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Proton Affinity and Acidity of Hypohalous Acids: A Density Functional Study

Tapan K. Ghanty and Swapan K. Ghosh*

Heavy Water Division, Bhabha Atomic Research Centre, Bombay 400 085, India

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The acidities and proton affinities of hypohalous acids HOX and also hydrohalic acids HX for X = F, Cl, Br, and I are calculated through the Kohn−Sham version of spin-polarized density functional theory with several available local as well as nonlocal gradient-corrected exchange−correlation functionals. The calculated values are observed to be in good agreement with the available reported results. Unlike the proton affinity or acidity values, the calculated gross electron populations at the atomic sites are not monotonic on going from HOF to HOI and thus cannot explain the calculated proton affinity or acidity trend. However, the trends in acidity as well as proton affinity are rationalized, in general, in terms of the calculated values of atomic Fukui reactivity indices.

1. Introduction

The proton affinity (or basicity) and acidity of a chemical species are two important thermochemical properties that have attracted considerable attention[1−6] in recent years. The site of protonation or deprotonation of a given base or acid possessing more than one possible site is usually difficult to determine experimentally, and the situation is even more complicated in the presence of a solvent. Moreover, the experimental results mostly correspond to the most reactive sites of the molecules. On the other hand, theoretically the properties of all the protonated and deprotonated species can be computed using the same level of theory, and one can thus obtain rather accurate estimates of relative proton affinity and acidity. There are several ab-initio methods, out of which, the Gaussian-2 (G2) model[7] is one of the best theoretical approaches available, which has been found[1] to provide reasonably accurate estimates of proton affinities.[1] But this method is not practicable for larger molecular systems. There are however several other more economical methods (such as G2(MP2))[8] for obtaining proton affinities, a relative comparison of which has been given by Smith and Radom.[9] In recent years, however, another approach that has become quite popular is the density functional theory (DFT),[10] which has established itself as a highly successful and versatile tool for the computation of molecular properties, maintaining a good compromise between accuracy and performance. Recently, predictions of several thermochemical properties including proton affinities based on calculations using DFT-based methods have been reported (see, for example, refs 2, 3, and references therein).

It is well-known[1] that the hypohalous acids, HOX (X = F, Cl, Br, and I), are important from an atmospheric chemistry point of view. Thus, HOCl and HOBr have been involved in catalytic cycles in the seasonal depletion of the ozone layer in the stratosphere and can also serve as temporary reservoirs for ClO_x and BrO_x. It has been suggested that HOI is involved in tropospheric iodide chemistry and also serves as a volatile carrier of radioactive iodine (^{131}I). The hypohalous acids are strong oxidizing agents and are of special interest[1] because they reflect an interplay between the σ-inductive effect and repulsive interactions between the lone pairs. The chemical instability of the hypohalous acids however renders the accurate experimental determination of their properties rather difficult. Theoretical studies on the properties of the hypohalous acids can thus play a very important role. Very recently, Glukhovtsev et al.[1] have calculated the acidities and proton affinities of hypohalous acids using the G2 theory.

In view of the simplicity of the density functional approach and its recent application to the study of proton affinities, it is of interest to investigate the performance of DFT for the calculation of proton affinities of this important class of molecules. An added advantage of a DFT-based procedure is that not only does it provide a simpler route to the electronic structure of atoms, molecules, and solids but it also often leads to means of rationalization and prediction of various physicochemical phenomena in terms of important chemical concepts such as electronegativity,[11] hardness,[12] softness and frontier orbital theory,[13] and generalized electronegativity equalization[14] by providing a foundation for the existing concepts or by introducing newer concepts. Thus, besides predicting the proton affinities through DFT calculation, our aim here is also concerned with rationalization of the observed trends in these quantities for the molecules studied in terms of the calculated reactivity indices, such as partial atomic charges[15] and the atomic Fukui indices.[16,17]

