



Article

Effect of the Nucleophile's Nature on Chloroacetanilide Herbicides Cleavage Reaction Mechanism. A DFT Study

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SUPPLEMENTARY MATERIAL

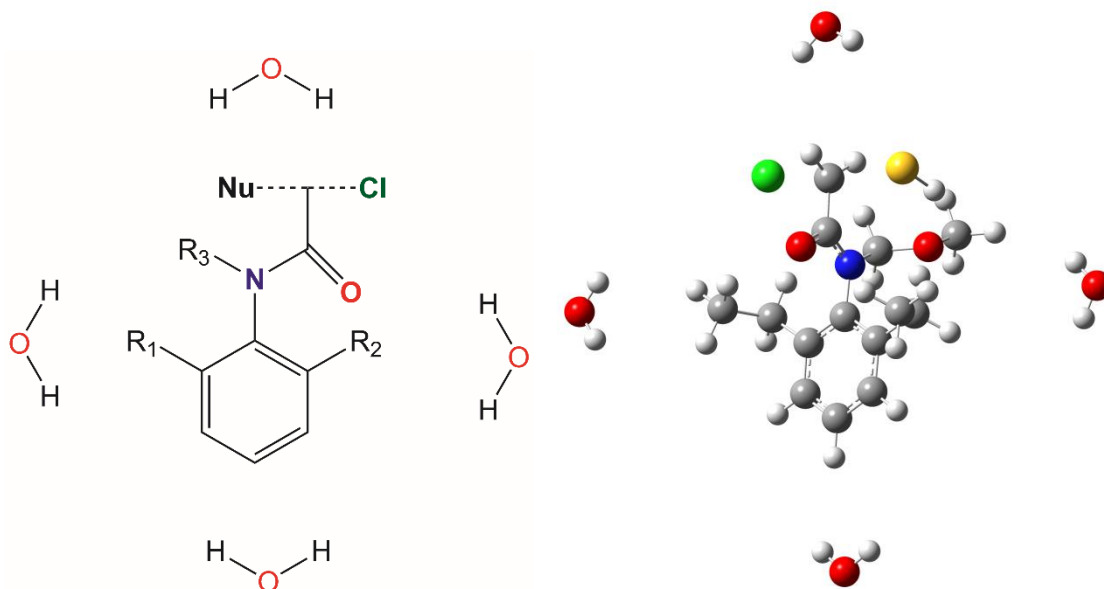


Figure S1. 2D and 3D representation of the 4-water model in the TS structure of Chloroacetanilide Herbicides

Table S1. Solvation electronic energy of chloroacetanilides and transition states

Chloroacetanilide	Nucleophile	Solvation Energy (kcal/mol)
Alachlor	<i>(Reagent)</i>	1.7
	<i>Br⁻ (TS)</i>	0.8
	<i>I⁻ (TS)</i>	1.3
	<i>HS⁻ (TS)</i>	1.2
	<i>S₂O₃⁻² (S) (TS)</i>	1.1
	<i>S₂O₃⁻² (O) (TS)</i>	1.0
Acetochlor	<i>(Reagent)</i>	1.3
	<i>Br⁻ (TS)</i>	0.7
	<i>I⁻ (TS)</i>	1.2
	<i>HS⁻ (TS)</i>	1.0
	<i>S₂O₃⁻² (S) (TS)</i>	1.2
	<i>S₂O₃⁻² (O) (TS)</i>	1.5
Propachlor	<i>(Reagent)</i>	1.5
	<i>Br⁻ (TS)</i>	0.4
	<i>I⁻ (TS)</i>	0.8
	<i>HS⁻ (TS)</i>	0.3
	<i>S₂O₃⁻² (S) (TS)</i>	1.2
	<i>S₂O₃⁻² (O) (TS)</i>	0.3
Metolachlor	<i>(Reagent)</i>	0.0
	<i>Br⁻ (TS)</i>	-0.3
	<i>I⁻ (TS)</i>	-0.4
	<i>HS⁻ (TS)</i>	0.7
	<i>S₂O₃⁻² (S) (TS)</i>	0.2
	<i>S₂O₃⁻² (O) (TS)</i>	0.9

