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Insertion Reactions Between Singlet Carbenes and Alcohols: Mechanistic insights from ab Initio and DFT Study

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Abstract

The insertion reactions of $^1CH_2$, ^1CHF and $^1CF_2$ into 1° and 2° polar O-H bonds of methanol, ethanol, 1-propanol and 2-propanol have been investigated at *ab initio* (HF, MP2) and DFT levels using 6-31g (d, p) basis set. In the two-step mechanism of carbene insertion into O-H bond, initially the reactants form an ylide-like complex, which then undergoes the 1, 2-proton shift concertedly giving the ether product. The barrier heights of the TSs in the concerted mechanism vary with the type of carbene and the O-H bond. Frontier orbital energies (FOE) indicate that the initial interactions between the alcohols and carbenes are controlled mainly by the HOMO of alcohols and the LUMO of carrbenes. This fact is substantiated by NBO charge analysis, which indicates the net amount of charge transfer from alcohol to carbene moiety in the transition states at B3LYP (MP2)/6-31g (d, p) levels.

Key words: Methylene, Flurocarbenes, ab initio, DFT, O-H insertion, Alcohol insertion, activation barriers.

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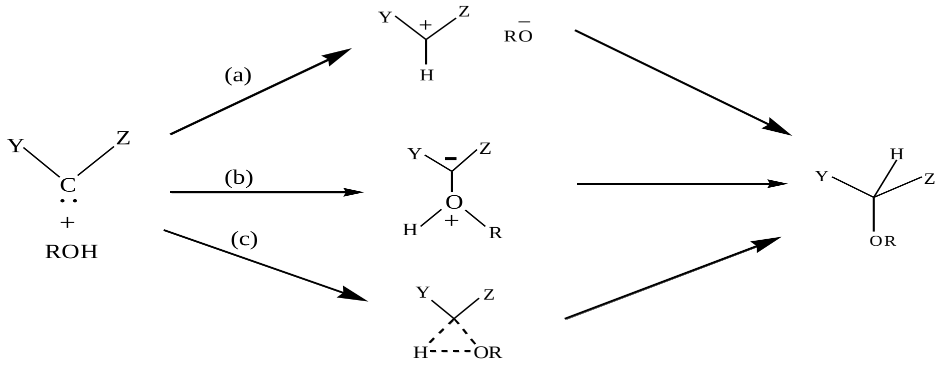
1. Introduction

Singlet carbenes have the tendency to readily insert into O-H bond [1]. The reaction mechanisms for this insertion process have been controversial for a long time [2-14]. Three general mechanisms have been proposed for their reaction with alcohols [2, 3]: (a) proton transfer from the hydroxyl group to the carbene, followed by addition of the ion pairs, (b) ylide formation followed by proton migration to form the corresponding ether, and (c) direct insertion of the carbene into the O-H bond as shown below.



Experimentally it has been shown that depending on the nature of substituent in carbene (:CXY) the insertion reaction may follow any one of the three mechanistic paths. Bethell et al. [4] have studied the reaction of :CPh2 with methanol and tert-buty1 alcohol in acetonitrile, and based on the analysis of product isotopic effect, they have concluded that in this case the reaction follows the mechanistic pathway (b). The reaction between CH_3OH and cyclopentadienylidene also follows the type (b) mechanism, while the type (a) path is followed if the carbene is cycloheptatrienylidene [5]. The reaction of fluorenylidene with ROH was studied by Zupancic et al. [3] using laser spectrophoto-metric techniques, and by measuring the kinetic and product isotopic effects in CH_3CN solution they concluded that the mechanism is not a one-step process, and suggested that there is an ylide formation, i.e., path (b). The formation of diarylcarbocation formed by the protonation of diaryl carbene in acetonitrile-water solution follows path (a) [7], which is in apparent conflict with the results of Bethell et al. [4] for diphenylcarbene. In a study of diphenylcarbene reactions with H_2O in acetonitrile-water solution and with methanol, ethanol and 2-propanol using laser flash photolysis, Chateauneuf [8] detected the diphenylcarbocation again in favor of the path (a) contradicting the conclusions of Bethell's first studies.

Theoretical studies have also been performed for some systems to predict the mechanism for these insertion reactions. Pople et al.[10] studied the potential-energy surface for the H_2O+CH_2 reaction at the MP4/6-31g(d)//HF/6-31g(d) level, and they found that the reaction proceeded by direct insertion, without an energy barrier. A correlated CASSCF study by Walch also supported this result [11]. Yates et al. determined optimized geometries and relative energies for H_2O-CH_2 at MP4/6-311g (d, p)//MP2/6-31g (d) [15]. At this level, they found that a barrier for rearrangement of H_2O-CH_2 to methanol exists, but the barrier is only 1 kcal/mol. Similar structures to those obtained for CH_2 interacting with H_2O were also found at the MP2/3-21g level for CCl_2 and CF_2 interacting with H_2O [16].

As the literature survey found little details about the carbene insertions into the O-H bond of aliphatic alcohols the researcher has been prompted to probe theoretically the various mechanistic pathways. For this, methylene and flurocarbenes have been chosen as the reagents and simple aliphatic alcohols like methanol, ethanol, 1-propanol and 2-propanol as the substrates. In addition to the reaction mechanisms, the influences of fluorine on the transition states, energetics, geometrical parameters etc., have also been investigated in this study at B3LYP and MP2 levels of theory using 6-31g (d, p) basis set.

2. Computational Details

Geometries of the reactants, ylide-like complexes the transition states and the products have been optimized first at HF/6-31g (d, p) level using Gaussian 03W suite of program [17]. The resultant HF geometries obtained were then optimized at MP2 [18] and B3LYP [19-23] levels. The standard 6-31g (d, p) [24, 25] basis set has been adopted in all the calculations for better treatment of 1, 2-hydrogen shift during the rearrangement of the ylide to the product through the transition state. All the stationary points found were characterized as either minima or transition states (TSs) by computing the vibrational harmonic frequencies – TSs have a Hessian index of one while minima have zero hessian index. TSs were further characterized by animating the imaginary frequency in MOLDEN [26] and by checking with intrinsic reaction coordinate (IRC) analyses. The calculated vibrational frequencies have been used to compute the thermodynamic parameter enthalpies of the reaction. The intrinsic reaction coordinate analyses have been done for some transition structures obtained at the MP2 level [27].

