Competitive Dynamics of Elimination and Substitution Reaction Modulated by

Nucleophile and Leaving Group

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Methods							_			
Species	MP2	B3LYP	B97-1	BHandH	BHandHLYP	M06	M06-2X	wb97XD	CCSD(T)	Ref ^d
anti-E2										
RC	-19.5	-19.2	-20.2	-24.5	-19.3	-21.5	-21.9	-19.8	-19.5	-19.3
TS(aE)	-15.2	-18.8	-19.8	-22.8	-16.3	-19.6	-19.5	-18.0	-15.0	-15.1
PC(aE)	-61.8	-65.0	-64.5	-68.8	-68.9	-65.1	-70.9	-66.4	-63.0	-65.5
P1(E)	-41.9	-49.7	-47.0	-45.8	-53.5	-47.6	-51.8	-48.6	-42.8	-47.4
P2(E)	-55.4	-61.9	-59.9	-61.1	-65.4	-60.2	-64.8	-61.0	-56.9	
P3(E)	-47.7	-53.3	-51.4	-51.6	-57.0	-52.0	-56.6	-52.8	-48.3	
P4(E)	-43.5	-50.5	-48.3	-50.5	-54.5	-48.4	-53.0	-51.5	-44.2	
					syn-E2					
TS(sE-Hendo)	-6.8	-10.4	-11.9	-15.3	-6.8	-11.6	-12.0	-9.5	-7.1	
TS(sE-Hexo)	-4.7		-9.8	-13.1	-4.8	-9.2	-10.1	-7.2	-5.0	-4.8
PC(sE-Hendo/Hexo)	-61.8	-65.0	-64.3	-68.8	-68.9	-65.8	-70.9	-66.4	-63.0	-65.2/-65/-60.3
inv-S _N 2										
TS(iS)	-15.8	-19.1	-19.9	-22.6	-17.7	-21.0	-20.1	-17.8	-16.8	-16.9
PC(iS)	-65.2	-76.1	-70.0	-80.6	-82.3	-72.1	-76.6	-73.0	-65.6	-76.2/-68.9
P(S)	-56.7	-63.4	-63.7	-72.4	-69.8	-65.2	-69.3	-66.4	-57.5	-62
					ret-S _N 2					
RC(Ha)	-9.5	-11.5	-13.7	-15.4	-8.6	-14.2	-11.8	-9.8	-10.1	-10.2
TS(rS-Hendo)	18.5	10.0	10.1	11.2	16.1	8.9	12.4	14.3	16.1	
TS(rS-Hexo)	24.4		16.9	18.4	23.6	15.6	18.9	21.2	22.8	22.4
PC(rS-Hendo/Hexo)	-73.1	-76.2	-77.7	-90.0	-82.5	-80.0	-84.6	-80.6	-74.5	
PT										
TS(PT)	-12.8	-14.7	-17.0	-21.9	-13.9	-17.1	-18.6	-15.5	-13.8	

Table S1. Classical relative energies for HO⁻ + CH₃CH₂Br stationary points.^{a,b,c}

PC(PT)	-12.9	-15.4	-17.7	-22.7	-16.1	-20.5	-21.0	-16.4	-14.5	
P(PT)	9.0	4.8	3.3	2.5	3.3	-0.5	0.1	4.8	6.3	
					Dits					
TS(Dits)	6.3	5.2	2.9	-4.4	4.8	-3.2	-1.9	3.3	5.3	4.8

^a The energy of the stationary points of the $HO^- + CH_3CH_2Br$ reaction is calculated relative to the reactants at 0 K in kcal mol⁻¹, excluding the zero point energy correction (ZPE).

^b For the elements C, H, and O, the aug-cc-pVDZ(abbreviation aVDZ) and aug-cc-pVTZ(abbreviation aVTZ) basis set are used, and for Br the pseudo basis set ECP/d and aug-cc-pVTZ-PP (abbreviation PP/t) are used. The aVDZ and ECP/d belong to the double zeta basis sets, while aVTZ and PP/t belong to the triple zeta basis sets. The MP2 and DFT methods are matched with a double zeta basis set, while the CCSD(T) method is matched with a triple zeta basis set and calculates the energy of the stationary point of the potential energy surface on the minimum energy configuration of MP2/ECP/d.

