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Quantum Mechanical Study of the Gas-Phase Reactions between a Series of Substituted Singlet Carbenes and Water

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The mechanisms and energetics governing the gas-phase reactions of a series of substituted singlet carbenes with water were studied using highly correlated ab initio molecular orbital calculations. Monosubstituted singlet carbenes (^{1}[X−C−H]) were allowed to react with one and two water molecules in the gas phase (X = H, Me, CN, Cl, F for reactions with one water molecule and X = CN, Cl, F for reactions with two water molecules). Our results indicate the presence of stable ylide-like intermediates in all cases studied, with overall and intrinsic barriers depending on the nature of the group bonded to the central carbon atom. For the reactions with one water molecule, it is found that, whereas all reaction profiles exhibit positive or near zero intrinsic barriers (intermediate → TS), carbenes substituted with strong electron withdrawing groups (X = Cl, F) have positive overall barriers but carbenes bearing other substituents react in an overall barrierless fashion to produce the respective alcohols. For reactions with two water molecules, only the fluorine-substituted carbene exhibits an overall barrier. Classical transition-state theory with Eckart tunneling corrections (TST/Eckart) predicts the intermediate → TS step to be about 3 to 6 orders of magnitude faster for the ^{1}[X−C−H] + 2H_2O reactions than for the corresponding 1 water molecule cases. The competitive mechanisms and the effects of substituent and level of theory on the reaction paths are discussed in detail.

1. Introduction

Carbenes are highly reactive intermediates with the ability to behave as both electrophiles and nucleophiles depending on the nature of the substituents bonded to the central carbon atom.[1] It is well-known that singlet carbenes have a strong tendency to react with molecules bearing single O−H bonds,[2] however many aspects of the mechanism governing such reactions remain obscure, and there is no agreement as to a systematic way to predict the reaction paths for particular cases.[3]

Until recently, three major mechanisms for the reaction of singlet carbenes with alcohols were generally accepted[4,5] (Figure 1): (i) a two-step mechanism with proton transfer followed by ionic reaction, (ii) a two-step mechanism with intermediate formation followed by proton transfer, and (iii) direct insertion of the carbene into the O−H bond. Occurrence of each of these mechanisms depending on the substituent attached to the carbene, all having experimental and theoretical support.[3,5−13] Singlet methylene for instance was theoretically predicted by Pople and co-workers[14] at the mp4/6-31g*//hf/6-31g* and by Walch[15] at the CASSCF level to react with water in the gas phase in a barrierless fashion to produce methanol in a direct insertion (type iii) mechanism. More sophisticated ab initio calculations performed by Gonzalez et al.[16] were in better agreement with the experimental results by Wesdemiotis et al.,[17] who found an intermediate with a molecular weight of 32 amu and a half-time of 1 μs, results that can best be explained by the general type ii reaction mechanism.

More recently, Pliego et al.[18,19] predicted the existence of yet another mechanism (iv in Figure 1) for the reaction of :CCl_2 with two water molecules. A similar mechanism was found by Marquez et al.[20] for the reactions of the isoelectronic monosubstituted nitrenium ions and water (below). Pliego and co-workers found that, whereas direct insertion (type iii) is a valid reaction path, it leads to a very low reaction rate, so an alternative mechanism (named OH group catalysis) was proposed; the mechanism features intermediate formation and affords a higher rate constant for the :CCl_2 + 2H_2O reaction. The proposed transition state involves a total of three molecules, a five-atom reaction center and double proton transfer in aqueous solution.

Singlet nitrenium ions ^{1}[H−N−X]$^+$ are isoelectronic to carbenes but bear a formal positive charge that changes the electrostatic interactions with molecules in the neighborhood. Marquez et al.[20] have studied the analogous reactions of monosubstituted singlet nitrenium ions with water to produce the corresponding protonated hydroxylamines [XNH_2OH]$^+$; it was reported that the gas-phase reaction is governed by a type ii mechanism with intermediate formation; moreover, the presence of one water molecule in the near vicinity of a methylnitrenium cation ^{1}[CH_3NH]$^+$ inhibits its rapid decomposition to ^{1}[HC=NH]$^+$ + H_2 by the competitive formation of an intermediate, thus suggesting that, while methylnitrenium ion is not observed in the gas phase, it could be isolated in solution, the intrinsic barrier for intermediate rearrangement being 102.80 kJ/mol. Reactions of singlet nitrenium ions ^{1}[NH_2]$^+$ with two