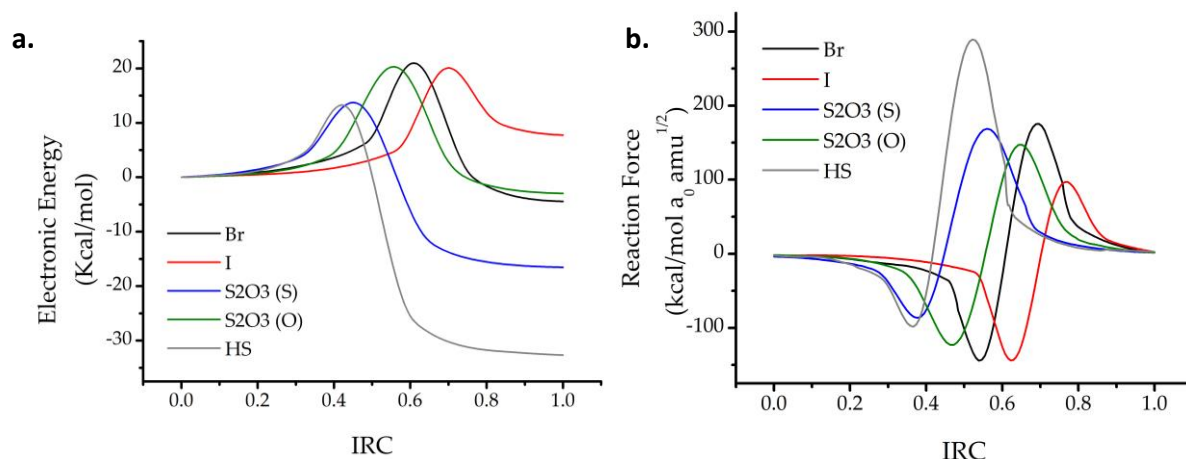


Figure S2. IRC (a) and RF (b) plots for the nucleophilic substitution of acetochlor

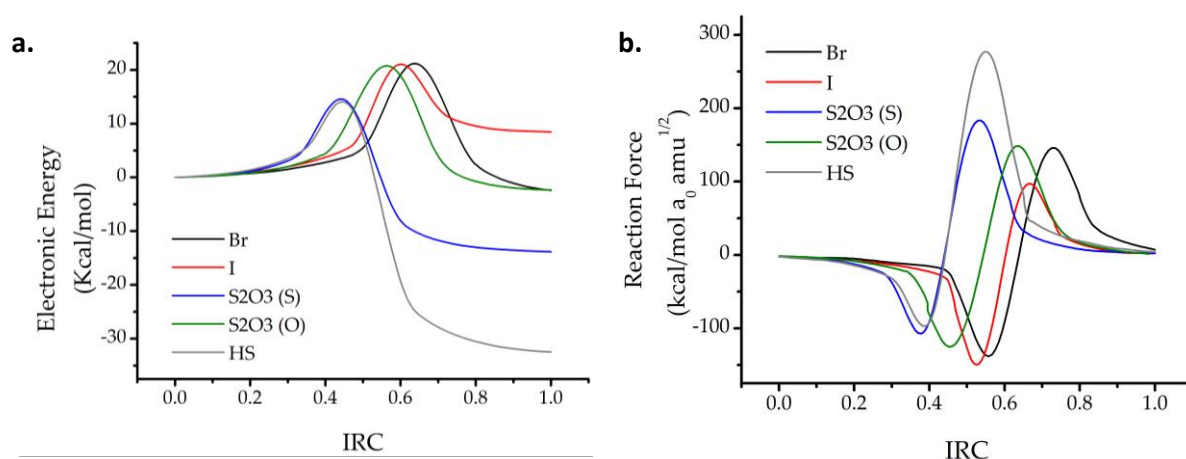


Figure S3. IRC (a) and RF (b) plots for the nucleophilic substitution of metolachlor.

Table S2. Reaction force Works (in Kcal/mol) involved in the nucleophilic substitution of propachlor

<i>Nucleophile</i>	<i>w1</i>	<i>w2</i>	<i>w3</i>	<i>w4</i>
<i>Br</i> ⁻	13.6	8.0	-11.0	-14.6
<i>I</i> ⁻	11.9	7.9	-4.4	-7.8
<i>HS</i> ⁻	9.1	4.4	-22.4	-26.2
<i>S</i> ₂ <i>O</i> ₃ ⁻² (<i>S</i>)	9.4	5.1	-10.9	-18.0
<i>S</i> ₂ <i>O</i> ₃ ⁻² (<i>O</i>)	12.5	8.7	-10.0	-14.3

Table S3. Reaction force Works (in Kcal/mol) involved in the nucleophilic substitution of metolachlor

<i>Nucleophile</i>	<i>w1</i>	<i>w2</i>	<i>w3</i>	<i>w4</i>
<i>Br</i> ⁻	13.1	8.0	-9.1	-14.4
<i>I</i> ⁻	13.0	8.0	-4.5	-8.1
<i>HS</i> ⁻	9.6	4.4	-19.2	-27.3
<i>S</i> ₂ <i>O</i> ₃ ⁻²	9.3	5.1	-12.4	-15.9
<i>O</i> ₂ <i>S</i> ₂ <i>O</i> ₃ ⁻²	13.1	7.4	-10.2	-12.9

Table S4. Reaction force Works (in Kcal/mol) involved in the nucleophilic substitution of alachlor

<i>Nucleophile</i>	<i>w1</i>	<i>w2</i>	<i>w3</i>	<i>w4</i>
<i>Br</i> ⁻	12.3	7.7	-9.5	-15.8
<i>I</i> ⁻	11.8	8.1	-4.6	-7.8
<i>HS</i> ⁻	8.9	4.3	-20.4	-29.2
<i>S</i> ₂ <i>O</i> ₃ ⁻²	8.9	5.0	-12.9	-17.8
<i>O</i> ₂ <i>S</i> ₂ <i>O</i> ₃ ⁻²	12.6	7.5	-10.3	-12.9

