ELECTRONIC SUPPORTING INFORMATION

Halonium, Chalconium, and Pnictonium Salts as Noncovalent Organocatalysts: A Computational Study on Relative Catalytic Activity

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Table of contents

Table S1. Calculated values of total electronic energies, enthalpies, and Gibbs free energies of activation ($\Delta E^{\neq}$, $\Delta H^{\neq}$, and $\Delta G^{\neq}$ in kJ mol^{-1}) for model reactions (**Method 1**).

Model reaction	$\Delta E^{\neq}$	$\Delta H^{\neq}$	$\Delta G^{\neq}$
$CH_3Cl + H_2O \rightarrow$ **TS1**	252.5	257.4	293.4
1 + $CH_3Cl + H_2O \rightarrow$ **1···TS1**	108.2	118.2	206.6
2 + $CH_3Cl + H_2O \rightarrow$ **2···TS1**	69.9	81.8	177.2
3 + $CH_3Cl + H_2O \rightarrow$ **3···TS1**	50.8	61.5	154.6
4 + $CH_3Cl + H_2O \rightarrow$ **4···TS1**	92.2	101.3	184.2
5 + $CH_3Cl + H_2O \rightarrow$ **5···TS1**	63.9	77.5	160.2
6 + $CH_3Cl + H_2O \rightarrow$ **6···TS1**	61.5	73.5	153.3
7 + $CH_3Cl + H_2O \rightarrow$ **7···TS1**	76.2	88.3	163.3
8 + $CH_3Cl + H_2O \rightarrow$ **8···TS1**	59.5	71.5	149.9
9 + $CH_3Cl + H_2O \rightarrow$ **9···TS1**	51.0	63.1	142.2
$H_2O + NH_3 + Me_2CO \rightarrow$ **TS2**	-10.6	-8.5	94.5
1 + $H_2O + NH_3 + Me_2CO \rightarrow$ **1···TS2**	-105.2	-96.8	63.1
2 + $H_2O + NH_3 + Me_2CO \rightarrow$ **2···TS2**	-140.9	-131.6	32.5
3 + $H_2O + NH_3 + Me_2CO \rightarrow$ **3···TS2**	-154.4	-147.1	18.5
4 + $H_2O + NH_3 + Me_2CO \rightarrow$ **4···TS2**	-120.9	-110.7	46.2
5 + $H_2O + NH_3 + Me_2CO \rightarrow$ **5···TS2**	-160.2	-149.6	10.7
6 + $H_2O + NH_3 + Me_2CO \rightarrow$ **6···TS2**	-152.2	-141.6	17.5
7 + $H_2O + NH_3 + Me_2CO \rightarrow$ **7···TS2**	-122.8	-112.5	35.4
8 + $H_2O + NH_3 + Me_2CO \rightarrow$ **8···TS2**	-142.5	-133.8	17.0
9 + $H_2O + NH_3 + Me_2CO \rightarrow$ **9···TS2**	-144.2	-134.6	13.3

Table S2. Calculated total electronic energies (E, in Hartree), enthalpies (H, in Hartree), Gibbs free energies (G, in Hartree), and entropies (S, cal/mol•K) for optimized equilibrium model structures (**Method 1**).

Model structure	E	H	G	S
CH_3Cl	-500.045423591	-500.002975	-500.029526	55.880
H_2O	-76.3733781385	-76.348059	-76.369493	45.112
NH_3	-56.5129432676	-56.474244	-56.496081	45.960
Me_2CO	-193.057343796	-192.966042	-193.000966	73.503
1	-1266.12783251	-1265.757874	-1265.827382	146.291
2	-3158.59676668	-3158.227463	-3158.299393	151.390
3	-930.159409533	-929.791625	-929.866364	157.302
4	-1091.36335793	-1091.092010	-1091.149704	121.428
5	-3092.65033011	-3092.379263	-3092.437972	123.563
6	-701.238385649	-700.968565	-701.029098	127.403
7	-921.752039426	-921.579216	-921.624391	95.079
8	-3033.37840425	-3033.205520	-3033.251785	97.374
9	-472.960287924	-472.788086	-472.835650	100.106
TS1	-576.322630312	-576.253009	-576.287275	72.119
1···TS1	-1842.50543382	-1842.063891	-1842.147714	176.420
2···TS1	-3734.98893299	-3734.547345	-3734.630907	175.871
3···TS1	-1506.55885228	-1506.119247	-1506.206494	183.627
4···TS1	-1667.74703571	-1667.404476	-1667.478572	155.948
5···TS1	-3669.04481092	-3668.700797	-3668.775960	158.194
6···TS1	-1277.63377319	-1277.291596	-1277.369711	164.407
7···TS1	-1498.14180729	-1497.896633	-1497.961220	135.934
8···TS1	-3609.77453667	-3609.529324	-3609.593697	135.485
9···TS1	-1049.35968192	-1049.115087	-1049.180493	137.659
TS2	-325.947695904	-325.791587	-325.830551	82.007
1···TS2	-1592.11155657	-1591.583074	-1591.669874	182.686
2···TS2	-3484.59410733	-3484.065932	-3484.153543	184.393
3···TS2	-1256.16187671	-1255.635987	-1255.725870	189.176
4···TS2	-1417.35308516	-1416.922522	-1416.998651	160.226
5···TS2	-3418.65502473	-3418.224586	-3418.300428	159.623
6···TS2	-1027.24001632	-1026.810841	-1026.888987	164.471
7···TS2	-1247.74248481	-1247.410409	-1247.477462	141.125
8···TS2	-3359.37633956	-3359.044840	-3359.111861	141.057
9···TS2	-798.958861144	-798.627710	-798.697117	146.078

