Supporting Information

Alkaline Hydrolysis of Organophosphorus Pesticides: the Dependence of the Reaction Mechanism on the Incoming Group Conformation.

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Performance of single reference computational methods

Table S1: Relative energies ($\mathbf{kcal \cdot mol^{-1}}$) from different computational approaches along the reaction pathway of the hydrolysis of selected organophosphorus pesticides.

		INTS→TSa	INTS→INTPa
paraoxon	HF	4.6	-54.7
	CASSCF	12.4	-79.7
	MP2	3.4	-46.6
	CASMP2	-0.8	-33.4
	DFT/B3LYP	5.3	-43.6
methyl parathion	HF	-6.8	-54.3
	CASSCF	-1.3	-68.0
	MP2	4.9	-45.6
	CASMP2	-6.7	-32.1
	DFT/B3LYP	5.8	-43.7
azinophos-ethyl	HF	1.1	-67.6
	CASSCF	4.3	-74.8
	MP2	4.4	-58.5
	CASMP2	17.1	-28.3
	DFT/B3LYP	4.3	-42.0

A and B path structures

The structures associated with all the stationary points along A reaction pathways of methyl parathion, fenitrothion, demeton-S, acephate, phosalone azinophos-ethyl and malathion hydrolysis are illustrated in Figures S1, S2, S3, S4, S5, S6, S7, respectively.

Figure S1: B3LYP/6-31+G(d) geometries of the stationary points along a reaction coordinate for the alkaline hydrolysis of methyl parathion (A path). Selected interatomic distances (Å) are indicated. The analogous distances associated with structures from B path are given in parentheses.

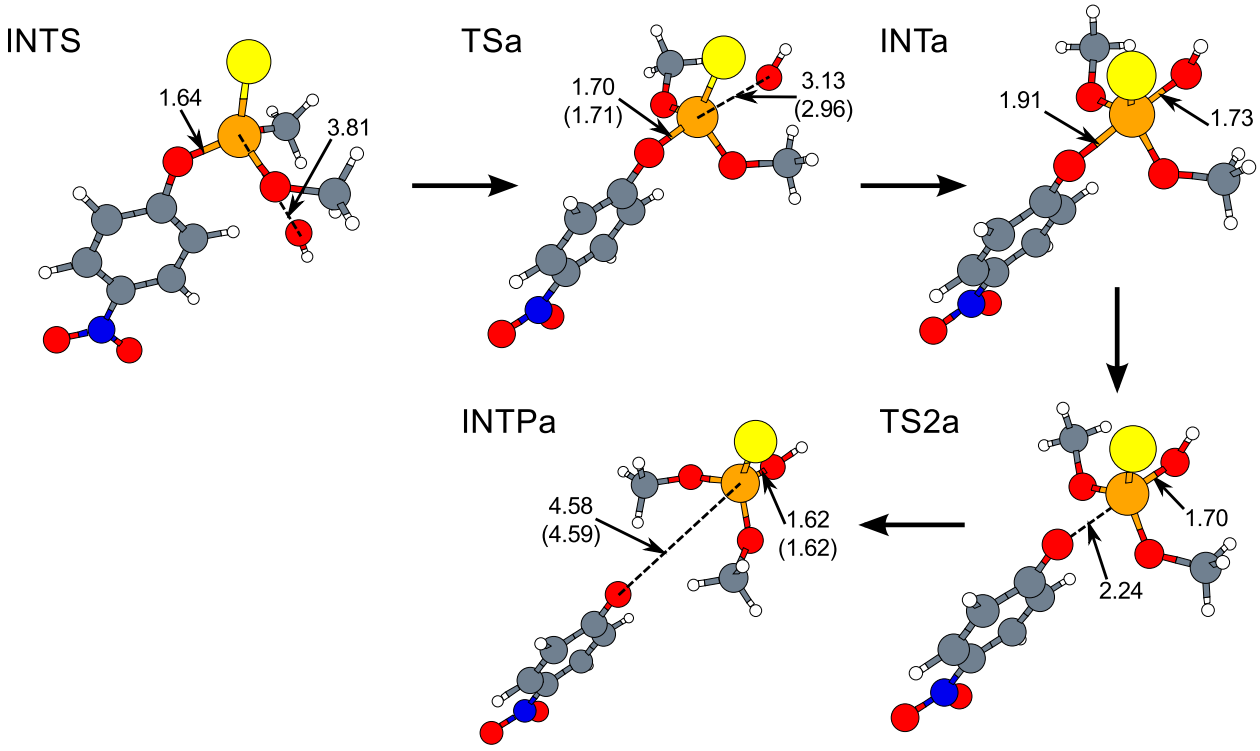


Figure S2: B3LYP/6-31+G(d) geometries of the stationary points along a reaction coordinate for the alkaline hydrolysis of fenitrothion (A path). Selected interatomic distances (Å) are indicated. The analogous distances associated with structures from B path are given in parentheses.

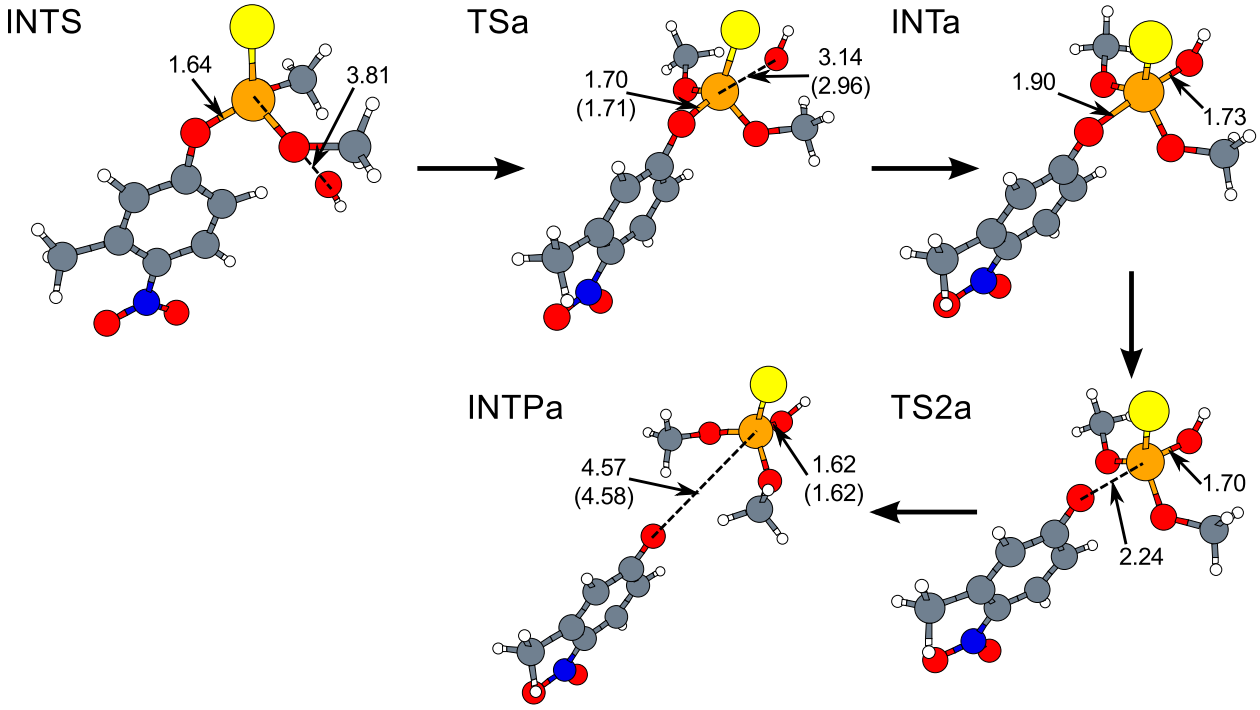


Figure S3: B3LYP/6-31+G(d) geometries of the stationary points along a reaction coordinate for the alkaline hydrolysis of demeton-S (A path). Selected interatomic distances (Å) are indicated. The analogous distances associated with structures from B path are given in parentheses.

