*Res.J.Chem.Sci.*_____*Research Journal of Chemical Sciences*
Vol. **1(4),** 40-48, July **(2011)** ISSN 2231-606X

Comparative Study of the Influence Effect of the Zinc Chloride ($ZnCl_2$) and the Aluminium Chloride ($AlCl_3$) on the 1h-azirene Hydrochlorination

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Available online at: www.isca.in
(Received 3rd May 2011, revised 19th May 2011, accepted 9th June 2011)

Abstract

Hydrochlorination of 1H-azirene (C_2H_3N) is modeled without catalyst and with two catalysts: alumina chloride ($AlCl_3$) and zinc chloride ($ZnCl_2$) respectively. The product of the reaction performed without catalyst is 2-chloroethanimine; the same product is obtained when the reaction performed on alumina chloride. With zinc chloride, the product of reaction is 2-chloroaziridine. On the basis of the calculations performed by HF, MP2 and DFT methods in lanl2dz basis set, a mechanism of each reaction has been proposed.

Keywords: hydrochlorination, hydrogen chloride, zinc chloride, alumina chloride, 2-chloroethanimine, 2-chloroaziridine, Hartree-Fock (HF), Möller Plesset of 2nd order (MP2), Density Functional Theory (DFT), lanl2dz basis set.

Introduction

The hydrohalogenation is the addition reaction of hydrogen halide HX on organic unsaturated cyclic or linear molecules. Most of these reactions are carried out in presence of catalysts and give halogenated widely used in organic synthesis to produce pesticides, anesthetics, solvents, refrigerants or dyes[1,2].

In the present works, we have carried out a comparative study of 1H-azirene (C_2H_3N) hydrochlorination without catalyst and in the presence of two catalysts which are zinc chloride ($ZnCl_2$) and aluminum chloride ($AlCl_3$), respectively. It is worth noting that the reaction of the molecule in the presence of aluminum chloride has already been published earlier[3].

Material and Methods

Calculation methods and drawings of chemical systemsThe calculations were performed using the program Gaussian-03W, by quantum methods HF, MP2 and DFT, in the basis Lanl2dz. Data obtained are geometry, multiplicity and charge of studied systems[4-9].

The drawings of chemical systems studied were jointly produced with ChemDraw Ultra 6.0, Chem3D Ultra 6.0 and GaussView 3.09; the curves were plotted with Microsoft Office Excel 2003 and 2007.

The work was done in the "Laboratoire de Chimie Théorique et de Spectroscopie Moléculaire (Lacthesmo)" of "Université d'Abomey-Calavi" in Republic of Benin on a HP Pentium 4 microcomputer.

Reaction Modeling: The modeling of the hydrochlorination reaction without catalyst was to gradually approach the two reactive molecules (HCl and C_2H_3N) by decreasing the distance between the C^3 atom of 1H-azirene and H^{10} atom of the hydrogen chloride until that the system reaches its lowest energy state (figure 1a). The reaction in the presence

of zinc chloride was modeled in the same way, but in two stages: the 1H-azirène adsorption on the catalyst and the approach of one molecule of hydrogen chloride to the complex (substrate-catalyst) (figure 1b). The reaction parameters are the N^1Zn^7 distance during the adsorption and C^3H^{10} distance during the hydrochlorination.

Results and discussion

Hydrochlorination in the presence of $ZnCl_2$ From a distance C^3H^{10} of 10 Å, the hydrogen chloride molecule was approached to the complex (substrate-catalyst) obtained by adsorption. The geometrical parameters (interatomic distances and angles), atomic charges and energy of the chemical system varied according to the reaction coordinate C^3H^{10}, on the reaction pathway.

The curve of figure 2 shows the variation of the system energy calculated in HF; it shows that the system is more stable at the end of the reaction than at the beginning. By quantum methods HF, MP2 and DFT, the additional reaction enthalpy (ΔH_r) and free energy (ΔG_r) were calculated (Table 1). The values of reaction enthalpy obtained by the three calculation methods are all negative; this means the reaction is exothermic. Also, negative values of the reaction energy mean that the reaction is thermodynamically favorable (Table1).

Some interatomic distances and bond angles, calculated by HF, at the beginning of the reaction, at the transition state and at the end of reaction, are reported in Table 2. Analysis of these results reveals that:

The bonds N^1C^3 and N^1C^4, initially equivalents (1.539 Å), become respectively 1.514 Å and 1.479 Å.

