Theoretical Study of SmI_2 Interaction with Monohaloethanes

Tácito D. F. Leite, José D. Santos & João B. L. Martins

SmI_2 é um reagente seletivo para reações de transferência de elétrons, promovendo importantes reações, tais como as reduções em síntese natural e hidrocarbonetos insaturados. Nós estudamos a formação de radical etil a partir de fluoroetano, cloroetano e bromoetano. Os cálculos foram realizados com funcional de densidade B3LYP, com pseudopotencial SDD para o samário e funções de base 6-31++G(2df,2pd) e 6-311++G(2df,2pd) para os outros átomos.

Palavras-chave: SmI_2 , transferência de elétrons, B3LYP.

SmI_2 is a selective reagent for electron transfer reactions, promoting important reactions such as reductions in the natural synthesis and unsaturated hydrocarbons. We have studied the formation of ethyl radical from fluoroethane, chloroethane and bromoethane. The calculations were carried out using the B3LYP density functional with SDD pseudopotential for samarium and 6-31++G(2df,2pd) and 6-311++G(2df,2pd) basis sets for the other atoms.

Keywords: SmI_2 , electron transfer, B3LYP.

Introdução

Single electron transfer chemistry constitutes an important field of organic chemistry^{1,2}. Their reactions with nucleofugal leaving groups of alkyl and aryl halides are the most widely investigated group of organic synthesis¹⁻⁴. The reactions of these groups with electron donors involve the breaking of the carbon-halogen bond and the reaction can be described as:

In a stepwise reaction^{1,2} the anion radical is formed as a first intermediate

From the hard and soft acid and bases (HSAB), it is well known that as the “hardness” of the ion is reduced through the introduction of electron-withdrawing groups at R, inductive and resonance stabilization combine to render the beta-elimination pathway increasingly feasible kinetically.

Samarium(II) iodide is a selective single electron transfer reagent that promotes a number of important reduction reactions in organic synthesis. The application potential of this compound may not be fully realized until its coordination chemistry and dynamics is better understood. These reduction reactions also require a proton source. Despite the wide application of SmI₂ in organic synthesis, the knowledge about the structure and mechanisms of these reduction reactions are unknown⁵⁻⁷. The effects of proton donors (alcohols and water) on the rate of reduction of acetophenone by SmI₂ have been examined utilizing stopped-flow^{6,8}.

We have studied the following reactions, in gas phase:

where X=F, Cl, and Br. The electronic structure calculations were done.

COMPUTATIONAL DETAILS

The geometries of the electronic ground and excited states have been optimized with standard Density Functional Theory (DFT) using the three-parameter Becke3-Lee-Yang-Parr (B3LYP) exchange-correlation (XC) functional in combination with 6-31++G(2df,2pd) and 6-311++G(2df,2pd) basis set. For samarium the Stuttgart/Dresden relativistic small core ECP (SDD) and basis set were used for the ground state calculations. The RHF method with the same basis set was also used for the optimization in order to compare the results. All calculations were carried out using the Gaussian03 program package⁹.

Results and Discussions

The results of interaction energy (ΔE) are shown in Table 1 for the reaction 1. The reactions are endothermic for both doublet and quartet states (Table 1). The B3LYP e HF results shows mainly the same values excepting the bromine results.

Table 1. The variations of energy (kcal.mol⁻¹) for the reactions are shown. Only doublet state results are shown.

		RHF (a)	RHF (b)	B3LYP (a)	B3LYP (b)
$\Delta H1$	F	116.91	20.89	17.31	18.20
kcal.mol ⁻¹	Cl	71.63	-24.89	-17.23	-17.09
	Br	66.29	1.90	-19.81	0.24
$\Delta H2$	F	181.39	180.59	171.51	170.82
kcal.mol ⁻¹	Cl	179.95	179.37	169.78	169.39
	Br	179.12	141.66	168.64	143.59

(a) 6-31++G(2df,2pd). (b) 6-311++G(2df,2pd)

The results are in accordance to the Bertran et al.² calculations for the dissociative electron transfer with fluorine. The 6-311 contraction scheme shows a large difference between the halogens in relation to the 6-31 contraction. In the case of quartet state, the ΔE values ranges between 200 and 250 kcal/mol.