Table S3. Calculated values of total electronic energies of activation ($\Delta E^{\neq}$ in kJ/mol) for model reactions at the M06-2X/MWB46 for Sb, Te, and I; 6-311G* for other atoms (single point calculations) // M06-2X/MWB46 for Sb, Te, and I; 6-31G* for other atoms (full geometry optimization) level of theory (**Method 2**).

Model reaction	$\Delta E^{\neq}$
$CH_3Cl + H_2O \rightarrow$ **TS1**	235.6
1 + $CH_3Cl + H_2O \rightarrow$ **1···TS1**	97.8
2 + $CH_3Cl + H_2O \rightarrow$ **2···TS1**	86.9
3 + $CH_3Cl + H_2O \rightarrow$ **3···TS1**	45.1
4 + $CH_3Cl + H_2O \rightarrow$ **4···TS1**	80.0
5 + $CH_3Cl + H_2O \rightarrow$ **5···TS1**	76.7
6 + $CH_3Cl + H_2O \rightarrow$ **6···TS1**	53.4
7 + $CH_3Cl + H_2O \rightarrow$ **7···TS1**	66.9
8 + $CH_3Cl + H_2O \rightarrow$ **8···TS1**	57.5
9 + $CH_3Cl + H_2O \rightarrow$ **9···TS1**	43.9
$H_2O + NH_3 + Me_2CO \rightarrow$ **TS2**	-7.6
1 + $H_2O + NH_3 + Me_2CO \rightarrow$ **1···TS2**	-100.7
2 + $H_2O + NH_3 + Me_2CO \rightarrow$ **2···TS2**	-110.9
3 + $H_2O + NH_3 + Me_2CO \rightarrow$ **3···TS2**	-147.8
4 + $H_2O + NH_3 + Me_2CO \rightarrow$ **4···TS2**	-120.5
5 + $H_2O + NH_3 + Me_2CO \rightarrow$ **5···TS2**	-127.0
6 + $H_2O + NH_3 + Me_2CO \rightarrow$ **6···TS2**	-150.4
7 + $H_2O + NH_3 + Me_2CO \rightarrow$ **7···TS2**	-120.4
8 + $H_2O + NH_3 + Me_2CO \rightarrow$ **8···TS2**	-120.4
9 + $H_2O + NH_3 + Me_2CO \rightarrow$ **9···TS2**	-138.4

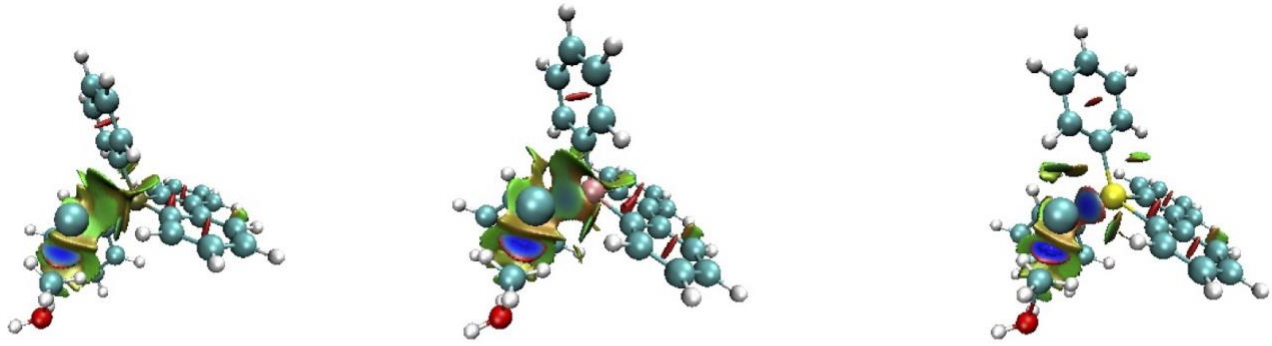
Table S4. Calculated total electronic energies (E, in Hartree) for model structures at the M06-2X/MWB46 for Sb, Te, and I; 6-311G* for other atoms (single point calculations) // M06-2X/MWB46 for Sb, Te, and I; 6-31G* for other atoms (full geometry optimization) level of theory (**Method 2**).

