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INSERTION REACTION OF Mg INTO THE CARBON-HALOGEN BOND IN CH_3X (X = F, Cl): A THEORETICAL STUDY

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ABSTRACT

Density functional calculations were used to study the insertion reaction of Mg into the Carbon-Halogen bond in CH_3X (X=F, Cl). For both the reactions, a 3-centered transition state with C_s symmetry has been predicted. Both the reactions are predicted to be exothermic in nature. The inclusion of electron correlation increases the exothermicity by a small amount. In CH_3MgX (X=F, Cl), all the bonds except Mg-C and X-Mg have covalent character. Second-order Moller-Plesset perturbation (MP2) has also been made for the reactants, transition states and product. Results of density functional calculations are in good agreement with those obtained from MP2 studies.

Keywords: Density Functional Theory, B3LYP, Insertion, Mg, Carbon-Halogen bond, CH_3X, CH_3MgX (X=F, Cl), ZPVE

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INTRODUCTION

The reaction of Mg atom and Mg clusters have received much attention as it relates to Grignard Chemistry. The chemistry of atomic Mg with alkyl halides to form a Grignard reagent under isolated conditions has received interest because the system is free from solvent perturbations. Ault reported the results of matrix isolation studies for the insertion of Mg atom into the carbon-halogen bond of methyl halides.[1] This study has provided the first spectroscopic characterization of an unsolvated Grignard species. Theoretical calculations have been carried out for the methyl magnesium halides CH_3MgX (X = F, Cl) to obtain equilibrium and transition state geometries, overall reaction energies, activation energy barrier and vibrational frequencies.[2-5] Liu and Davis (have also studied the reaction between Mg atom and fluoroethylene and chloroethylene.[6] In this work, we report the result of our density functional study of the insertion reaction of Mg atom into the carbon-halogen bond of CH_3MgX (X = F, Cl).

EXPERIMENTAL

Method of Calculations

In the present work, the calculations were carried out by ab-initio and density functional method.[7-9] Here the B3LYP functional, which is formed by combining Becke's three-parameter exchange and the non-local correlation functional of Lee, Yang and Parr has been used.[10,11] B3LYP function predicts the activation energy barrier for a number of reactions.[12-20] Hartree-Fock (HF), second-order Moller - Plesset (MP2) calculations have also been done for comparison. The geometries were optimized by the analytical gradient. For all calculations reported here, 6-31G(d) basis set was used. Examination of the number of imaginary frequencies and eigenvalues of the Hessian matrix was done to characterize all stationary points. All calculations were made using GAUSSIAN-94 quantum chemistry package.[19]

RESULTS AND DISCUSSION

Structures of Reactants, Transition states and Products

Optimized geometries of CH_3X, the transition state for the reaction $CH_3X + Mg \rightarrow CH_3MgX$ (X=F, Cl) and the product CH_3MgX are listed in Tables-1,2 and 3, respectively. The inclusion of electron correlation increases all bond lengths in CH_3F and CH_3MgF, excepting Mg2-C1 bond in CH_3MgF. This bond becomes shorter with the inclusion of electron correlation. The transition state geometries obtained using MP2 and B3LYP methods are very much similar to each other but differ considerably from SCF