Bond orders reported here are Wiberg [28] bond indices calculated by Natural Bond Orbital (NBO) program [29]. From this bond orders, bond formation index BFi, bond cleavage index BCj are calculated as follows [30, 31].

$$BF_i \, or \, BC_j = \frac{BO_i^{TS} - BO_i^{R}}{BO_i^{P} - BO_i^{R}} \times 100$$

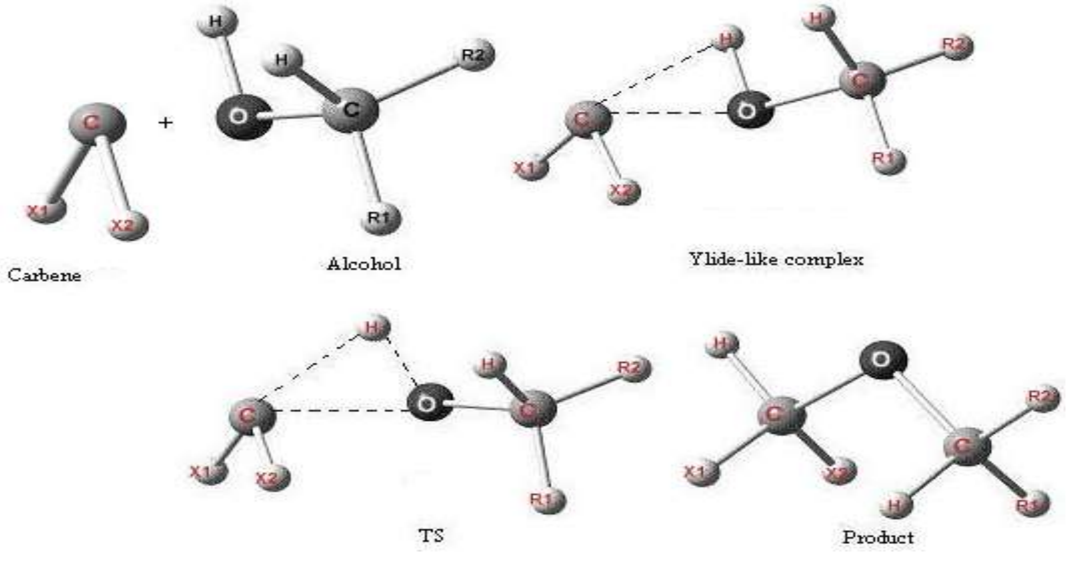
BFC_{Ave} is the average percentage of all bond forming and cleaving indices of various species in the reaction step.

$$BFC_{Ave} = \frac{\sum_{i,j} \left(BF_i + BC_j \right)}{n}$$

where n is the total number of bonds that undergo major changes during the reaction. Deformation energy analyses also have been done as reported earlier [31].

3. Results and discussion

The O-H bond of alcohols (methanol/ethanol/1-propanol/2-propanol) undergoes insertion reactions with $^1CH_2$, ^1CHF and $^1CF_2$ forming methoxyalkanes, fluromethoxyalkanes and difluromethoxyalkanes respectively. Reactants first form the ylide-like complex. The ylide proceeds to form a concerted transition state which then converges into a product as shown in Figure 1.



X1, X2=H, F, Cl; R1=H, CH_3, C_2H_5; R2=H, CH3

Figure 1. Reaction pathways for the insertion of carbenes into O-H bond of alcohols

3.1. Reaction energetics

Frontier orbital energies (FOE) indicate that the initial interaction between the aforesaid alcohols and $^1CH_2$ are controlled mainly by the HOMO of alcohol and the LUMO of $^1CH_2$ i.e., HLEG ($HOMO_{ROH} - LUMO_{^1CH_2}$). The HLEG values and the q_{Ct} (amount of charge transfer) during the TS formation are presented in Table 1 at MP2/6-31g (d, p) and B3LYP/6-31g (d, p) levels. The lower HLEG, the higher the q_{ct} as well as lower the E_a is the correlated trend observed in the insertion reaction (Table 1) if the mechanism (b) is followed. Further the HLEG and consequently the Ea varies linearly with the nucleophilicity of the carbon bearing the hydroxyl group. From the above facts, the following trend emerges in the insertion reaction in terms of the type of the alcohol and the nature of the hydroxyl group bearing carbon: 2-propanol > 1-propanol > ethanol > methanol. The same trend is noticed in the quantum of charge transferred at the TS from the alcohol to the carbene [2-propanol (0.206 a.u.) >1-propanol (0.205 a.u.) > ethanol (0.206 a.u.) > methanol (0.203 a.u.)]. All the above facts reveal that HLGE is the controlling factor in the insertion reaction of $^1CH_2$ into O-H of alcohol. This conclusion is in consonance with MP2/6-31g (d, p) calculations; but no such correlation could be arrived at from B3LYP/6-31g (d, p) results.

The energy profile diagram of the insertion of $^1CH_2$ into O-H of methanol at MP2 and B3LYP levels is shown in Figure 2. In the diagram the energies of ylides, transition states and products are shown with reference to the reactants. The intermediate ylide formed is quite obvious from its lower energy point in the energy profile on comparison with either the reactants or the TS and moreover its zero hessian index confirms that it is a stationary point. The binding energy of the CH_3OH with $^1CH_2$ (22.38 kcal/mol) at MP2 level is stronger. The value of energy barrier for the formation of transition state from the complex is 2.3 and 0.9 kcal/mol at MP2 and B3LYP levels respectively. Computed deformation energies of methanol (0.9kcal/mol) and $^1CH_2$ (0.0 kcal/mol) in the ylide at MP2 level show that the methanol distorts to a small extent during the formation of the ylide.

Table 1 Relative energies of ylides, TSs and products relative to reactants activation barriers (E_a), enthalpy of reactions (ΔHr) in kcal/mol and q_{ct} at B3LYP (MP2)/6-31g (d, p) levels for the $^1CH_2$ insertion insertion into O-H bond of alcohols.

Alcohol	ylide	TS	product	HLEG (eV)	E_a	q_{ct}	ΔHr
methanol	-22.5 (-22.4)	-21.6 (-20.1)	-111.2 (-114.6)	0.143 (0.517)	0.9 (2.3)	0.217 (0.203)	-104.9 (-108.1)
ethanol	-22.8 (-22.7)	-21.8 (-20.5)	-111.2 (-114.8)	0.140 (0.509)	1.0 (2.2)	0.218 (0.206)	-105.4 (-108.9)
1-propanol	-22.8 (-22.8)	-21.9 (-20.6)	-111.1 (-114.8)	0.139 (0.508)	1.0 (2.2)	0.217 (0.205)	-105.3 (-108.9)
2-propanol	-22.8 (-22.5)	-21.5 (-20.7)	-109.3 (-113.5)	0.139 (0.504)	1.3 (1.8)	0.215 (0.206)	-103.5 (-107.6)

q_{ct} = quantum of charge transferred from alcohol to $^1CH_2$ moiety.