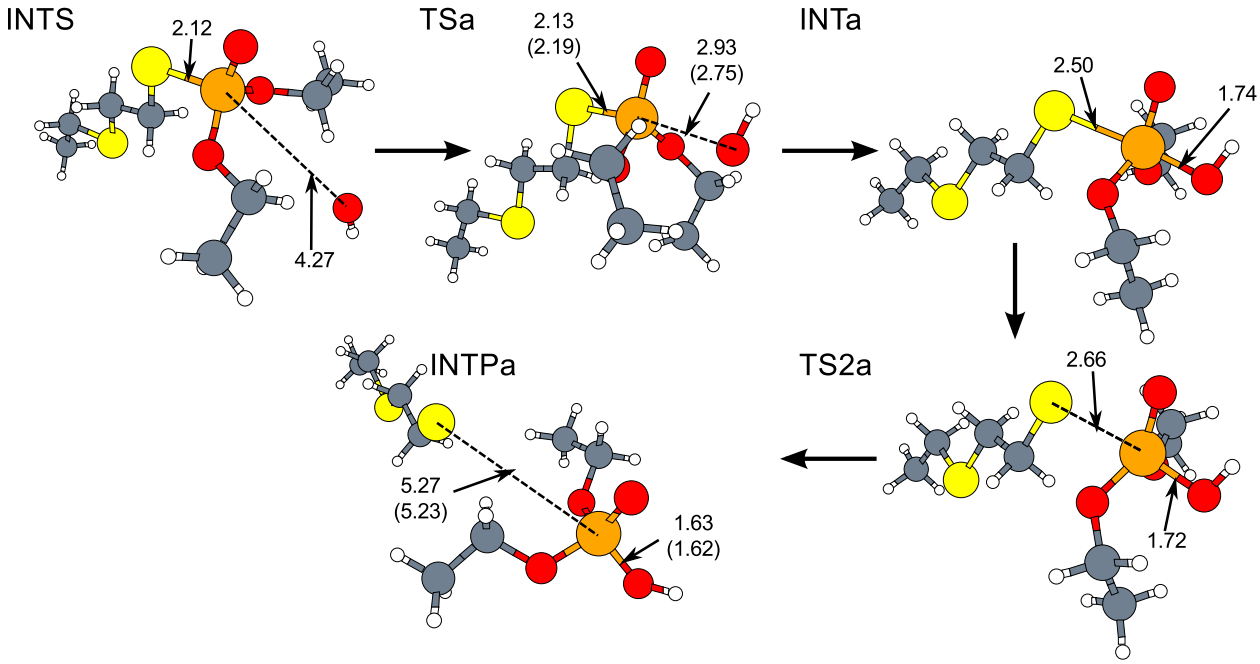


Figure S4: B3LYP/6-31+G(d) geometries of the stationary points along a reaction coordinate for the alkaline hydrolysis of acephate. Selected interatomic distances (Å) are indicated.

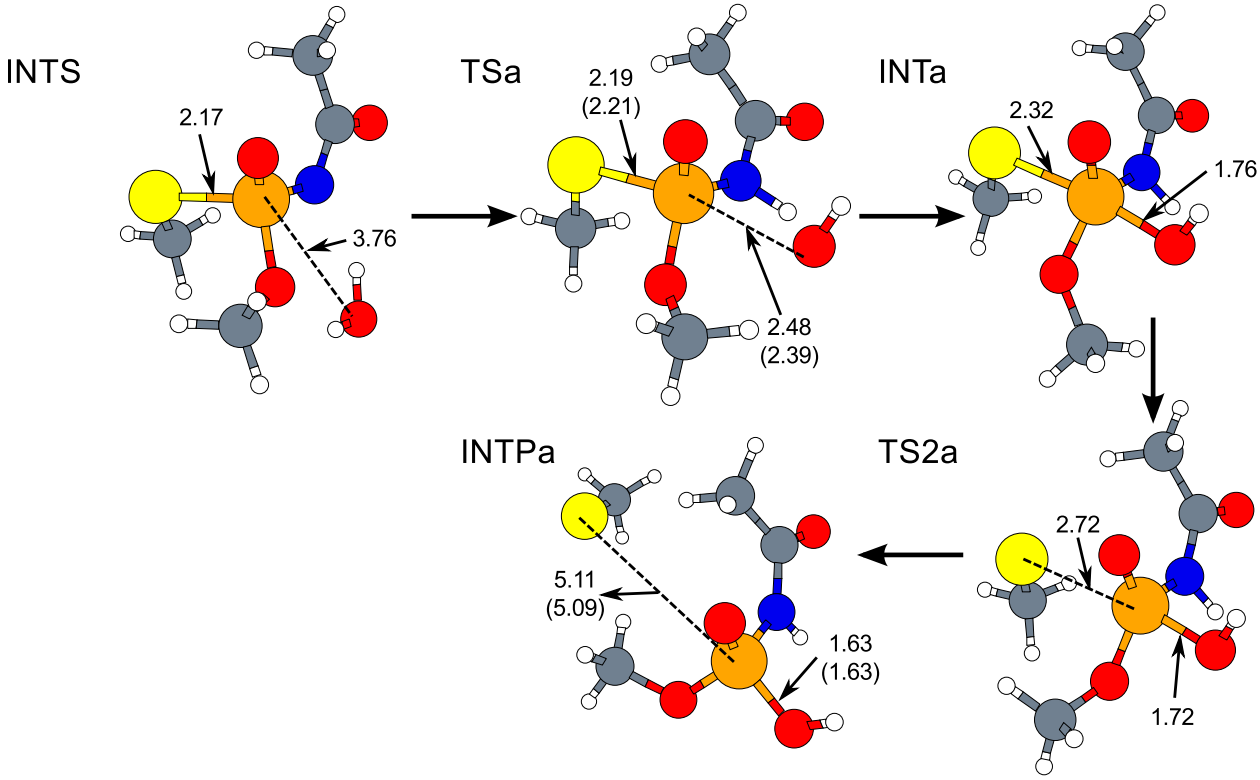


Figure S5: B3LYP/6-31+G(d) geometries of the stationary points along a reaction coordinate for the alkaline hydrolysis of phosalone (A path). Selected interatomic distances (Å) are indicated. The analogous distances associated with structures from B path are given in parentheses.