The C^3C^4distance increases from1.271 Å to 1.473 Å. This shows probably the transformation of C = C double bond between two atoms into a single bond C – C.

The C^4Cl^{11}distance changes from 9.050 Å to 1.805 Å, when the $H^{10}Cl^{11}$distance between atoms of hydrogen chloride molecule increases from 1.289 Å to 2.937 Å. Concurrently, the value of the reaction coordinate C^3H^{10} varied from 10 Å to 1.077 Å.

The bond angles $N^1C^3C^4$ and $N^1C^4C^3$ almost identical at baseline (65,618° and 65,607 respectively) differ slightly at the end of reaction (59,356° and 61,711° respectively), but the sum of the three angles $N^1C^3C^4$, $N^1C^4C^3$ and $C^3N^1C^4$ remained equal to 180°, which means that the atoms C^3, C^4 and N^1 form a triangular cycle (because N^1C^3, N^1C^4 and C^3C^4 bonds exist) (table 2).

Figure 3 shows drawings of the system at the beginning of reaction, at the transition state and at the reaction end.

From these observations it seems that H^{10} - Cl^{11} bond of the molecule of hydrogen chloride was broken during the reaction and atoms H^{10} and Cl^{11} have established new chemical bonds with atoms C^3 and C^4 of the 1H - azirene molecule; then C^3 and C^4 pass from sp^2 hybridization state into sp^3 hybridization state after the opening of the π bond existing between them. The reaction product observed is a three-membered nitrogen heterocycle, saturated and chlorinated: this is probably the 2-chloroaziridine. The values of various geometric parameters calculated for this product are close to the standard and experimental values published in the literature[10-16].

Furthermore, the optimized geometry of a molecule of 2-chloroaziridine has been directly calculated and the parameters were compared with those of the product of the reaction (table 3).

The differences observed between the values of calculated data and those of experimental crystallographic data are not significant, especially as regards the interatomic distances. Because our calculations are performed on an isolated molecule, small differences as regards angles raise no problem especially since the crystallographic data concern a

non-isolated molecule contained in a macrosystem. Thus on the basis of these comparisons, the hypothesis of the formation of 2-chloroaziridine at the end of the process, is well confirmed.

In order to determine the mechanism of the reaction that occurred during the addition of hydrogen chloride on the 1H-azirene, we used the population analysis of Mulliken of the system on the reaction pathway (table 4) and the analysis of the vibrational modes in the transition state.

The population analysis of Mulliken of the system reveals that at the transition state, the charges brought by the atoms C^3 (-0.260 au), C^4 (0.226 au), H^{10} (0.230 au) and Cl^{11} (-0.514 au) favor an electrostatic attraction between C^3 and H^{10}, on the one hand, between C^4 and Cl^{11}, on the other hand. From the initial state to the transition state, the atom C^3 was enriched in electronic charge to the detriment of C^4 while H^{10} is impoverished for the benefit of Cl^{11} (table 4). This means that bonds cleavage between C^3 and C^4, on the one hand, and between H^{10} and Cl^{11}, on the other hand, are all heterolytic.

Note that the transition state of reaction, determined by the method QST2-QST3 was reached when the value of the reaction coordinate C^3H^{10} is 1.274 Å. The calculation of the IR spectrum of the reaction system in this state has revealed the existence of a single negative vibrational frequency (-1037.9445 cm^{-1}); this is a characteristic of transition state.

On the basis of these results, the probable mechanism of the reaction between 1H-azirene and hydrogen chloride in the presence of zinc chloride has been proposed (figure 4).

Comparison of the influence of catalysts $ZnCl_2$ and $AlCl_3$ on the1H-azirene hydrochlorination Hydrochlorination of 1H-azirene in the presence of aluminum chloride ($AlCl_3$), had already been studied in previous works[3]. In this condition, we observed the opening of the 1H-azirene molecule ring between the nitrogen atom and a carbon atom. The product of the reaction is the 2-chloroethanimine; the proposed mechanism is shown in figure 5.