HLEG = $HOMO_{ROH} - LUMO^1{}_{CH_2}$

The deformation energies (DE1) of the alcohols (methanol, ethanol, 1-propanol and 2-propanol) and (DE2) $^1CH_2$, in the TSs, both at B3LYP and MP2 levels are found to be very small (Table 2) and hence the insertion through the TSs becomes easier. This aspect is further supported by the exothermicity (Table 1) [the reaction enthalpy values -105.4(-108.9), -104.8(-108.1), -105.3(-108.9) and -103.5(-107.6) kcal/mol corresponding to methanol, ethanol, 1-propanol and 2-propanol] of all the insertion reactions investigated here. Moreover reaction enthalpy values are consistent with the Hammond

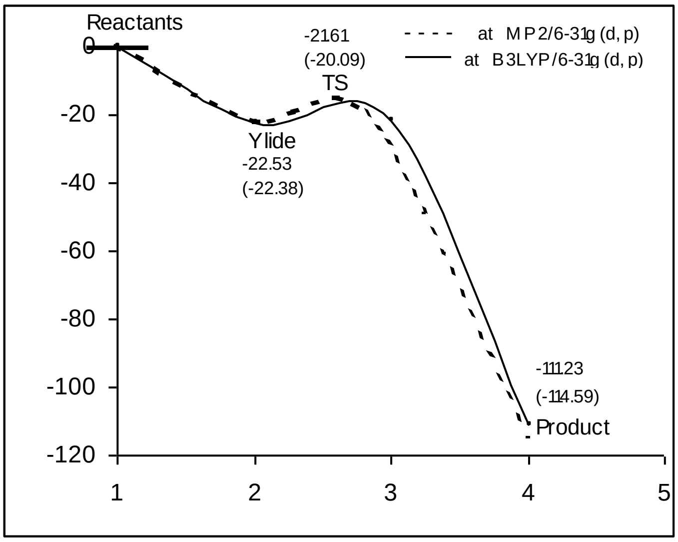


Figure 2. Energy profile for $^1CH_2 + CH_3OH \rightarrow CH_3\text{-}O\text{-}CH_3$

postulate [32], i.e., the TSs is more reactants like rather than the products. A very little decreasing trend in barrier is observed as we move from methanol to 2-propanol at MP2 level (Table 1). This is due to the increase in electron repelling alkyl substituent at the nucleophilic carbon, bearing the O-H group.

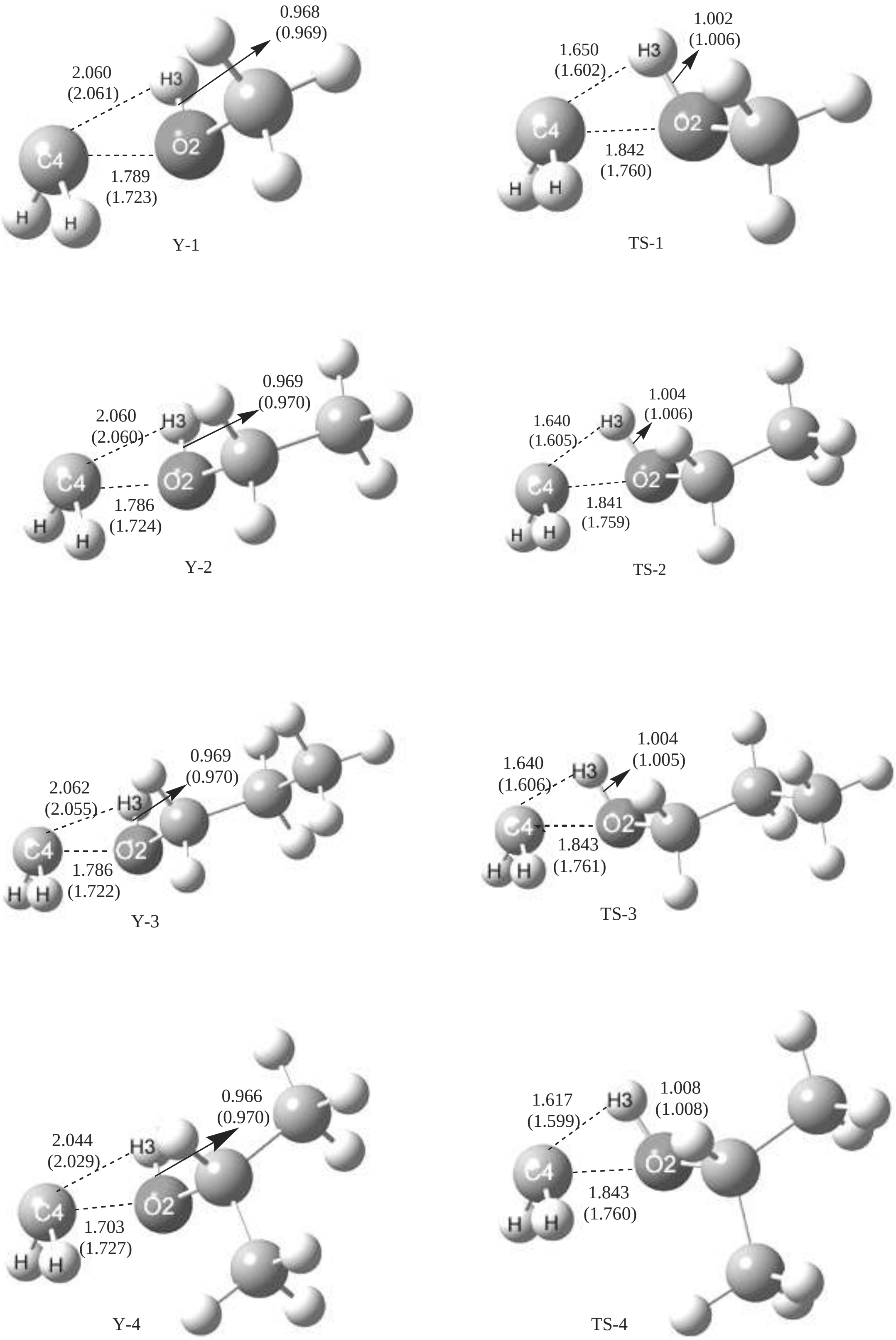
3.2. Geometry of the ylide and the transition state

The optimized structures of the ylides, and the TSs formed between $^1CH_2$ and methanol, ethanol, 1-prapanol and 2-propanol at MP2/6-31G (d, p) level are shown in Figure 3. When $^1CH_2$ approaches the O-H of methanol the O2-H3 bond gets weakened (elongation from 0.963 to 0.969 Å), while the interactions among the pairs C4 : H3 (2.061Å) and C4 : O2 (1.723 Å) get stabilized, resulting in a lower energy ylide formation. As the ylide moves up nearing the TS, the O2-H3 bond starts cleaving (1.006Å) with the formation of C4-H3 (1.602) and C4-O2 (1.760Å) bonds.

Table 2 Selected geometrical parameters (distances in Å) and deformation energies (kcal/mol) for the $^1CH_2$ insertion into O-H bond of alcohols B3LYP (MP2) / 6-31g(d, p) at levels

Alcohol	Species	C4-O2	C4-H3	O2-H3	Deformation energies	
					DE1	DE2
methanol	ylide	1.789(1.723)	2.060(2.061)	0.968(0.969)	0.8(0.9)	0.1(0.0)
	TS	1.842(1.760)	1.650(1.602)	1.002(1.006)	1.9 (2.3)	0.4(0.3)
ethanol	ylide	1.786(1.724)	2.060(2.060)	0.969(0.970)	0.5(0.8)	0.1(0.0)
	TS	1.841(1.759)	1.640(1.605)	1.004(1.006)	1.7(2.1)	0.4(0.3)
1-propanol	ylide	1.786(1.722)	2.062(2.055)	0.69(0.970)	0.4(0.6)	0.1(0.0)
	TS	1.843(1.761)	1.640(1.606)	1.004(1.006)	1.5 (2.0)	0.4(0.3)
2-propanol	ylide	1.703(1.727)	2.044(2.029)	0.966(0.970)	1.4(1.2)	0.2(0.0)
	TS	1.843(1.760)	1.617(1.599)	1.008(1.007)	2.2(2.2)	0.4 (0.3)

For numbering refer Figure 3



Y-1 TS-1

Y-2 TS-2

Y-3 TS-3

Y-4 TS-4

Figure 3. Y1, Y2, Y3, and Y4 are ylides formed by methanol, ethanol, 1-propanol and 2-propanol with $^1CH_2$ respectively. TS-1, TS-2, TS-3 and TS-4 are the corrersponding transition states. Bond distances are in Å unit.

