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A COMPARATIVE THEORETICAL INVESTIGATION OF MAGNESIUM INSERTION INTO THE C-X BOND IN VINYL HALIDES (X = F, Cl, AND Br)

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ABSTRACT

In the present study, the insertion of the magnesium atom into the carbon halogen bond of vinyl halides (X = F, Cl, and Br) is studied via B3LYP density functional calculations with a 6-311G(d,p) basis set. A 3-centered transition state with a single imaginary frequency is obtained for all three reactions. The potential energy profile is determined in both directions for all the systems along the intrinsic reaction coordinate. All the transition states obtained lie on the potential energy surface. The three Grignard reactions are exothermic in nature, as indicated by the energetics of the reactions. Electron correlation inclusion has increased the exothermicity of the reactions. Atom in molecules (AIM) analysis predicted the ionic character of the Mg-C and X-Mg bond in the product, C_2H_3MgX, where X = F, Cl, and Br, as compared to all the other bonds. Results obtained in our study at the DFT level are in agreement with the previous MP2 and HF calculations.

Keywords: Atom in Molecules, B3LYP, Density Functional Theory, Grignard Reagent, Insertion, Transition State, C_2H_3X (X = F, Cl, and Br).

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INTRODUCTION

Organomagnesium compounds (R-Mg-X), more commonly known as Grignard reagents, are one of the best reagents for introducing carbon-carbon bonds. Insertion of Mg into the C-X bond was reported by Ault using matrix isolation studies.[1] It is interesting to note that the solvent perturbations do not affect Mg insertion in alkyl halides under isolated conditions. Theoretical investigation of organomagnesium compounds has been carried out to explore the equilibrium geometries of these moieties along with their transition state.[2-6] Overall reaction energies, activation barriers, and harmonic vibrational frequencies were also calculated for such systems. Ab initio calculations for the reaction between vinyl fluoride and chloride and the Mg atom were reported by Liu and Davis.[7] However, density functional calculations are not reported for these systems. Furthermore, theoretical calculations for vinyl bromide are not reported in the literature. This paper presents a density functional study of the insertion of Mg in vinyl halides (C_2H_3MgX, where X = F, Cl, and Br) to form the corresponding Grignard reagents.

EXPERIMENTAL

Method of Calculations

B3LYP density functional with 6-311G(d,p) basis set has been used for all geometry optimizations.[8,9] RHF/6-311G(d,p) and MP2/6-311G(d,p) have also been performed for the comparison.[10-12] All the stationary points have been identified by their number of negative frequencies and corresponding eigenvalues of the Hessian matrix. The type of bonding, i.e., ionic or covalent, for the reaction pathway of the several stationary points, has been analyzed by the values of electronic charge density (ρ_c), Laplacian density ($\nabla^2\rho_c$), which is known as Bader's topological analysis.[13] B3LYP functional is used to calculate activation energy since it is known to predict the same for the various types of reactions.[14-19] For all the calculations in the present study, GAUSSIAN-09 quantum chemistry software was used.

RESULTS AND DISCUSSION

Structural Analysis

The reactant (R), C_2H_3X (X = F, Cl, and Br), the transition state (TS) of the Grignard reaction, and the product (P), CH_3MgX, are fully optimized (Fig.-1) and geometrical parameters for these are listed in Tables-