2. Theory and Computational Method

For the present calculations, we employ the spin-polarized Kohn−Sham version of DFT, where up- and down-spin electron densities $\rho_\alpha(\mathbf{r})$ and $\rho_\beta(\mathbf{r})$ are the basic variables and are obtained by solving the Kohn−Sham equations[18] for the spin orbitals (with $i = 1-N$) given by (atomic units are used throughout)

$$\left[-\frac{1}{2}\nabla^2 + v^{\sigma}_{\rm eff}(\mathbf{r},\{\rho_\sigma\})\right]\psi_{i\sigma}(\mathbf{r}) = \epsilon_{i\sigma}\psi_{i\sigma}(\mathbf{r}) \qquad (1)$$

where $\rho_\sigma(\mathbf{r}) = \sum_i n_{i\sigma}\rho_{i\sigma}(\mathbf{r})$ and $\rho_{i\sigma}(\mathbf{r}) = |\psi_{i\sigma}(\mathbf{r})|^2$, with the occupation numbers $n_{i\sigma}$ satisfying $\sum_i n_{i\sigma} = N_\sigma$, where N_σ (for $\sigma = \alpha$ or β) denotes the number of up- or down-spin electrons and $N = N_\alpha + N_\beta$. Here, the spin-dependent Kohn−Sham effective potential is given by

$$v^{\sigma}_{\rm eff}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{d\mathbf{r}'\,\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \mu^{\sigma}_{\rm XC}(\mathbf{r};[\{\rho_\sigma\}]) \qquad (2)$$

where the exchange−correlation (XC) potential, $\mu^{\sigma}_{\rm XC}$, is given by the functional derivative $[\delta E^{\sigma}_{\rm XC}[\rho_\alpha,\rho_\beta]/\delta\rho_\sigma(\mathbf{r})]$ of the XC energy functional $E_{\rm XC}[\{\rho_\sigma\}]$. The total energy can be obtained by evaluating the expression

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$$E = \sum_{\sigma}\sum_{i} \epsilon_{i\sigma} - \frac{1}{2}\int\int \frac{d\mathbf{r}\, d\mathbf{r}'\rho(\mathbf{r})\, \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{XC}[\{\rho_\sigma\}] - \sum_{\sigma}\int d\mathbf{r}\, \mu^{\sigma}_{XC}[\{\rho_\sigma\}]\rho_\sigma(\mathbf{r}) \quad (3)$$

and hence the proton affinity can easily be estimated from the calculated energies of a molecule and the corresponding protonated species. The solution of the Kohn−Sham equations also leads to the partial atomic charges as well as other new reactivity indices such as the Fukui function,[13] defined within the framework of DFT as

$$f(\mathbf{r}) = \left[\frac{\delta\mu}{\delta v(\mathbf{r})}\right] = \left[\frac{\partial\rho(\mathbf{r})}{\partial N}\right]_v \quad (4)$$

which are useful for the prediction of chemical reactivity. The derivative discontinuity associated with this function can lead to three derivatives, viz., the right, left, and the average, denoted as $f^+(\mathbf{r})$, $f^-(\mathbf{r})$, and $f^0(\mathbf{r})$, respectively. For the investigation of the proton affinity, however, the electron density transfer that is encountered is from the attacking site of the molecule to the proton, and hence the quantity of interest is $f^-(\mathbf{r})$, which can be expressed within the finite difference approximation as

$$f^-(\mathbf{r}) = [\rho_N(\mathbf{r}) - \rho_{N-1}(\mathbf{r})] \quad (5)$$

While the position-dependent Fukui function provides a detailed picture, one can often obtain averaged but sufficient information from the corresponding condensed Fukui functions on each atom.[16,17] The condensed Fukui function f_A^- on atom A is given by

$$f_A^- = [q_A(N) - q_A(N-1)] \approx q_A(\mathrm{HOMO}) \quad (6)$$

where $q_A(N)$ and $q_A(\mathrm{HOMO})$ represent respectively the total charge on atom A and the contribution of the highest occupied molecular orbital (HOMO) to it in the N-electron molecule.

All the calculations in this work have been done using the Gaussian density functional program deMon,[19] where the Kohn−Sham molecular orbitals are expanded in a basis of Gaussian type orbitals. We have used the DZVP orbital basis set[20] and the fine grid option of deMon for density calculation here. In DFT, the form of the XC energy density functional is not yet known exactly and hence has to be approximated. The simplest approximation is the local spin density approximation (LSD),[21] which however is known to yield[2,3] underestimated values for the proton affinity calculation, and hence one requires a nonlocal gradient-corrected XC functional. For the present calculations, we have employed three common standard nonlocal functional forms, viz., (i) the Perdew−Wang XC functional (PW91),[22] (ii) the Perdew XC potential (PP86),[23,24] and (iii) the Becke exchange and Perdew correlation functionals (BP).[24,25] For the purpose of comparison, we have also carried out the calculations using an LSD approximation to the XC functionals due to Vosko, Wilk, and Nusair (VWN).[26]