The structural variations along the IRC around the TS1 are shown in Figure 4. The O2-H3 bond cleaves to a small extent until TS and the cleavage of this bond takes place suddenly after the TS. Thus, the reaction is a two-stage process.

Selected geometrical parameters of the TSs are shown in the Table 2. The trend observed in the variation of geometrical parameters in the TSs of the insertion of $^1CH_2$ into O-H of ethanol, 1-propanol and 2-propanol is similar to that observed in the insertion of methanol.

3.3. Bond order analysis

Computed bond indices listed in Table 3 for $^1CH_2$ insertion reactions into O-H bond of alcohols show that the bond formation and cleavage take place systematically as the reaction progresses. Bond indices for the methanol substrate reveal that the initial ylide formed is appreciably stronger. In this ylide the C4-O2 bond is formed to 54.24(49.95%). The C4-H3 bond formation index of 1.2 (0.4%) at B3LYP (MP2)/6-31G (d, p) levels shows that it is only a stabilizing electrostatic interaction at this stage of the insertion reaction. The cleavage of O2-H3 bond takes place to 9.2 (8.7%). In the TS, the C4-O2 bond is formed to 58.2(52.1%) and the C4-H3 bond formation is 15.8(11.6%). The cleavage of O2-H3 bond is 25.9 (26.8%). The BFC_{Ave} value of 33.3(30.2%) in the TS shows that the TS is more “reactant like”.

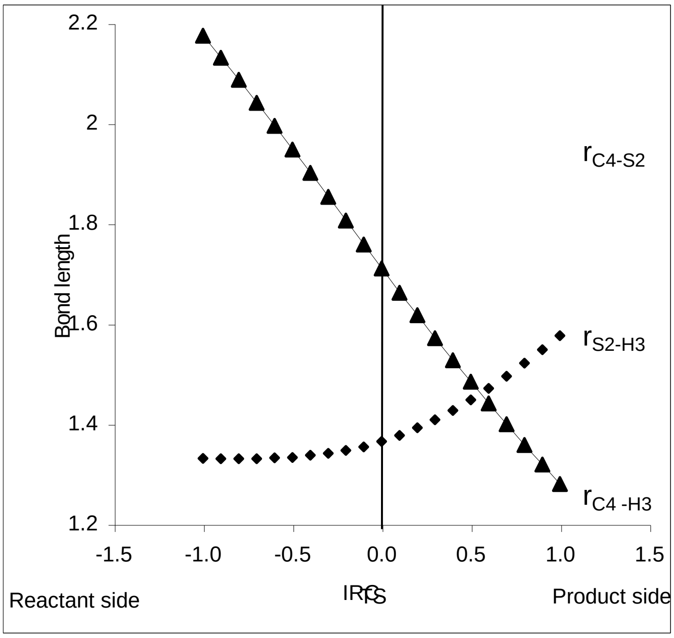


Figure 4. Bond lengths variations ($amu^{-1/2}bohr$) along the IRC around the TS in the insertion of $^1CH_2$ into O-H bond of methanol at the MP2/6-31G (d, p) level.

BFi and BCj values listed in Table 3 for the insertion reactions between ethanol, 1-propanol or 2-propanol with $^1CH_2$ predict similar trend in the ylide formation in comparison with that of methanol and the same is extendable to the formation of TSs also. Both DFT and MP2 values of BFC_{Ave} for these TSs show that they are reactant like.

3.4. Effect of B3LYP and MP2 methods

Table1 lists the relative energies of the ylides, TSs and products at different computational levels for these insertion reactions. Activation barriers, binding energy of ylides, deformation energies and enthalpy of reactions computed by MP2 method are slightly higher than B3LYP/6-31G (d, p) values. But BFC_{Ave} values predicted by MP2 method for these insertion reactions are slightly lower than DFT values.

Table 3 Wiberg bond order analysis for the $^1CH_2$ insertion into O-H bond of alcohols at B3LYP (MP2) / 6-31g (d, p) levels.

Alcohol	Species	Bond formation		Bond cleavage	BFC_{Ave}
		C4-O2	C4-H3	O2-H3	
methanol	ylide	54.2(50.0)	1.2 (0.4)	9.2 (8.7)	21.6(19.7)
	TS	58.2(52.1)	15.8(11.6)	25.9 (26.8)	33.3(30.2)
ethanol	ylide	54.8 (50.2)	1.2 (0.4)	8.9(8.3)	21.6 (19.6)
	TS	58.8(52.4)	16.3 (11.4)	26.2(26.2)	33.8(30.0)
1-propanol	ylide	54.8(50.4)	1.2 (0.4)	9.0(8.4)	21.6 (19.7)
	TS	58.6 (52.2)	16.4(11.4)	26.2 (26.2)	33.7 (29.9)
2-propanol	ylide	61.0 (50.4)	0.8(0.5)	9.8 (9.1)	23.9(20.0)
	TS	59.8(52.8)	17.6 (11.7)	27.6(26.9)	35.0(30.5)

For numbering, refer Figure 3.

3.5. NBO analyses

NBO analyses of charge distribution in the transition states give some insight into the insertion reactivity. For all the transition states, the second-order perturbative analyses were carried out for all possible interactions between filled Lewis-type NBOs and empty non-Lewis NBOs. These analyses show that the interaction between the lone pair of electrons of the carbenic carbon and the antibonding orbital of O2-H3 ($n_C \rightarrow \sigma^*_{OH}$) seems to give the strongest stabilization (for e.g., this stabilization energy: 23.1(31.5) kcal/mol for the methanol and $^1CH_2$ TSs at B3LYP (MP2) levels). Finally we observed that there was a net charge flow from the alcohol moiety to the inserting carbene moiety. The quantum of charge transfer from alcohol to carbene supporting the donor-acceptor interaction in the transition states for all the insertion reactions, both at B3LYP and MP2 levels, have been presented in Table 1. The inverse relationship between the quantum of

charge transfer and the activation barriers reveals the fact that for the favorable insertion, the nucleophilicity of the alcohol should have been enhanced either sterically or electronically. This correlation holds good for the reactions analysed in this investigation.