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1, 2 and 3, respectively. All bond lengths in 'R' and 'P' except C2-Mg7 in the 'P' increase upon electron correlation inclusion. A longer Mg7-C2 bond in the TS than Mg7-F1 suggests a strong interaction between the latter. Also, the Mg7-F1 bond is found to be shorter than Mg7-Cl1 and Mg7-Br1 (Table-2). This suggests a strong Mg-F interaction as compared to Mg-Cl or Mg-Br when moving from 'TS' towards 'P'. Similar geometries of 'TS' were obtained from the MP2 and B3LYP calculations. However, 'TS' geometries obtained at the SCF level are different from the other two methods. The Mg-C bond length comparison between CH_3MgX and C_2H_3MgX shows that the bond is shorter in the latter, but the Mg-X bond lengths are identical in the two.[6] All vinyl products were found to be planar with a linear C-Mg-X arrangement. Atom in molecules (AIM) analysis of 'R', 'TS', and 'P' has been carried out to analyze the bonding characteristics of all the considered systems. The values of electronic charge density (ρ_c), Laplacian density ($\nabla^2\rho_c$) and ellipticity (ϵ) at the bond critical points are tabulated in Table-4 and 5, calculated using B3LYP/6-311G(d,p) and MP2/6-311G(d,p), respectively. Using B3LYP/6-311G(d,p), the $\nabla^2\rho_c$ value of the C2-X1 bond (Table-4) in 'R' changes from positive (X = F) to negative (X = Cl and Br), depicting the nature of bonding changes from ionic to covalent. The rest of the bonds in all three reactants have shown covalent character since $\nabla^2\rho_c$ values are negative. In the 'TS', $\nabla^2\rho_c$ values are positive for the C2-X1 (X = F, Cl, and Br) and X1-Mg7 (X = F and Cl) bonds (Table-4) which shows the ionic nature of these two bonds. In the case of vinyl bromide, 'TS' is slightly different from the other two 'TS' since the $\nabla^2\rho_c$ value of the C2-Mg7 bond is observed and not for the X1-Mg7 bond that was observed in the case of F and Cl. In the product, i.e., C_2H_3MgX (X = F, Cl, and Br), all bonds have negative values of $\nabla^2\rho_c$ except for C2-Mg7 and X1-Mg7 bonds, which show the ionic character of these two bonds and are covalent for the rest of the bonds. Furthermore, the $\nabla^2\rho_c$ value for the C2-Mg7 bond (Table-4) is almost equal in all three products (X = F, Cl, and Br), showing a similar ionic nature of the bond. On the other hand, the $\nabla^2\rho_c$ value of the X1-Mg7 bond decreases from F to Br, describing the decreasing ionic character of the bond. At the MP2/6-311G(d,p) level of theory, similar bonding characteristics are observed for all the considered structures of 'R', 'TS', and 'P' (Table-5) except for the 'TS' of the reaction $C_2H_3Cl + Mg \rightarrow C_2H_3MgCl$. In this case, the $\nabla^2\rho_c$ value of the C2-Mg7 bond is observed (Table-5) and not for the X1-Mg7 bond as in the case of B3LYP/6-311G(d,p) calculations.

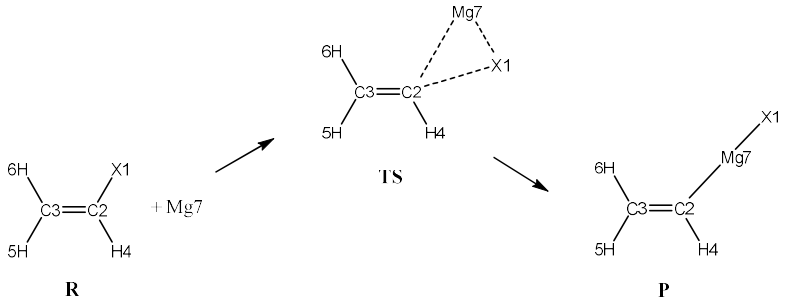

Fig.-1: Insertion Reaction of Mg in vinyl halides (X = F, Cl, and Br)

Table-1: Optimized Geometry Parameters of 'R'[a], C_2H_3X (X = F, Cl, and Br)

	X=F			X=Cl			X=Br		
Parameters	A	B	C	A	B	C	A	B	C
Lengths (in Å)									
C3-C2	1.307	1.329	1.320	1.310	1.334	1.322	1.310	1.334	1.322
X1-C2	1.325	1.343	1.349	1.741	1.730	1.753	1.896	1.888	1.910
H4-C2	1.073	1.084	1.084	1.071	1.083	1.081	1.072	1.083	1.081
H5-C3	1.073	1.081	1.081	1.075	1.084	1.084	1.076	1.084	1.085
H6-C3	1.074	1.082	1.082	1.074	1.083	1.082	1.074	1.084	1.083
Angles (in Degrees)									
X1-C2-C3	122.3	122.3	122.3	123.1	123.1	123.4	123.2	123.1	123.5
H4-C2-C3	125.6	125.4	125.9	124.4	123.6	124.5	124.2	123.5	124.5
H5-C3-C2	119.5	119.2	119.6	119.4	119.1	119.3	119.4	119.1	119.3
H6-C3-C2	121.3	121.0	121.4	122.3	121.9	122.5	122.7	122.2	122.8