3. Results and Discussions

We have calculated the electronic structure of different hypohalous acids HOX and the corresponding protonated species H_2OX^+ and $HOXH^+$ as well as the deprotonated ions OX^- for X = F, Cl, Br, and I. Calculations are also performed for the species HX, X^-, and H_2X^+. The geometries of all these molecules and ions have been optimized using the PW91 XC functional, and the resulting optimized geometries are reported in Table 1. The bond lengths and bond angles obtained are comparable to those reported earlier by Glukhovtsev et al.[1] based on G2 calculation, and the trend of their variation for different X is also consistent with the electronegativity parameter of X. The same optimized geometries are then used as inputs for the energy calculation of all these species using the other three XC energy functionals mentioned earlier. The proton affinity values are obtained from the calculated total energies of the species reported in Table 2 involved in the different proton transfer processes and are reported in Table 3 along with the results of G2 calculations of Glukhovtsev et al.[1] It is interesting to note that the proton affinity values obtained by the present method using XC functionals (PW91, PP86, BP) are always higher than the predictions of the G2 method, while that of the LSD approximation does not show such systematic trend. While it is difficult to assess whether this trend is a consequence of the electron correlation effects as included in DFT, it is interesting to note that the available experimental values[1,27] also reported

TABLE 1: Calculated Geometries of HX, HOX, OX^-, H_2X^+, H_2OX^+, and $HOXH^+$ Species (X = F, Cl, Br, and I)

species	R(O−X) (Å)	R(H−O) (Å)	R(X−H) (Å)	∠HOX (deg)	∠HXH (deg)	∠OXH (deg)	∠HOXH (deg)
HF			0.926				
HCl			1.284				
HBr			1.426				
HI			1.625				
HOF	1.457	0.975		94.4			
HOCl	1.740	0.976		100.2			
HOBr	1.884	0.977		100.0			
HOI	2.056	0.977		101.8			
OF^-	1.552						
OCl^-	1.769						
OBr^-	1.886						
OI^-	2.013						
H_2F^+			0.963		111.1		
H_2Cl^+			1.306		91.7		
H_2Br^+			1.445		88.5		
H_2I^+			1.636		87.2		
H_2OF^+	1.423	0.993		100.8			111.0
H_2OCl^+	1.771	0.987		107.9			114.7
H_2OBr^+	1.939	0.985		107.3			112.9
H_2OI^+	2.156	0.981		109.6			114.6
$HOFH^+$	1.518	0.994	0.967	93.8		101.1	158.9
$HOClH^+$	1.687	0.986	1.314	102.9		96.7	96.8
$HOBrH^+$	1.826	0.985	1.453	103.0		93.8	91.7
$HOIH^+$	2.987	0.984	1.644	105.1		91.5	90.3

TABLE 2: Calculated Total Energies of HX, H_2X^+, X^-, HOX, OX^-, H_2OX^+, and $HOXH^+$ Species (X = F, Cl, Br, and I) Using Different Exchange−Correlation Functionals