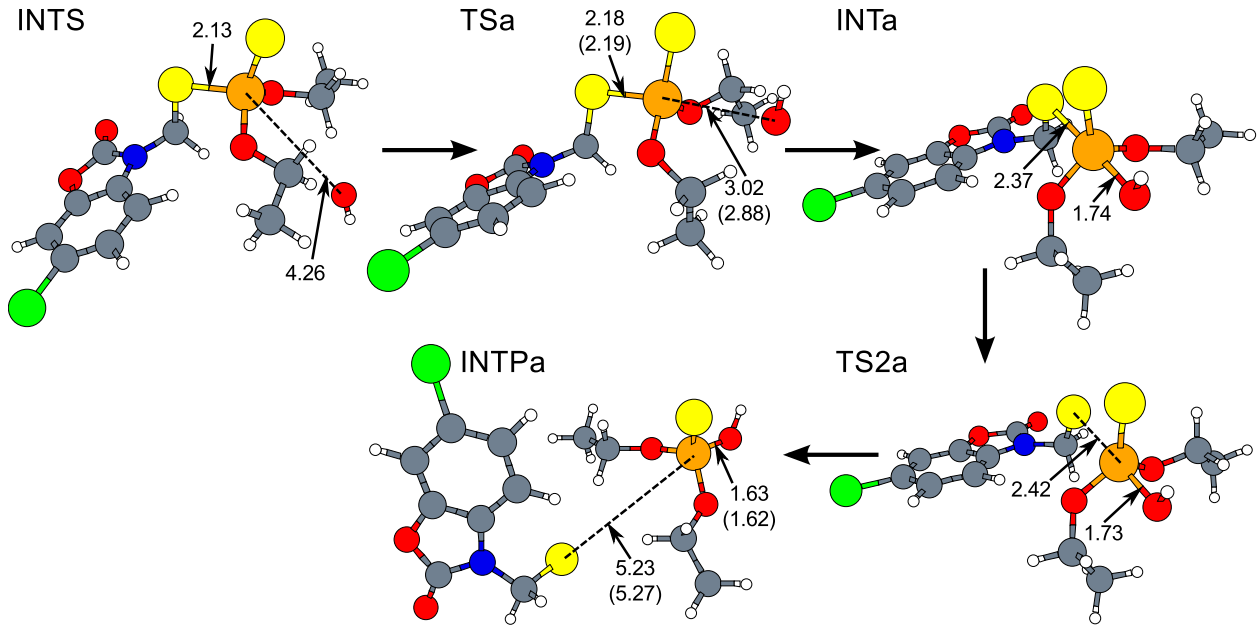


Figure S6: B3LYP/6-31+G(d) geometries of the stationary points along a reaction coordinate for the alkaline hydrolysis of azinophos-ethyl (A path). Selected interatomic distances (Å) are indicated. The analogous distances associated with structures from B path are given in parentheses.

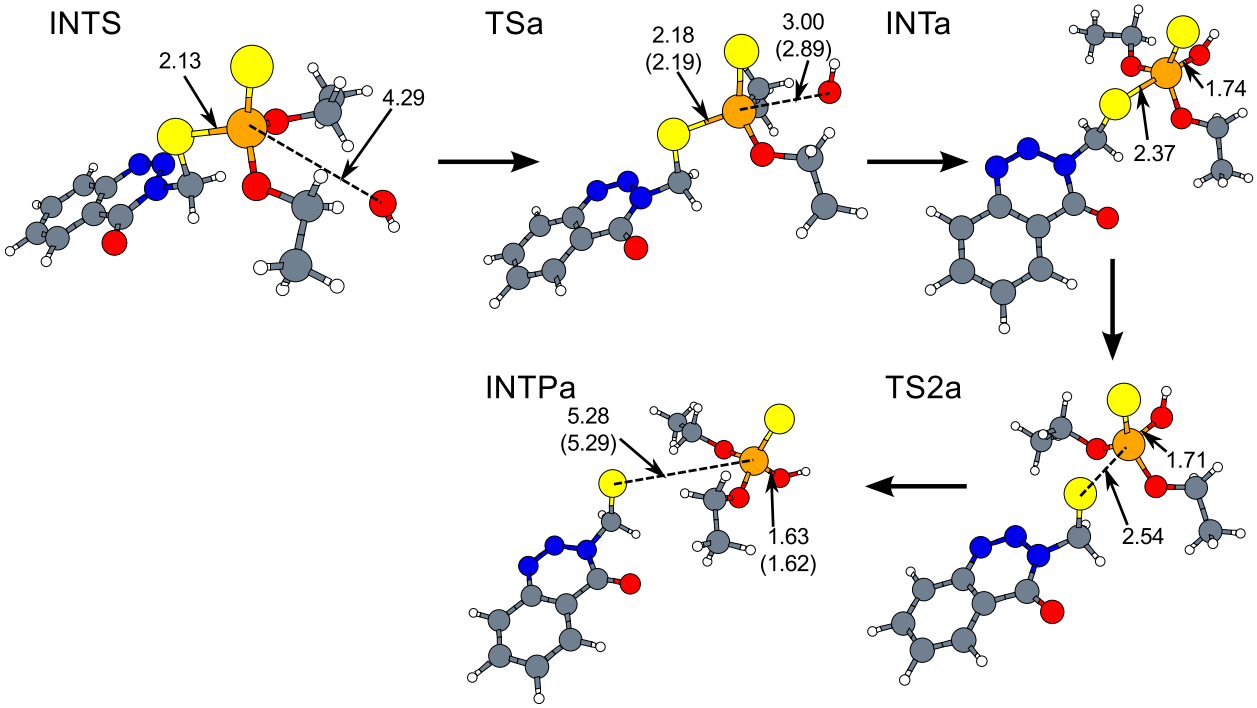
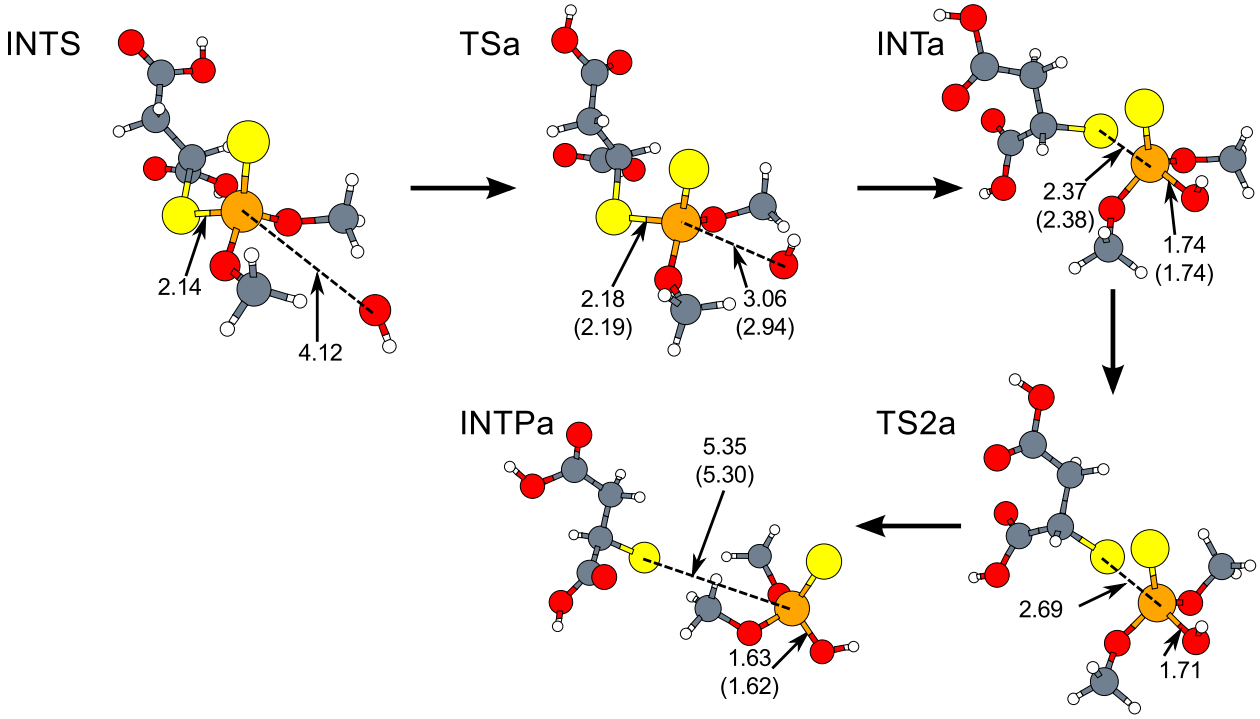


Figure S7: B3LYP/6-31+G(d) geometries of the stationary points along a reaction coordinate for the alkaline hydrolysis of malathion (A path). Selected interatomic distances (Å) are indicated. The analogous distances associated with structures from B path are given in parentheses.



A' and B' path structures

The structures associated with all the stationary points along A‘ reaction pathways reported in this contribution are illustrated in Figures S8, S9, and S10.

Figure S8: B3LYP/6-31+G(d) geometries of the stationary points along a reaction coordinate for the alkaline hydrolysis of fenitrothion (A' path). Selected interatomic distances (Å) are indicated. The analogous distances associated with structures from B' path are given in parentheses.

