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The performance of density function theory in describing gas-phase S_N2 reactions at saturated nitrogen

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Abstract

The prototype gas-phase identity S_N2 reactions at neutral nitrogen $X^- + NH_2X \rightarrow NH_2X + X^-$ (where X = F, Cl, Br, I) were studied using the three hybrid Hartree–Fock DFT methods B3LYP, MPW1PW and MPW1K in conjunction with the 6-31+G(d,p) basis sets. Comparison of the results with the high-level G2(+) theory indicated that all of the three hybrid DFT methods can give reasonable values of the complexation energies (ΔH_{comp}) for the ion–molecule complex formed in the reaction $X^- + NH_2X$ (X = Cl, Br, I). The overall barriers ($\Delta H^{\neq}_{\text{ovr}}$) and central barriers ($\Delta H^{\neq}_{\text{cent}}$) for all of the reactions calculated using B3LYP functional are significantly underestimated. The best transition structures were obtained using MPW1K/6-31+G(d,p) level, which appears to exhibit the best performance in describing the potential energy surface for S_N2 reactions at neutral nitrogen. Some correlations of central barriers found at the G2(+) level of theory are reproduced by the results of three hybrid DFT methods for the reactions $X^- + NH_2X \rightarrow NH_2X + X^-$ (X = Cl, Br, I). (Int J Mass Spectrom 221 (2002) 59–65)

Keywords: Complexation energies; Nucleophilic substitution reaction; Transition state

1. Introduction

In the last decade, the nucleophilic substitution reaction at a formally neutral saturated nitrogen has become the focus of increasing attention, both experimental [1–5] and theoretical [6–9], because of their synthetic, biochemical, chemical and theoretical importance. Although the mechanism of S_N2 process at nitrogen remain poorly understood comparing with the S_N2 at carbon, all of the theoretical studies support the existence of conventional backside S_N2 transition state in the reaction $X^- + NH_2X \rightarrow NH_2X + X^-$ [6,8], which is characterized, in the gas phase, by double-well energy profile, with two minima corresponding to the formation of a pre- and post-reaction ion–molecule complex and with a transition structure of C_{2V} symmetry (see Fig. 1).

From a theoretical point of view, several studies have shown the S_N2 reactions to be extremely sensitive to the theoretical model used [10–14]. The high-level G2(+) theory appeared to be able to reproduce quite well the experimental available data in the studies of nucleophilic reactions at neutral carbon [15–17] and was also applied to the nucleophilic substitution reactions at neutral nitrogen [8,9] and oxygen [18]. Hybrid Hartree–Fock density function theory

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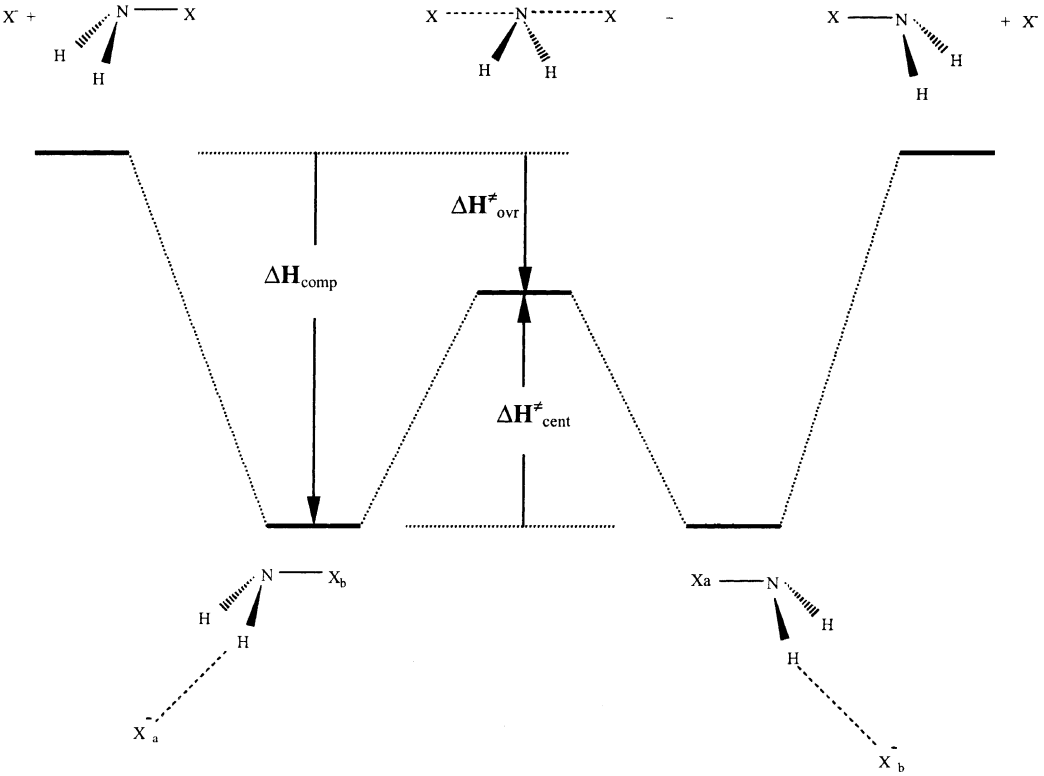