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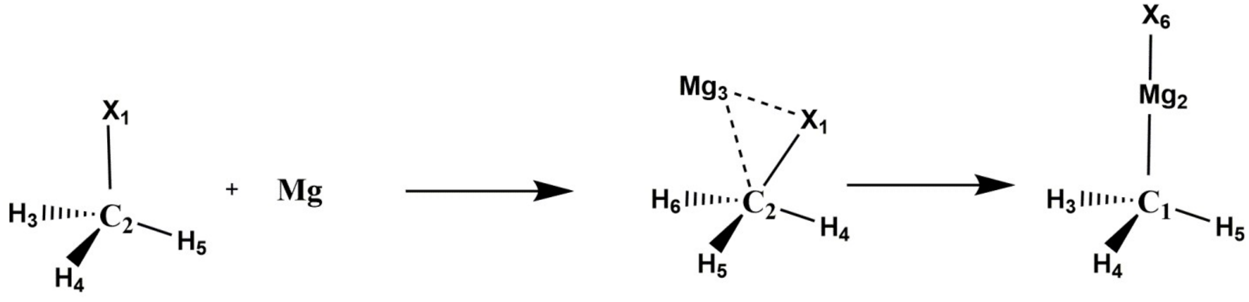
level HF studies. The dihedral angles H4-C2-F1-Mg3 (Fig.-1) is 0^0 at SCF level but changes to 180^0 with the inclusion of electron correlation. This is in agreement with the observation made earlier by Davis (2). At a correlated level of theory (i.e. MP2 and B3LYP), as shown in Table 2, the equivalent C-H bonds (H5-C2 and H6-C2) in the transition state have longer bond length than H4-C2 bonds. As shown in Table 4, the electronic charge densities for H4-C2 bond are larger than those of H5-C2 and H6-C2. C2-F1 and Mg3-F1 bonds in the transition state are somewhat ionic since $\nabla^2\rho_c$ values (Table-4) are positive. In CH_3MgF, all bonds have pronounced covalent characters except the Mg2-C1 and F6-Mg2 bonds. ∇^2P_c values for these two bonds are positive, while negative for other bonds (Table-5).



(TS)

X = F, Cl

Fig.-1: Insertion Reaction of Mg Atom into CH_3X

Calculated equilibrium geometries for CH_3Cl, the transition state in the reaction $CH_3Cl + Mg \rightarrow CH_3MgCl$ and CH_3MgCl using B3LYP are in good agreement with the results of MP2 studies. For this transition state, the H4-C2 is shorter than those of H5-C2 and H6-C2. It can be seen from Table 4 that the electronic charge density at the bond critical point of H4-C2 is larger than those of H5-C2 and H6-C2. $\nabla^2\rho_c$ (Table-4) values for these bonds are positive for C2-Cl1 and Mg3-Cl1 bonds, indicating ionic type interaction. In CH_3MgCl, all bonds have covalent characters except Mg2-Cl and Cl6-Mg2 bonds. $\nabla^2\rho_c$ values for these bonds are positive (Table-5), Density functional predicted equilibrium geometries for CH_3MgF and CH_3MgCl are in good agreement with the post-SCF results of Davis.[2]

Table-1: Calculated Equilibrium Geometry (C_{3v}) of CH_3X^a (X=F, Cl)

	X=F			X=Cl		
Parameters[b]	HF	MP2	B3LYP	HF	MP2	B3LYP
Lengths						
C2-X1	1.364	1.392	1.383	1.784	1.780	1.803
H3-C2	1.082	1.092	1.097	1.078	1.089	1.090
Angles						
H3-C2-X1	109.1	109.1	109.6	108.5	108.8	108.6

a) See Fig. 1
b) All bond length in Å and angles in degrees

Table-2: Calculated Equilibrium Geometry of Transition State [a] (TS) for the Reaction ($CH_3X + Mg \rightarrow CH_3MgX$) (X =F, Cl)

	X=F			X=Cl		
Parameters[b]	HF	MP2	B3LYP	HF	MP2	B3LYP
Lengths						
C2-X1	2.036	1.881	1.974	2.522	2.283	2.396
Mg3-X1	1.805	1.852	1.834	2.395	2.378	2.405
H4-C2	1.070	1.082	1.080	1.067	1.083	1.081
H5-C2	1.068	1.084	1.083	1.070	1.084	1.083
H6-C2	1.068	1.084	1.083	1.070	1.084	1.083
Angles						

Mg3-X1-C2	91.6	90.1	90.7	73.7	73.4	75.7
H4-C2-X1	124.2	84.2	82.5	76.9	84.1	83.5
H5-C2-X1	85.1	112.0	109.7	107.6	112.7	108.8
H6-C2-X1	85.1	112.0	109.7	107.6	112.7	108.8
Dihedral angles						
H4-C2-X1-Mg3	0.0	180.0	180.0	180.0	180.0	180.0
H5-C2-X1-Mg3	-120.4	-65.5	-64.6	-64.2	-66.4	-64.4
H6-C2-X1-Mg3	120.4	65.5	64.6	64.2	66.4	64.4

a) See Fig.-1
b) All bond length in Å and angles in degrees

Table-3: Calculated Equilibrium Geometry (C_{3v}) of CH_3X^a (X = F, Cl)