species	PW91	BP	PP86	VWN
HF	−100.4403	−100.4746	−100.5503	−99.8239
HCl	−460.7451	−460.8116	−460.9429	−459.2674
HBr	−2574.4182	−2574.5680	−2574.5574	−2570.7285
HI	−6920.8090	−6921.0396	−6920.6218	−6914.6001
H_2F	−100.6363	−100.6707	−100.7437	−100.0160
H_2Cl	−460.9631	−461.0301	−461.1601	−459.4775
H_2Br	−2574.6462	−2574.7969	−2574.7852	−2570.9482
H_2I	−6921.0524	−6921.2836	−6920.8653	−6914.8333
F^-	−99.8167	−99.8519	−99.9297	−99.2075
Cl^-	−460.2028	−460.2701	−460.4018	−458.7349
Br^-	−2573.8956	−2574.0459	−2574.0363	−2570.2162
I^-	−6920.3039	−6920.1178	−6920.1178	−6914.1064
HOF	−175.5408	−175.6004	−175.7448	−174.4181
HOCl	−535.9003	−535.9918	−536.1901	−533.9199
HOBr	−2649.5896	−2649.7644	−2649.8218	−2645.3957
HOI	−6995.9995	−6996.2549	−6995.9051	−6989.2863
OF^-	−174.9457	−175.0064	−175.1543	−173.8287
OCl^-	−535.3114	−535.4038	−535.6038	−533.3380
OBr^-	−2649.0033	−2649.1788	−2649.2374	−2644.8171
OI^-	−6995.4180	−6995.6738	−6995.3247	−6988.7134
H_2OF^+	−175.7633	−175.8257	−175.9671	−174.6379
H_2OCl^+	−536.1516	−536.2432	−536.4399	−534.1644
H_2OBr^+	−2649.8543	−2650.0291	−2650.0858	−2645.6524
H_2OI^+	−6996.2805	−6996.5360	−6996.1857	−6989.5582
$HOFH^+$	−175.7361	−175.7961	−175.9391	−174.6050
$HOClH^+$	−536.1236	−536.2154	−536.4121	−534.1349
$HOBrH^+$	−2649.8232	−2649.9989	−2650.0547	−2645.6211
$HOIH^+$	−6996.2491	−6996.5052	−6996.1546	−6989.5262

TABLE 3: Calculated Values of Proton Affinities (in kcal/mol) of HX, X^-, HOX, and OX^- Species (X = F, Cl, Br, and I)

	present calculation					
species	PW91	BP	PP86	VWN	lit.[a]	expt[b]
HF	123.0	123.0	121.4	120.5	114.5	117.0
HCl	136.8	137.1	136.3	131.8	133.0	136.5
HBr	143.1	143.6	143.0	137.9	138.6	139.1
HI	152.7	153.1	152.8	146.3	148.2	147.0
F^-	391.3	390.7	389.4	386.8	369.8	371.4
Cl^-	340.3	339.8	339.5	334.1	333.3	333.4
Br^-	327.9	327.6	326.9	321.5	323.3	323.6
I^-	317.0	316.7	316.2	309.8	314.4	314.3
HOF	141.5[c]	141.4	139.5	137.9	133.8	
	122.6[d]	122.8	121.9	117.3	115.9	
HOCl	157.7	157.7	156.8	153.4	152.0	
	140.1	140.3	139.3	134.9	137.7	
HOBr	166.0	166.1	165.7	161.1	160.7	
	146.6	147.1	146.2	141.5	142.4	
HOI	176.3	176.3	176.0	170.6	172.0	
	156.6	157.1	156.5	150.5	152.3	
OF^-	373.4	372.8	370.5	369.8	359.2	368 ± 4
OCl^-	369.6	369.0	367.9	365.1	354.8	359 ± 2
OBr^-	367.9	367.4	366.7	363.0	355.0	
OI^-	364.9	364.7	364.2	359.5	354.1	355 ± 6

[a] Literature values calculated by using the G2 method (from ref 1). [b] Experimental values from ref 27 as also quoted in ref 1. [c] Proton affinities corresponding to the process HOX + H^+ = H_2OX^+. [d] Proton affinities corresponding to the process HOX + H^+ = $HOXH^+$.

in Table 3 are intermediate in most of the cases between the present results using the nonlocal functionals and the G2 results, and in general the agreement is good in both cases. We have reported in Table 4 the calculated total charges q_H, q_O, and q_X on the H, O, and X atoms in various species and the respective atomic Fukui indices f_H^-, f_O^-, and f_X^- obtained as charges contributed by the HOMO using the approximation of eq 6. From the reported results it is clear that the gross atomic charges as well as the Fukui indices are quite less sensitive to the forms of the XC energy functional used.

TABLE 4: Calculated Values of Atomic Charges and Atomic Fukui Indices of HOX and OX^- Species (X = F, Cl, Br, and I)[a]