Table S5. Reaction force Works (in Kcal/mol) involved in the nucleophilic substitution of acetochlor

<i>Nucleophile</i>	<i>w1</i>	<i>w2</i>	<i>w3</i>	<i>w4</i>
<i>Br</i> ⁻	13.2	7.7	-11.1	-14.2
<i>I</i> ⁻	11.7	8.1	-4.6	-7.7
<i>HS</i> ⁻	8.7	4.5	-19.6	-26.1
<i>S</i> ₂ <i>O</i> ₃ ⁻²	8.7	5.0	-12.9	-17.3
<i>O</i> ₂ <i>S</i> ₂ <i>O</i> ₃ ⁻²	12.6	7.5	-10.4	-12.8

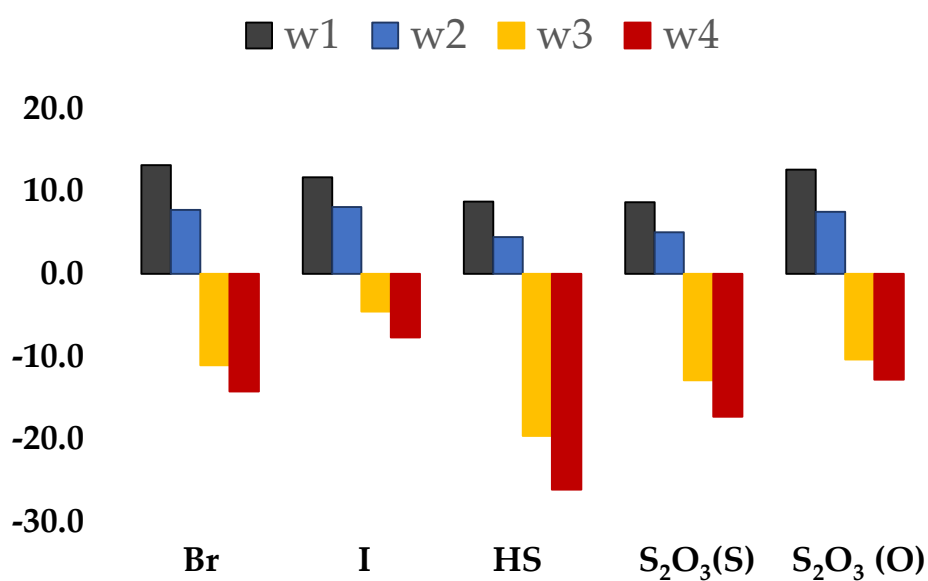


Figure S4. Reaction force work 1 and 2 for the nucleophilic substitution reaction of acetochlor.

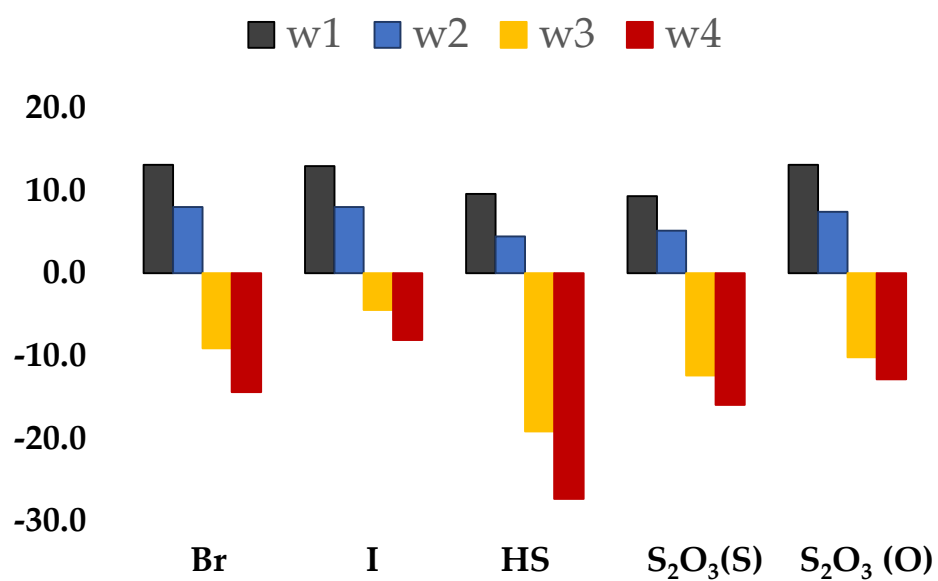


Figure S5. Reaction force work 1 and 2 for the nucleophilic substitution reaction of metolachlor.