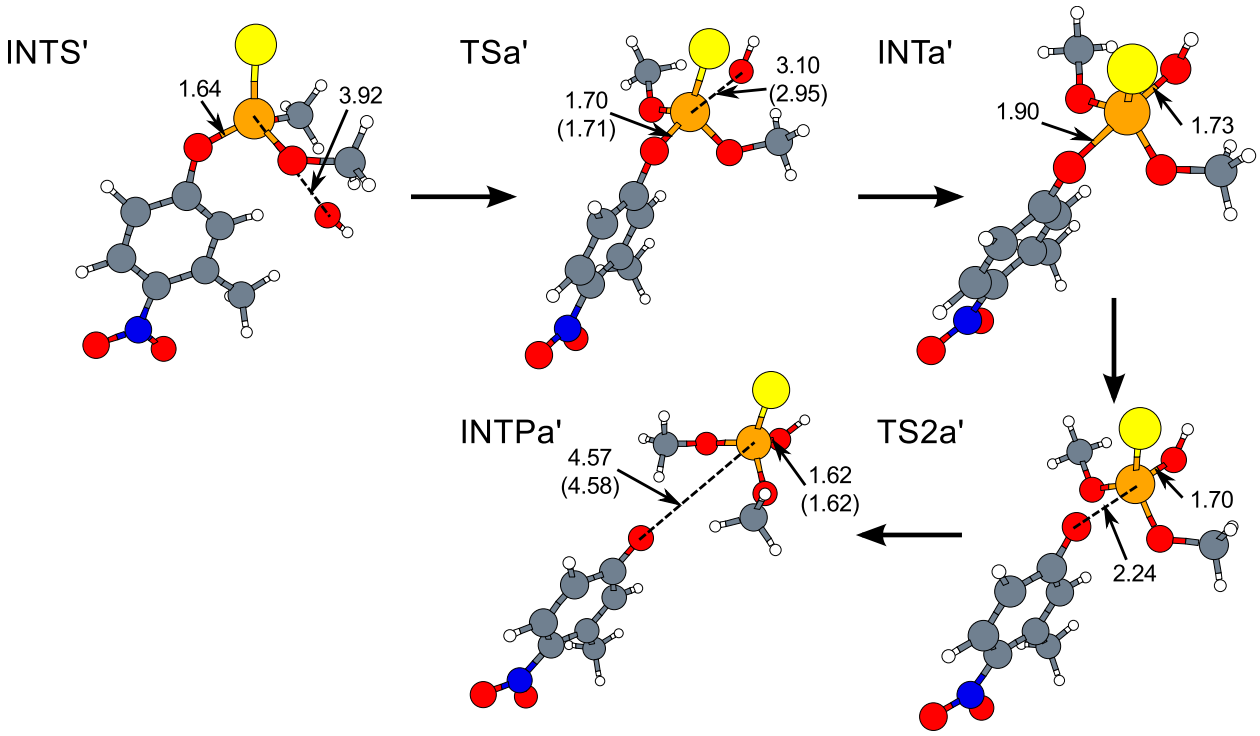


Figure S9: B3LYP/6-31+G(d) geometries of the stationary points along a reaction coordinate for the alkaline hydrolysis of demeton-S (A' path). Selected interatomic distances (Å) are indicated. The analogous distances associated with structures from B' path are given in parentheses.

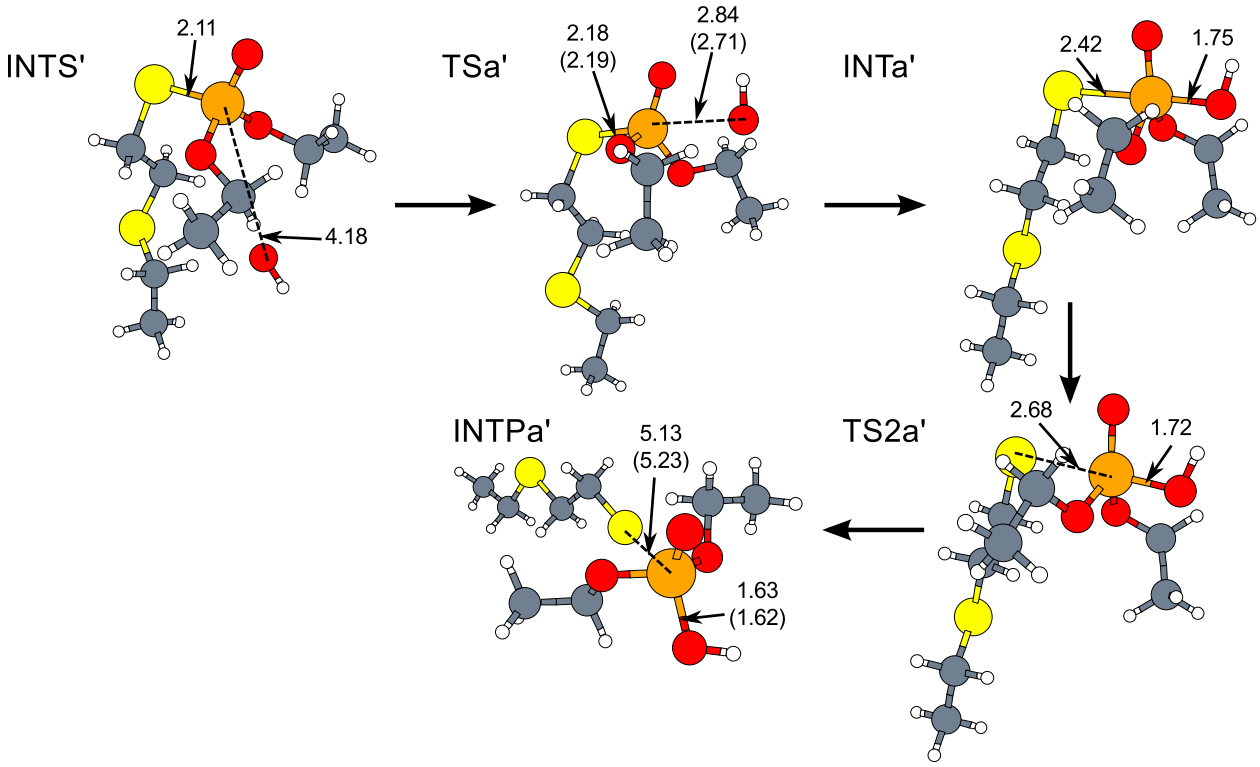
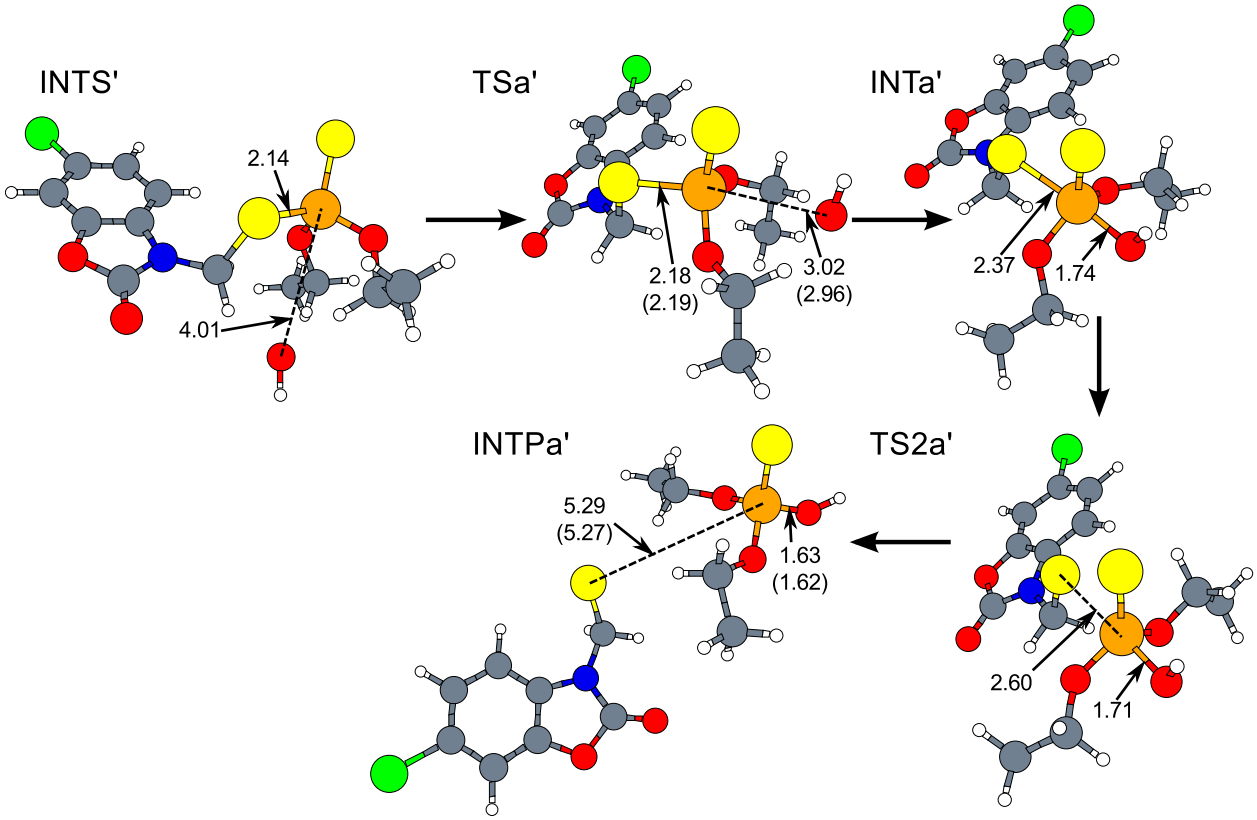