^c The P2 (E), P3 (E) and P4 (E) are $CH_2=CH_2 + Br^-(H_2O)$, $CH_2=CH_2(Br^-) + H_2O$ and $CH_2=CH_2(H_2O) + Br^-$ complex products, respectively.

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Fig. S1. Schematic potential energy surface of the $HO^- + CH_3CH_2Br$ (black), $HO^- +$ CH₃CH₂Cl (red), and F⁻ + CH₃CH₂Br (blue) reactions showing stationary points along the substitution, elimination, and proton transfer pathways at the CCSD(T)/PP/t//MP2/ECP/d level of theory. The energies in kcal mol⁻¹ are relative to isolated molecules and ions without zero-point energy (ZPE). Numbers in parentheses include ZPEs and compare well with available experimental data given in brackets. The data of F⁻ + CH₃CH₂Br and HO⁻ + CH₃CH₂Cl are from ref (J. Am. Chem. Soc. 2018, 140 (35), 10995-11005.) and ref (J. Chem. Phys., 2025, 162(2): 024304.), respectively.



Fig. S2. Stationary point structures of E2, S_N2 , and PT channels in the HO⁻ + CH₃CH₂Br reaction optimized at the B3LYP/ECP/d level of theory.

Bond distances (in Å) and angles (in degree) are shown for each reaction pathway, and the available experimental data ^{a,b} are given in brackets.

^a Lide, D. R. CRC Handbook of Chemistry and Physics; CRC Press: Boca Raton, FL, 2005. ^b Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.;

Frurip, D. J.; McDonald, R. A.; Syverud, A. N. JANAF Thermochemical Tables; National Bureau of Standards: Washington, D.C., 1985; Vol. 14



Fig. S3. Schematic representation of the different geometrical configurations of TS (rS) and TS (sE). Notes: HO⁻ is a diatomic nucleophilic reagent that produces different geometrical configurations when close to the reaction substrate. Fig. S3 shows two structures in the transition structures of ret-S_N2 and syn-E2, Hendo and Hexo, respectively. The energy data in Table S1 illustrate that the energies of the Hendo configuration are lower than that of Hexo under all methods, and the energies of the Hendo configuration in the syn-E2 transition structure are 2 kcal mol⁻¹ lower than that of Hexo, whereas those of ret-S_N2 are nearly 6~8 kcal mol⁻¹ lower. Therefore, in discussing this paper, if not remarkable, the ret-S_N2 and syn-E2 transition structures refer the Hendo-type structures by default. to



Fig. S4. The histograms show differences between the stationary point energies using the CCSD(T)/PP/t benchmark method and MP2 or DFT functionals with the basis set ECP/d in $HO^- + CH_3CH_2Br$ system. Each histogram contains stationary point energies in the potential energy surface, each fitting with the normal distribution of the error curve.

(a)	(b)	(C)	(d)	(e)	(f)
inv-S _N 2	inv-S _N 2	inv-S _N 2	anti-E2	anti-E2	PT-iRe
pre+PE(I)	pre+PE(II)	post+Roaming	pre+PE(I)	pre+PE(Ⅱ)	post
900.0 fs	1395.0 fs	1845.0 fs	1260.0 fs	1800.0 fs	855.0 fs
Ηα	Ηα	→	+ 	→ Hα	** **
982.5 fs	1567.5 fs	2017.5 fs	1342.5 fs	1890.0 fs	1207.5 fs
ο γ Hα	Hα *****	•	β Ηα	Ha	*
1162.5 fs	1845.0 fs	2032.5 fs	1582.5 fs	2175.0 fs	1357.5 fs
Ηα	Ηα	9	На	Ha	,
1762.5 fs	2745.0 fs	2107.5 fs	1905.0 fs	2505.0 fs	1410.0 fs
Ηα	Ha e	*** **	Ηα	Ha	• •
2452.5 fs	2842.5 fs	2550.0 fs	3082.5 fs	2595.0 fs	2842.5 fs
Ηα	Ha	*	Ηα	Ha	¢ مې
2842.5 fs	2940.0 fs	10807.5 fs	3210.0 fs	2842.5 fs	3742.5 fs
Hα	Ha	••••••••••••••••••••••••••••••••••••••	Ηα	Ha Ha Ha	• •
2917.5 fs	3097.5 fs	11115.0 fs	3390.0 fs	2932.5 fs	5872.5 fs
Ha	Ηα		7• Ηα Δ	Ηα 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4	/• ***

Fig. S5. Snapshots of atomic-level mechanistic trajectories of $S_N 2$, E2, and PT-iRe channels in the HO⁻ + CH₃CH₂Br reaction.