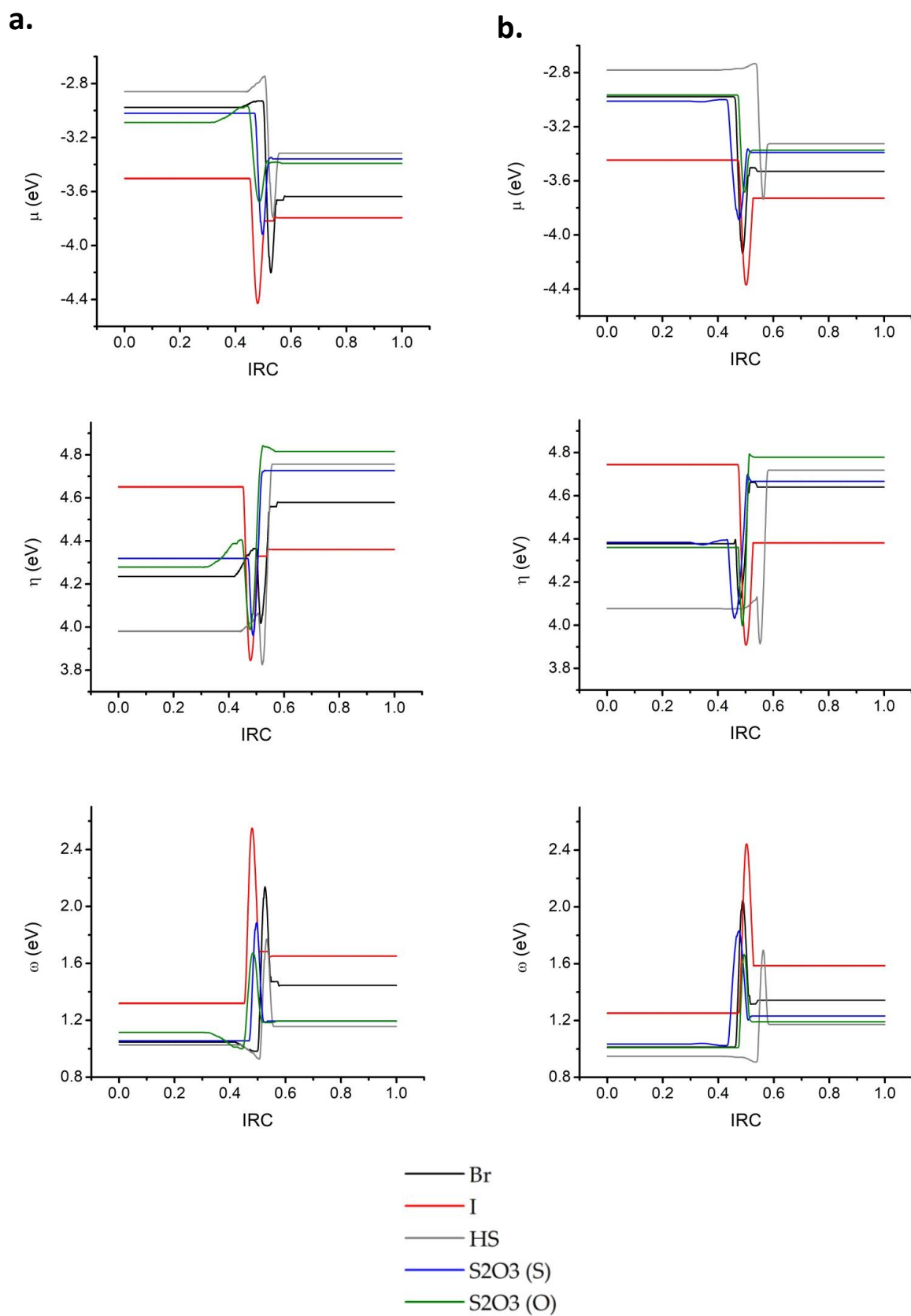


Figure S6. μ , η , and ω plots for the nucleophilic substitution of alachlor (a) and propachlor (b).