	X=F				X=Cl			
Parameters[b]	HF	MP2	B3LYP	Other[c]	HF	MP2	B3LYP	Other[c]
Lengths								
Mg2-C1	2.097	2.092	2.084	2.085	2.090	2.084	2.080	2.080
H3-C1	1.088	1.094	1.097	1.095	1.088	1.094	1.097	1.095
F6-Mg2	1.734	1.757	1.749	1.778	2.218	2.208	2.219	2.199
Angles								
H3-C1-Mg2	111.7	111.4	111.4	111.4	111.7	111.4	111.5	111.5

a) See Fig. 1
b) All bond length in Å and angles in degrees
c) Obtained from reference (2)

Table 4: Bonding characteristics in Transition state [a] (TS) for the Reaction, ($CH_3X + Mg \rightarrow CH_3MgX$) (X = F, Cl)

Bond	MP2						B3LYP					
	X = F			X =Cl			X = F			X = Cl		
	ρ_c	$\nabla^2\rho_c$	ϵ	ρ_c	$\nabla^2\rho_c$	ϵ	ρ_c	$\nabla^2\rho_c$	ϵ	ρ_c	$\nabla^2\rho_c$	ϵ
C2-X1	0.084	0.152	0.217	0.062	0.079	0.158	0.068	0.148	0.215	0.050	0.078	0.155
Mg3-X1	0.057	0.541	0.020	0.030	0.175	0.029	0.060	0.574	0.019	0.030	0.158	0.011
H4-C2	0.283	-1.057	0.013	0.281	-1.036	0.007	0.286	-1.063	0.012	0.284	-1.048	0.006
H5-C2	0.278	-1.009	0.009	0.278	-1.011	0.008	0.281	-1.013	0.009	0.281	-1.017	0.007
H6-C2	0.278	-1.009	0.009	0.278	-1.011	0.008	0.281	-1.013	0.009	0.281	-1.017	0.007

a)See Fig. 1, ρ_c in e/au^3 and $\nabla^2\rho_c$ in e/au^5

Table 5: Bonding characteristics in CH_3MgX^a (X = F, Cl)

Bond	MP2						B3LYP					
	X = F			X = Cl			X = F			X = Cl		
	ρ_c	$\nabla^2\rho_c$	ϵ	ρ_c	$\nabla^2\rho_c$	ϵ	ρ_c	$\nabla^2\rho_c$	ϵ	ρ_c	$\nabla^2\rho_c$	ϵ
Mg2-C1	0.053	0.274	0.0	0.054	0.275	0.000	0.055	0.272	0.0	0.055	0.275	0.0
H3-C1	0.260	-0.831	0.037	0.260	-0.821	0.036	0.261	-0.820	0.037	0.261	-0.821	0.036
H4-C1	0.260	-0.831	0.037	0.260	-0.821	0.036	0.261	-0.820	0.037	0.261	-0.821	0.036
H5-C1	0.260	-0.831	0.037	0.260	-0.821	0.036	0.261	-0.831	0.037	0.261	-0.821	0.036
F6-Mg2	0.076	0.791	0.0	0.047	0.281	0.000	0.078	0.808	0.0	0.047	0.047	0.0

a) See Fig.1. ρ_c in e/au^3 and $\nabla^2\rho_c$ in e/au^5

Harmonic Vibrational Frequencies

Calculated harmonic vibrational frequencies for CH_3X, TS1 and CH_3MgX are listed in Tables 6,7 and 8, respectively. As can be seen, vibrational frequencies are positive for CH_3X, CH_3MgX. For these systems, the frequencies obtained at the correlated level of theory (MP2 and B3LYP) are smaller than those obtained at the SCF level. This is in agreement with the results of earlier work on a number of systems[7]. The transition states TS (X=F, Cl) each has one imaginary frequency (Table 7). It can also be seen (Tables 6,7,8) the B3LYP calculated zero-point vibrational energies (ZPVE) are in good agreement with those obtained from MP2 studies.