Model structure	E
CH_3Cl	-500.088390368
H_2O	-76.3992479578
NH_3	-56.5331544923
Me_2CO	-193.110607217
1	-1266.35325710
2	-3160.84548733
3	-930.362495636
4	-1091.54113600
5	-3094.90541799
6	-701.390320287
7	-921.880663921
8	-3035.86476051
9	-473.058566934
TS1	-576.397921387
1···TS1	-1842.80365191
2···TS1	-3737.30002302
3···TS1	-1506.83295292
4···TS1	-1667.99829928
5···TS1	-3671.36384466
6···TS1	-1277.85763388
7···TS1	-1498.34283600
8···TS1	-3612.33048656
9···TS1	-1049.52948570
TS2	-326.045892600
1···TS2	-1592.43460333
2···TS2	-3486.93074864
3···TS2	-1256.46181762
4···TS2	-1417.63002728
5···TS2	-3420.99681132
6···TS2	-1027.49062991
7···TS2	-1247.96954398
8···TS2	-3361.95364130
9···TS2	-799.154275002

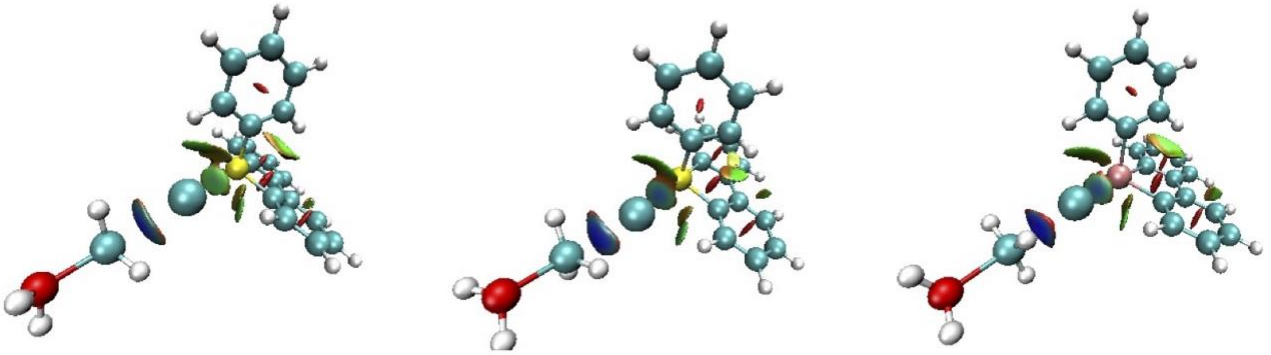
Table S5. Values of the density of all electrons – $\rho(\mathbf{r})$, Laplacian of electron density – $\nabla^2\rho(\mathbf{r})$, energy density – H_b, potential energy density – $V(\mathbf{r})$, Lagrangian kinetic energy – $G(\mathbf{r})$, and electron localization function – ELF (a.u.) at the bond critical points (3, –1) for contacts X···Y (X = P, As, Sb, S, Sb, Te, Cl, Br, I,; Y = Cl in **TS1** and O in **TS2**) as well as approximately estimated strength of these noncovalent interactions $E_{int} = -V(\mathbf{r})/2$ (kJ/mol).