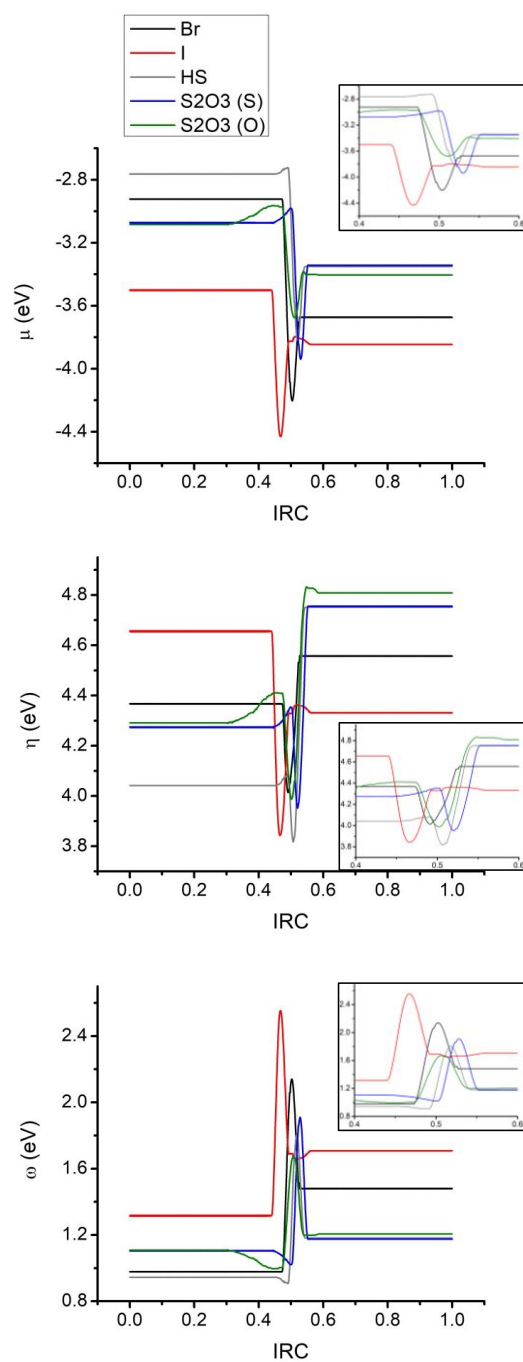


Figure S7. μ , η , and ω plots for the nucleophilic substitution of acetochlor.

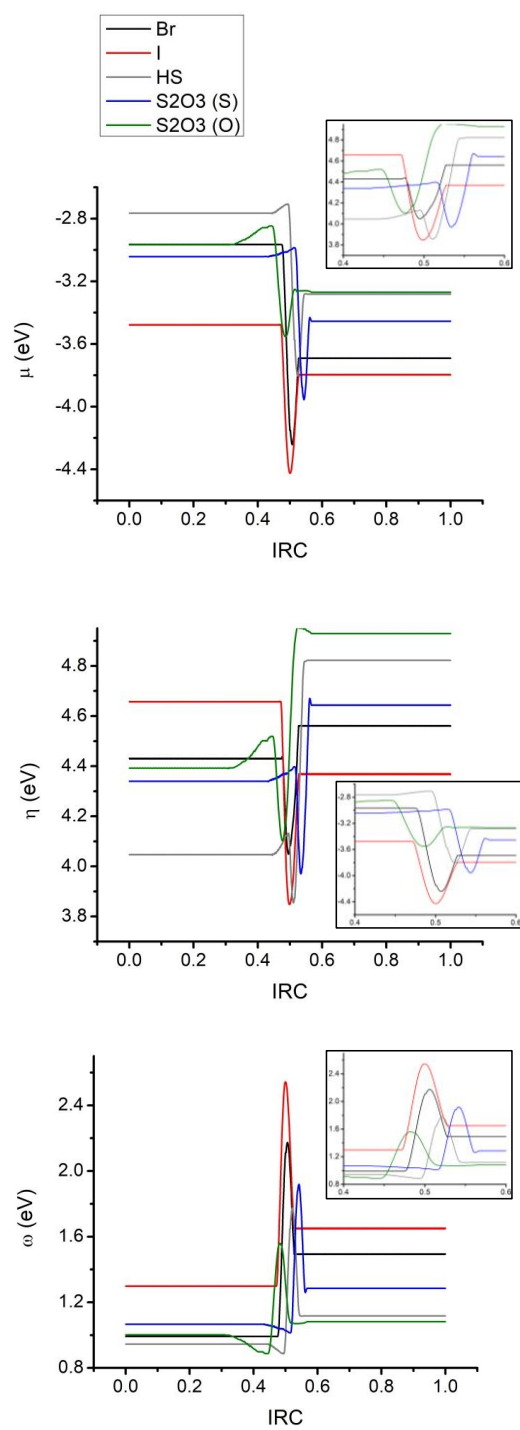


Figure S8. μ , η , and ω plots for the nucleophilic substitution of metolachlor.

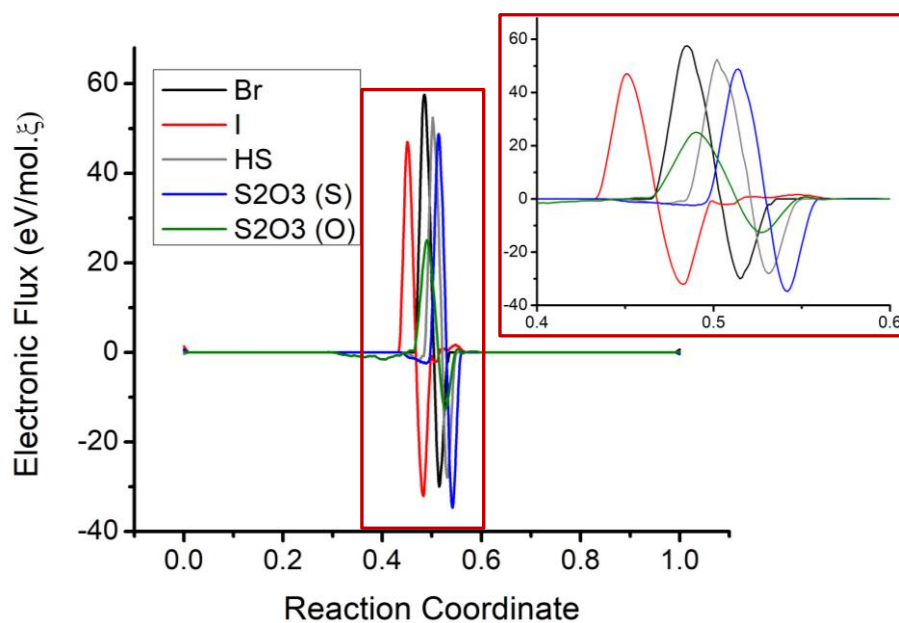


Figure S9. REF plots for the nucleophilic substitution of acetochlor.