Dihedral Angles (in Degrees)									
H4-C2-C3-X1	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0
H5-C3-C2-X1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H6-C3-C2-X1	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0

a. See Fig.-1
A. HF/6-311G(d, p) optimized geometry
B. MP2/6-311G(d, p) optimized geometry
C. B3LYP/6-311G(d, p) optimized geometry

Table-2: Optimized Geometry Parameters of Transition State **'TS'**[a]

	X=F			X=Cl			X=Br		
Parameters	A	B	C	A	B	C	A	B	C
Lengths (in Å)									
C3-C2	1.309	1.350	1.327	1.313	1.368	1.336	1.315	1.368	1.338
H4-C2	1.067	1.084	1.080	1.070	1.087	1.082	1.071	1.088	1.083
Mg7-C2	2.442	2.340	2.396	2.254	2.304	2.391	2.485	2.323	2.389
X1-Mg7	1.854	1.951	1.919	2.440	2.513	2.551	2.638	2.731	2.746
H6-C3	1.072	1.084	1.082	1.073	1.088	1.082	1.073	1.085	1.083
H5-C3	1.081	1.089	1.089	1.080	1.088	1.088	1.080	1.089	1.088
Angles (in Degrees)									
H4-C2-C3	130.7	122.3	126.3	128.3	118.4	123.4	127.0	118.3	122.6
Mg7-C2-C3	125.0	127.8	127.2	125.9	129.9	127.7	125.8	129.3	127.2
X1-Mg7-C2	49.5	44.6	47.2	54.4	49.4	51.4	55.5	50.2	52.4
H6-C3-C2	124.1	123.3	123.8	124.0	122.8	123.7	124.0	122.8	123.7
H5-C3-C2	117.9	118.4	119.0	118.1	118.6	118.9	118.2	118.5	119.1
Dihedral Angles (in Degrees)									
Mg7-C2-C3-H4	-175.7	-164.4	-168.1	-151.5	-149.1	-149.9	-153.4	-144.8	-145.6
X1-Mg7-C2-C3	-91.8	-97.8	-94.2	-99.9	-106.9	-105.3	-102.6	-109.2	-108.0
H5-C3-C2-H4	13.5	12.4	12.8	13.8	14.1	13.3	11.8	14.8	12.3
H6-C3-C2-H5	176.7	173.6	176.1	175.8	172.5	176.1	177.2	172.1	176.4

a. See Fig.-1
A. HF/6-311G(d, p) optimized geometry
B. MP2/6-311G(d, p) optimized geometry
C. B3LYP/6-311G(d, p) optimized geometry

Table-3: Optimized Geometry Parameters of **'P'**[a], C_2H_3MgX (X=F, Cl, and Br)

	X=F			X=Cl			X=Br		
Parameters	A	B	C	A	B	C	A	B	C
Lengths (in Å)									
C3-C2	1.331	1.353	1.340	1.331	1.353	1.340	1.331	1.353	1.340
H4-C2	1.085	1.094	1.093	1.085	1.094	1.093	1.084	1.094	1.093
Mg7-C2	2.076	2.077	2.070	2.070	2.072	2.067	2.072	2.074	2.070
H5-C3	1.082	1.092	1.091	1.082	1.091	1.091	1.082	1.090	1.091
H6-C3	1.081	1.090	1.089	1.081	1.090	1.089	1.081	1.091	1.089
X1-Mg7	1.773	1.776	1.773	2.204	2.197	2.208	2.356	2.351	2.357
Angles (in Degrees)									
H4-C2-C3	114.5	114.2	115.0	114.5	114.2	115.0	114.5	114.3	115.1
Mg7-C2-C3	123.1	122.1	123.8	123.2	122.4	124.0	123.1	122.0	123.8
H5-C3-C2	122.8	122.7	122.8	122.7	122.8	122.7	122.8	122.7	122.7
H6-C3-C2	122.9	122.7	123.0	122.9	122.7	123.1	122.9	122.7	123.1
X1-Mg7-C2	179.0	178.3	179.0	179.1	178.5	179.3	179.1	178.4	179.3
Dihedral Angles (in Degrees)									

