Ab Initio Study of the Stability of the Ylide-like Intermediate Methyleneoxonium in the Reaction between Singlet Methylene and Water

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Abstract: Highly correlated ab initio molecular orbital calculations have been used to study the energetics and mechanism governing the reaction between the radical $^1CH_2$ and H_2O in gas phase and in solution. It was found that methylene reacts in a barrierless fashion to produce the ylide-like intermediate methyleneoxonium, H_2C--OH_2, which in turn undergoes a 1,2-hydrogen shift to produce CH_3OH. Results obtained at the QCISD(T)/6-311++G**//QCISD/6-311++G** level indicate that in the gas phase, the ylide and the transition state are located 6.4 and 4.9 kcal/mol below reactants, respectively, with an intrinsic barrier for the 1,2-hydrogen shift of 1.4 kcal/mol. In the presence of the solvent, the ylide remains more stable than reactants by 5.5 kcal/mol, while the energy of the transition state is now 1.96 kcal/mol higher than reactants giving a barrier of 7.49 kcal/mol for the 1,2-hydrogen shift.

Introduction

Carbenes, R_2C:, are sp^2-hybridized divalent species where two bonding electrons exist in sp^2 orbitals and two nonbonding electrons belong to the central carbon atom.[1] They can exist in both the singlet and triplet states, the relative stability of these states being dependent on the substituents bonded to the central atom that is deficient in electrons. In the lowest singlet state, the nonbonding electrons occupy an sp^2 orbital, leaving an empty p orbital on the central carbon, making these species very reactive toward nucleophiles. In the triplet state, the nonbonding electrons have parallel spins and occupy an sp^2 orbital as well as an orbital with large p character, usually behaving as diradicals.

Methylene, H_2C:, is the simplest carbene. Experimental studies[2] have shown that the triplet is in the ground state with a singlet−triplet gap, **S**−**T**, equal to ca. 9 kcal/mol. Results provided by highly correlated ab initio molecular orbital calculations are in excellent agreement with this value.[3−7]

Given their relatively high electrophilicity, it is reasonable to expect that the behavior of the singlet and triplet carbene radicals would be significantly affected in the presence of polar solvents as a result of the dipole created by charge transfer. Even though the use of Polarized Continuum Models,[8−11] PCM, together with conventional ab initio molecular orbital theory calculations seems to be a reasonable method to study the effects of polar solvents on the **S**−**T** gaps of carbenes, these models are not appropriate in the case of protic solvents, due to the large affinity these species have for such molecules.

It is well-known that singlet carbenes have the tendency to readily insert into single O−H bonds.[12] Thus, the reaction between singlet methylene and water affording methanol is expected to be very fast. The mechanism governing this reaction is the subject of a long-standing controversy. Most of the theoretical studies to date have proposed a barrierless mechanism where $^1[H_2C:]$ inserts into one of the O−H bonds in water producing CH_3OH.[13−15] These results have led theoreticians to conclude that the lifetime of the intermediate H_2C--OH_2 is too short for its direct experimental observation. On the other hand, Wesdemiotis et al. have used mass spectrometric techniques[16] to study the same reaction in the gas phase and have found the existence of an intermediate with a molecular weight of 32 amu and a half-life time of 1 μs, indicating the formation of the ylide-like intermediate H_2C-OH_2. Needless to say, this is an undesirable state of affairs.

In this work, we use highly correlated ab initio molecular orbital calculations to study the mechanism and energetics of the reaction $^1[H_2C:] + H_2O \rightarrow CH_3OH$. The results of this study show the formation of the ylide methyleneoxonium, H_2C-

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-OH_2, which undergoes a 1,2-hydrogen shift to produce methanol involving an intrinsic barrier of 1.4 kcal/mol. It is also shown that solvent effects computed by Polarizable Continuum Models, PCM,[8−11] have a significant impact on the stability of this species, leading to the suggestion that methyleneoxonium should be stable enough to be detected in solution under the right experimental conditions.

