

A minimum electrophilicity perspective of the HSAB principle

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Abstract : Some exchange reactions are studied, both at the gas and the solution phases, at the B3LYP/6-31+G(d) level of theory. The favourable direction of a reaction as dictated by the HSAB principle often produces the least electrophilic species. The average electrophilicity of the products is less than that of the reactants in most cases as would have been predicted by a minimum electrophilicity principle.

Keywords : DFT, electrophilicity, HSAB principle.

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1. Introduction

Several popular qualitative chemical concepts like electronegativity [1,2], hardness [3-5], electrophilicity [6] *etc.* have been introduced into the chemistry vocabulary to explain various aspects of chemical bonding and reactivity. Pauling [1] introduced the concept of electronegativity as "the power of an atom in a molecule to attract electron itself" which was later made use of by Sanderson [7] to propose his electronegativity equalization principle [7] which states that, "the electronegativities of all the constituent atoms in a molecule have the same value which can be expressed as the geometric mean of the electronegativity value of the associated isolated atoms". The concept of hardness was introduced by Pearson [3] in the context of his famous hard-soft acids and bases (HSAB) principle [8] which may be stated as, "hard acids prefer to coordinate with hard bases and soft acids prefer to coordinate with soft bases for both their thermodynamic and kinetic properties". Different organic reactions have been analyzed through the behaviour of molecules in terms of their electrophilic ('electron loving') and nucleophilic ('nucleus loving') nature originally proposed by Ingold [9].

Conceptual density functional theory (CDFT) [10] has been quite successful in

providing theoretical definitions of these qualitative concepts and the associated electronic structure principles. For an N-electron system with total energy E , the electronegativity (χ) is defined as [2]

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(r)} \quad (1)$$

where μ and $v(r)$ are the chemical and external potentials respectively.

The hardness (η) of that system is defined as [5]

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(r)} \quad (2)$$

Parr *et al* [6(a)] have made use of the above definitions of χ and η to variationally obtain the following quantitative definition of the electrophilicity (ω), originally suggested by Maynard and coworkers [11],

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta} \quad (3)$$

Attempts have been made to theoretically justify the electronegativity equalization principle [2] and the HSAB principle [12,13] as well as other structure principles. Another hardness related principle is the maximum hardness principle (MHP) [14] which may be stated as, "there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible". Owing to the inverse relationships between hardness and polarizability [15] (magnetizability as well) a minimum polarizability principle (MPP) [16] and a minimum magnetizability principle (MMP) [17] have been proposed.

It has been observed through the analysis of some selected molecular vibrations, internal rotations and chemical reactions that the electrophilicity ω often corresponds to a minimum value for the equilibrium configurations/conformations, stable systems and favourable processes [18]. To be precise, the change in ω associated with any physico-chemical process and attainment of an extremum may be analyzed through the following derivative :

$$\frac{\partial \omega}{\partial y} = \frac{\mu}{\eta} \left(\frac{\partial \mu}{\partial y} \right) - \frac{1}{2} \left(\frac{\mu}{\eta} \right)^2 \left(\frac{\partial \eta}{\partial y} \right) \quad (4)$$

where y may be a bond length (a stretching mode of vibration), bond angle (a bending mode of vibration), dihedral angle (internal rotation) or a reaction coordinate (chemical reaction). The extremal behaviour of ω would be dictated by that of μ and η . Note that if both μ and η attain their extremum (maximum or minimum) values for a given y , ω would also be an extremum at that point. It can be easily shown that the corresponding slopes of μ and η changes will be of opposite sign. According to the MHP [14] when

μ remains constant ($(\partial\mu/\partial y) = 0$) and hardness gets maximized ($(\partial\omega/\partial y) = 0$) the system attains a stable state which corresponds to an extremal situation for ω which has been numerically verified to be a minimum for a stable state or a favourable process.

It has been shown that the HSAB principle is in conformity with the MHP [12,13,19,20] as well as the MPP [12(d),16(b)]. In the present work we would like to analyze whether the HSAB principle is compatible with a minimum electrophilicity principle (MEP).