H4-C3-C4-Mg7	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0
X1-Mg7-C2-C3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

a. See Fig.-1
A. HF/6-311G(d, p) optimized geometry
B. MP2/6-311G(d, p) optimized geometry
C. B3LYP/6-311G(d, p) optimized geometry

Table-4: Bonding Characteristics (in 'R', 'TS' and 'P')[a] using B3LYP/6-311G(d,p)

		X = F			X= Cl			X= Br		
	Bond	ρ_c	$\nabla^2\rho_c$	ϵ	ρ_c	$\nabla^2\rho_c$	ϵ	ρ_c	$\nabla^2\rho_c$	ϵ
R	C2-H4	0.289	-1.028	0.055	0.287	-1.003	0.036	0.286	-0.996	0.030
	C2-C3	0.352	-1.073	0.424	0.348	-1.043	0.382	0.347	-1.039	0.372
	C2-X1	0.252	0.144	0.069	0.194	-0.279	0.062	0.157	-0.145	0.069
TS	C2-H4	0.286	-1.001	0.049	0.283	-0.979	0.043	0.282	-0.970	0.039
	C2-C3	0.344	-1.025	0.316	0.337	-0.989	0.302	0.336	-0.981	0.300
	C2-X1	0.098	0.174	0.115	0.081	0.058	0.119	0.072	0.043	0.130
	X1-Mg7	0.048	0.401	0.013	0.023	0.091	1.396	0.030*	0.082*	0.125*
P	C2-H4	0.271	-0.890	0.028	0.271	-0.890	0.027	0.271	-0.890	0.028
	C2-C3	0.334	-0.967	0.253	0.334	-0.967	0.253	0.334	-0.967	0.253
	C2-Mg7	0.057	0.266	0.056	0.058	0.266	0.055	0.058	0.264	0.055
	X1-Mg7	0.072	0.703	0.004	0.051	0.270	0.007	0.045	0.204	0.007

a. Fig.-1, $\nabla^2\rho_c$ are in e/au^5 and ρ_c values in e/au^3
*Consider C2-Mg7 instead of X1-Mg7

Table-5: Bonding Characteristics (in 'R', 'TS' and 'P')[a] using MP2/6-311G(d,p)

		X = F			X= Cl			X= Br		
	Bond	ρ_c	$\nabla^2\rho_c$	ϵ	ρ_c	$\nabla^2\rho_c$	ϵ	ρ_c	$\nabla^2\rho_c$	ϵ
R	C2-H4	0.288	-1.036	0.057	0.284	-1.000	0.037	0.283	-0.991	0.032
	C2-C3	0.344	-1.030	0.463	0.338	-0.987	0.414	0.337	-0.978	0.402
	C2-X1	0.253	0.244	0.064	0.204	-0.334	0.068	0.164	-0.171	0.072
TS	C2-H4	0.283	-0.994	0.051	0.280	-0.961	0.046	0.278	-0.953	0.041
	C2-C3	0.327	-0.932	0.339	0.315	-0.867	0.312	0.314	-0.862	0.313
	C2-X1	0.126	0.116	0.112	0.105	0.021	0.103	0.091	0.018	0.101
	X1-Mg7	0.043	0.358	0.047	.034*	0.120*	0.108*	0.033*	0.111*	0.083*
P	C2-H4	0.269	-0.887	0.024	0.269	-0.887	0.024	0.269	-0.888	0.024
	C2-C3	0.323	-0.901	0.272	0.323	-0.901	0.271	0.323	-0.900	0.271
	C2-Mg7	0.055	0.280	0.056	0.056	0.283	0.054	0.056	0.280	0.054
	X1-Mg7	0.070	0.708	0.004	0.051	0.295	0.008	0.045	0.220	0.007

a. Fig.-1, $\nabla^2\rho_c$ are in e/au^5 and ρ_c values in e/au^3
*Consider C2-Mg7 instead of X1-Mg7

Table-6: Harmonic Vibrational Frequencies (cm^{-1}) and ZPVE (kcal mol^{-1}) of **R**[a], C_2H_3X (X = F, Cl, and Br)