Fig. 1. Schematic energy profile for the $X^- + NH_2X$ identity exchange reaction ($X = F, Cl, Br, I$).

(hereafter called hybrid DFT) is of great interest for computational thermochemistry and thermochemical kinetics. Its low computational cost compares to ab initio methods makes it a very attractive alternative for many applications. Two very promising hybrid DFT method are B3LYP [19] and MPW1PW [20], both of them have been proven to be a successful approach to obtaining accurate molecular structures, vibrational frequencies and bond energies. Recently, Truhlar and coworkers proposed a new hybrid DFT model called the modified Perdew–Wang one parameter model for kinetics (MPW1K) [21]. They checked the 20 test reactions and found that the MPW1K/6-31+G(d,p) level reduced the mean unsigned error in reaction barrier heights by a factor of 2.4 over MPW1PW and by a factor of 3 over B3LYP. Martin and coworkers studied the gas-phase S_N2 reactions at carbon $Y^- + CH_3X \rightarrow CH_3Y + X^-$ ($X, Y = F, Cl, Br$) using a serious of high level ab initio computational thermochemistry methods and eight density functional methods and concluded that the MPW1K functional appeared to put in the best performance on all DFT methods considered [22].

In the present study, the three hybrid DFT methods B3LYP, MPW1PW and MPW1K have been applied to the calculation for the following identity gas-phase S_N2 exchange reactions at neutral nitrogen atom:

$$F^- + NH_2F \rightarrow FNH_2 + F^- \tag{1}$$

$$Cl^- + NH_2Cl \rightarrow ClNH_2 + Cl^- \tag{2}$$

$$Br^- + NH_2Br \rightarrow BrNH_2 + Br^- \tag{3}$$

$$I^- + NH_2I \rightarrow INH_2 + I^- \tag{4}$$

Because the direct experimental data for the above four reactions are not available, the G2(+) results [8] are claimed as the reference data in our paper. Our principal aim is to study a variety of hybrid DFT methods to determine how accurately available hybrid DFT methods can predict the geometrical structures and potential energy surfaces involved in the reactions (1)–(4).

2. Computational methods

All of the calculations presented in this paper were performed with the GAUSSIAN-98 program [23]. All electron (AE) calculation were done for first- and second-row atoms, while Wadt and Hay effective core potential (ECP) [24] were used for bromine- and iodine-containing species. The B3LYP, MPW1PW, MPW1K procedures were employed in the hybrid DFT calculation. All reactants, ion–molecular complexes and transition state structures for the four reactions were completely optimized at the three hybrid DFT methods, in all cases using the recommended 6-31+G(d,p) basis set [21]. The nature of all saddle points were determined using frequencies analysis. Un-scaled zero-point vibrational energy (ZPVE) at the 6-31+G(d,p) basis set were used in the calculation of the relative energies.

Throughout this paper, bond lengths are in angstroms (Å), and bond angles are in degrees (°). Relative energies correspond to enthalpy changes at 0 K [ΔH (0 K)] in kJ/mol.