2. Exchange reactions in the gas phase :

Ten selected exchange reactions are studied in the gas phase at the B3LYP/6-31+G(d) level of theory. The forward direction of the reactions are considered to be associated with the negative reaction enthalpy values [20] which coincide with that dictated by the HSAB principle. In fact these directions are shown to be favourable in terms of both ΔE and ΔH values. Required χ and η values are obtained through the following approximate formulas derived by using a finite difference approximation and Koopmans' theorem:

$$\chi = \frac{(IP + EA)}{2}; \quad \eta = \frac{(IP - EA)}{2} \quad (5)$$

$$IP \approx -E_{\text{HOMO}}; \quad EA \approx -E_{\text{LUMO}}$$

$$\chi = -\frac{1}{2}(E_{\text{LUMO}} + E_{\text{HOMO}}); \quad \eta = \frac{1}{2}(E_{\text{LUMO}} - E_{\text{HOMO}}). \quad (6)$$

Table 1 presents different reactivity descriptors for the molecules present in the studied exchange reactions. As it is shown in Table 2, ΔE values are negative in all cases like the corresponding ΔH values. As prescribed by the MHP [14], $\Delta\eta$ values are positive [20] in all cases. Out of the four molecules involved in a reaction one with the least ω value often (two exceptions) lies in the product side and $\Delta\omega$ is negative in seven reactions. Three exceptions in the latter includes the two obtained in the former. In order to check whether the individual electrophilicity values change with the variation in the level of calculation we calculate the CDFT reactivity descriptors for HF and HCl (Tables 3 and 4) at various levels of theory which are then compared with other available data [20–23]. Wide variation in these values is easily discernible.

3. Exchange reactions in the aqueous phase :

Since most of the reactions were studied experimentally in the aqueous phase we analyze the selected ten reactions within the same level of theory in the aqueous phase as well. Table 5 presents various CDFT reactivity descriptors of all the molecules involved in those reactions. It is transparent that not only the numerical values change as we move from the gas phase to the solution phase the qualitative trends also get

Table 1. Properties of the molecules involved in the exchange reactions (gas phase):

Molecule	IP (eV)	EA (eV)	Energy (<i>E</i> , au)	Electronegativity (χ , eV)	Hardness (η , eV)	Electrophilicity (ω , eV)
LiH	5.3228	1.3164	-8.082	3.3196	2.0032	2.7506
LiF	7.6142	1.4772	-107.435	4.5457	3.0685	3.3671
LiCl	6.8907	1.6897	-467.800	4.2902	2.6005	3.5390
LiBr	6.5440	1.7319	-2579.330	4.1380	2.4060	3.5583
NaF	6.5334	1.8669	-262.186	4.2001	2.3333	3.7804
NaCl	6.2733	2.1036	-622.564	4.1884	2.0848	4.2073
KF	5.9106	1.4827	-699.799	3.6966	2.2139	3.0861
KCl	5.6918	1.7801	-1060.180	3.7359	1.9559	3.5681
KBr	5.4782	1.8070	-3171.710	3.6426	1.8356	3.6143
HF	11.4513	-0.9883	-100.443	5.2315	6.2198	2.2001
HCl	9.1828	0.4702	-460.798	4.8265	4.3563	2.6737
HBr	8.4541	0.8321	-2572.310	4.6431	3.8110	2.8284
H ₂	11.808	-2.7234	-1.176	4.5423	7.2658	1.4198
H ₂ O	8.6871	-0.6773	-76.423	4.0049	4.6822	1.7128
CH ₃ F	9.6544	-0.2892	-139.751	4.6826	4.9718	2.2051
CH ₃ SH	6.5818	0.2547	-438.701	3.4183	3.1636	1.8467
CH ₃ SCH ₃	6.0719	-0.1200	-478.018	2.9760	3.0960	1.4303
SiH ₄	9.6756	-0.0204	-291.886	4.8276	4.8480	2.4036
SiH ₃ F	9.6821	0.6305	-391.194	5.1563	4.5258	2.9373
HO ₂	9.1317	2.2791	-175.541	5.7054	3.4263	4.7503

IP = Ionization potential; EA = Electron affinity.