Theoretical Method

All geometry optimizations and gas-phase energy calculations were carried out with the Gaussian 92 suite of programs.[17] Unless otherwise specified, all geometries (reactants, intermediates, transition states, and products) have been fully optimized with the 6-311++G** basis at the MP2(Full) and QCISD levels of theory. Analytical second derivatives were used to compute vibrational frequencies at MP2/6-311++G**, while numerical second derivatives were computed in order to calculate vibrational frequencies at the QCISD/6-311++G** level. These frequencies were used to characterize the stationary points as minima or saddle points. In addition, relative energies were also computed at the QCISD(T)/6-311++G**//MP2/6-311++G** and QCISD(T)/6-311++G**//QCISD/6-311++G** levels. Zero point energy corrections were also computed and used to obtain the energetics of the reaction. Energies in solution were computed using a recent implementation of the Isodensity Polarizable Continuum Model, IPCM, by Foresman et al.[10] at MP2/6-311++G** and QCISD/6-311++G** in a local version of the Gaussian ab initio package. In order to simulate water as the solvent interacting with the substrate, a dielectric constant of 80 was used. In the IPCM model, the solute is placed inside a cavity surrounded by a continuous medium (the solvent) with a bulk dielectric constant ϵ. The charge distribution of the solute generates an electric field that induces a dipole density distribution on the solvent. Making use of Gauss' law, the virtual charge distribution $\sigma(\mathbf{r}_s)$ at point $\mathbf{r}_s$ on the cavity surface can be written as:

$$\sigma(\mathbf{r}_s) = \frac{1-\epsilon}{4\pi\epsilon}\frac{\partial}{\partial\vec{n}}[\Phi_\rho(\mathbf{r}_s) + \Phi_\sigma(\mathbf{r}_s)] = \frac{1-\epsilon}{4\pi\epsilon}[\vec{E}_0(\mathbf{r}_s) + \vec{E}_P(\mathbf{r}_s)]\cdot\vec{n}(\mathbf{r}_s)$$

where $\Phi_\rho(\mathbf{r}_s)$ and $\Phi_\sigma(\mathbf{r}_s)$ are the electrostatic potential due to the solute charge distribution and the virtual charges, respectively, $E_0(\mathbf{r}_s)$ and $E_P(\mathbf{r}_s)$ are the electric fields of the solute and the virtual charges, and $n(\mathbf{r}_s)$ is a unit vector perpendicular to the cavity and pointing in the outward direction. The solute Hamiltonian in solution is then given by:

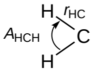
$$\mathbf{H} = \mathbf{H}_0 - \sum_i^n \int \frac{\sigma(\mathbf{r}_s)\,d\mathbf{r}_s}{|\mathbf{r}_i - \mathbf{r}_s|} + \sum_A^M Z_A \int \frac{\sigma(\mathbf{r}_s)\,d\mathbf{r}_s}{|\mathbf{R}_A - \mathbf{r}_s|}$$

where $\mathbf{H}_0$ is the gas-phase Hamiltonian, the first summation is over electrons, and the second summation is over nuclei. As observed in these expressions, the wave function of the system can be obtained from a modified set of Hartree−Fock equations where an additional level of self-consistency has been included to account for the interdependability of the Fock operator, the one-electron density matrix, and the virtual charge distribution $\sigma(\mathbf{r}_s)$. It is well-known that the description of the cavity is central for the performance of the PCM models. In the IPCM method employed in this work, the volume of the cavity surrounding the solute is computed by an isosurface of electron density obtained from standard quantum chemistry calculations (in this work QCISD and QCISD(T)).[10,11]

Results

Methylene S−T Gap. In order to calibrate the methodology to be used in the determination of the energetics as well as the mechanism governing the title reaction, full geometry optimization of the species $^1[H_2C:]$ and $^3[H_2C:]$ at the QCISD/6-311++G** level was carried out (see Table 1, parts a and b). The geometric parameters obtained at the MP2 and QCISD levels are very similar, and agree with results previously reported by other investigators. The corresponding geometries for singlet and triplet methylene obtained at the QCISD/6-311++G** level were used to calculate the **S−T** energy separation, T_e, at QCISD(T)/6-311++G**. The results shown on Table 2 indicate that the T_e value obtained at this level (12.11 kcal/mol) is in excellent agreement with the value reported by Bauschlicher and Taylor[5] (11.96 kcal/mol) using full configuration interaction, FCI, with a double-ζ plus polarization basis, DZP. This result is encouraging especially in view of the recent findings reported by Li and Paldus[6] where they show that limited CI truncated methods should include more expensive quadruple excitations in order to get a similar agreement with the FCI value. As seen in Table 2, the **S−T** gap obtained at the QCISD(T)/6-311++G**//QCISD/6-311++G** level after zero point energy corrections are taken into account is ca. 2.6 kcal/mol higher than the experimental value. This could be attributed to lack of extension as well as neglect of relativity effects in the one-particle basis sets used. The use of a basis set accounting for all these factors could become prohibitively expensive when mapping potential energy surfaces. Based on the results previously discussed, it seems that the choice of the 6-311++G** basis offers a good compromise between accuracy and computational expense.