3.6. Singlet fluorocarbenes insertion into methanol and ethanol

Reaction energetics

The HOMO and the LUMO energies of the alcohols and the fluorocarbenes (^1CHF and $^1CF_2$) appear to have the pivotal role in the initial interaction, i.e., lower the HOMO-LUMO gap, higher the reactivity corresponding to smaller activation barrier (Table 4.). The q_{ct} at B3LYP (MP2)/6-31g (d, p) to the fluorocarbene unit at the transition state substantiates this observation

Table 4 Relative energies of ylides, TSs and products relative to reactants, activation barriers (E_a), enthalpy of reactions (ΔHr) in kcal/mol and q_{ct} at B3LYP (MP2)/6-31g(d, p) levels for the ^{1}CHF and $^1CF_2$ insertions into O-H bond of alcohols

Reactants	ylide	TS	product	HLEG (eV)	E_a	q_{ct}	ΔHr
methanol +^{1}CHF	-10.5	-5.6	-87.2	0.170	4.9	-0.023	-82.8
	(-9.3)	(-2.5)	(-90.8)	(0.534)	(6.8)	(-0.035)	(-86.3)
ethanol +^{1}CHF	-10.6	-5.7	-87.1	0.167	4.9	-0.025	-82.7
	(-9.5)	(-3.0)	(-91.0)	(0.526)	(6.5)	(-0.028)	(-86.5)
1-propanol +^{1}CHF	-10.7	-5.8	-87.1	0.166	4.9	-0.024	-82.7
	(-9.7)	(-3.2)	(-91.1)	(0.525)	(6.5)	(-0.026)	(-86.5)
2-propanol +^{1}CHF	-10.6	-3.9	-90.1	0.166	6.8	-0.030	-85.5
	(-10.2)	(-3.1)	(-94.8)	(0.521)	(7.1)	(-0.030)	(-90.1)
methanol +$^1CF_2$	-5.3	14.1	-65.4	0.187	19.3	0.051	-62.0
	(-5.1)	(17.4)	(-68.2)	(0.545)	(22.5)	(0.050)	(-64.6)
ethanol +$^1CF_2$	-5.1	14.1	-65.5	0.184	19.2	0.054	-62.1
	(-5.3)	(16.9)	(-68.4)	(0.537)	(22.2)	(0.055)	(-64.8)
1-propanol +$^1CF_2$	-5.6	14.0	-65.5	0.183	19.6	0.054	-62.0
	(-5.5)	(16.6)	(-68.4)	(0.537)	(22.2)	(0.056)	(-64.9)
2-propanol +$^1CF_2$	-5.3	14.5	-64.1	0.183	19.8	0.046	-60.7
	(-5.9)	(16.3)	(-67.4)	(0.532)	(22.2)	(0.049)	(-63.9)

q_{ct} = quantum of charge transfer from alcohol to ^{1}CHF or $^1CF_2$ moiety; HLEG = $HOMO_{ROH}$ - $LUMO^1{}_{CHF\ or\ ^1CF_2}$.

The schematic energy profile diagram for the insertion of ^{1}CHF / $^1CF_2$ into O-H of methanol at MP2 and B3LYP levels are shown in Figures 5 and 6. The energies of ylides, transition states and products are shown with reference to the reactants in the diagram. The computed low binding energy [10.5(9.3) kcal/mol at B3LYP (MP2)] between methanol and singlet monofluorocarbene shows that the ylide-like complex Y5 is weak in nature. In this ylide-like complex simultaneous partial bond formation (between the atom-pairs- C4:O2 and C4:H3) and bond breaking (atom pair-O2: H3) occur leading to the transition state species TS-5 (Figure 6). This is associated with a barrier height of 4.9(6.8) kcal/mol at B3LYP (MP2) level calculation. The computed deformation energies of alcohols (DE1) and monofluorocarbene (DE2) in the ylide-like complexes (Y5 to Y8) as well as in the TS-5 to TS-8 at B3LYP (MP2) levels are presented in Table 5. The deformation energies of the reactants from the ylide-like complexes to the corresponding transition states have been also included in the Table 5. From these data, it is obvious that the carbene moiety is more deformed during the ylide-like complex formation. But when the TS is reached from the ylide-like complex

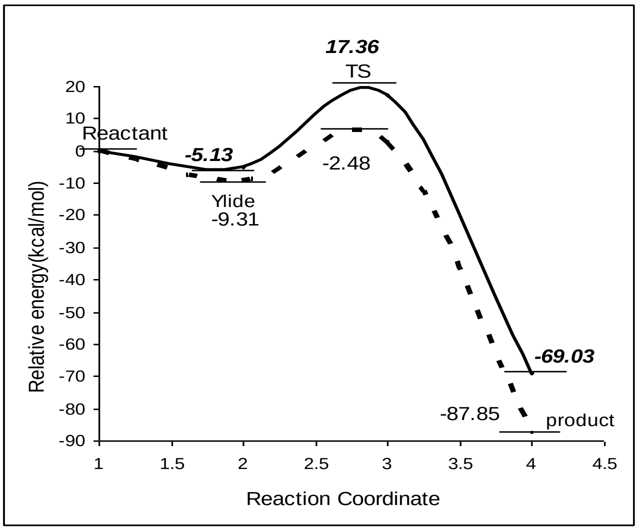


Figure 5. (a). - - - - Energy profile for $^1CHF+CH_3OH \longrightarrow CH_3$-O-CH2F
at MP2/6-31g (d, p)
(b). —— Energy profile for $^1CF_2+CH_3OH \longrightarrow CH_3$-O-$CHF_2$
at MP2/6-31g (d, p)

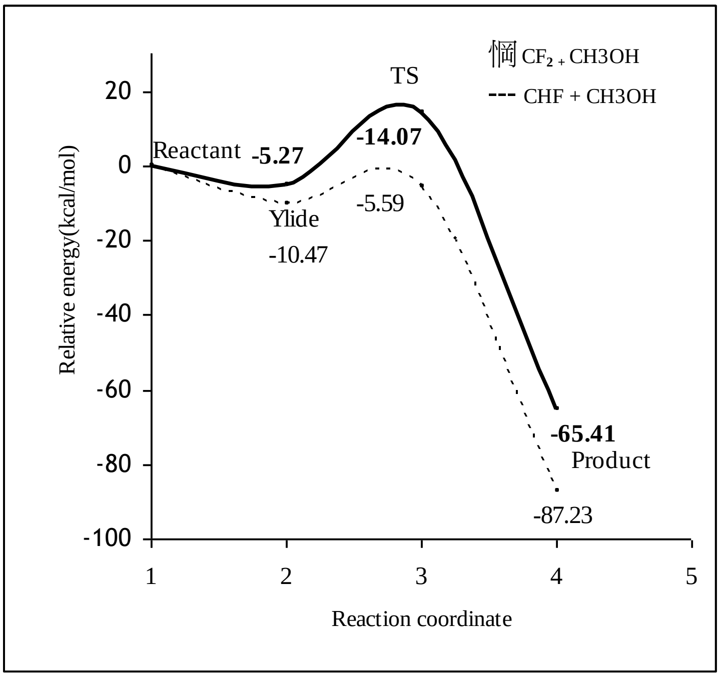


Figure 6. (a). - - - - Energy profile for ^{1}CHF+CH3OH ⟶ CH3-O-CH2F
at B3LYP/6-31g (d, p)
(b). —— Energy profile for $^1CF_2$+CH3OH ⟶ CH3-O-CHF_2
at B3LYP/6-31g (d, p)

the alcohol unit of the complex is distorted largely in comparison with the fluorocarbene part. If the reagent is difluorocarbene the deformation energies are insignificant for the ylide-like complex formation, while the distortions are large from the ylide-like complex to the TS.