Table 2. Exchange reactions (gas phase):

Reaction : 1	CH ₃ F +	CH ₃ SH =	CH ₃ SCH ₃ +	HF	$\Delta H =$	-12.9000
Energy (<i>E</i> , au)	-139.7510	-438.7010	-478.0180	-100.4430	$\Delta E =$	-0.0090
Electronegativity (χ , eV)	4.6826	3.4183	2.9760	5.2315	$\Delta\chi =$	0.1067
Hardness (η , eV)	4.9718	3.1636	3.0960	6.2198	$\Delta\eta =$	1.1804
Electrophilicity (ω , eV)	2.2149	1.8467	1.4303	2.2001	$\Delta\omega =$	-0.4312
Reaction : 2	LiCl +	NaF =	LiF +	NaCl	$\Delta H =$	-9.5000
Energy (<i>E</i> , au)	-467.8000	-262.1860	-107.4350	-622.5640	$\Delta E =$	-0.0130
Electronegativity (χ , eV)	4.2902	4.2001	4.5457	4.1884	$\Delta\chi =$	0.2438
Hardness (η , eV)	2.6005	2.3333	3.0685	2.0848	$\Delta\eta =$	0.2196
Electrophilicity (ω , eV)	3.5390	2.2038	3.3671	4.2073	$\Delta\omega =$	1.8316
Reaction : 3	LiCl +	KF =	LiF +	KCl	$\Delta H =$	-10.0000
Energy (<i>E</i> , au)	-467.8000	-699.7990	-107.4350	-1060.1800	$\Delta E =$	-0.0151
Electronegativity (χ , eV)	4.2902	3.6966	4.5457	3.7359	$\Delta\chi =$	0.2948
Hardness (η , eV)	2.6005	2.2139	3.0685	1.9559	$\Delta\eta =$	0.2099
Electrophilicity (ω , eV)	3.5390	3.0861	3.3671	2.043	$\Delta\omega =$	-1.2150
Reaction : 4	LiBr +	KF =	LiF +	KBr	$\Delta H =$	-10.5000
Energy (<i>E</i> , au)	-2579.3300	-699.7990	-107.4350	-3171.7100	$\Delta E =$	-0.0160
Electronegativity (χ , eV)	4.1380	3.6966	4.5457	3.6426	$\Delta\chi =$	0.3537
Hardness (η , eV)	2.4060	2.2139	3.0685	1.8356	$\Delta\eta =$	0.2841
Electrophilicity (ω , eV)	3.5583	3.0861	3.3671	3.6143	$\Delta\omega =$	0.3369

Table 2. (Contd)

Reaction 5	LiF +	HBr =	LiBr +	HF	$\Delta H =$	-10 8000
Energy (E , au)	-107 4350	-2572 3100	-2579 3300	-100 4430	$\Delta E =$	-0 0280
Electronegativity (χ , eV)	4 5457	4 6431	4 1380	5 2315	$\Delta\chi =$	0 1807
Hardness (η , eV)	3 0685	3 8110	2 4060	6 2198	$\Delta\eta =$	1 7463
Electrophilicity (ω , eV)	3 3671	2 8284	3 5583	2 2001	$\Delta\omega =$	-0 4371
Reaction 6	NaF +	HCl =	NaCl +	HF	$\Delta H =$	-16 2000
Energy (E , au)	-262 1860	-460 7980	-622 5640	-100 4430	$\Delta E =$	-0 0230
Electronegativity (χ , eV)	4 2001	4 8265	4 1884	5 2315	$\Delta\chi =$	0 3933
Hardness (η , eV)	2 3333	4 3563	2 0848	6 2198	$\Delta\eta =$	1 6150
Electrophilicity (ω , eV)	2 2038	2 6737	4 2073	2 2001	$\Delta\omega =$	1 5299
Reaction 7	SiH ₄ +	HF =	SiH ₃ F +	H ₂	$\Delta H =$	-26 2000
Energy (E , au)	-291 8860	-100 4430	-391 1940	-1 1760	$\Delta E =$	-0 0410
Electronegativity (χ , eV)	4 8276	5 2315	5 156295	4 5423	$\Delta\chi =$	-0 3605
Hardness (η , eV)	4 8156	6 2198	4 507881	7 2658	$\Delta\eta =$	0 7382
Electrophilicity (ω , eV)	2 4036	2 2001	2 937287	1 4198	$\Delta\omega =$	-0 2466
Reaction 8	LiH +	HF =	LiF +	H ₂	$\Delta H =$	-49 0000
Energy (E , au)	-8 0822	-100 4430	-107 4350	-1 1760	$\Delta E =$	-0 0858
Electronegativity (χ , eV)	3 3196	5 2315	4 5457	4 5423	$\Delta\chi =$	0 5369
Hardness (η , eV)	2 0032	6 2198	3 0685	7 2658	$\Delta\eta =$	2 1112
Electrophilicity (ω , eV)	2 7506	2 2001	3 3671	1 4198	$\Delta\omega =$	-0 1638
Reaction 9	HCl +	LiH =	LiCl +	H ₂	$\Delta H =$	-56 1000
Energy (E , au)	-460 7980	-8 0822	-467 8000	-1 1760	$\Delta E =$	-0 0958
Electronegativity (χ , eV)	4 8265	3 3196	4 2902	4 5423	$\Delta\chi =$	0 6864
Hardness (η , eV)	4 3563	2 0032	2 6005	7 2658	$\Delta\eta =$	3 5067
Electrophilicity (ω , eV)	2 6737	2 7506	3 5390	1 4198	$\Delta\omega =$	-0 4655
Reaction 10	HO ₂ +	LiH =	LiF +	H ₂ O	$\Delta H =$	-144 1000
Energy (E , au)	-175 5400	-8 0822	-107 4350	-76 4230	$\Delta E =$	-0 2358
Electronegativity (χ , eV)	5 7054	3 3196	4 5457	4 0049	$\Delta\chi =$	-0 4744
Hardness (η , eV)	3 3920	2 0032	3 0685	4 6822	$\Delta\eta =$	2 3554
Electrophilicity (ω , eV)	4 7503	2 7506	3 3671	1 7128	$\Delta\omega =$	-2 4210