Table 1. Optimized Geometries for Singlet and Triplet Methylene Obtained at the MP2/6-311++G** and QCISD/6-311++G** Levels



species	r_{CH}[a]	A_{HCH}[b]
(a) MP2/6-311++G** Level		
$^1CH_2$	1.100	101.8
$^3CH_2$	1.080	132.7
(b) QCISD/6-311++G** Level		
$^1CH_2$	1.115	101.4
$^3CH_2$	1.083	133.0

[a] In Å. [b] In deg.

Table 2. Energies and ZPE for Singlet and Triplet Methylene Computed at QCISD(T)

species	E[a,b]	ZPE (kcal/mol)	T_e (kcal/mol)[c]	S−T gap (kcal/mol)[d]
$^1CH_2$	−39.036 762 8	10.46	12.11	11.65
$^3CH_2$	−39.056 057 9	10.92		

[a] Computed at QCISD(T)/6-311++G**. [b] In au. [c] $E(^1CH_2) - E(^3CH_2)$. [d] T_e + ZPE($^1CH_2$) − ZPE($^3CH_2$).

Geometries. Using eigenfollowing techniques[18] as well as the IRC method developed by Gonzalez and Schlegel,[19] it was found that singlet methylene reacts with water in a barrierless path to produce an intermediate, H_2C--OH_2, with C_s symmetry where the dipole moments of both fragments (H_2O and $^1CH_2$) are antiparallel to each other. The structure of this intermediate is very similar to the one previously reported in the literature.[13−15] Using the same techniques, another minimum was found with C_1 symmetry. Even though this minimum is actually 0.16 kcal/mol higher in energy than the one with C_s symmetry, IRC calculations indicate this is the one connected to products via a

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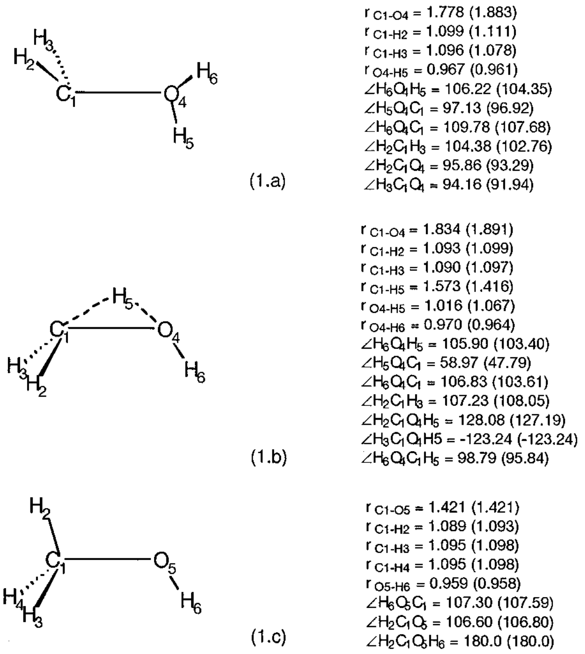

Figure 1. Optimized geometries calculated at MP2/6-311++G** and QCISD/6-311++G** (in parentheses) for ylide (a), transition state (b), and methanol (c) for the reaction $^1CH_2 + H_2O \rightarrow CH_3OH$. Bond lengths in angstroms, and bond angles in degrees. Redundant geometric parameters have been included for clarity purpose.

