33379
H	3.44103	-0.56060	-0.37554
H	2.58196	-0.05062	1.09403
H	-0.00009	-0.00464	1.09212

C	-1.236070	0.000000	-0.691170
C	1.259460	0.000000	-0.647560
H	-0.019040	0.000000	1.089540
C	-1.906707	-1.123190	-1.066168
H	-2.851713	-1.070908	-1.594585
H	-1.512928	-2.111694	-0.845980
C	1.942790	1.123198	-0.998899
H	2.905684	1.070921	-1.493977
H	1.541557	2.111705	-0.792602
H	1.698861	-0.971962	-0.873481
H	-1.667307	0.971965	-0.932304

CH_3--H•--CH_3 PC

10
0 2

H	0.628838	0.000000	0.000000
C	1.710915	0.000000	0.000000
C	-2.339762	0.000000	0.000000
H	-2.339052	0.000000	1.072286
H	-2.339052	0.928627	-0.536142
H	-2.339052	-0.928626	-0.536143
H	2.072388	0.000000	-1.019531
H	2.072388	-0.882940	0.509765
H	2.072388	0.882939	0.509765
–XX	-0.314425	-5.000000	0.000000

CH_3--H•--CH_3 TS

10
0 2

–XX	0.000000	0.000000	0.000000
H	0.000000	0.000000	5.000000
C	1.336614	0.000000	4.907815
C	-1.336614	0.000000	4.907815
H	-1.508835	0.000000	3.831922
H	-1.664964	-0.911798	5.407159
H	-1.664964	0.911798	5.407159
H	1.664964	-0.911798	5.407159
H	1.664964	0.911798	5.407159
H	1.508835	0.000000	3.831922

OH--H•--OH PC

6
0 2

–XX	0.000000	0.000000	0.000000
O	1.841969	0.000000	6.938397
O	-0.126211	1.837640	6.938397
H	0.733612	2.062028	6.547406
H	-0.755968	1.834147	6.204551
H	1.443276	-0.325989	6.103633

OH--H•--OH TS

6
0 2

–XX	0.000000	0.000000	0.000000
H	0.000000	0.000000	7.000000
O	1.117188	0.000000	6.679969
O	-1.115970	-0.013334	6.680159
H	-1.179858	0.574275	5.904210
H	1.187033	-0.646376	5.952927

SH--H•--SH PC

6
0 2

–XX	0.000000	0.000000	0.000000
S	1.491122	0.000000	6.556839
S	-1.491088	0.010002	6.556839
H	-1.581942	0.983415	5.637111
H	-1.591874	-0.961820	5.636511
H	1.374010	-0.000136	5.215536

SH--H•--SH TS

6
0 2

–XX	0.000000	0.000000	0.000000
H	0.000000	0.000000	7.000000
S	1.574974	0.000000	6.855828
S	-1.574914	0.003290	6.855841
H	1.496971	-0.091217	5.515045
H	-1.497007	0.094114	5.515026

NH_2--H•--NH_2 PC

8
0 2

–XX	0.000000	0.000000	0.000000
N	1.366397	0.000000	4.711764
N	-1.366397	-0.000246	4.711764
H	1.343917	0.003762	3.692207

NH_2--H•--NH_2 TS

8
0 2

–XX	0.000000	0.000000	0.000000
H	0.000000	0.000000	5.000000
N	1.209005	0.000000	4.687371
N	-1.197088	0.169630	4.687360

H	0.845827	-0.808700	5.036164
H	0.860891	0.816780	5.040115
H	-1.353957	0.796790	4.059711
H	-1.362584	-0.796039	4.057990

PH_2--H•--PH_2 PC

8

0 2

–XX	0.000000	0.000000	0.000000
P	1.779206	0.000000	4.552625
P	-1.779200	0.004478	4.552625
H	0.995419	1.025426	5.136709
H	1.083175	-0.000936	3.321186
H	1.004679	-1.033557	5.134716
H	-1.529527	-1.053039	3.644899
H	-1.528908	0.978370	3.555998

PH_4--H•--PH_4 PC

12

0 2

–XX	0.000000	0.000000	0.000000
P	1.699978	0.000000	4.740294
P	-1.699429	0.043224	4.740294
H	1.344990	1.284315	5.251277
H	2.831610	-0.052144	5.710356
H	2.621903	-0.111000	3.663095
H	1.148869	-1.168397	5.348883
H	-3.026581	-0.058346	5.211174
H	-1.926928	-0.020700	3.357963
H	0.582056	0.052583	3.805716
H	-1.724120	1.571394	4.768891
H	-1.452796	-1.464390	4.866158