Table 3. Properties of HF molecule at different levels of calculation

Level	IP (eV)	EA (eV)	E (au)	χ (eV)	η (eV)	ω (eV)
HF/6-31G	17 1613	-5 6752	-99 983	5 7431	11 4180	1 4443
HF/6-31+G(d)	17 7303	-5 1960	-100 015	6 2671	11 4630	1 7132
HF/6-311+G**	17 7722	-3 1906	-100 053	7 2908	10 4810	2 5357
HF/6-31+G**	17 7466	-5 2583	-100 024	6 2442	11 5020	1 6948
B3LYP/6-31G	10 2184	-1 2900	-100 404	4 4642	5 7542	1 7317
B3LYP/6-31+G(d)	11 4513	-0 9883	-100 443	5 2315	6 2198	2 2001
B3LYP/6-311+G**	11 5338	-0 0522	-100 482	5 7408	5 7930	2 8445
MNDO ^a				4 77	10 05	1 1320
Experimental ^b	16	-6		5	11	1 1364

^ataken from Reference 20^btaken from Reference 4(b) [Experimental values of ionization potential (IP) and electron affinity (EA) are used]

Table 4. Properties of HCl molecule at different levels of calculation.

Level	IP (eV)	EA (eV)	E (au)	χ (eV)	η (eV)	ω (eV)
HF/6-31G	13.0352	-4.1691	-460.037	4.4331	8.6022	1.1423
HF/6-31+G(d)	12.9910	-2.3692	-460.061	5.3110	7.6802	1.8363
HF/6-311+G**	12.9903	-2.5243	-460.095	5.2330	7.7573	1.7651
HF/6-31+G**	12.9895	-2.3790	-460.067	5.3053	7.6842	1.8314
B3LYP/6-31G	9.0691	0.1088	-460.776	4.5890	4.4801	2.3502
B3LYP/6-31+G(d)	9.1828	0.4702	-460.798	4.8265	4.3563	2.6737
B3LYP/6-311+G**	9.2190	0.3227	-460.834	4.7709	4.4482	2.5585
MNDO ^c				6.04	6.96	2.6208
HF/6-31G(d,p) ^d					7.875	
B3LYP/6-31G(d,p) ^d					8.020	
HF/6-311G***					7.325	
B3LYP/6-311G***					7.475	
B3LYP/6-31++G*** ^f					4.190	
B3LYP/6-31++G*** ^f					6.675	
Experimental ^g	12.7	-3.3		4.7	8	1.3806

^ctaken from Reference 20; ^dtaken from Reference 21; ^etaken from Reference 22; ^ftaken from Reference 23, ^gtaken from Reference 4(b) [Experimental values of ionization potential (IP) and electron affinity (EA) are used] In the References 21–23, $\eta = (I-A)$, where I and A are vertical ionization potential and vertical electron affinity respectively, was used except for the value $\eta = 4.190$ where the frontier orbital energies were used. We have divided their numbers by 2 (*cf.* eq. (5)).