A	B	C	D	A	B	C	D	A	B	C	D
X = F				X= Cl				X= Br			
523	483	485	490	428	404	400	395	374	352	347	344
800	739	732	713	691	630	633	620	649	592	598	582
1019	849	888	923	761	753	698	720	653	636	598	612
1023	948	937	863	1066	883	926	896	1073	888	931	901
1085	979	970	929	1081	986	977	941	1078	982	975	941
1272	1190	1167	1 I57	1128	1053	1040	1030	1108	1027	1019	1005
1437	1345	1331	1305	1412	1324	1306	1279	1390	1297	1282	1258
1533	1427	1412	1380	1518	1419	1404	1369	1517	1416	1403	1373
1865	1715	1714	656	1814	1660	1668	1608	1802	1646	1659	1602
3312	3217	3162	3052	3301	3199	3149	3030	3295	3191	3140	3027
3377	3254	3196	3080	3379	3256	3210	3086	3376	3251	3210	3087
3410	3329	3258	3115	3397	3307	3242	3121	3391	3298	3234	3112

ZPVE											
29.5	27.8	27.5	27.5	28.6	27.0	26.7	26.7	28.2	26.6	26.3	26.3

a. See Fig.-1
A. HF/6-311G(d, p) optimized geometry
B. MP2/6-311G(d, p) optimized geometry
C. B3LYP/6-311G(d, p) optimized geometry
D. From reported experimental data[7,20]

Table-7: Harmonic Vibrational Frequencies (cm^{-1}) and ZPVE (kcal mol^{-1}) of **'TS'**[a] for the Reaction $C_2H_3X + Mg \rightarrow C_2H_3MgX$ Where (X = F, Cl, and Br)

	A	B	C	A	B	C	A	B	C
	X = F			X= Cl			X= Br		
	657i	601i	412i	667i	593i	401i	641i	583i	359i
	178	185	176	171	175	162	153	145	140
	256	293	259	228	263	244	212	242	227
	330	346	323	289	303	283	253	277	261
	483	522	484	335	376	341	323	351	329
	607	550	557	473	498	486	449	473	463
	920	738	830	943	706	834	954	711	838
	1000	931	915	1001	939	930	1001	943	935
	1005	1002	961	1028	1016	967	1037	1000	966
	1178	1232	1163	1183	1240	1173	1186	1220	1170
	1471	1366	1375	1475	1327	1371	1476	1325	1371
	1713	1537	1576	1702	1502	1547	1699	1500	1544
	3252	3157	3101	3258	3156	3109	3256	3153	3105
	3379	3235	3207	3379	3197	3192	3375	3189	3180
	3435	3263	3227	3404	3260	3214	3389	3259	3209
ZPVE	27.5	26.2	26.0	27.0	25.7	25.5	26.8	25.4	25.4

a. See Fig.-1
A. HF/6-311G(d, p) optimized geometry
B. MP2/6-311G(d, p) optimized geometry
C. B3LYP/6-311G(d, p) optimized geometry

Table-8: Calculated Harmonic Vibrational Frequencies (cm^{-1}) and ZPVE (kcal mol^{-1}) of **'P'**[a], C_2H_3MgX (X = F, Cl, and Br)

	A	B	C	A	B	C	A	B	C
	X = F			X= Cl			X= Br		
	101	94	95	85	80	81	77	71	73
	141	135	134	126	120	118	115	109	108
	248	235	244	236	224	231	221	210	215
	404	360	390	390	361	375	327	323	315
	492	480	472	403	388	390	402	358	388
	818	796	788	649	643	625	623	614	599
	1077	951	982	1077	954	985	1077	953	983
	1095	1002	1004	1097	1002	1004	1097	1002	1003
	1163	1072	1069	1162	1071	1068	1162	1070	1068
	1379	1269	1273	1380	1270	1275	1380	1269	1274
	1539	1437	1437	1538	1437	1438	1538	1436	1437
	1748	1612	1622	1747	1612	1622	1747	1611	1621
	3202	3115	3056	3203	3116	3057	3203	3116	3057
	3227	3131	3075	3229	3132	3076	3228	3132	3075
	3285	3200	3134	3288	3201	3135	3287	3201	3135
ZPVE	28.5	27.0	26.8	28.0	26.6	26.4	27.9	26.4	26.2

a. See Fig.-1
A. HF/6-311G(d, p) optimized geometry
B. MP2/6-311G(d, p) optimized geometry