3. Results and discussion

The complexation energy (ΔH_{comp}), central activation barrier ($\Delta H^{\neq}_{\mathrm{cent}}$) and the overall activation barrier relative to the separated reactants $\Delta H^{\neq}_{\mathrm{ovr}}$ for the reactions $X^- + NH_2X \rightarrow NH_2X + X^-$ (X = F, Cl, Br, I) are defined in Fig. 1. The values of ΔH_{comp}, $\Delta H^{\neq}_{\mathrm{cent}}$ and $\Delta H^{\neq}_{\mathrm{ovr}}$ calculated at various level of theory are compared with G2(+) theory in Table 1. All geometries of the reactants, ion–molecule complexes and transition state structures at various computational levels are given in the supporting information. Table 2 summarizes the mean unsigned error (MUE) and mean signed error (MSE) for the ΔH_{comp}, $\Delta H^{\neq}_{\mathrm{cent}}$ and

Table 2
Complexation energies of the ion–molecule complex (ΔH_{comp}), overall barrier relative to reactants ($\Delta H^{\neq}_{\mathrm{ovr}}$) and central barriers ($\Delta H^{\neq}_{\mathrm{cent}}$) for the reactions of X^- with H_2NX (X = F, Cl, Br, I) calculated at various levels of theory (kJ/mol)

Computational level	ΔH_{comp}	$\Delta H^{\neq}_{\mathrm{ovr}}$	$\Delta H^{\neq}_{\mathrm{cent}}$
X = F			
G2(+)[a]	114.0	−55.8	58.2
B3LYP/6-31+G(d,p)	126.1	−78.0	48.1
MPW1PW/6-31+G(d,p)	127.2	−66.6	60.6
MPW1K/6-31+G(d,p)	124.9	−46.1	78.8
X = Cl			
G2(+)[a]	67.8	−9.3	58.5
B3LYP/6-31+G(d,p)	66.3	−37.5	28.8
MPW1PW/6-31+G(d,p)	68.0	−27.0	41.0
MPW1K/6-31+G(d,p)	66.5	−5.7	60.8
X = Br			
G2(+)[a]	58.4	−13.7	44.7
B3LYP/6-31+G(d,p)	57.2	−38.6	18.6
MPW1PW/6-31+G(d,p)	59.5	−33.1	26.4
MPW1K/6-31+G(d,p)	58.0	−13.9	44.1
X = I			
G2(+)[a]	50.0	−10.8	39.1
B3LYP/6-31+G(d,p)	47.8	−36.1	11.7
MPW1PW/6-31+G(d,p)	50.1	−33.6	16.5
MPW1K/6-31+G(d,p)	47.9	−14.4	33.5

[a] From [8].

Table 1
Mean errors (kJ/mol) of ΔH_{comp}, $\Delta H^{\neq}_{\mathrm{ovr}}$ and $\Delta H^{\neq}_{\mathrm{cent}}$ for reactions (1)–(4)

Method (6-31+G(d,p))	ΔH_{comp}		$\Delta H^{\neq}_{\mathrm{ovr}}$		$\Delta H^{\neq}_{\mathrm{cent}}$	
	MUE	MSE	MUE	MSE	MUE	MSE
B3LYP	4.230	1.831	25.17	−25.17	23.34	−23.34
MPW1PW	3.627	3.627	17.54	−17.54	15.09	−13.92
MPW1K	3.730	1.704	4.372	2.616	7.143	4.321

Table 3
Mean signed errors in selected inter-nuclear distances for reactions (1)–(4)

Method	r(N–X) in NH_2X	$r(X_a \cdots H_a)$ in complex	$r(N \cdots X)$ in TS
B3LYP	0.011	−0.042	0.063
MPW1PW	−0.012	−0.078	0.027
MPW1K	−0.033	−0.059	0.005

$\Delta H^{\neq}_{\text{ovr}}$ values for the four prototype reactions. Table 3 displays the MSE for some important bond lengths. Table 4 compares some linear correlations of various characteristics of $X^- + NH_2X \rightarrow NH_2X + X^-$ reactions calculated at three hybrid DFT methods and G2(+) theory.

3.1. Complexation energies

Inspection of Table 1 shows that the complexation energies for $X^- \cdots NH_2X$ (X = F, Cl, Br, I) are rather insensitive to the computational levels used. The ΔH_{comp} values vary in the small range of just 2.3 kJ/mol for the reactions (1)–(4). The complexation energies calculated by the three hybrid DFT methods for the reactions (2)–(4) are close to the corresponding values at the G2(+) level. As for the reaction (1), all of the three hybrid DFT functionals overestimate the ΔH_{comp} values by more than 10 kJ/mol. The MUE for the complexation energies of the reactions (1)–(4) are about 4 kJ/mol (see Table 2).

Three hybrid DFT methods complexation energies for $X^- \cdots NH_2X$ (X = F, Cl, Br, and I) are found to decrease in the order F > Cl > Br > I and show a good linear correlation with halogen electronegativities (see Table 4), that is the same as the G2(+) theory.