Table 5. Properties of the molecules involved in the exchange reactions (aqueous phase):

Molecule	IP (eV)	EA (eV)	Energy (E , au)	Electronegativity (χ , eV)	Hardness (η , eV)	Electrophilicity (ω , eV)
LiH	5.5786	0.0324	-8.133	2.8055	2.7731	1.4191
LiF	7.8770	0.2411	-107.486	4.0591	3.8180	2.1577
LiCl	7.2985	0.2297	-467.890	3.7641	3.5344	2.0043
LiBr	6.8498	0.2830	-2579.400	3.5664	3.2834	1.9369
NaF	7.8664	0.3004	-262.270	4.0834	3.7830	2.2038
NaCl	7.2006	0.3317	-622.650	3.7661	3.4344	2.0649
KF	7.6735	0.3102	-699.870	3.9918	3.6816	2.1641
KCl	7.1083	0.3328	-1060.300	3.7206	3.3878	2.0430
KBr	6.6928	0.3652	-3171.778	3.5290	3.1638	1.9682
HF	11.216	-1.7716	-100.460	4.7223	6.4939	1.7170
HCl	9.0166	-0.0174	-460.810	4.4996	4.5170	2.2411
HBr	8.2816	0.4343	-2572.300	4.3580	3.9237	2.4201
H ₂	11.806	-2.7507	-1.175	4.5275	7.2781	1.4082
H ₂ O	8.6250	-1.0035	-76.429	3.8108	4.8143	1.5082
CH ₃ F	9.7874	-0.323	-139.750	4.7322	5.0552	2.2149
CH ₃ SH	6.6779	0.1804	-438.700	3.4291	3.2487	1.8098
CH ₃ SCH ₃	6.2646	-0.0805	-478.020	3.0920	3.1725	1.5068
SiH ₄	9.4908	-0.1404	-291.890	4.6752	4.8156	2.2695
SiH ₃ F	9.4274	0.4117	-391.200	4.9196	4.5079	2.6844
HO ^f	8.9238	2.1398	-175.560	5.5318	3.3920	4.5107

IP = Ionization potential; EA = Electron affinity.

altered in some cases Details of these exchange reactions are provided in Table 6 The forward directions are depicted as in Table 2. For three reactions which were

Table 6. Exchange reactions (aqueous phase)