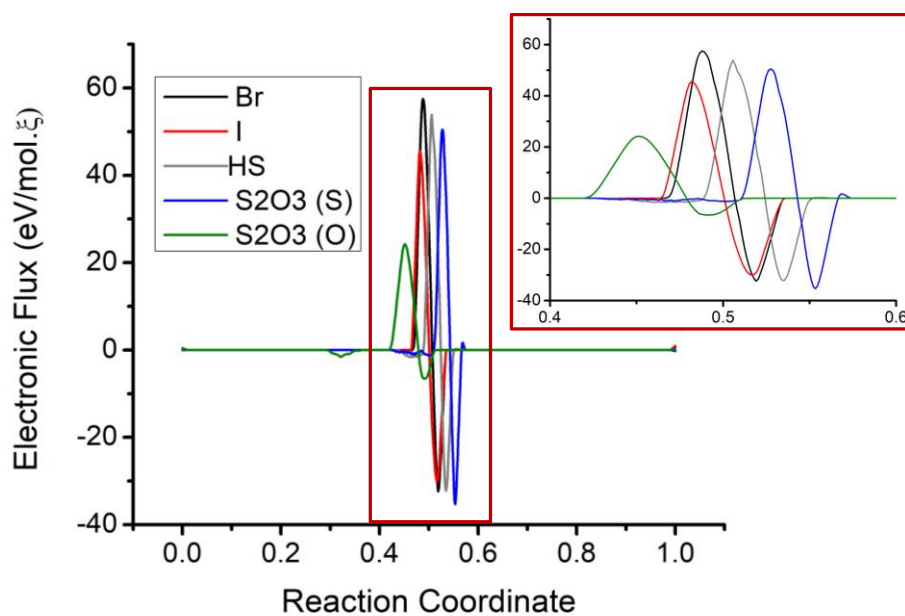


Figure S10. REF plots for the nucleophilic substitution of metolachlor.

Table S6. Charge analysis of the nucleophilic attack mechanism of Acetochlor

Nucleophile		Cl	C	Nu
Br ⁻	<i>R</i>	-0.123	-0.397	-1.000
	<i>TS</i>	-0.577	-0.330	-0.576
	<i>P</i>	-1.000	-0.489	-0.034
	δQi	0.454	-0.067	-0.424
I ⁻	<i>R</i>	-0.123	-0.397	-1.000
	<i>TS</i>	-0.622	-0.382	-0.500
	<i>P</i>	-1.000	-0.630	0.108
	δQi	0.499	-0.015	-0.500
HS ⁻	<i>R</i>	-0.123	-0.397	-1.108
	<i>TS</i>	-0.509	-0.356	-0.744
	<i>P</i>	-1.000	-0.557	-0.121
	δQi	0.386	-0.041	-0.364
S ₂ O ₃ ²⁻ (S)	<i>R</i>	-0.123	-0.397	-0.843
	<i>TS</i>	-0.541	-0.356	-0.545
	<i>P</i>	-1.000	-0.584	-0.089
	δQi	0.418	-0.041	-0.298
S ₂ O ₃ ²⁻ (O)	<i>R</i>	-0.123	-0.397	-1.125
	<i>TS</i>	-0.606	-0.183	-0.981
	<i>P</i>	-1.000	-0.131	-0.794
	δQi	0.483	-0.214	-0.144

Table S7. Charge analysis of the nucleophilic attack mechanism of Alachlor

Nucleophile		Cl	C	Nu
Br ⁻	<i>R</i>	-0.123	-0.396	-1.000
	<i>TS</i>	-0.578	-0.329	-0.576
	<i>P</i>	-1.000	-0.488	-0.033
	δQi	0.455	-0.067	-0.424
I ⁻	<i>R</i>	-0.123	-0.396	-1.000
	<i>TS</i>	-0.621	-0.381	-0.500
	<i>P</i>	-1.000	-0.629	0.108
	δQi	0.498	-0.015	-0.500
HS ⁻	<i>R</i>	-0.123	-0.396	-1.108

	<i>TS</i>	-0.497	-0.357	-0.746
	<i>P</i>	-1.000	-0.558	-0.120
	δQi	0.374	-0.039	-0.362
S₂O₃⁻² (S)	<i>R</i>	-0.123	-0.396	-0.843
	<i>TS</i>	-0.539	-0.354	-0.544
	<i>P</i>	-1.000	-0.584	-0.089
	δQi	0.416	-0.042	-0.299
S₂O₃⁻² (O)	<i>R</i>	-0.123	-0.396	-1.125
	<i>TS</i>	-0.607	-0.181	-0.981
	<i>P</i>	-1.000	-0.131	-0.794
	δQi	0.484	-0.215	-0.144