3.2. Central barriers

The central barriers $\Delta H^{\neq}_{\text{cent}}$ obtained by the B3LYP functional are significantly underestimated for all of the prototype reactions. The MPW1PW model gives a little bit better $\Delta H^{\neq}_{\text{cent}}$ results than B3LYP. It is obvious that the MPW1K method predicts the most accurate $\Delta H^{\neq}_{\text{cent}}$ values except for the reaction (1). The MSE for the central barriers for the reactions (1)–(4) are −23.4 kJ/mol (B3LYP), −13.9 kJ/mol (MPW1PW) and 4.3 kJ/mol (MPW1K), respectively. All of the three DFT methods give significantly greater barrier range (more than 35 kJ/mol) than the G2(+) theory (∼19 kJ/mol).

3.3. Overall barriers

The overall barrier values ($\Delta H^{\neq}_{\text{ovr}}$) for all of the reactions also display a large variation with the computational level. In comparison, calculations using B3LYP and MPW1PW functionals uniformly give negative values for the overall barriers, both of the methods underestimate the overall barrier. The $\Delta H^{\neq}_{\text{ovr}}$ values calculated by the MPW1K/6-31+G(d,p) appear to agree well with the results of G2(+) theory. Especially, the overall barriers for reaction (3) calculated by MPW1K/6-31+G(d,p) level is −13.8 kJ/mol, which is lower than the corresponding value at the G2(+) level by only 0.1 kJ/mol.

Table 4
Linear correlations of various characteristics of $X^- + NH_2X$ reactions calculated by the three hybrid DFT methods and at the G2(+) level[a]

Parameter 1	Parameter 2	R^2 (B3LYP)	R^2 (MPW1PW)	R^2 (MPW1K)	R^2 (G2(+))
% N–H_a[b]	ΔH_{comp}	0.987	0.995	0.990	0.981
Electronagitivities of X[c]	ΔH_{comp}	0.961	0.960	0.964	0.975
% N–$X^{\neq}$ (X = Cl, Br, I)	$\Delta H^{\neq}_{\text{cent}}$	0.999	1.000	0.995	0.990
IE(X^-) (X = Cl, Br, I)	$\Delta H^{\neq}_{\text{cent}}$	0.988	0.981	0.970	0.937
PA(X^-) (X = Cl, Br, I)	$\Delta H^{\neq}_{\text{cent}}$	0.997	0.997	0.995	0.971
$D_{\text{N–X}}$ (X = Cl, Br, I)	$\Delta H^{\neq}_{\text{cent}}$	0.997	0.995	0.993	0.993

[a] From [8].
[b] X = F, Cl, Br, I.
[c] Mulliken scale.

3.4. Geometries

The geometries of at the B3LYP/6-31+G(d,p) and MPW1PW/6-31+G(d,p) levels generally agree well with the results of G2(+) calculation. The N–X bond lengths in reactants NH_2X are a little bit underestimated by the MPW1K method and the MSE for the N–X (X = F, Cl, Br, I) bond lengths in NH_2X are −0.03 Å at the level of MPW1K/6-31+G(d,p).

The geometries of ion–molecule complex $X^- \cdots NH_2X$ (X = F, Cl, Br, I) optimized by three hybrid DFT methods are generally close to the MP2/6-31+G(d) geometries except for the $F_a \cdots H_a$ distance. All of the three hybrid DFT methods predict too short $F_a \cdots H_a$ distance (see Table 2) and too high interaction energy, which will induce the overestimation of the complexation energy for the $F^- + NH_2F$ system. The geometries of NH_2X moieties in the $X^- \cdots NH_2X$ complexes differ from those of the unperturbed NH_2X molecules. Our studies show that there is a well defined linear relationship between the extent of elongation of the $N–H_a$ bonds in the complex, defined by % $N–H_a$ [8], and the complexation energies (see Table 4).

The key parameters for transition state $[X \cdots NH_2 \cdots X]^{-\neq}$ (X = F, Cl, Br, I) in rationalizing the behavior of the different hybrid DFT methods are the distance between the halogen anion and the nitrogen atom of NH_2X. The $N \cdots X$ bond lengths calculated by the MPW1K model can well reproduce the result of MP2/6-31+G(d) level (MSE is 0.005), but B3LYP and MPW1PW models estimate too long bond lengths for the N–X bonds (see Table 2), that induces a significant stabilization of the transition structure with respect to the ion–molecule complex. The effect may be so relevant to induce the underestimation of $\Delta H^{\neq}_{\mathrm{cent}}$ and $\Delta H^{\neq}_{\mathrm{ovr}}$.