C. B3LYP/6-311G(d, p) optimized geometry

Frequency Analysis

Harmonic vibrational frequencies are calculated for the 'R', 'TS', and 'P' and tabulated in Table-6, 7, and 8, respectively. All the vibrational frequencies are observed to be positive for 'R' and 'P', suggesting a stable geometry. At the MP2 and SCF levels of theory, frequencies are larger in magnitude than those observed at the B3LYP level for all the systems. Furthermore, the frequencies at the B3LYP level are in good agreement with the experiment values for the reactants as compared to values obtained at MP2 and SCF levels (Table-6).[7,20] Only one imaginary frequency, i.e., a negative force constant, is obtained for each 'TS' (X = F, Cl, and Br), implying a valid structure of 'TS' (Table-7). The zero-point vibrational energies (ZPVE) calculated at the B3LYP and MP2 levels of theory are in good agreement. Furthermore, ZPVE at the SCF level is slightly greater than the other two methods of calculation.

Energetics of the Reactions

Mg atom insertion into the carbon halogen bond of vinyl halide (X = F, Cl, and Br) is exothermic in nature, as indicated by the negative values of the energy of the reaction. The exothermicity is found to follow the order F<Cl<Br at all the levels of calculations (Table-9). The calculations at the MP2 level showed an increment in the exothermicity as compared to that at the SCF level for all the systems. However, B3LYP calculations did not display a trend in the energetics of the reaction when compared to the corresponding SCF level of calculations for the considered systems. For vinyl fluoride, reaction exothermicity increases, and for chloride and bromide, exothermicity decreases when compared to the values obtained at the SCF level of theory. Activation energies (E_a) are also calculated, and it was observed that the magnitude of E_a decreases significantly upon electron correlation inclusion, as can be seen in Table-9. Furthermore, the activation energy at the B3LYP level for the vinyl fluoride (24.4 kcal mol^{-1}) is the least among the three reactions studied, which is in accordance with the previous ab initio calculations.[7] The activation barrier for the vinyl chloride is found to be maximum, followed by the vinyl bromide, with E_a equal to 27.4 and 25.1 kcal mol^{-1}, respectively. The potential energy surface (PES) for all three Grignard reactions along the intrinsic reaction coordinate (IRC) in both directions, calculated at the B3LYP/6-311G(d,p), is shown in Fig.-2. It was observed from the IRC plot that the Grignard product (all three) lies on the PES. The 'TS' obtained for the vinyl fluoride reaction lies more toward the product side when compared to the analogous vinyl chloride and bromide reactions. These observations are supported by the E_a data as discussed earlier.

Table-9: Calculated E_a and Energy of Reaction (ΔE) (kcal mol^{-1}) for the Reaction using HF (A), MP2 (B), and B3LYP (C) using 6-311G(d,p) Basis Set

	Method of Calculation	E_a	ΔE
$C_2H_3F + Mg \rightarrow C_2H_3MgF$	A	56.4	-40.8
	B	29.5	-51.1
	C	24.4	-45.2
	D	22.6	-53.8
$C_2H_3Cl + Mg \rightarrow C_2H_3MgCl$	A	54.7	-50.8
	B	32.2	-52.4
	C	27.4	-49.8
	D	29.7	-53.7
$C_2H_3Br + Mg \rightarrow C_2H_3MgBr$	A	51.7	-52.4
	B	29.3	-53.4
	C	25.1	-50.2
	D	-	-

A. HF/6-311G(d, p) optimized geometry
B. MP2/6-311G(d, p) optimized geometry
C. B3LYP/6-311G(d, p) optimized geometry
D. obtained from reference (7)

CONCLUSION

Insertion of the magnesium atom into the carbon halogen bond of C_2H_3X, where X = F, Cl, and Br via DFT calculations (B3LYP/6-311G(d,p)), shows that the three reactions considered in the study are exothermic

in nature. A 3-centered transition state is obtained for all three systems with C_s symmetry. Transition state geometry was characterized by a single negative frequency.