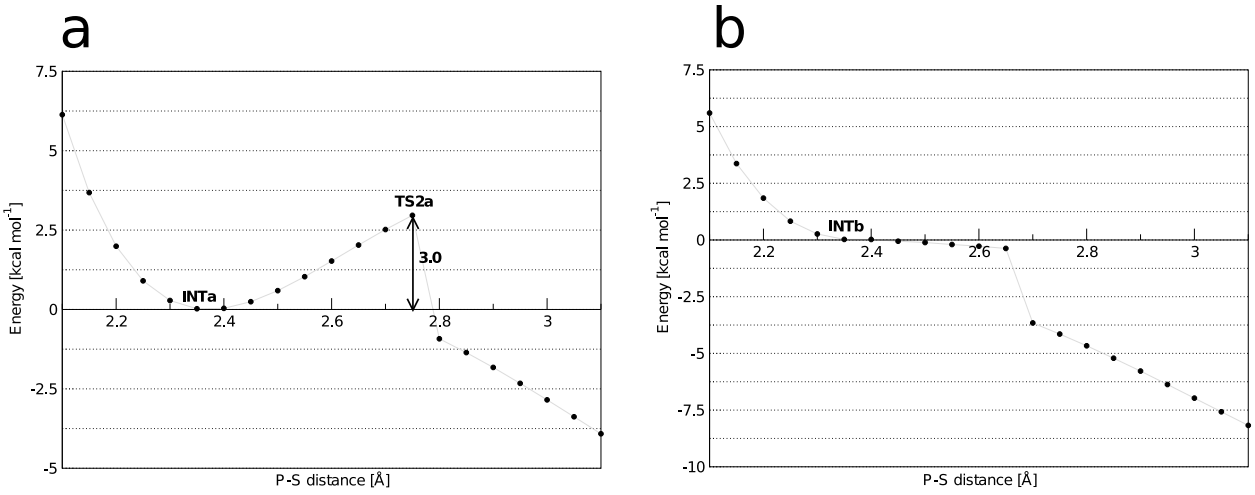
Figure S10: B3LYP/6-31+G(d) geometries of the stationary points along a reaction coordinate for the alkaline hydrolysis of phosalone (A' path). Selected interatomic distances (Å) are indicated. The analogous distances associated with structures from B' path are given in parentheses.



Malathion hydrolysis

Relaxed potential energy surface (PES) scans for A and B paths of malathion hydrolysis were performed to analyze the structural and energetic changes upon stretching of the P-S bond. Scans corresponding to A and B paths (Figure S11) start from TSa and TSb geometries, respectively.

Figure S11: B3LYP/6-31+G(d) energy changes accompanying the stretching of P-S bond in (a) TSa and (b) TSb structures. Relative energy is calculated with respect to the intermediate geometry (INTa or INTb). Scan points corresponding to the intermediate (INTa or INTb) and transistion state (TS2a) geometry are distinguished by respective labels. The value of 3.0 kcal $\cdot$ mol^{-1} reflects the difference between the point that resembles TS2a geometry the most and the energy associated with INTa structure.



Alternative leaving group conformations: more examples

To further explore the influence of the leaving group conformation on the reaction energy barrier, additional conformations of the departing groups of paraoxon, methyl parathion, acephate, azinophos-ethyl, and malathion were identified. The corresponding reaction pathways of A‘, B‘ (paraoxon, methyl parathion, acephate) or A’, B’, A”, B” (azinphos-ethyl, malathion) are described in what follows.

The structures associated with all these stationary points are illustrated in Figures S12, S13, S14 (A’ reaction pathway) and S15, S16 (A’, A” reaction pathways).

Figure S12: B3LYP/6-31+G(d) geometries of the stationary points along a reaction coordinate for the alkaline hydrolysis of paraoxon (A’ path). Selected interatomic distances (Å) are indicated. The analogous distances associated with structures from B’ path are given in parentheses.

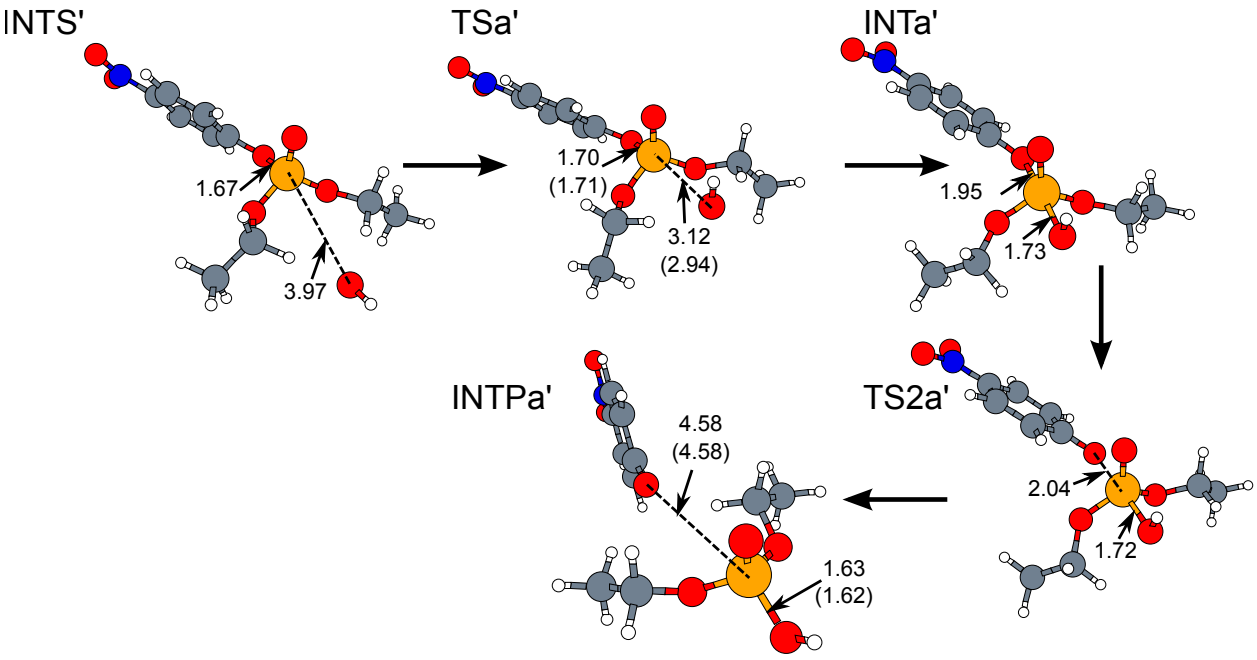


Figure S13: B3LYP/6-31+G(d) geometries of the stationary points along a reaction coordinate for the alkaline hydrolysis of methyl parathion (A' path). Selected interatomic distances (Å) are indicated. The analogous distances associated with structures from B' path are given in parentheses.