Table S8. Charge analysis of the nucleophilic attack mechanism of Metolachlor

Nucleophile		Cl	C	Nu
Br⁻	<i>R</i>	-0.124	-0.391	-1.000
	<i>TS</i>	-0.586	-0.325	-0.569
	<i>P</i>	-1.000	-0.483	-0.035
	δQi	0.462	-0.066	-0.431
I⁻	<i>R</i>	-0.124	-0.391	-1.000
	<i>TS</i>	-0.629	-0.375	-0.497
	<i>P</i>	-1.000	-0.624	0.107
	δQi	0.505	-0.016	-0.503
HS⁻	<i>R</i>	-0.124	-0.391	-1.108
	<i>TS</i>	-0.511	-0.349	-0.737
	<i>P</i>	-1.000	-0.552	-0.122
	δQi	0.387	-0.042	-0.371
S₂O₃⁻² (S)	<i>R</i>	-0.124	-0.391	-0.843
	<i>TS</i>	-0.555	-0.349	-0.551
	<i>P</i>	-1.000	-0.579	-0.088
	δQi	0.431	-0.042	-0.292
S₂O₃⁻² (O)	<i>R</i>	-0.124	-0.391	-1.125
	<i>TS</i>	-0.616	-0.179	-0.989
	<i>P</i>	-1.000	-0.129	-0.794
	δQi	0.492	-0.212	-0.136

Table S9. Charge analysis of the nucleophilic attack mechanism of Propachlor

Nucleophile		Cl	C	Nu
Br ⁻	<i>R</i>	-0.128	-0.394	-1.000
	<i>TS</i>	-0.586	-0.321	-0.581
	<i>P</i>	-1.000	-0.486	-0.040
	δQi	0.458	-0.073	-0.419
I ⁻	<i>R</i>	-0.128	-0.394	-1.000
	<i>TS</i>	-0.631	-0.372	-0.503
	<i>P</i>	-1.000	-0.633	0.098
	δQi	0.503	-0.022	-0.497
HS ⁻	<i>R</i>	-0.128	-0.394	-1.108
	<i>TS</i>	-0.509	-0.345	-0.740
	<i>P</i>	-1.000	-0.556	-0.123
	δQi	0.381	-0.049	-0.368
S ₂ O ₃ ²⁻ (S)	<i>R</i>	-0.128	-0.394	-0.843
	<i>TS</i>	-0.561	-0.345	-0.548
	<i>P</i>	-1.000	-0.583	-0.090
	δQi	0.433	-0.049	-0.295
S ₂ O ₃ ²⁻ (O)	<i>R</i>	-0.128	-0.394	-1.125
	<i>TS</i>	-0.623	-0.174	-0.987
	<i>P</i>	-1.000	-0.130	-0.793
	δQi	0.495	-0.220	-0.138

Table S10.Wiberg bond indexes (Bi), evolution percent, synchronicity (Sy) and average value (%Evav) for the nucleophilic substitution of acetochlor

		Wiberg bond index (Bi)	Sy	%Evav	
Br ⁻		$B_{(C-Cl)}$	$B_{(C-Nu)}$		
	<i>R</i>	0.979	0.000		
	<i>TS</i>	0.453	0.437	0.904	48.9
	<i>P</i>	0.000	0.987		
	% <i>Evi</i>	53.67	44.23		
I ⁻		$B_{(C-Cl)}$	$B_{(C-Nu)}$		
	<i>R</i>	0.979	0.000		
	<i>TS</i>	0.384	0.513	0.928	56.7
	<i>P</i>	0.000	0.974		
	% <i>Evi</i>	60.80	52.61		

HS⁻		<i>B_(C-Cl)</i>	<i>B_(C-Nu)</i>	0.897	41.8
	<i>R</i>	0.979	0.000		
	<i>TS</i>	0.528	0.376		
	<i>P</i>	0.000	1.003		
	<i>%Evi</i>	46.09	37.46		
S₂O₃²⁻ (S)		<i>B_(C-Cl)</i>	<i>B_(C-Nu)</i>	0.892	45.2
	<i>R</i>	0.979	0.000		
	<i>TS</i>	0.489	0.398		
	<i>P</i>	0.000	0.987		
	<i>%Evi</i>	50.08	40.35		
S₂O₃²⁻ (O)		<i>B_(C-Cl)</i>	<i>B_(C-Nu)</i>	0.839	45.7
	<i>R</i>	0.979	0.000		
	<i>TS</i>	0.460	0.331		
	<i>P</i>	0.000	0.863		
	<i>%Evi</i>	53.03	38.32		

Table S11.Wiberg bond indexes (Bi), evolution percent, synchronicity (Sy) and average value (%Evav) for the nucleophilic substitution of alachlor