The enthalpy changes of the insertion reactions of of flurocarbenes into O-H of alcohols selected here have been listed in Table 4. Irrespective of the type of carbene or alcohol, all such reactions are exothermic in nature and this shows that the transition states are reactant-like rather than the products [32]. The exothermicity is less in the case of $^1CF_2$ in comparison with that of ^1CHF. A gradual decreasing trend in the barrier height is observed as we move from methanol to 2-propanol (Table 4). This is due to the increase in the electron repelling alkyl substituent at the nucleophilic carbon that bears the O-H group.

3.7. Geometry of the ylide and the transition state

The necessary optimized bond parameters of the ylides and TSs formed between $^1CHF/^1CF_2$ and methanol, ethanol, 1-prapanol or 2-propanol at B3LYP (MP2)/6-31g (d, p) level are shown in Figures 7 and 8. Replacement of hydrogen by fluorine in $^1CH_2$ decreases its electron affinity [33] and also the electrophilicity [34, 35]. As a result, the barrier heights increase spectacularly from 4.9 to 19.3 kcal/mol at B3LYP and 6.8 to 22.5 kcal/mol at MP2 calculations respectively for methanol on moving from ^1CHF to $^1CF_2$ insertions. In the ylides and TSs formed between methanol and $^1CHF/^1CF_2$, the O2-H3 bond weakens, C4-H3 bond formation starts and the C4-O2 bond formation is stronger (Table 5). A similar type of changes observed in the ylides and TSs formed by above mentioned alcohols and $^1CHF/^1CF_2$ during the insertion processes. The structural variations along the IRC around these TSs are shown in Figures 9 and 10.

Table 5 Selected geometrical parameters (bond distances in Å) and deformation energies (kcal/mol) for the ^1CHF and $^1CF_2$ insertions into O-H bond of alcohols at B3LYP (MP2) / 6-31g(d, p) levels

Reactants	Species	C4-O2	C4-H3	O2-H3	Deformation energies	
					DE1	DE2
methanol	ylide	2.160(2.075)	2.153(2.299)	0.969(0.966)	0.3(0.3)	0.5(0.7)
$+^1CHF$	TS	2.005(1.940)	1.332(1.387)	1.130(1.080)	12.9(7.9)	0.7(0.2)
ethanol	ylide	2.160(2.075)	2.176(2.303)	0.969(0.967)	0.1(0.2)	0.5(0.4)
$+^1CHF$	TS	2.001(1.945)	1.33(1.390)	1.132(1.079)	13.1(7.6)	0.7(0.5)
1-propanol	ylide	2.185(2.155)	2.183(2.183)	0.969(0.969)	0.2(0.1)	0.5(0.4)
$+^1CHF$	TS	2.002(1.947)	1.328(1.389)	1.134(1.08)	13.2(7.6)	0.7(0.5)
2-propanol	ylide	2.128(2.042)	2.270(2.270)	0.968(0.968)	0.3 (0.4)	0.6 (0.9)
$+^1CHF$	TS	2.000(1.944)	1.321(1.389)	1.141(1.081)	13.3 (7.6)	0.6(0.0)
methanol	ylide	2.606(2.625)	2.321(2.623)	0.967(0.965)	0.1(0.0)	0.1(0.0)
$+^1CF_2$	TS	1.956(1.903)	1.21(1.236)	1.273(1.213)	31.5 (24.6)	1.2(0.9)
Ethanol	ylide	2.526(2.622)	2.663(2.647)	0.966(0.966)	0.1 (0.1)	0.1(0.0)
$+^1CF_2$	TS	1.960(1.909)	1.207(1.234)	1.28(1.216)	31.8 (24.7)	1.2(0.9)
1-propanol	ylide	2.606(2.621)	2.343(2.648)	0.968(0.966)	0.4(0.2)	0.1(0.0)
$+^1CF_2$	TS	1.960(1.911)	1.207(1.234)	1.279(1.217)	32.0(24.8)	1.2 (0.9)
2-propanol	ylide	2.534(2.620)	2.602(2.846)	0.967(0.966)	0.1(0.0)	0.1(0.1)
$+^1CF_2$	TS	1.952(1.908)	1.211(1.237)	1.271(1.215)	31.3 (24.4)	1.1(0.8)

For numbering, refer Figures7 and 8.