In order to have a good basis for comparison, and for a correct appreciation of the influence of the two catalysts on 1H-azirene hydrochlorination, the reaction without catalyst was also modeled. The product obtained in this case is the same as that obtained when operating in the presence of $AlCl_3$ catalyst, it is 2-chloroethanimine. However, it was noticed that the energy barrier reached by the system during the reaction without catalyst is higher and the difference between the two energy barriers is about 37.55 kJ (figure 6): alumina chloride accelerates the 1H-azirene hydrochlorination reaction that provides 2-chloroéthanimine. Indeed, the reaction rate is even larger than its activation energy is lower.

Finally, one notice that the energy of the system obtained at the end of the reaction in the presence of alumina chloride (-147.1443 Hartree) is less than the one obtained in the presence of zinc chloride (-147.1004 Hartree). So alumina chloride leads to the more stable system.

Conclusion

At the end of this study, it appears that the addition reaction of hydrogen chloride on the 1H-azirene leads to the formation of 2-chloroethanimine after opening of the1H-azirene molecule ring. This reaction can be accelerated by alumina chloride acting as a catalyst.

When the catalyst is zinc chloride, the addition reaction leads to the formation of 2-chloroaziridine. In this case, ring opening of 1H-azirene is not observed. Zinc chloride and alumina chloride did not have the same influence on the reaction between 1H-azirene and hydrogen chloride. Given that the nature of the reaction product was dependent on the type of catalyst used; our results also highlight the selectivity that is one role that we recognize to the catalysts.

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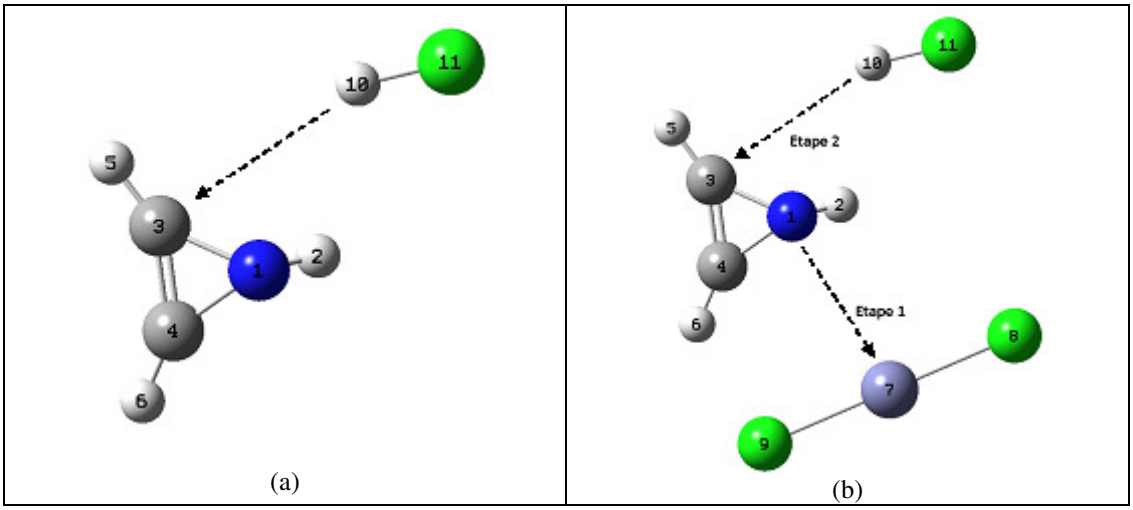

Figure-1: Modeling of the 1H-azirene hydrochlorination (a) without catalyst (b) in the presence of $ZnCl_2$

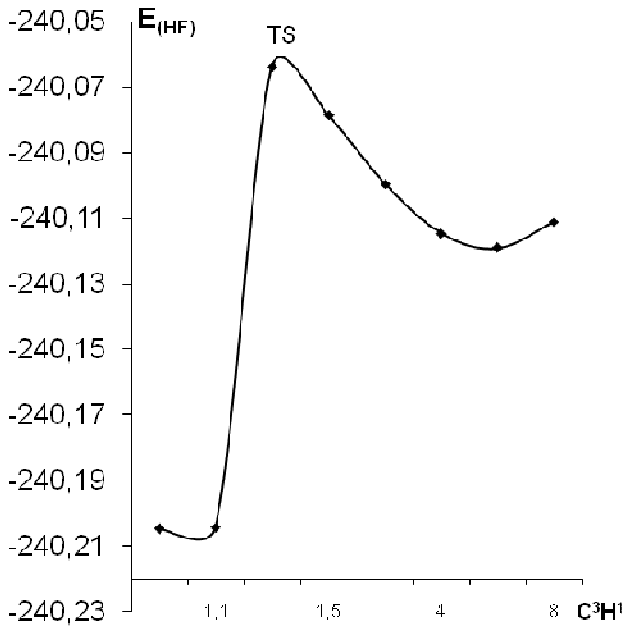

Figure-2: Path of the 1H-azirene hydrochlorination reaction in the presence of zinc chloride ($ZnCl_2$).