1,2-OH shift (optimized) PC

11

0 2

C	0.713329	-0.772745	0.023966
C	0.653483	0.617911	0.538073
O	2.050571	-1.268639	-0.075102
H	0.195359	-1.448021	0.707711
H	0.220206	-0.822385	-0.956864
H	2.540068	-0.674688	-0.663103
O	1.143909	1.530625	-0.358334
H	0.813199	0.831567	1.592736
H	1.206345	2.407357	0.043917
XX	-4.303542	-0.162302	-0.069904
XX	7.665133	0.041413	0.772310

1,2-OH shift (optimized) PR

11

0 2

C	0.755667	1.362288	0.286276
C	0.967418	0.001510	-0.275142
H	1.206172	2.212109	-0.209686
H	0.073620	1.505371	1.113848
H	0.567063	-0.087521	-1.295571
O	0.331814	-0.910380	0.585694

H	-1.321374	-0.376637	3.826832
H	-1.257075	1.139416	4.360431
H	1.403600	0.950171	4.355310
H	1.255535	-0.562674	3.829698

PH_2--H•--PH_4 TS

8

0 2

–XX	0.000000	0.000000	0.000000
H	0.000000	0.000000	5.000000
P	1.650168	0.000000	4.674522
P	-1.636707	-0.209090	4.674579
H	1.401824	0.056356	3.281006
H	1.671220	-1.419058	4.697622
H	-1.456645	-1.613112	4.577356
H	-1.411405	-0.005321	3.291187

PH_2--H•--PH_4 TS

12

0 2

–XX	0.000000	0.000000	0.000000
H	0.000000	0.000000	5.000000
P	1.638926	0.000000	4.371354
P	-0.959363	-1.342669	4.367112
H	1.995767	1.274253	4.864431
H	2.918540	-0.320857	3.828661
H	1.072932	0.389457	3.087415
H	1.881892	-0.774688	5.616819
H	-1.507173	-2.598898	3.962233
H	-1.111312	-0.644593	3.153784
H	-2.190046	-0.942151	5.018384
H	0.540754	-1.697274	4.053711

1,2-OH shift (optimized) TS

11

0 2

C	0.606119	-0.802718	-0.236737
C	0.566877	0.377760	0.407528
O	2.807333	-0.854223	0.103253
H	0.529146	-1.723560	0.323460
H	0.596318	-0.847036	-1.320285
H	2.981538	-0.146337	-0.546113
O	0.611142	1.548042	-0.275035
H	0.548312	0.444224	1.491965
H	0.661201	2.296367	0.333886
XX	-4.411366	-0.336051	0.007400
XX	7.583508	-0.039471	0.194580

H	0.475440	-1.801025	0.232681
O	2.336543	-0.307657	-0.430629
H	2.771286	-0.143467	0.422138
XX	-4.086549	-0.013773	-0.174526
XX	7.788871	1.655812	0.257697

1,2-OH shift (enzyme) PC

13
0 2

–XX	-0.02513	-1.46821	-3.31566
–XX	-0.04113	3.39779	-2.41566
–XX	3.32487	-0.53221	3.57834
+XX	0.40087	0.48679	-0.82166
C	3.22948	-1.16586	-0.54056
C	3.46203	-0.53078	-1.86132
O	1.96106	-1.82017	-0.45723
H	3.97670	-1.94109	-0.36037
H	3.31430	-0.40785	0.25057
H	1.27754	-1.15680	-0.63293
O	2.65658	0.55780	-2.06957
H	3.71157	-1.13047	-2.73400
H	2.74016	0.87787	-2.97783

1,2-OH shift (enzyme) TS

13
0 2

–XX	-0.02513	-1.46821	-3.31566
–XX	-0.04113	3.39779	-2.41566
–XX	3.32487	-0.53221	3.57834
+XX	0.40087	0.48679	-0.82166
C	3.16484	-1.03921	-0.50128
C	3.38632	-0.48041	-1.70495
O	2.04421	-2.67043	-1.52447
H	3.84650	-1.78716	-0.12234
H	2.37936	-0.66972	0.14884
H	1.28592	-2.09347	-1.73714
O	2.57544	0.49542	-2.18208
H	4.18504	-0.81685	-2.36041
H	2.81715	0.72697	-3.08830

1,2-OH shift (enzyme) PR

13
0 2

–XX	-0.02513	-1.46821	-3.31566
–XX	-0.04113	3.39779	-2.41566
–XX	3.32487	-0.53221	3.57834
+XX	0.40087	0.48679	-0.82166
C	3.21187	-1.19483	-0.50048
C	3.39074	-0.46170	-1.78199
H	3.15713	-2.27552	-0.51570
H	3.24477	-0.65811	0.43834
H	4.33191	-0.73373	-2.28168
O	3.36880	0.91234	-1.48513
H	3.47306	1.39727	-2.31728
O	2.40352	-0.79726	-2.73439
H	1.53757	-0.67834	-2.31113