Fig. S6. Distribution of entrance channel interaction time in the $HO^- + CH_3CH_2Br$ system, defined as the time interval from the first collision event to the transition structure. A star corresponds to an individual molecular dynamics trajectory. Red stars denote trajectories with interaction time in the 0 ~ 1 ps range, and blue stars represent those in the 1 ~ 2 ps range.

Animations S1 - S12

Animation S1. A trajectory following the direct rebound (DR) mechanism for the anti-E2 reaction $HO^- + CH_3CH_2Br \rightarrow H_2O + CH_2=CH_2 + Br^-$.

Animation S2. A trajectory following the direct stripping (DS) mechanism for the anti-E2 reaction $HO^- + CH_3CH_2Br \rightarrow H_2O + CH_2=CH_2 + Br^-$.

Animation S3. A typical indirect trajectory trapped in RC pre-reaction potential energy well and forming a reaction intermediate (see Fig. 1) for the anti-E2 reaction HO⁻ + $CH_3CH_2Br \rightarrow H_2O + CH_2=CH_2 + Br^-$.

Animation S4. A indirect trajectory (pre + PE) for the anti-E2 reaction HO⁻ + $C(H_{\beta})_{3}C(H_{\alpha})_{2}Br \rightarrow H_{\alpha}O-H_{\beta} + C(H_{\beta})_{2}=CH_{\alpha}H + Br^{-}.$

Animation S5. A indirect trajectory (pre + PE) for the anti-E2 reaction HO⁻ + $C(H_{\beta})_{3}C(H_{\alpha})_{2}Br \rightarrow HO-H_{\beta} + C(H_{\beta})_{2}=C(H_{\alpha})_{2} + Br^{-}$.

Animation S6. A trajectory following the direct rebound (DR) mechanism for the inv-S_N2 reaction HO⁻ + CH₃CH₂Br \rightarrow CH₃CH₂OH + Br⁻.

Animation S7. A trajectory following the direct stripping (DS) mechanism for the inv-S_N2 reaction HO⁻ + CH₃CH₂Br \rightarrow CH₃CH₂OH + Br⁻.

Animation S8. A typical indirect trajectory trapped in RC pre-reaction potential energy well and forming a reaction intermediate (see Fig. 1) for the inv-S_N2 reaction HO⁻ + CH₃CH₂Br \rightarrow CH₃CH₂OH + Br⁻.

Animation S9. A indirect trajectory (pre + PE) for the inv-S_N2 reaction HO⁻ + $C(H_{\beta})_3C(H_{\alpha})_2Br \rightarrow C(H_{\beta})_3CH_{\alpha}H-OH_{\alpha} + Br^-$.

Animation S10. A indirect trajectory (pre + PE) for the inv-S_N2 reaction HO⁻ + $C(H_{\beta})_3C(H_{\alpha})_2Br \rightarrow C(H_{\beta})_3(CH_{\alpha})_2$ -OH + Br⁻.

Animation S11. A indirect trajectory (post + Roaming) for the inv-S_N2 reaction HO⁻ + $CH_3CH_2Br \rightarrow CH_3CH_2OH + Br^-$.

Animation S12. A typical indirect trajectory trapped in PC (PT) postreaction potential energy well and induce rearrangement reaction PT-iRe HO⁻ + C(H_{β})₃C(H_{α})₂Br \rightarrow HO-H_{α} + C(H_{β})₂=CH_{α}H_{β} + Br⁻.

In the animation, the color coding for atoms is as follows: C_{α} , C_{β} , H, H in hydroxide

ion, O, and Br for blue, cyan, white, silver, magenta, and pink, respectively.