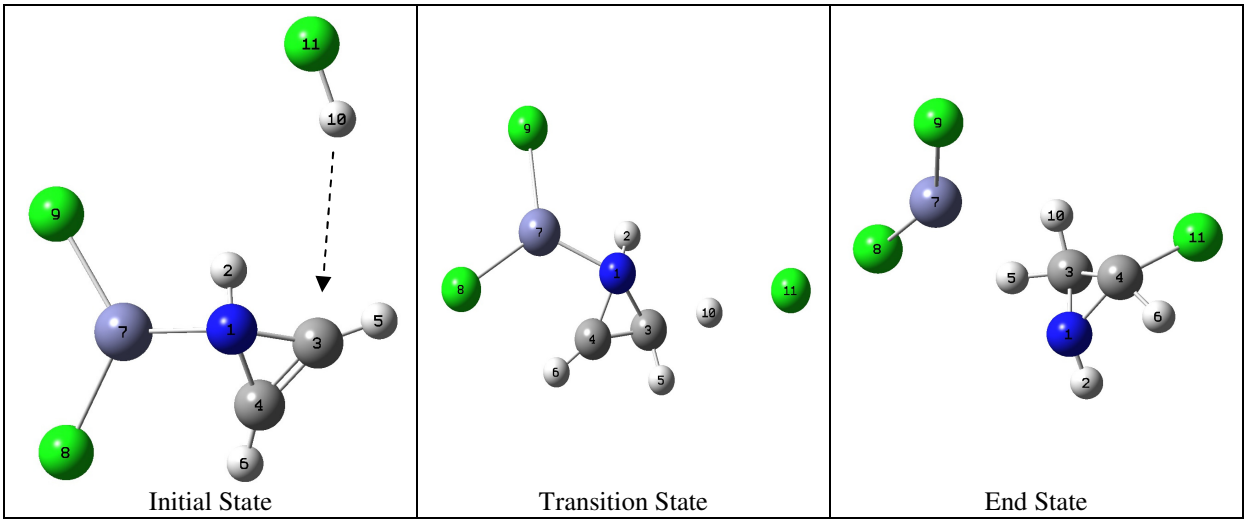

Figure-3: Drawings of the system at the beginning of reaction, at the transition state and at the reaction end.