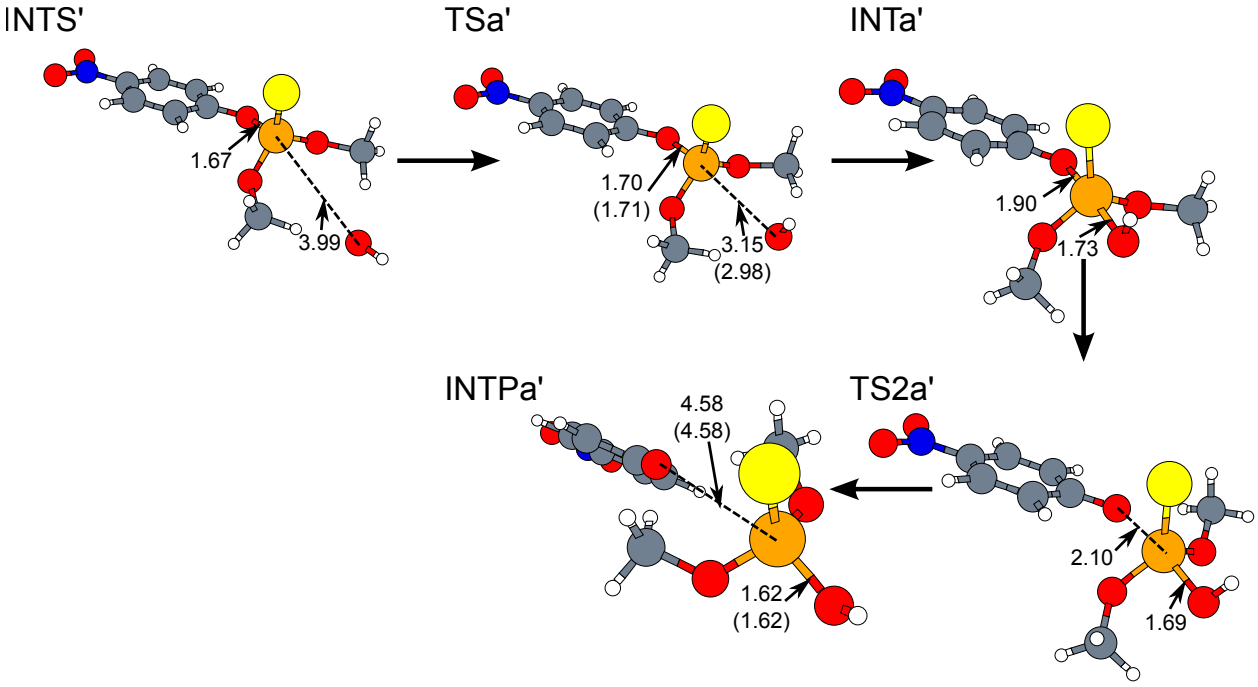


Figure S14: B3LYP/6-31+G(d) geometries of the stationary points along a reaction coordinate for the alkaline hydrolysis of acephate (A' path). Selected interatomic distances (Å) are indicated. The analogous distances associated with structures from B' path are given in parentheses.

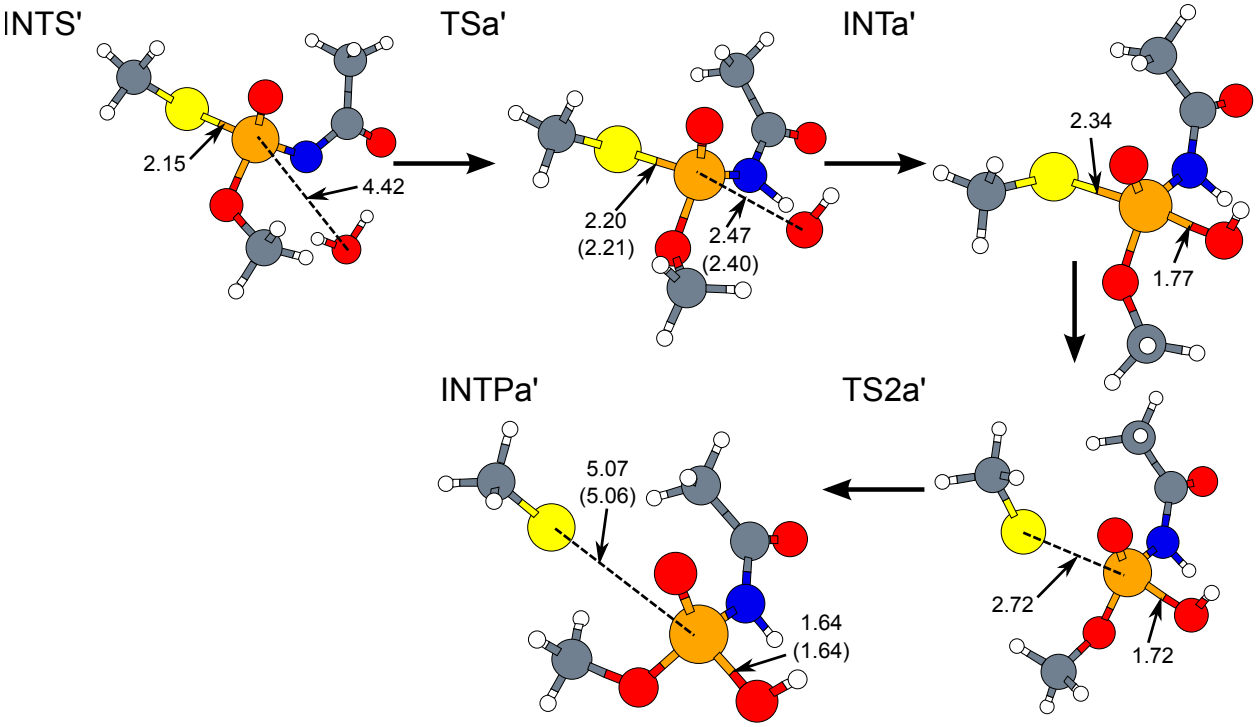


Figure S15: B3LYP/6-31+G(d) geometries of the stationary points along a reaction coordinate for the alkaline hydrolysis of azinophos-ethyl (A' and A" paths). Selected interatomic distances (Å) are indicated. The analogous distances associated with structures from B' and B" paths are given in parentheses.