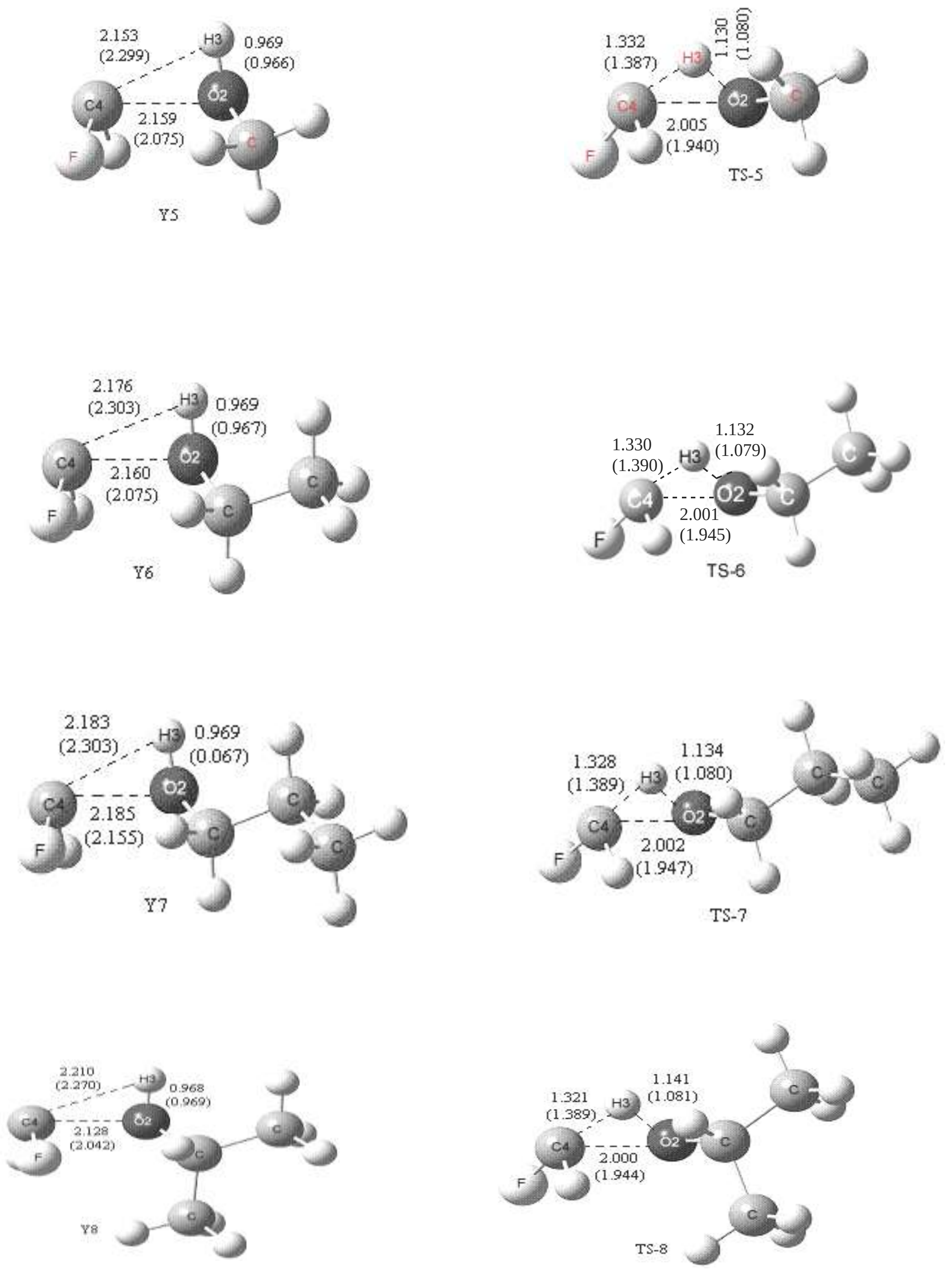


Figure 7 Y5, Y6, Y7, and Y8 are ylides formed by methanol, ethanol, 1-propanol and 2-propanol with ^{1}CHF respectively. TS-5, TS-6, TS-7 and TS-8 are the corres-ponding transition states. Bond distances are in Å unit.

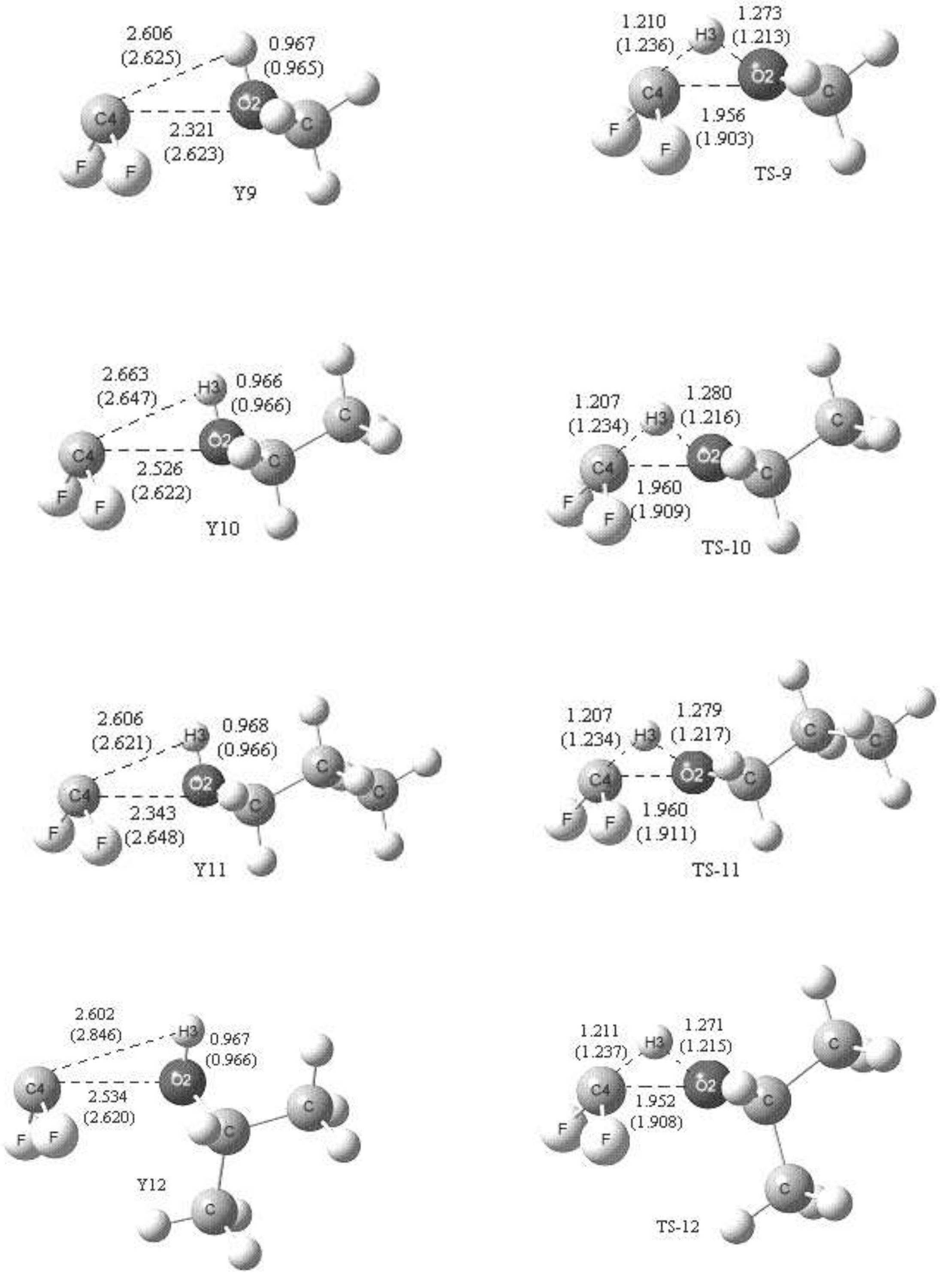


Figure 8. Y9, Y10, Y11, and Y12 are ylides formed by methanol, ethanol, 1-propanol and 2-propanol with $^1CF_2$ respectively. TS-9, TS-10, TS-11 and TS-12 are the corresponding transition states. Bond distances are in Å unit.

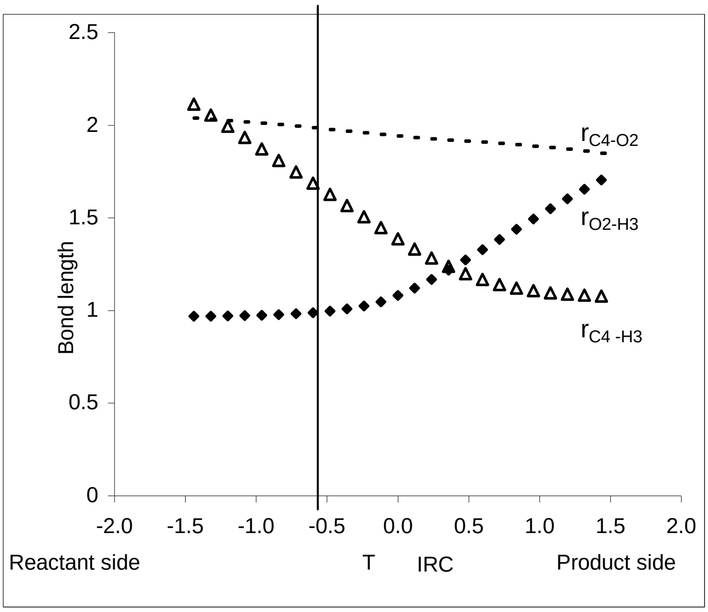


Figure .9. Bond lengths variations ($amu^{-1/2}bohr$) along the IRC around the TS in the insertion of ^1CHF into O-H bond of methanol at the MP2/6-31G (d, p) level.