Table-6: Calculated Harmonic Vibrational Frequencies (cm^{-1}) and Zero Point Vibrational Energy (ZPVE) ($kcal\ mol^{-1}$) of CH_3X (X = F, Cl)

	HF	MP2	B3LYP	HF	MP2	B3LYP
	X = F			X = Cl		
	1187	1106	1093	784	783	722
	1312	1225	1206	1139	1086	1045
	1312	1225	1206	1139	1086	1045
	1652	1556	1524	1538	1467	1415
	1653	1566	1524	1629	1546	1511
	1653	1566	1532	1629	1546	1511
	3233	3115	3037	3268	3150	3095
	3313	3215	3111	3371	3262	3194
	3313	3215	3111	3371	3262	3194
ZPVE	26.6	25.4	24.8	25.5	24.6	23.9

Table-7: Calculated Harmonic Vibrational Frequencies (cm^{-1}) and Zero Point Vibrational Energy (ZPVE) ($kcal\ mol^{-1}$) of Transition state (TS1) for the Reaction ($CH_3X + Mg \rightarrow CH_3MgX$) (X = F, Cl)

	HF	MP2	B3LYP	HF	MP2	B3LYP
	X = F			X = Cl		
	609i	726i	390i	513i	811i	354i
	45	99	92	66	134	108
	266	260	226	205	198	148
	605	585	583	316	351	320
	692	675	635	647	668	616
	800	840	769	728	766	720
	1156	1118	1023	1148	1126	1008
	1566	1504	1454	1553	1493	1445
	1584	1516	1469	1573	1514	1464
	3356	3189	3162	3352	3193	3163
	3528	3334	3310	3533	3333	3318
	3550	3344	3326	3546	3344	3323
ZPVE	24.5	23.5	22.9	23.8	23.0	22.3

Table-8: Calculated Harmonic Vibrational Frequencies (cm^{-1}) and Zero Point Vibrational Energy (ZPVE) ($kcal\ mol^{-1}$) of CH_3MgX (X = F, Cl)

	HF	MP2	B3LYP	HF	MP2	B3LYP
	X = F			X = Cl		
	135	129	128	119	111	108
	135	129	128	119	111	108
	488	479	473	377	379	366
	638	625	625	639	621	622
	638	625	625	639	621	623
	836	813	806	640	638	623
	1322	1234	1207	1324	1236	1209
	1603	1524	1492	1602	1520	1491
	1603	1524	1492	1602	1520	1491
	3168	3099	3036	3170	3099	3037
	3236	3192	3113	3238	3192	3113
	3236	3192	3113	3238	3192	3113
ZPVE	24.4	23.7	23.2	23.9	23.2	22.7

Energetics of the Reactions

Mg atom insertion into the C-X bonds of CH_3X is predicted to be exothermic. At SCF level, exothermicity for X = F is predicted to be smaller than that for X = Cl. At correlated levels of theory

(B3LYP and MP2), the order gets reversed. This is in agreement with the results of Davis (2). The inclusion of electron correlation increases the exothermicity by a small amount. However, the energy barriers are lowered significantly with the inclusion of electronic correlation (Table-9).

Table-9: Relative Energies (kcal mol^{-1}) of Reactants, Products and Transition States[a]

System[b]	HF	MP2	B3LYP	Other[c]	HF	MP2	B3LYP	Other[c]
	X=F				X=Cl			
ΔE	-44.1	-55.6	-51.3	-55.7	-47.4	-51.6	-49.0	-54.4
E_a	50.0	28.4	21.0	31.2	54.8	42.1	32.4	39.4

a) ΔE is the difference in energies of products and reactants and E_a is the activation energy barrier
b) See Fig.-1
c) Obtained from reference (2)

From the study, we can conclude that the method used there is attractive because of its ability to include exchange and correlation for only a moderate cost in comparison to the ab-initio post-SCF method.

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