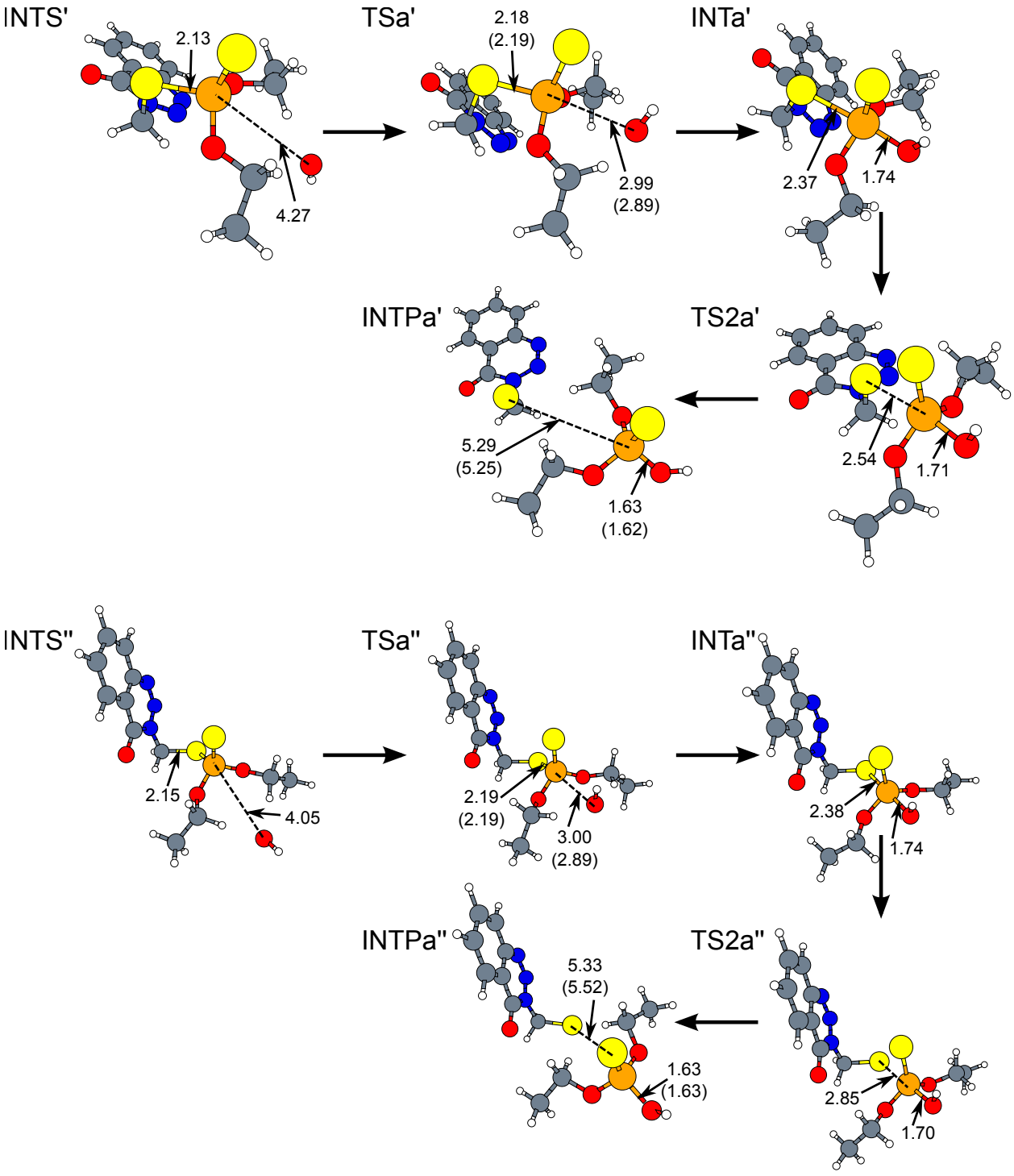


Figure S16: B3LYP/6-31+G(d) geometries of the stationary points along a reaction coordinate for the alkaline hydrolysis of malathion (A' and A" paths). Selected interatomic distances (Å) are indicated. The analogous distances associated with structures from B' and B" paths are given in parentheses.

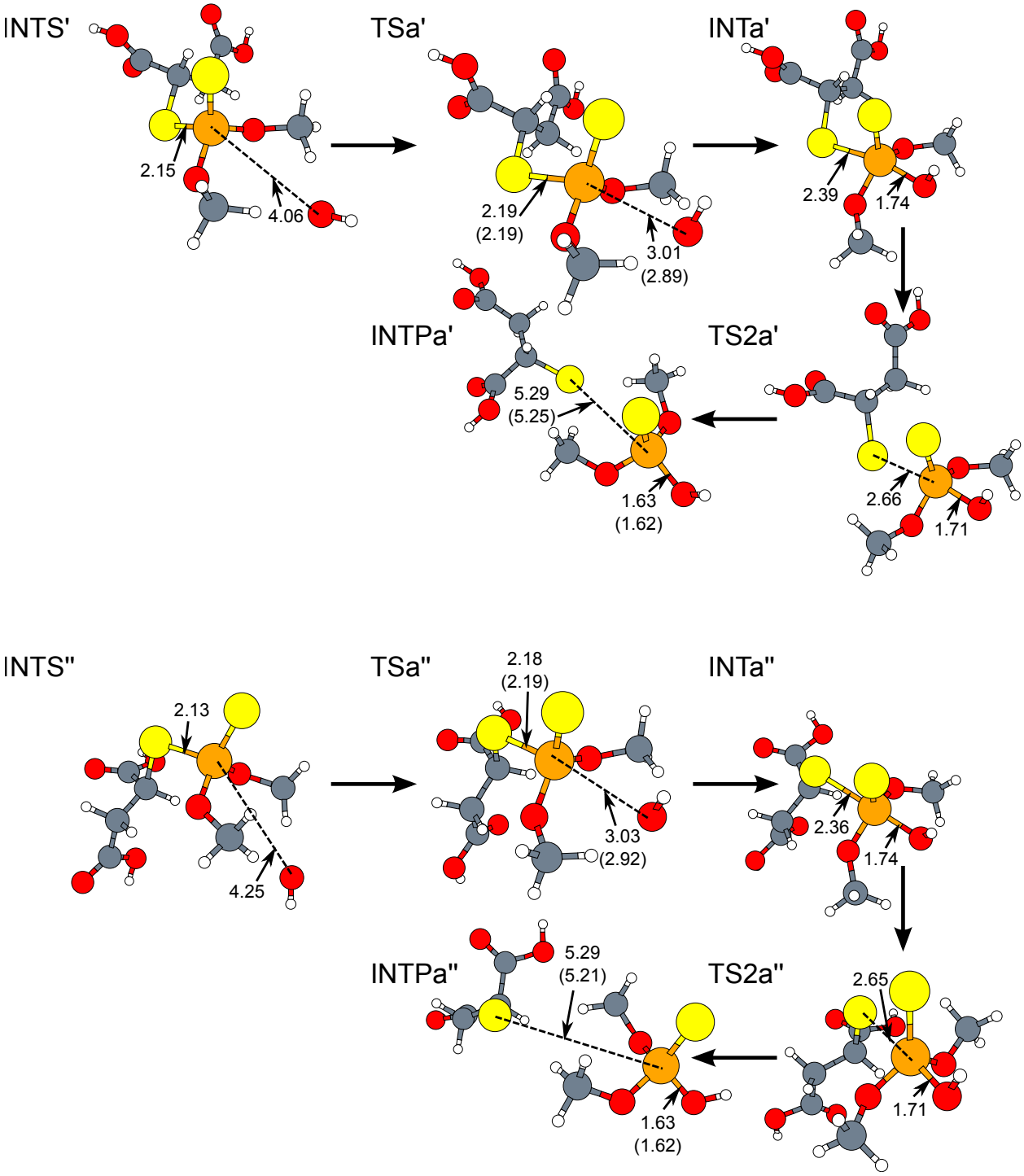


Table S2: MP2/6-311++G(2d,2p)//B3LYP/6-31+G(d) relative energies[a] for the hydrolysis reactions involving alternative conformations.