Reaction 1	CH ₃ F +	CH ₃ SH =	CH ₃ SCH ₃ +	HF		
Energy (E, au)	-139 7500	-438 7000	-478 0200	-100 4600	ΔE =	-0 0300
Electronegativity (χ, eV)	4 7322	3 4291	3 092	4 7223	Δχ =	-0 3471
Hardness (η, eV)	5 0552	3 2487	3 1725	6 4939	Δη =	1 3625
Electrophilicity (ω, eV)	2 2149	1 8098	1 5068	1 7170	Δω =	-0 8010
Reaction 2	LiCl +	NaF =	LiF +	NaCl		
Energy (E, au)	-467 8900	-262 2700	-107 4860	-622 6500	ΔE =	0 0200
Electronegativity (χ, eV)	3 7641	4 0834	4 0591	3 7661	Δχ =	-0 0223
Hardness (η, eV)	3 5344	3 7830	3 8180	3 4344	Δη =	-0 0650
Electrophilicity (ω, eV)	2 0043	2 2038	2 1577	2 0649	Δω =	0 0144
Reaction 3	LiCl +	KF =	LiF +	KCl		
Energy (E, au)	-467 8900	-699 8700	-107 4860	-1060 2550	ΔE =	0 0190
Electronegativity (χ, eV)	3 7641	3 9918	4 0591	3 7206	Δχ =	0 0237
Hardness (η, eV)	3 5344	3 6816	3 8180	3 3878	Δη =	-0 0103
Electrophilicity (ω, eV)	2 0043	2 1641	2 1577	2 0430	Δω =	0 0323
Reaction 4	LiBr +	KF =	LiF +	KBr		
Energy (E, au)	-2579 4000	-699 8700	-107 4860	-3171 7780	ΔE =	0 0060
Electronegativity (χ, eV)	3 5664	3 9918	4 0591	3 5290	Δχ =	0 0298
Hardness (η, eV)	3 2834	3 6816	3 818	3 1638	Δη =	0 0167
Electrophilicity (ω, eV)	1 9369	2 1641	2 1577	1 9682	Δω =	0 0248
Reaction 5	LiF +	HBr =	LiBr +	HF		
Energy (E, au)	-107 4860	-2572 3000	-2579 4000	-100 4600	ΔE =	-0 0740
Electronegativity (χ, eV)	4 0591	4 3580	3 5664	4 7223	Δχ =	-0 1283
Hardness (η, eV)	3 818	3 9237	3 2834	6 4939	Δη =	2 0357
Electrophilicity (ω, eV)	2 1577	2 4201	1 9369	1 717	Δω =	-0 9239
Reaction 6	NaF +	HCl =	NaCl +	HF		
Energy (E, au)	-262 2700	-460 8100	-622 6500	-100 4600	ΔE =	-0 0300
Electronegativity (χ, eV)	4 0834	4 4996	3 7661	4 7223	Δχ =	-0 0946
Hardness (η, eV)	3 7830	4 5170	3 4344	6 4939	Δη =	1 6284
Electrophilicity (ω, eV)	2 2038	2 2411	2 0649	1 7170	Δω =	-0 6630
Reaction 7	SiH ₄ +	HF =	SiH ₃ F +	H ₂		
Energy (E, au)	-291 8900	-100 4600	-391 2000	-1 1750	ΔE =	-0 0250
Electronegativity (χ, eV)	4 6752	4 7223	5 5318	4 5275	Δχ =	0 6618
Hardness (η, eV)	4 8156	6 4939	4 5079	7 2781	Δη =	0 4764
Electrophilicity (ω, eV)	2 2695	1 7170	2 6844	1 4082	Δω =	0 1061
Reaction 8	LiH +	HF =	LiF +	H ₂		
Energy (E, au)	-8 1330	-100 4600	-107 4860	-1 1750	ΔE =	-0 0680
Electronegativity (χ, eV)	2 8055	4 7223	4 0591	4 5275	Δχ =	1 0587
Hardness (η, eV)	2 7731	6 4939	3 8180	7 2781	Δη =	1 8291
Electrophilicity (ω, eV)	1 4191	1 7170	2 1577	1 4082	Δω =	0 4298
Reaction 9	HCl +	LiH =	LiCl +	H ₂		
Energy (E, au)	-460 8100	-8 1330	-467 8900	-1 1750	ΔE =	-0 1220
Electronegativity (χ, eV)	4 4996	2 8055	3 7641	4 5275	Δχ =	0 9865
Hardness (η, eV)	4 5170	2 7731	3 5344	7 2781	Δη =	3 5225
Electrophilicity (ω, eV)	2 2411	1 4191	2 0043	1 4082	Δω =	-0 2477
Reaction 10	HO ⁻ +	LiH =	LiF +	H ₂ O		
Energy (E, au)	-175 5600	-8 1330	-107 4860	-76 4290	ΔE =	-0 2220
Electronegativity (χ, eV)	5 5318	2 8055	4 0591	3 8108	Δχ =	-0 4675
Hardness (η, eV)	3 3920	2 7731	3 8180	4 8143	Δη =	2 4671
Electrophilicity (ω, eV)	4 5107	1 4191	2 1577	1 5082	Δω =	-2 2640

^aΔH in kcal mole⁻¹

energetically favourable in the forward direction in the gas phase, have become favourable in the backward directions in presence of water. All three reactions obey the MEP in the backward direction (now energetically favourable) whereas two of them follow the MHP. For the remaining seven reactions forward directions are energetically favourable and the MHP is valid in all cases while the MEP is not valid in two cases although the least electrophilic species lie in the product side.

4. Concluding remarks

Although there are marked variations in numerical values of different conceptual DFT based reactivity descriptors and also in their qualitative trends in some cases for the calculations in the gas and the aqueous phases using different levels of theories and basis sets, the favourable directions of the exchange reactions as dictated by the HSAB principle coincide in many cases with that from the maximum hardness and minimum electrophilicity principles.

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