Table 3. Relative Energies[a] (in kcal/mol) for $^1CH_2 + H_2O \rightarrow CH_3OH$ Computed in the Gas Phase

species	MP2// MP2	QCISD// MP2	QCISD(T)// MP2	QCISD// QCISD	QCISD(T)// QCISD
$CH_2 + H_2O$	0.0	0.0	0.0	0.0	0.0
H_2C--OH_2	−9.30	−4.55	−6.03	−5.02	−6.37
TS	−7.66	−2.24	−4.62	−1.99	−4.94
MeOH	−94.74	−87.06	−88.20	−87.05	−88.18
barrier[b]	1.64	2.31	1.41	3.03	1.43

[a] Energies computed at the 6-311++G** basis set and corrected for ZPE. [b] Barrier for 1,2-hydrogen shift in H_2C--$OH_2 \rightarrow$ TS $\rightarrow$ MeOH.

transition state corresponding to a 1,2-hydrogen shift (see below). The optimized geometry corresponding to this intermediate is depicted on Figure 1a. QCISD predicts a C−O bond length approximately 0.1 Å larger than the value obtained at MP2, indicating the importance of correlation in the correct description of the attack of the vacant 2p orbital on the singlet methylene by the oxygen's lone pair. This ylide resembles a long-range complex between water and singlet methylene where the geometries of the two moieties do not change considerably. Further optimization at the MP2 and QCISD levels led to the stationary point depicted in Figure 1b. Harmonic vibrational frequency calculations indicate that this geometry corresponds to a first-order saddle-point leading to a 1,2-hydrogen shift from the water fragment toward the methylene to afford methanol. It is interesting to notice that Harding et al.[13] could not locate this transition structure at the MP2 level when using the smaller 6-31G* basis sets. Even though the geometry of methanol is well-known, the corresponding optimized structures obtained in this work are also shown in Figure 1c for comparison purposes.

Energetics. The relative energies for the reaction in the gas phase are listed in Table 3 while the corresponding energies in solution are shown in Table 4. The results on Table 3 indicate that in the gas phase, $^1CH_2$ readily reacts with H_2O to form the ylide methyleneoxonium which in turn undergoes a 1,2-hydrogen shift to afford methanol. It is observed that MP2 predicts lower relative energies than QCISD and QCISD(T). The inclusion of triple excitations in the QCISD formalism tends to stabilize the ylide by approximately 1 kcal/mol and the transition structure by ca. 3 kcal/mol. The values of the Norm-(A)[20] obtained for $^1[H_2C:]$ (1.0412), the ylide (1.0253), and the transition state (1.0757) were found to be very close to 1.00, indicating a good correlation correction to the wave function from the QCISD and QCISD(T) procedures. The energy values obtained with the highest correlated method used in this work (QCISD(T)/6-311++G**//QCISD/6-311++G**) place the intermediate methyleneoxonium ca. 6.4 kcal/mol below reactants. This result is in excellent agreement with the value of 6.5 kcal/mol obtained by Walch,[15] who performed contracted configuration interaction (CCI) energy calculations on stationary points optimized with CASSCF using the polarized double-ζ basis set of Dunning and Hay.[21] On the other hand, the barrier corresponding to the 1,2-hydrogen shift to afford methanol was found to be ca. 1.4 kcal/mol at the same level, while Walch's study predicts a barrier of only 0.5 kcal/mol. It is interesting to notice that Yates et al.[14] have obtained a barrier of 0.96 kcal/mol for the same process at MP4/6-311G(dg,p)//MP2/6-31G*. The formation of methanol from $^1[H_2C:]$ and H_2O was found to be an exothermic process with a heat of reaction equal to −88.2 kcal/mol (see Table 3). This result is in very good agreement with the value obtained by Walch's study (−88.8 kcal/mol) and by the value obtained using experimental heats of formation from the JANAF tables[22] reported in the same work (−89.5 kcal/mol).

Table 4. Relative Energies[a] (in kcal/mol) for $^1CH_2 + H_2O \rightarrow CH_3OH$ Computed in Solution Using the IPCM Model

species	MP2//MP2	QCISD//MP2	QCISD//QCISD
$CH_2 + H_2O$	0.0	0.0	0.0
H_2C--OH_2	−10.76	−6.25	−5.53
TS	−4.38	0.66	1.96
MeOH	−89.71	−82.53	−82.13
barrier[b]	6.38	6.92	7.49

[a] Energies computed at the 6-311++G** basis set and corrected for ZPE. [b] Barrier for 1,2-hydrogen shift in H_2C--$OH_2 \rightarrow$ TS $\rightarrow$ MeOH.