		Wiberg bond index (Bi)		Sy	%Evav
Br⁻		<i>B_(C-Cl)</i>	<i>B_(C-Nu)</i>	0.904	49.1
	<i>R</i>	0.978	0.000		
	<i>TS</i>	0.452	0.438		
	<i>P</i>	0.000	0.987		
	<i>%Evi</i>	53.80	44.41		
I⁻		<i>B_(C-Cl)</i>	<i>B_(C-Nu)</i>	0.928	56.8
	<i>R</i>	0.978	0.000		
	<i>TS</i>	0.383	0.513		
	<i>P</i>	0.000	0.974		
	<i>%Evi</i>	60.82	52.69		
HS⁻		<i>B_(C-Cl)</i>	<i>B_(C-Nu)</i>	0.899	40.8
	<i>R</i>	0.978	0.000		
	<i>TS</i>	0.539	0.368		
	<i>P</i>	0.000	1.002		
	<i>%Evi</i>	44.93	36.69		
S₂O₃²⁻ (S)		<i>B_(C-Cl)</i>	<i>B_(C-Nu)</i>	0.892	45.0
	<i>R</i>	0.978	0.000		
	<i>TS</i>	0.490	0.397		

	<i>P</i>	0.000	0.987		
	% <i>Evi</i>	49.92	40.18		
		<i>B</i> _(C-Cl)	<i>B</i> _(C-Nu)		
	<i>R</i>	0.978	0.000		
S₂O₃²⁻ (O)	<i>TS</i>	0.459	0.331	0.839	45.8
	<i>P</i>	0.000	0.862		
	% <i>Evi</i>	53.11	38.40		

Table S12. Wiberg bond indexes (Bi), evolution percent, synchronicity (Sy) and average value (%Evav) for the nucleophilic substitution of metolachlor

		Wiberg bond index (Bi)		Sy	%Evav
		<i>B</i> _(C-Cl)	<i>B</i> _(C-Nu)		
Br⁻	<i>R</i>	0.976	0.000		
	<i>TS</i>	0.441	0.446	0.904	50.0
	<i>P</i>	0.000	0.985		
	% <i>Evi</i>	54.84	45.21		
		<i>B</i> _(C-Cl)	<i>B</i> _(C-Nu)		
I⁻	<i>R</i>	0.976	0.000		
	<i>TS</i>	0.377	0.517	0.928	57.3
	<i>P</i>	0.000	0.973		
	% <i>Evi</i>	61.40	53.14		
		<i>B</i> _(C-Cl)	<i>B</i> _(C-Nu)		
HS⁻	<i>R</i>	0.976	0.000		
	<i>TS</i>	0.525	0.377	0.898	42.0
	<i>P</i>	0.000	1.001		
	% <i>Evi</i>	46.26	37.67		
		<i>B</i> _(C-Cl)	<i>B</i> _(C-Nu)		
S₂O₃²⁻ (S)	<i>R</i>	0.976	0.000		
	<i>TS</i>	0.474	0.410	0.893	46.5
	<i>P</i>	0.000	0.986		
	% <i>Evi</i>	51.48	41.52		
		<i>B</i> _(C-Cl)	<i>B</i> _(C-Nu)		
S₂O₃²⁻ (O)	<i>R</i>	0.976	0.000		
	<i>TS</i>	0.446	0.333	0.832	46.5
	<i>P</i>	0.000	0.860		
	% <i>Evi</i>	54.28	38.65		

Table S13.Wiberg bond indexes (Bi), evolution percent, synchronicity (Sy) and average value (%Evav) for the nucleophilic substitution of propachlor

		Wiberg bond index (Bi)		Sy	%Evav
		$B_{(C-Cl)}$	$B_{(C-Nu)}$		
Br⁻	<i>R</i>	0.978	0.000	0.903	49.2
	<i>TS</i>	0.450	0.438		
	<i>P</i>	0.000	0.987		
	<i>%Evi</i>	53.94	44.38		
		$B_{(C-Cl)}$	$B_{(C-Nu)}$		
I⁻	<i>R</i>	0.978	0.000	0.917	56.4
	<i>TS</i>	0.381	0.512		
	<i>P</i>	0.000	0.991		
	<i>%Evi</i>	61.03	51.70		
		$B_{(C-Cl)}$	$B_{(C-Nu)}$		
HS⁻	<i>R</i>	0.978	0.000	0.895	41.2
	<i>TS</i>	0.532	0.370		
	<i>P</i>	0.000	1.004		
	<i>%Evi</i>	45.56	36.87		
		$B_{(C-Cl)}$	$B_{(C-Nu)}$		
S₂O₃²⁻ (S)	<i>R</i>	0.978	0.000	0.892	46.4
	<i>TS</i>	0.475	0.409		
	<i>P</i>	0.000	0.989		
	<i>%Evi</i>	51.39	41.35		
		$B_{(C-Cl)}$	$B_{(C-Nu)}$		
S₂O₃²⁻ (O)	<i>R</i>	0.978	0.000	0.833	46.5
	<i>TS</i>	0.447	0.334		
	<i>P</i>	0.000	0.862		
	<i>%Evi</i>	54.24	38.73		