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Comparison between Experimental and Theoretical Scales of Electrophilicity Based on Reactivity Indexes

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A comparative study between a relative experimental scale of electrophilicity and a theoretical absolute scale based on electronic reactivity indexes is presented. The theoretical scale correctly predicts the experimental electrophilicity within the dihalogen and inter-halogen subseries (XY) including F_2, Cl_2, Br_2, BrCl, and ClF and the HX (X = F, Cl, Br) series. It is shown that the best correlation is obtained for the local electrophilic index that encompasses the global electrophilicity power weighted by a local factor described by the electrophilic Fukui function. This result is in agreement with the electrostatic model of Legon (*Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2686), as the electrophilic power of molecules is mainly determined by the local properties of the electrophilic ends of HX and XY species. We also evaluated the electrophilicity of Li_2, LiH, LiF, and LiCl species for which experimental data are not available. Whereas LiH is predicted to have an electrophilic potential comparable to that shown by the dihalogen and inter-halogen series but higher than that of the HX species, LiF and LiCl are predicted to display an electrophilic pattern even higher that those of the XY and HX molecules. On the other hand, Li_2 displays an electrophilic pattern even lower than that of F_2.

Introduction

It has been recently proposed that the electrophilic power of XY and HX (X,Y = halogen atom) species may be conveniently accommodated within a relative scale.[1,2] The electrophilic scale of XY species has been established with reference to BrCl[2], and the electrophilic scale of HX species has been established with reference to HF using H_2O as the reference nucleophile.[1] The experimental model of electrophilicity is based on the remarkable parallelism found between the angular geometry of the B···HX and B···XY hydrogen-bonded complexes, where B is a Lewis base; these complexes are expected to share bonding properties including the force constant k_s.[1−3] This quantity determines the strength of the intermolecular interaction. It has been further proposed that k_s may be partitioned to define the nucleophilicity of the Lewis base B and the electrophilicity of the HX and XY species within a relative scale. For instance, the B···HX hydrogen bond has been interpreted as the electrophilic site of HX (the hydrogen atom) seeking the most nucleophilic site of B, whereas the nucleophilic end of HX (the halogen atom) will avoid the nucleophilic site of B[1]. This framework is within a model similar to the classical rules used to predict geometries in molecules proposed by Nyholm and Gillespie.[4] The local electrophilicity of H in HX is therefore determined by its ability to seek the most electron-rich region in the Lewis base B. The same model seems to apply to the electrophilicity of inter-halogen (XY) and dihalogen (X_2) species.[1−3] It is important to mention that the experimental electrophilicity of BrCl was arbitrarily assigned the value $E_{BrCl} = 9.0$ for the X_2 and XY subseries,[2] and $E = 10.0$ for HF was also arbitrarily assigned for the HX subseries.[1]

Global and local electrophilicity, on the other hand, may be conveniently represented by reactivity indexes. For instance, the global electrophilic power of atoms and molecules have been given the following definition:[5]

$$\omega = \frac{\mu^2}{2\eta} \qquad (1)$$

$\mu \approx -(I + A)/2$ and $\eta \approx (I - A)$ are the electronic chemical potential and the chemical hardness of the ground state of atoms and molecules, respectively, approximated in terms of the vertical ionization potential I and the electron affinity A. The electrophilicity index simultaneously encompasses both the propensity of the electrophile to acquire an additional electronic charge, driven by μ^2, and the resistance of the system to exchange electronic charge with the environment, described by η. A good electrophile is therefore characterized by a high value of μ and a low value of η. It is also possible to define a semilocal (regional) electrophilic power[6] associated with a site k in a molecule with the aid of the electrophilic Fukui function f_k^+,[7,8] namely,[6]

$$\omega_k = \omega f_k^+ \qquad (2)$$

Equation 2 predicts that the most electrophilic site in a molecule is the one displaying the maximum value of f_k^+ (i.e., the active site of the electrophile). This site also coincides with the softest region in a molecule.