The results on Table 4 show that the relative energy of the ylide is not significantly affected by the solvent. In fact, comparing with the corresponding results in the gas phase at QCISD(T)/6-311++G**//QCISD/6-311++G** (see Table 3) it is observed that the ylide is stabilized by less than 1 kcal/mol when the solvent is present. In the case of the transition structure, however, the relative energy increases by up to 4 kcal/mol. This can be attributed to stronger electrostatic interactions between the reactants and the ylide with the solvent that led to a net stabilization of these species with respect to the transition state. The gas-phase dipole moment values listed on Table 5 provide evidence supporting this view. As can be seen in this table, the predicted dipole moment (calculated at the QCISD/6-311++G** level) for the transition state (1.79 D) is substantially lower than the corresponding dipole moments for the ylide (3.05 D), water (2.25 D), and singlet methylene (2.11 D). The effect of the solvent on the energetics of the reaction can be seen on Figure 2, where the corresponding reaction profiles in the gas phase as well as in the presence of the solvent are shown. The results obtained at the QCISD/6-311++G**//QCISD/6-

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(20) Norm(A) is defined as the normalization factor for the wave function projected into the CISD space. Thus, $\text{Norm}(A)^2 = \langle \Psi^{(0)} + \Psi^{(1)} | \Psi^{(0)} + \Psi^{(1)} \rangle$.

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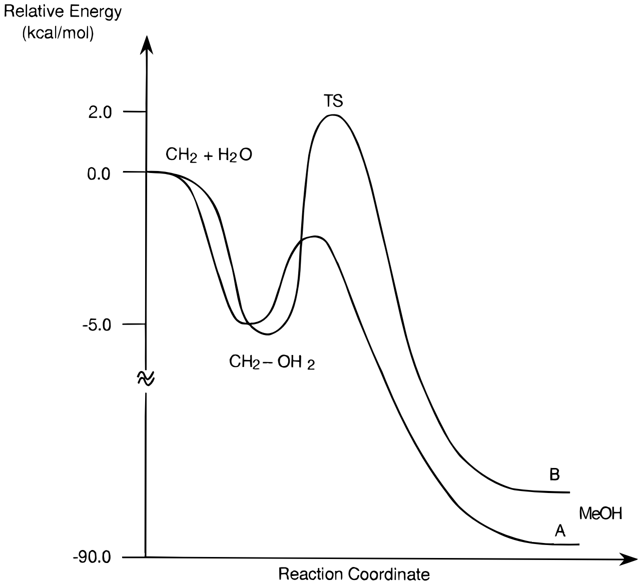

Figure 2. Energy profiles for $^1CH_2 + H_2O \rightarrow CH_3OH$ computed at the QCISD/6-311++G** level of theory: (a) gas phase; (b) in the presence of a solvent with a dielectric constant $\epsilon = 80$. Relative energies in kcal/mol.

311++G** level using the IPCM model predict the methyleneoxonium to be 5.5 kcal/mol lower than reactants while the relative energy of the transition state is ca. +2 kcal/mol, giving a barrier for the 1,2-hydrogen shift of 7.49 kcal/mol.

Conclusions

The highly correlated ab initio molecular orbital calculations used in this work to study the reaction between H_2O and $^1CH_2$ indicate the formation of a stable ylide-like intermediate, H_2C--OH_2 (methylenoxonium), that undergoes a 1,2-hydrogen shift to produce CH_3OH. The stability of this intermediate is dramatically increased by the presence of a polar solvent and suggests that these species might actually exist long enough to be observed under experimental conditions. Even though these results are very encouraging, they are by no means definitive, and more studies involving the energetics as well as the dynamics of these reactions are needed before a final conclusion can be reached. In particular, it is very important to determine first solvation shell effects on the potential energy surface of this reaction. Work is currently under way where extra molecules of water are treated explicitly in the ab initio geometry optimization as well as in the energetics of the reaction. The results will be reported in a future publication.

Table 5. Dipole Moments (in D) for $^1CH_2 + H_2O \rightarrow CH_3OH$ Computed in the Gas Phase at the MP2 and QCISD Levels[a]

species	MP2	QCISD
$^1CH_2$	2.11	2.11
H_2O	2.26	2.25
ylid	3.64	3.05
TS	2.06	1.79
CH_3OH	2.02	2.02

[a] Using the 6-311++G** basis set.

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