3.5. Correlations of central barrier heights

Because $F^- + NH_2F^-$ system behaves in many respects different than the other $X^- + NH_2X$ reactions (X = Cl, Br, I), in this context, we will analysis our results calculated by three hybrid DFT methods and give some important correlations between the central barriers and the geometrical and energetic characteristics of the transition states for the reactions, $X^- + NH_2X \rightarrow XNH_2 + X^-$ (X = Cl, Br, I).

The main geometric feather in the transition structure $[X \cdots NH_2 \cdots X]^{-\neq}$ is the elongation of the N–X bond relative to the ion–molecular complex. Our hybrid DFT results show very well correlations between the central barriers and the looseness of the transition state geometries, defined by % $N–X^{\neq}$ [8].

We have calculated the gas-phase ionization energies of X^-[IE(X^-)], proton affinities of X^-[PA(X^-)] and bond dissociation energies $D_{N–X}$ in NH_2X by the three hybrid DFT levels. The results show that IE(X^-) and PA(X^-) values are close to the corresponding G2(+) values, and $D_{N–X}$ are significantly underestimated (see Table 5). Plots of DFT central barriers vs. IE(X^-), PA(X^-) and $D_{N–X}$ (where X = Cl, Br, I), respectively, generate very good linear correlations (see Table 4).

Table 5
Ionization energies, gas-phase proton affinity of X^- and dissociation energies of the N–X (X = Cl, Br, I) calculated at various levels of theory

Method[a]	IE(X^-) (eV)			PA(X^-) (kJ/mol)			$D_{N–X}$ (kJ/mol)		
	Cl	Br	I	Cl	Br	I	Cl	Br	I
B3LYP	3.674	3.357	3.042	1370	1333	1303	219.3	179.8	147.1
MPW1PW	3.599	3.332	3.039	1378	1336	1301	227.7	187.8	153.1
MPW1K	3.560	3.322	3.043	1379	1334	1297	214.4	173.9	138.9
G2(+)	3.602	3.293	2.969	1395	1353	1320	252.3	210.8	187.1

[a] All of the DFT methods are in conjunction with 6-31+G(d,p).

3.6. Concluding remarks

Three promising hybrid DFT models B3LYP, MPW1PW and MPW1K are applied to study the gas-phase identity S_N2 reaction at neutral nitrogen. Several important general conclusions emerge from our calculations:

(1) The patterns of potential energy surface for the reactions $X^- + NH_2X \rightarrow XNH_2 + X^-$ described by all of the three hybrid DFT methods are analogous to the results of G2(+). B3LYP and MPW1PW generally systematically underestimate the barrier heights, and the MPW1K functional gives more reasonable $\Delta H^{\neq}_{\text{ovr}}$ and $\Delta H^{\neq}_{\text{cent}}$ values.

(2) The complexation energies ΔH_{comp} for the $X^- \cdots NH_2X$ complex are not very sensitive to the functional considered. The calculated ΔH_{comp} values by the three hybrid DFT methods are close to the corresponding G2(+) values for the reactions $X^- + NH_2X \rightarrow XNH_2 + X^-$ (X = Cl, Br, I).

(3) All of the three hybrid DFT methods predict that the overall barriers are negative for the S_N2 reactions at neutral nitrogen, which is the same as the conclusion of G2(+) level.

(4) Our studies indicates that MPW1K/6-31+G(d,p) can well reproduce the results of G2(+) theory in describing the potential energy surface for S_N2 reactions at neutral nitrogen and reduce the mean unsigned errors over all of the complexation energies, central barriers and overall barriers, by a factor of 7 over MPW1PW and by a factor of 12.5 over B3LYP.

(5) For the reactions $X^- + NH_2X \rightarrow XNH_2 + X^-$ (X = Cl, Br, I), all of the hybrid DFT methods show that there exist the excellent correlations between the DFT central barriers with % $N\text{–}X^{\neq}$, IE(X^-), PA(X^-) and D_{N-X}. These correlations are also found at the G2(+) level of theory.

(6) All of the three hybrid DFT methods underestimate the $X_a \cdots H_a$ distance in the ion–molecular complexes. Both of the B3LYP and MPW1PW methods significantly overestimate the $N \cdots X$ bond lengths in transition structures.

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