To make a comparison between the experimental electrophilicity scale proposed by Legon and Millen[1,2] and the theoretical scale based on Parr's definition of electrophilicity, high-level

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TABLE 1: Electronic Chemical Potential (μ), Chemical Hardness (η), Global Electrophilicity (ω), Local Electrophilicity (ω_k), Fukui Function for Electrophilic Attack (f_k^+), and Experimental Relative Electrophilicity (E_{XY}) for a Series of Diatomic Molecules

species[a]	μ (eV)	η (eV)	ω (eV)	f_k^+	ω_k (eV)	E_{XY}[b]
F_2	−6.67	18.15	1.23	0.5000	0.62	1.9
	−7.07	16.91	1.48	0.5000	0.74	
Cl_2	−5.68	11.38	1.41	0.5000	0.71	5.1
	−6.28	10.71	1.84	0.5000	0.92	
Br_2	−5.40	9.86	1.48	0.5000	0.74	7.4
	−5.80	9.46	1.78	0.5000	0.89	
BrCl	−5.62	10.60	1.49	0.5887	0.88	9.0
	−6.04	9.98	1.83	0.5707	1.04	
ClF	−5.44	13.11	1.13	0.8234	0.93	9.8
	−6.22	12.80	1.51	0.7243	1.09	
HBr	−3.55	14.34	0.44	0.6534	0.29	4.2
	−4.41	14.61	0.66	0.6254	0.41	
HCl	−3.73	15.75	0.44	0.8127	0.36	5.0
	−4.71	16.04	0.69	0.7679	0.53	
HF	−4.23	19.88	0.45	0.9989	0.46	10.0
	−5.33	20.76	0.69	0.9865	0.68	
Li_2	−1.62	5.28	0.25	0.5000	0.13	
	−2.75	5.15	0.73	0.5000	0.37	
LiH	−3.42	7.13	0.82	0.9834	0.81	
	−4.17	8.23	1.06	0.9537	1.01	
LiF	−4.84	9.94	1.18	0.9995	1.18	
	−5.95	11.79	1.50	0.9997	1.50	
LiCl	−4.52	8.47	1.21	0.9982	1.21	
	−5.22	9.56	1.43	0.9945	1.42	

[a] For each species, the first entry corresponds to HF/6-31G(d,p) calculations and the second entry corresponds to B3LYP/6-31G(d,p) calculations. [b] Values of E_{XY} are from refs 1−3.

ab initio calculations were performed on a series of dihalogen, inter-halogen, and HX species for which experimental electrophilicity E_{XY} values are available.[1−3] We also include the global and local electrophilic propensities of Li_2, LiH, LiF, and LiCl to test the predictive power of the theoretical scale. The results are summarized in Table 1.

The global electrophilicity index ω was evaluated at the ground state of molecules using Hartree−Fock HF/6-31G(d,p) and B3LYP/6-31G(d,p) levels of theory, as implemented in the Gaussian 98 package.[9] The electronic chemical potential and chemical hardness were evaluated with the adiabatic approach by using I and A values obtained from the energy difference between the system with N electrons and the systems with $N - 1$ and $N + 1$ electrons, respectively, at a constant external potential. Electrophilic Fukui functions f_k^+, needed to project the regional electrophilic potential condensed at the atomic centers of the molecules ω_k, were obtained from single-point calculations on the optimized structures by a method described elsewhere.[10−12]