species	q_H	q_O	q_X	f_H^-	f_O^-	f_X^-
HOF	0.311	−0.163	−0.149	0.008	0.678	0.315
	0.329	−0.177	−0.152	0.008	0.681	0.312
	0.326	−0.175	−0.151	0.008	0.678	0.315
	0.347	−0.200	−0.147	0.008	0.684	0.309
HOCl	0.311	−0.441	0.130	0.005	0.483	0.512
	0.325	−0.460	0.135	0.006	0.495	0.505
	0.320	−0.452	0.131	0.005	0.490	0.505
	0.343	−0.475	0.132	0.005	0.485	0.510
HOBr	0.306	−0.392	0.086	0.005	0.400	0.595
	0.322	−0.424	0.102	0.005	0.410	0.585
	0.316	−0.419	0.102	0.005	0.404	0.592
	0.340	−0.430	0.091	0.005	0.410	0.590
HOI	0.308	−0.472	0.164	0.004	0.315	0.682
	0.323	−0.511	0.189	0.004	0.313	0.684
	0.316	−0.504	0.187	0.004	0.309	0.688
	0.341	−0.510	0.170	0.004	0.312	0.685
OF^-		−0.621	−0.379		0.891	0.109
		−0.618	−0.382		0.892	0.109
		−0.614	−0.386		0.889	0.111
		−0.625	−0.375		0.892	0.108
OCl^-		−0.812	−0.188		0.865	0.135
		−0.814	−0.186		0.864	0.137
		−0.804	−0.196		0.864	0.136
		−0.813	−0.187		0.862	0.138
OBr^-		−0.747	−0.253		0.846	0.154
		−0.756	−0.244		0.843	0.157
		−0.750	−0.251		0.843	0.157
		−0.746	−0.254		0.844	0.157
OI^-		−0.780	−0.220		0.812	0.188
		−0.798	−0.202		0.804	0.196
		−0.780	−0.220		0.806	0.194
		−0.793	−0.207		0.807	0.193

[a] The four rows for each of the species correspond respectively to the calculated values using PW91, BP, PP86, and VWN prescriptions of the XC functionals.

The proton affinity corresponding to the process HOX + H^+ = H_2OX^+ is always found to be higher than the same for the formation of $HOXH^+$, indicating that protonation is favored at oxygen rather than the halogen atom. This is consistent with the much higher gross negative charges at the oxygen atoms as reported in Table 4. Also, the proton affinity values of HOX are found to increase from HOF to HOI as the electronegativity of the halogen atom (X) decreases from F to I, and there exists an almost linear correlation between the proton affinities of HOX and the electronegativities of X. The trend in proton affinities of OX^- forming HOX is however reverse, and the values decrease as one moves from F to I. This can be rationalized by the decrease in the atomic Fukui index on the oxygen atom f_O^- in this series. The trend in the net atomic charges on the oxygen atoms is however opposite and cannot explain the observed trend in proton affinities in these species. Analogously, the increase in proton affinity for protonation at the halogen atoms in HOX forming $HOXH^+$ for X = F to I can also be explained by the increasing trend in the atomic Fukui index at X, but the gross atomic charge at X fails to provide any prediction.

Thus, the atomic Fukui index is found to serve as a good criterion for explaining the trend in proton affinities for protonation at the terminal atoms such as oxygen in OX^- or X in HOX, where the gross atomic charge fails to provide any systematic trend. For protonation at the central atom such as oxygen in HOX, however, no reactivity index seems to work well. This is probably because the geometry change (see Table 1) on protonation at this atom is rather large, and for such large perturbation, any prediction based on calculation of indices of the unperturbed system is unlikely to be successful. Even the atomic Fukui indices for HOX calculated for the distorted geometry corresponding to the protonated species are found to be unable to provide any conclusive prediction in this regard. In this connection it may be mentioned that recent studies have demonstrated[28] the role of the atomic Fukui index in correct prediction of the protonation site and proton affinities in amides and thioamides. Intuitively this is appealing since although the site with higher gross negative charge would exert more electrostatic attraction for the proton, the electron density transfer which mainly takes place from the HOMO is expected to be larger from the site with the higher value of the atomic Fukui index, leading to increased proton affinity.

4. Concluding Remarks

The present work has been concerned with a density functional investigation of the protonation of hypohalous acids, which are known to play an important role in many situations. Proton affinity values are known[2] to be dominated by a delicate balance of contributions from various energy components, and hence the ability to predict it properly is a good criterion for assessing the suitability of the approximations used in a theoretical approach. The present work shows that good prediction of proton affinities is possible through a density functional calculation with nonlocal XC functionals. We have also calculated the partial atomic charges and atomic Fukui reactivity indices. The Fukui index is shown to be a good criterion for explaining the observed trend in proton affinities of different HOX and OX^- species for protonation at the terminal atoms, while for protonation at central atoms, which is associated with large geometry changes, consideration of other effects might be essential.

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