Length of contacts X···Y	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	H_b	$V(\mathbf{r})$	$G(\mathbf{r})$	ELF	$-G(\mathbf{r})/V(\mathbf{r})$	E_{int}
1···**TS1** 3.404 Å	0.011	0.028	0.001	-0.006	0.006	0.053	1.00	7.9
2···**TS1** 3.069 Å	0.019	0.046	0.000	-0.011	0.012	0.107	1.09	14.4
3···**TS1** 2.917 Å	0.032	0.097	-0.002	-0.017	0.015	0.243	0.88	22.3
4···**TS1** 3.154 Å	0.015	0.049	0.001	-0.009	0.011	0.062	1.22	11.8
5···**TS1** 2.976 Å	0.023	0.065	0.001	-0.014	0.015	0.107	1.07	18.4
6···**TS1** 3.074 Å	0.023	0.078	0.000	-0.014	0.014	0.109	1.00	18.4
7···**TS1** 2.968 Å	0.019	0.070	0.002	-0.013	0.015	0.064	1.15	17.1
8···**TS1** 2.958 Å	0.023	0.073	0.002	-0.014	0.016	0.094	1.14	18.4
9···**TS1** 3.051 Å	0.024	0.086	0.001	-0.015	0.016	0.096	1.07	19.7
1···**TS2** 3.070 Å	Bond critical point for P···O contact was not found							
2···**TS2** 2.678 Å	0.023	0.066	-0.001	-0.019	0.018	0.089	0.95	24.9
3···**TS2** 2.406 Å	0.056	0.226	-0.004	-0.034	0.030	0.300	0.88	44.6
4···**TS2** 2.797 Å	0.018	0.060	0.000	-0.014	0.015	0.054	1.07	18.4
5···**TS2** 2.775 Å	0.020	0.067	0.000	-0.016	0.016	0.067	1.00	21.0
6···**TS2** 2.747 Å	0.027	0.105	-0.001	-0.020	0.019	0.101	0.95	26.3
7···**TS2** 2.699 Å	0.021	0.078	0.001	-0.018	0.019	0.060	1.06	23.6
8···**TS2** 2.627 Å	0.030	0.095	0.000	-0.024	0.024	0.114	1.00	31.5
9···**TS2** 2.579 Å	0.040	0.164	-0.001	-0.031	0.030	0.144	0.97	40.7

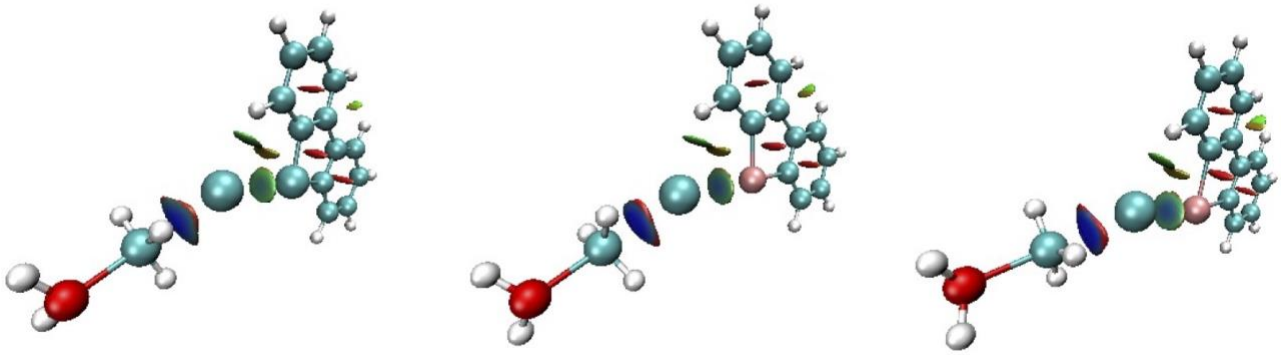
NCI plots for the catalyst···TS1 species



1···TS1 **2···TS1** **3···TS1**

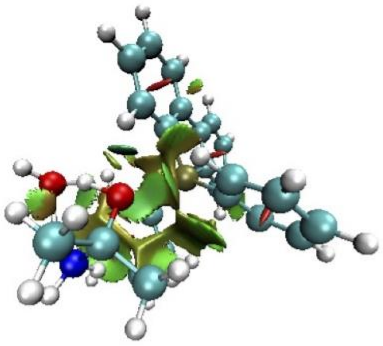


4···TS1 **5···TS1** **6···TS1**

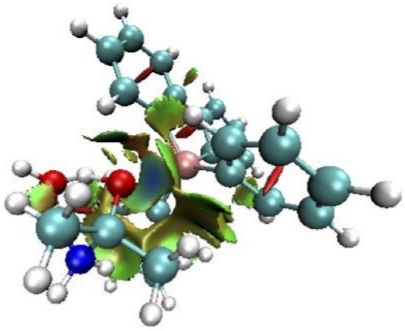


7···TS1 **8···TS1** **9···TS1**

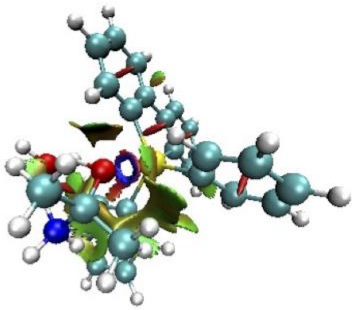
NCI plots for the catalyst···TS2 species