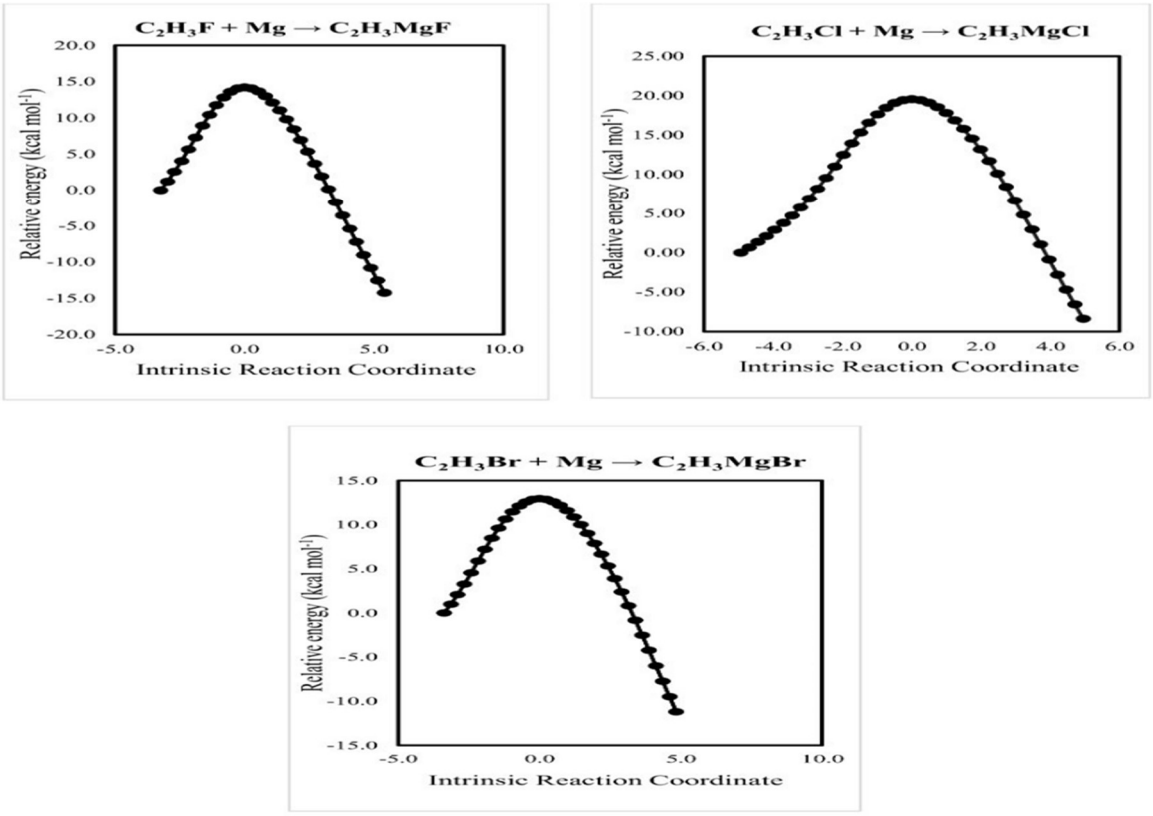

Fig.-2: Potential energy profile(PES) along the reaction coordinate for C2H3X + Mg C2H3MgX (X= F, Cl and Br) using B3LYP/6-311G(d.p) basis set. The zero point along the IRC represents the transition state and the reactant and products are towards the negative and positive directions respectively.

The energy profile along the IRC of all three reactions is plotted. In the case of vinyl fluoride, TS lies more toward the product compared to the corresponding vinyl chloride and bromide, which is supported by the lowest E_a value (24.4 kcal mol^{-1}). AIM analysis indicated that the Mg-C and X-Mg bonds are ionic in nature in the C_2H_3MgX (X=F, Cl, and Br) in comparison to all the other bonds. The results obtained are in accordance with previous calculations at the MP2 and SCF levels of theory. It can be concluded from the present study that only at a modest computational cost, exchange, and correlation can be effectively included as compared to the ab initio method of calculations.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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