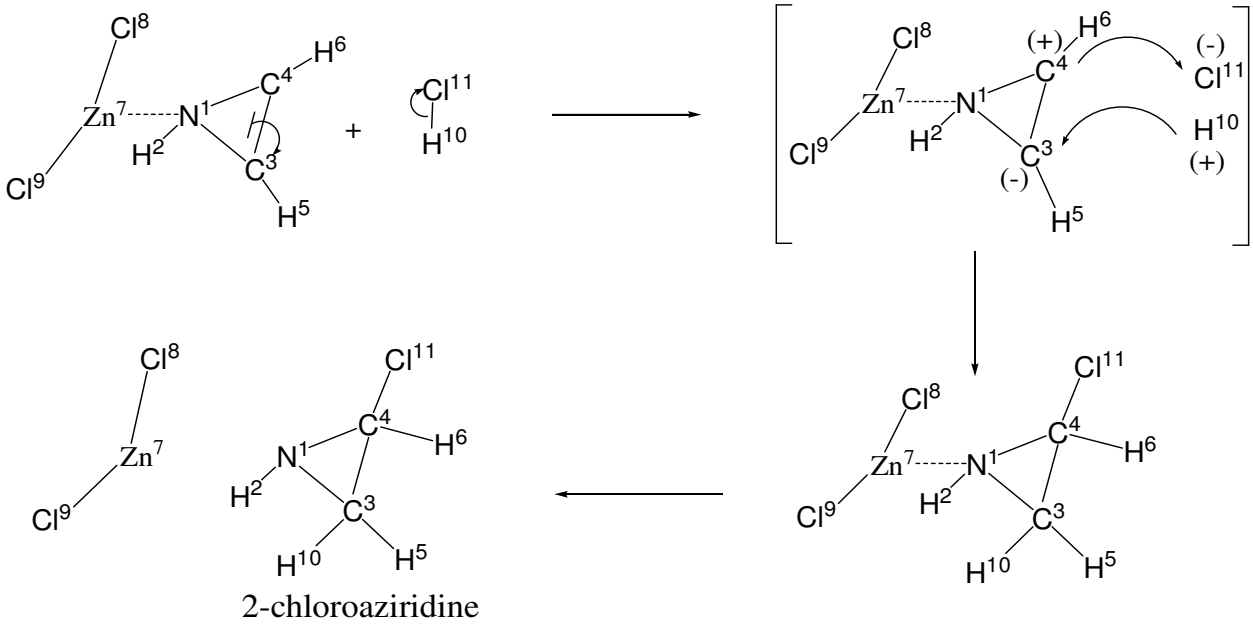

Figure-4: probable mechanism of the reaction between 1H-azirene and hydrogen chloride in the presence of $ZnCl_2$