A first glance, Table 1 reveals the absence of significant correlation between the experimental scale of electrophilicity E_{XY} and the theoretical scale defined on the basis of the global ω index. This is true for the whole series and also within the HX and XY subseries at both the Hartree−Fock and density functional levels of theory. To discuss the electrophilicity concept within a general framework, we may start by assuming a very crude model that is based on the global electronegativity of molecules: the higher the electronegativity, the higher the electrophilicity of the molecule. This is, of course, a very candid definition of electrophilicity, as this property should be expected to depend also on the chemical softness, which is correctly taken into account in Parr's model that is condensed in eq 1. Chemical softness (S) is defined as the reciprocal of molecular hardness ($S = 1/\eta$).[7] To illustrate this argument, let us compare F_2 and HF molecules. According to their global electronegativities, F_2 ($\chi = -\mu = 6.67$ eV) is predicted to be more electrophilic than HF ($\chi = -\mu = 4.23$ eV) at the Hartree−Fock level. Note that at the B3LYP level of theory a similar result is obtained. Because the electrophilicity index is second degree in electronic chemical potential and first degree in global softness, we expect the electrophilic power defined in eq 1 to be mostly μ-dependent. The global electrophilic order predicted on the basis of the ω index for this pair of molecules is $F_2 > HF$, in contrast with the experimental result (see Table 1). Note that according to the hardness values the difference in global softness for these molecules is about 0.005 $(eV)^{-1}$, whereas the difference in μ^2 is 2.44 eV at the Hartree−Fock level. B3LYP calculations predict $\Delta S \approx 0.01$ $(eV)^{-1}$ and a difference in μ^2 of 1.74 eV (see Table 1). Despite the fact that the molecular electronegativity has been defined as a uniform property (i.e., a property displaying the same value at each point of the molecular region), we may still use Politzer's model of electronegativity for atoms in their valence states[13] to check whether the electrophilic pattern of molecules may be traced to a regional property associated with the most electrophilic ends, as suggested by Legon and Millen.[1,2] Within Politzer's model, the ability of the system to acquire additional electronic charge from the environment is driven by its charge capacity, a quantity proportional to the first derivative of the electronegativity with respect to the net charge of the atom in the molecule. Within this approach, the F atom in F_2 would be expected to have a higher charge capacity than would the F atom in HF; therefore, F_2 would again be incorrectly predicted as being more electrophilic than HF.

These results suggest that the electrophilic power of molecules may be mostly related to a genuine local (regional) property rather than to a global property of the molecules, in agreement with the proposal of Legon and Millen:[1] the electrophilicity of HX is mainly determined by the most electrophilic site of HX (i. e.; the H atom). A genuine local index to describe the regional electrophilicity of molecules is the Fukui function f_k^+ for a nucleophilic attack at site k.[7,8] The values of f_k^+ are also listed in Table 1. Note that with the exception of dihalogens this local reactivity index correctly assesses the electrophilic sites in the whole series: the Br atom in BrCl, the Cl atom in ClF, and the H atom in the HX species. For the short series LiH, LiF, and LiCl, the electrophilic site is correctly predicted at the Li atom. A comparison between the theoretical electrophilic pattern described by the f_k^+ index with the experimental scale is, however, limited because as a result of symmetry considerations the f_k^+ index cannot discriminate the experimental electrophilic patterns for the X_2 species (they are all predicted to display the same electrophilicity).

To raise the ambiguity in the prediction of the electrophilic pattern in the X_2 species described by the Fukui functions, we also evaluated the local (regional) electrophilicity defined in eq 2. According to this model, the global counterpart ω helps to discriminate the electrophilic power within this series. The results are listed in Table 1. According to the local electrophilicity index evaluated at the HF/6-31G(d,p) level of theory, the expected order of electrophilicity is F_2 ($\omega_k = 0.62$ eV) < Cl_2 ($\omega_k = 0.71$ eV) < Br_2 ($\omega_k = 0.74$ eV) < BrCl ($\omega_k = 0.88$ eV) < ClF ($\omega_k = 0.93$ eV), in complete agreement with the relative experimental E_{XY} scale.[2] Note that B3LYP/6-31G(d,p) calculations predict, in general, the same trends, the only exception being the Cl_2 and Br_2 pairs that appear to be inverted with respect to the experimental scale. Within the subseries of HX species, the same result is obtained,[1] yet the model based on the local electrophilicity cannot accommodate the XY and HX species within a unique scale. On the other hand, LiH is predicted to have an electrophilic potential comparable to that shown by the dihalogen and inter-halogen series but higher than that of the HX species, whereas LiF and LiCl are predicted to display an electrophilic pattern even higher that those of XY and HX molecules. This pattern is mostly determined by the powerful electrophilic Li site.

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