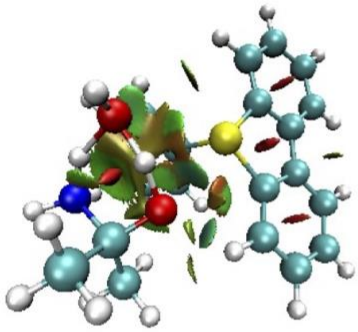
1···TS2



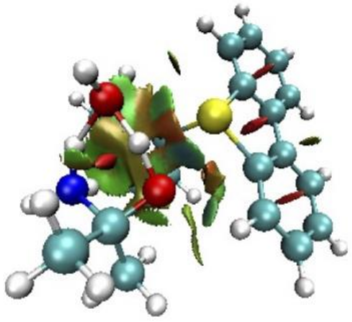
2···TS2



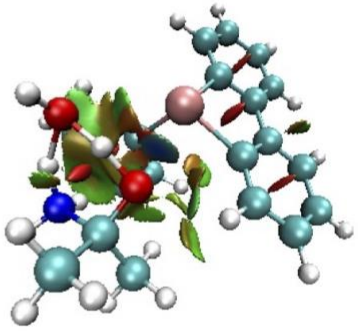
3···TS2



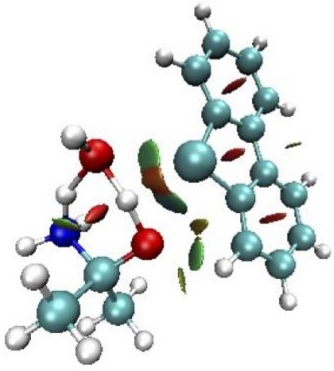
4···TS2



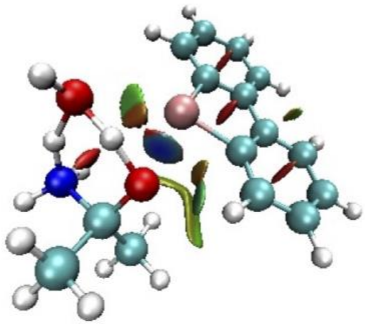
5···TS2



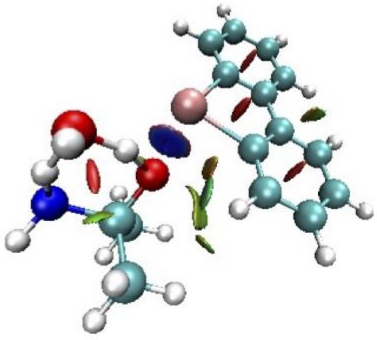
6···TS2



7···TS2



8···TS2



9···TS2

Table S6. Calculated values of total electronic energies of activation ($\Delta E^{\neq}$ in kJ/mol) for selected model reactions at the M06-2X/MWB46 for Sb, Te, and I; aug-cc-pVTZ for other atoms (single point calculations) // M06-2X/MWB46 for Sb, Te, and I; 6-31G* for other atoms (full geometry optimization) level of theory.

Model reaction	$\Delta E^{\neq}$
$CH_3Cl + H_2O \rightarrow$ **TS1**	264.6
5 + $CH_3Cl + H_2O \rightarrow$ **5···TS1**	112.7
9 + $CH_3Cl + H_2O \rightarrow$ **9···TS1**	73.6
$H_2O + NH_3 + Me_2CO \rightarrow$ **TS2**	22.3
5 + $H_2O + NH_3 + Me_2CO \rightarrow$ **5···TS2**	-71.9
9 + $H_2O + NH_3 + Me_2CO \rightarrow$ **9···TS2**	-95.5

Table S7. Calculated total electronic energies (E, in Hartree) for model structures at the M06-2X/MWB46 for Sb, Te, and I; aug-cc-pVTZ for other atoms (single point calculations) // M06-2X/MWB46 for Sb, Te, and I; 6-31G* for other atoms (full geometry optimization) level of theory.

Model structure	E
CH_3Cl	-500.108386688
H_2O	-76.430435048
NH_3	-56.553341719
Me_2CO	-193.141728941
5	-3095.085544346
9	-473.142500640
TS1	-576.438049301
5···TS1	-3671.581448575
9···TS1	-1049.653278540
TS2	-326.117020707
5···TS2	-3421.238447412
9···TS2	-799.304392198