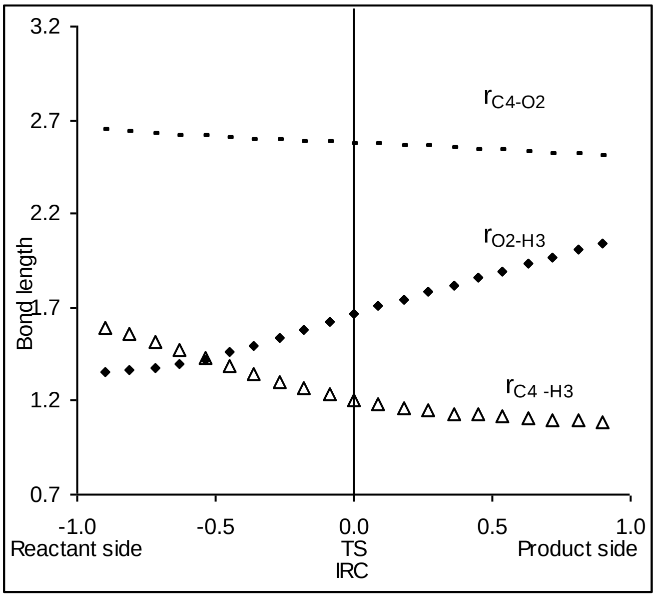


Figure 10. Bond lengths variations ($amu^{-1/2}bohr$) along the IRC around the TS in the insertion of $^1CF_2$ into O-H bond of methanol at the MP2/6-31G (d, p) level.

At an early stage of the reaction, the carbene carbon C4 starts bonding with the H3 and O2 of the alcohol.and simultaneously the O2-H3 bond starts weakening. The O2-H3 bond is nearly intact until TS and then it breaks suddenly after the TS (Figure 9.). The bond formation of C4-H3 is significant till the TS and is insignificant after the TS (Figure 10). These bond variations of O2-H3 and C4-H3 clearly support the two-step mechanism involving the weak ylide-like complex.

3.8. Bond order analysis

The computed Wiberg bond order indices listed in Table 6 for ^1CHF and $^1CF_2$ insertions into O-H bond of alcohols show that the bond formation and cleavage take place systematically as the reaction progresses. Bond indices for the ^1CHF and

Table 6. Wiberg bond order analysis for the ^{1}CHF and $^1CF_2$ insertions into O-H bond of alcohols at B3LYP (MP2) / 6-31G(d, p) levels

Reactants	Species	Bond formation		Bond cleavage	BFC_{Ave}
		C4-O2	C4-H3	O2-H3	
methanol +^{1}CHF	ylide	27.3(20.3)	2.4(0.3)	7.6(5.3)	12.4 (8.6)
	TS	56.1 (42.6)	47.8 (31.6)	50.4 (40.6)	51.5(38.3)
ethanol +^{1}CHF	ylide	27.3(20.4)	2.1 (0.3)	7.0(4.8)	12.1 (8.5)
	TS	56.5(42.3)	48.0(31.3)	50.5(39.9)	51.7(37.8)
1-propanol +^{1}CHF	ylide	27.3 (16.7)	2.0 (0.9)	6.9 (5.6)	12.1(7.7)
	TS	56.5(42.2)	48.2 (31.4)	50.7(40.0)	51.8(37.8)
2-propanol +^{1}CHF	ylide	72.3 (21.6)	1.6 (0.3)	64.8 (5.4)	46.3(9.1)
	TS	53.7 (40.8)	48.8 (31.4)	51.3(40.3)	51.3(37.5)
methanol +$^1CF_2$	ylide	8.4(3.5)	2.1(0.3)	4.3(1.7)	4.9 (1.8)
	TS	58.6(51.5)	66.2 (53.7)	67.4 (61.5)	64.1(55.6)
ethanol +$^1CF_2$	ylide	8.9 (3.5)	0.47(0.27)	2.2 (1.3)	3.9(1.7)
	TS	58.4 (51.1)	66.5 (53.9)	67.6(61.4)	64.2(55.5)
1-propanol +$^1CF_2$	ylide	8.7(3.6)	1.9 (0.3)	3.8(1.3)	4.7 (1.7)
	TS	60.4(52.4)	66.5 (54.4)	67.6(61.5)	64.8 (56.1)
2-propanol +$^1CF_2$	ylide	9.1 (3.5)	0.6(0.1)	2.4 (1.3)	4.0 (1.7)
	TS	58.5 (51.3)	65.6(53.2)	67.0(61.1)	63.7 (55.2)

For numbering, refer Figures7 and 8.

methanol insertion reaction reveal that the C4-O2 bond is formed to the extent of 27.3(20.3%) and the weak C4-H3 bond to the extent of 2.4(0.3%) in the complex at B3LYP (MP2)/6-31G (d, p) levels. The percentage cleavage of O2-H3 bond is 7.6 (5.3%). In the TS, 56.1 (42.6%) of the C4-O2 bond is formed and the C4-H3 bond formation is 47.8 (31.6%). The cleavage of O2-H3 bond is 50.4 (40.6%). The BFC_{Ave} value of 51.5(38.3%) in the TS shows that the TS is more “reactant like” as per MP2 theory calculations. A similar trend is observed for the $^1CF_2$ and methanol insertion reaction.

BFi and BCj values listed in Table 6 for the insertion reactions between ethanol, 1-propanol, 2-propanol with ^{1}CHF and $^1CF_2$ predict somewhat strong ylides and weak ylides respectively. In the TSs, calculated bond indices for the insertion reactions of ^{1}CHF and $^1CF_2$ into O-H bond of these alcohols predict the same trend as found in the case of methanol.

4. Conclusions

The insertion reactions of $^1CH_2$, ^1CHF and $^1CF_2$ into 1^o and 2^o polar O-H bonds of methanol, ethanol, 1-propanol and 2-propanol have been investigated at MP2 and DFT levels using 6-31g (d, p) basis set. The influences of fluorine on the transition states, energetics, geometrical parameters etc., have been studied both at B3LYP and MP2 levels of theory. Alcohols first react with singlet carbenes to form ylide-like complexes which inturn produce products via concerted transition states. Frontier orbital energies indicate that the initial interactions between the alcohols and carbenes are mainly controlled by the HOMO of alcohols and the LUMO of carbenes. This fact is substantiated by NBO charge analysis, which indicates that the net amount of charge transfer from alcohol to carbene moiety in the transition states at B3LYP (MP2)/6-31g (d, p) levels. Computations at B3LYP and MP2 levels show that these insertion reactions are highly exothermic. The decreasing order of insertion reactivity of carbenes with O-H bond of alcohols is: $^1CH_2 > {}^1CHF > {}^1CF_2$. Bond order analyses reveal that these reactions pass through "early" transition states. Geometrical changes around TSs for methanol and carbenes reactions through IRC and bond order analyses explain and support the ylide formation followed by proton migration mechanism to form the corresponding ether. The ylide formations and bond order analyses of the insertion reactions of above mentioned alcohols with carbenes also show the above type of mechanism is operating in these substrates.

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