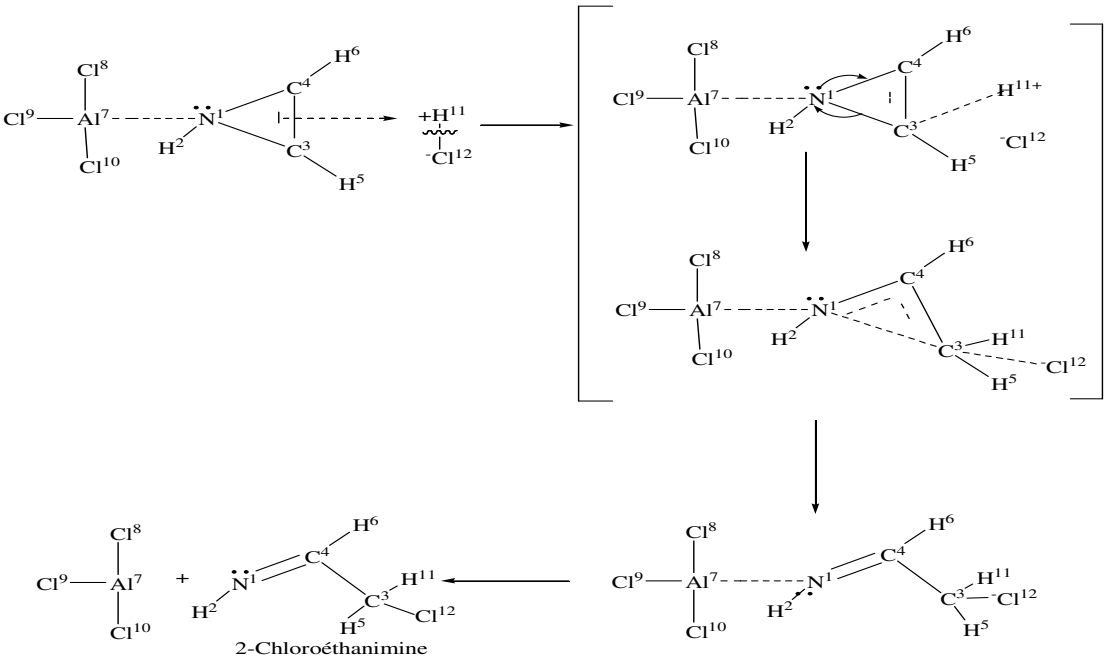

Figure-5: Mechanism hydrochloride 1H-azirene in the presence of $AlCl_3$

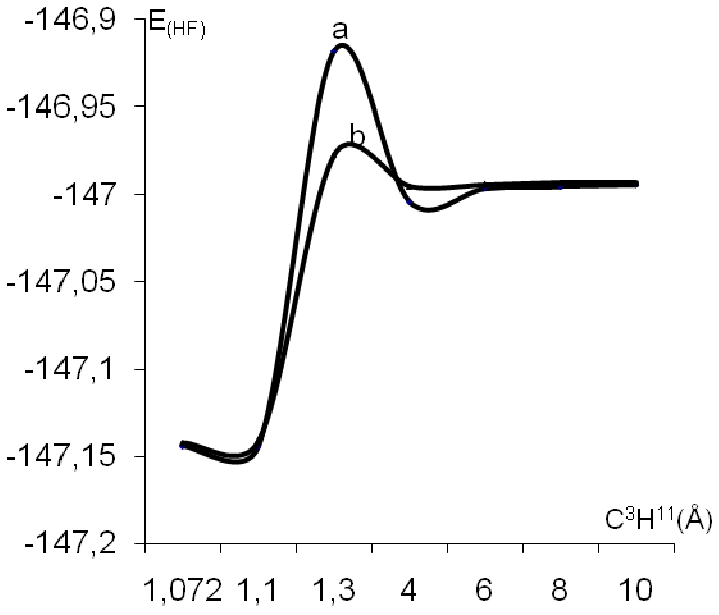

Figure-6: Paths of 1H-azirene hydrochlorination reaction (a) reaction without catalyst ; (b) reaction in the presence of $AlCl_3$

Table-1: Energy of the1H-azirene hydrochlorination reaction in the presence of $ZnCl_2$

Method	Enthalpies			
	$\Delta H_{Reactants}$(ua)	$\Delta H_{Product}$(ua)	$\Delta H_{Reaction}$(ua)	$\Delta H_{Reaction}$ (kJ.mol^{-1})
HF	-240.038	-240.123	-0.085	-222.317
MP2	-240.619	-240.695	-0.076	-198.778
DFT	-243.709	-243.793	-0.084	-219.702
Method	**Gibbs Energies**			
	$\Delta G_{Reactants}$(ua)	$\Delta G_{Product}$(ua)	$\Delta G_{Reaction}$(ua)	$\Delta G_{Reaction}$ (kJ.mol^{-1})
HF	-240.103	-240.172	-0.069	-180.469
MP2	-240.684	-240.743	-0.059	-154.314
DFT	-243.766	-243.842	-0.076	-198.778

Table-2: Interatomic distances (Å) and bond angles of the system during the hydrochlorination of 1H-azirène in the presence of $ZnCl_2$

Parameters	Initial State	Transition State	End State
Distances **(Å)**			
N^1C^3	1.539	1.584	1.514
N^1C^4	1.539	1.415	1.479
C^3H^{10}	10	1.274	1.077
C^3C^4	1.271	1.364	1.473
C^4Cl^{11}	9.05	1.805	1.805
$H^{10}Cl^{11}$	1.289	1.67	2.937
Angles **(°)**			
$N^1C^3C^4$	65.618	56.785	59.356
$N^1C^4C^3$	65.607	69.479	61.711
$C^3N^1C^4$	48.775	53.736	58.933

Table-3: Calculated data for 2-chloroaziridine and thoses for the reaction product

Parameters	**Reaction product**			**2-chloroaziridine**		
Distance (Å)	HF	DFT	MP2	HF	DFT	MP2
C^4Cl^{11}	1.838	1.871	1.863	1.838	1.872	1.863
C^3H^5	1.07	1.088	1.094	1.07	1.088	1.094
C^3H^{10}	1.073	1.085	1.091	1.073	1.086	1.091
C^3C^4	1.491	1.508	1.519	1.491	1.508	1.519
N^1C^3	1.485	1.519	1.557	1.486	1.518	1.556
N^1C^4	1.442	1.459	1.497	1.442	1.458	1.497
Angles(°)						
$N^1C^4C^3$	60.81	61.57	62.17	60.85	61.56	62.13
$N^1C^3C^4$	57.94	57.64	58.24	57.92	57.62	58.24
$C^4C^3H^{10}$	117.12	116.46	118.92	117.15	116.46	117.03
$C^4C^3H^5$	120.09	120.57	120.16	120.08	120.56	120.03
$Cl^{11}C^4C^3$	117.3	116.43	117.37	117.29	116.39	1117.47
Energy *(hartree)*	-147.1005	-148.2288	-147.4153	-147.1005	-148.2288	-147.4153

Table 4: Populations of Mulliken (au) of atoms in the system hydrochloride, 1H-azirène in the presence of $ZnCl_2$

Parameters	**Initial state**	**Transition state**	**End State**
Charges (u.a)			
N^1	-0.781	-0.751	-0.724
C^3	-0.016	-0.26	-0.22
C^4	-0.017	0.226	-0.172
H^{10}	0.227	0.23	0.255
Cl^{11}	-0.227	-0.514	-0.036