In the formation of ethyl radical (reaction 2), the calculations of doublet state using RHF/6-31++G(2df,2pd) are shown in Figure 1. The bromine atom is the best leaving group and is the most soft group from the HSAB theory, with the largest electronegativity (3.0) and ionic radii (196 pm).

Figure 1. Energy difference of reaction-2 in relation to the electronegativity of leaving halogen at RHF/6-311++G(2df,2pd) level.

The HOMO orbitals of C_2H_5F , C_2H_5Cl , and C_2H_5Br at RHF/6-311++G(2df,2pd) are shown in Figure 2. C_2H_5Cl and C_2H_5Br show the same contribution mainly on chlorine and bromine, while C_2H_5F has a contribution over fluorine and C-H bond.

Figure 2. HOMO orbital of C_2H_5F , C_2H_5Cl , C_2H_5Br at RHF/6-311++G(2df,2pd) level.

Conclusions

The Hartree-Fock and hybrid B3LYP density functional methods show the same trend for the reaction with SmI_2 . The analysis of reaction energy shows a linear relation with the electronegativity.

Table 2. Interatomic distance (Å) for the calculated C_2H_5 radical.

C2H5	RHF (a)	RHF (b)	B3LYP (a)	B3LYP (b)
D(C-C) (C2H5) Å	1.498	1.494	1.488	1.484
HOMO (eV)	-13.6	-13.6	-5.61	5.63

(a) 6-31++G(2df,2pd). (b) 6-311++G(2df,2pd)

Table 3. Interatomic distance (Å) for the calculated C_2H_5X and $C_2H_5X^-$ species at the ground state.

		RHF (a)	RHF (b)	B3LYP (a)	B3LYP (b)
D(C-C) Å	F	1.512	1.508	1.515	1.510
(C_2H_5X)	Cl	1.516	1.512	1.517	1.513
	Br	1.516	1.511	1.517	1.511
D(C-C) Å	F	1.508	1.504	1.512	1.506
($C_2H_5X^-$)	Cl	1.512	1.508	1.514	1.509
	Br	1.512	1.495	1.514	1.488
D(C-X) Å	F	1.370	1.368	1.401	1.401
(C_2H_5X)	Cl	1.799	1.798	1.818	1.816
	Br	1.936	1.959	1.954	1.980
D(C-X) Å	F	1.384	1.381	1.414	1.413
($C_2H_5X^-$)	Cl	1.822	1.820	1.843	1.840
	Br	1.958	4.271	2.013	????

(a) 6-31++G(2df,2pd). (b) 6-311++G(2df,2pd)

Table 4. HOMO energies (eV) and charge of heteroatom (Q, au) for the calculated C_2H_5X molecule at the ground state.

C2H5		RHF (a)	RHF (b)	B3LYP (a)	B3LYP (b)
HOMO	F	-13.51	-13.52	-9.01	-9.25
(C_2H_5X)	Cl	-11.73	-11.73	-8.11	-8.13
	Br	-10.82	-10.82	-7.59	-7.61
HOMO	F	-9.71	-9.77	1.78	1.74
($C_2H_5X^-$)	Cl	-8.37	-8.40	1.73	1.70
	Br	-7.59	-3.94	1.70	-0.92
Q(X)	F	-0.33	-0.25	-0.24	-0.21
(C_2H_5X)	Cl	-0.24	-0.18	-0.18	-0.12
	Br	-0.14	-0.26	-0.09	-0.20
Q(X)	F	-0.41	-0.33	-0.33	-0.30
($C_2H_5X^-$)	Cl	-0.24	0.45	-0.20	-0.45
	Br	0.11	-1.00	-0.11	-0.97

(a) 6-31++G(2df,2pd). (b) 6-311++G(2df,2pd)

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