		ΔE^b		ΔG^c	
		A path	B path	A path	B path
paraoxon	INTS'→TS'	2.4	2.9	3.5	4.5
	INTS'→INT'	-23.5		-22.5	
	INT'→TS2'	0.9		1.2	
	INT'→INTP'	-15.1		-18.9	
	INTS'→INTP'	-38.6	-39.7	-41.5	-42.8
methyl parathion	INTS'→TS'	2.0	2.9	3.3	4.4
	INTS'→INT'	-28.1		-27.0	
	INT'→TS2'	-0.3		0.2	
	INT'→INTP'	-11.5		-16.5	
	INTS'→INTP'	-39.6	-39.3	-43.5	-42.7
acephate	INTS'→TS'	36.3	40.2	38.5	42.1
	INTS'→INT'	21.4		23.3	
	INT'→TS2'	1.5		2.0	
	INT'→INTP'	-6.8		-10.2	
	INTS'→INTP'	14.6	14.2	13.1	13.8
azinophos-ethyl	INTS'→TS'	4.2	5.1	5.0	6.4
	INTS'→INT'	-25.8		-24.7	
	INT'→TS2'	1.8		2.1	
	INT'→INTP'	-11.7		-15.2	
	INTS'→INTP'	-37.5	-38.3	-39.9	-40.8
	INTS"→TS"	2.6	3.2	4.2	4.9
	INTS"→INT"	-26.8		-25.1	
	INT"→TS2"	4.9		4.2	
	INT"→INTP"	-13.4		-17.4	
	INTS"→INTP"	-40.2	-40.1	-42.5	-41.5
malathion	INTS'→TS'	2.8	3.6	4.3	4.8
	INTS'→INT'	-26.2		-25.2	
	INT'→TS2'	2.7		2.5	
	INT'→INTP'	-12.3		-15.9	
	INTS'→INTP'	-38.5	-38.2	-41.1	-40.8
	INTS"→TS"	3.3	4.4	4.3	5.9
	INTS"→INT"	-26.3		-25.4	
	INT"→TS2"	0.0		-0.1	
	INT"→INTP"	-12.2		-15.2	
	INTS"→INTP"	-38.6	-38.7	-40.6	-40.5

[a] In units of $\text{kcal} \cdot \text{mol}^{-1}$.

[b] ΔE corresponds to the sum of electronic and zero-point energies.

[c] ΔG stands for the Gibbs free energy.

Table S3: 6-311++G(2d,2p)//B3LYP/6-31+G(d) activation energy barriers[a] for the hydrolysis reactions involving alternative conformations.

		A path/I[b]	A path/II[c]	B path
paraoxon[d]	ΔE_a[e]	2.4	0.9	2.9
	ΔG_a[f]	3.5	1.2	4.5
	ΔE_a^{PCM}[g]	4.3	0.8	4.0
methyl parathion[d]	ΔE_a	2.0	-0.3	2.9
	ΔG_a	3.3	0.2	4.4
	ΔE_a^{PCM}	4.4	1.3	4.4
acephate[d]	ΔE_a	36.3	1.5	40.2
	ΔG_a	38.5	2.0	42.1
	ΔE_a^{PCM}	34.9	1.4	36.6
azinophos-ethyl[d]	ΔE_a	4.2	1.8	5.1
	ΔG_a	5.0	2.1	6.4
	ΔE_a^{PCM}	7.1	3.0	6.4
azinophos-ethyl[h]	ΔE_a	2.6	4.9	3.2
	ΔG_a	4.2	4.2	4.9
	ΔE_a^{PCM}	5.4	2.2	5.1
malathion[d]	ΔE_a	2.8	2.7	3.6
	ΔG_a	4.3	2.5	4.8
	ΔE_a^{PCM}	5.4	2.8	5.3
malathion[h]	ΔE_a	3.3	0.0	4.4
	ΔG_a	4.3	-0.1	5.9
	ΔE_a^{PCM}	5.6	0.7	5.1

[a] In units of $\text{kcal} \cdot \text{mol}^{-1}$.
[b] Intermediate formation.
[c] Intermediate decomposition.
[d] A', B' path conformations
[e] ΔE_a corresponds to the sum of electronic and zero -point energies.
[f] ΔG_a stands for the Gibbs free energy.
[g] ΔE_a^{PCM} represents electronic energy in solution.
[h] A", B" path conformations

Table S4: 6-311++G(2d,2p)//B3LYP/6-31+G(d) relative energies[a] for the alternative conformations of the stationary points along reaction coordinate of the hydrolysis of paraoxon, methyl parathion and acephate.

		ΔE^b	ΔG^c	$\Delta E^{PCM\,d}$
paraoxon	INTS'-INTS	5.8	4.4	1.5
	TSa'-TSa	-0.5	-0.8	-0.5
	TSb'-TSb	-1.1	-1.7	-1.0
	INTa'-INTa	-1.1	-1.4	-0.4
	TS2a'-TS2a	-0.7	-0.8	0.2
	INTPa'-INTPa	0.7	0.1	0.1
	INTPb'-INTPb	-0.1	-1.2	0.0
methyl parathion	INTS'-INTS	5.9	4.8	0.6
	TSa'-TSa	-0.8	-0.6	-1.3
	TSb'-TSb	-1.3	-1.4	-1.8
	INTa'-INTa	-1.2	-1.2	-1.3
	TS2a'-TS2a	-4.0	-2.5	-2.5
	INTPa'-INTPa	0.1	-0.5	0.2
	INTPb'-INTPb	0.2	-0.1	0.2
acephate	INTS'-INTS	0.6	0.4	1.1
	TSa'-TSa	0.6	0.2	0.9
	TSb'-TSb	0.6	0.1	1.3
	INTa'-INTa	1.1	0.5	1.7
	TS2a'-TS2a	0.4	0.6	1.1
	INTPa'-INTPa	-0.2	-1.0	-0.3
	INTPb'-INTPb	-0.2	1.0	-0.4

[a] In units of $\text{kcal} \cdot \text{mol}^{-1}$.
[b] ΔE corresponds to the sum of electronic and zero-point energies.
[c] ΔG stands for the Gibbs free energy.
[d] ΔE^{PCM} represents the electronic energy in solution.

Table S5: 6-311++G(2d,2p)//B3LYP/6-31+G(d) relative energies[a] for the alternative conformations of the stationary points along reaction coordinate of the hydrolysis of azinophos-ethyl and malathion.

		ΔE^b	ΔG^c	$\Delta E^{PCM\,d}$
azinophos-ethyl	INTS'-INTS	-1.5	-1.0	-2.1
	TSa'-TSa	-2.5	-2.3	-2.5
	TSb'-TSb	-2.0	-1.6	-2.3
	INTa'-INTa	-3.2	-2.3	-3.0
	TS2a'-TS2a	0.0	0.0	0.0
	INTPa'-INTPa	0.6	0.8	0.3
	INTPb'-INTPb	0.2	-0.5	0.0
	INTS"-INTS	-1.4	-0.6	-2.1
	TSa"-TSa	-3.9	-2.6	-4.1
	TSb"-TSb	-3.8	-2.8	-3.6
	INTa"-INTa	-4.1	-2.4	-2.8
	TS2a"-TS2a	2.1	2.1	-0.6
	INTPa"-INTPa	-2.0	-1.3	-1.9
	INTPb"-INTPb	-1.4	-0.6	-1.9
malathion	INTS'-INTS	-0.8	-0.5	-1.2
	TSa'-TSa	0.4	1.0	0.2
	TSb'-TSb	0.1	-0.3	0.2
	INTa'-INTa	1.4	1.2	0.2
	TS2a'-TS2a	0.4	0.8	0.3
	INTPa'-INTPa	-0.4	-0.5	-0.1
	INTPb'-INTPb	-0.3	-0.5	0.0
	INTS"-INTS	-0.7	-0.6	-0.1
	TSa"-TSa	1.2	0.9	1.4
	TSb"-TSb	1.2	0.7	1.2
	INTa"-INTa	1.5	0.9	0.5
	TS2a"-TS2a	-2.2	-2.1	-1.5
	INTPa"-INTPa	-0.3	-0.1	-0.3
	INTPb"-INTPb	-0.7	-0.2	-0.7

[a] In units of $\mathrm{kcal \cdot mol^{-1}}$.
[b] ΔE corresponds to the sum of electronic and zero-point energies.
[c] ΔG stands for the Gibbs free energy.
[d] ΔE^{PCM} represents the electronic energy in solution.