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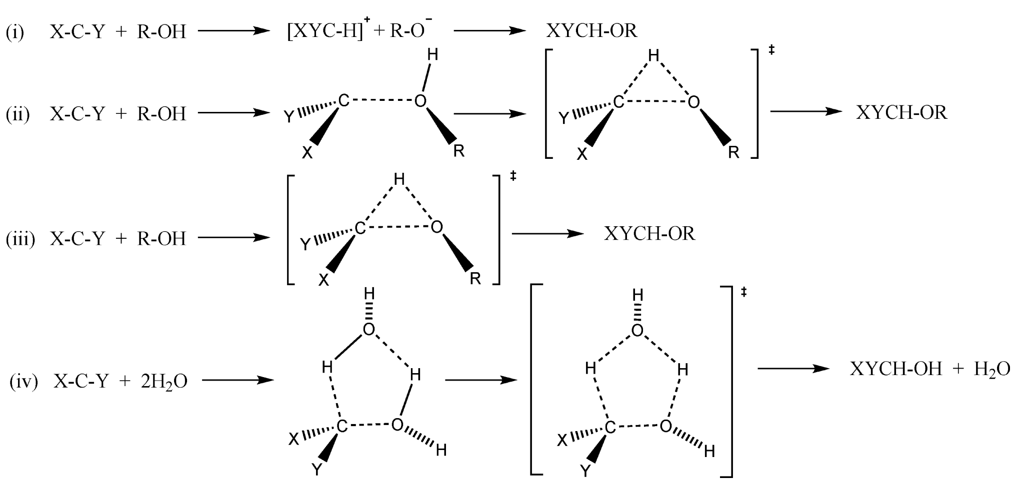


Figure 1. Possible reactions paths for the reactions of singlet monosubstituted carbenes with one and two water molecules.

water molecules exhibit a mechanism that features a five-member ring transition state with lowering of the intrinsic barrier by the catalytic action of the second water molecule. Such a mechanism, proposed by Marquez et al. for the $^1[NH_2]^+ + 2H_2O$ reaction, is in complete agreement with the (type iv) mechanism proposed by Pliego et al. for the $:CCl_2 + 2H_2O$ reaction. It is interesting to notice that those two studies were completely independent and were published within months of each other.

Whereas the findings of Pliego et al. and those of Marquez et al. are encouraging and give new insights into the intricacies of the reaction paths of water with both carbenes and nitrenium ions, their results are by no means conclusive when the reactions take place in solution; in particular, it is very important to determine first solvation shell effects on the potential energy surface (PES) by explicitly adding more water molecules to the calculations. In the gas phase, however, the situation is different because on statistical grounds a five-member ring transition state involving contributions from three different molecules (type iv mechanism) seems less probable to arise from molecular collisions than a bimolecular interaction leading to a three-member ring transition state as in the type ii mechanism.

In this work, we present the results of highly correlated ab initio molecular orbital theory calculations on the gas-phase reactions of a series of singlet monosubstituted carbenes with one and two water molecules to produce the corresponding alcohols. The chosen substituents are X = Me, CN, H, Cl, and F for the reactions with one water molecule; for reactions with two water molecules the chosen substituents are X = CN, Cl, and F. The above series were selected to study the effect of the substituent in the general mechanism and to compare it to the reactions of the analogous series of substituted singlet nitrenium ions, which were the subject of the study by Marquez et al.[20] The $^1[:CH_2] + H_2O$ reaction was previously studied at the same levels of theory as this work, the results were reported by Gonzalez et al.;[16] our calculations, which agree in every aspect with the above-mentioned publication, are reported here for completeness.

2. Computational Details

Stationary points within a given PES corresponding to reactants, intermediates, transition states, and products were calculated by fully optimizing the geometries at the MP2(Full)[21−23] level of theory in conjunction with the 6-311++G** basis set. Atom charges were calculated by fits to the electrostatic potential at points selected according to the MK,[24,25] CHelp,[26] and CHelpG[27] schemes as implemented in *Gaussian 03*.[28] The three methods of fitting the electrostatic potential yielded similar trends, so we only report the results obtained by the CHelp methodology. Comparison of the performances of the various charge-predicting models can be found elsewhere.[27]

Characterizations of all of the molecular species as minima or first-order saddle points and determination of their zero-point vibrational energies were carried out by calculating analytical second derivatives at the same MP2(Full)/6-311++G** level. Relative energies for all reactions were calculated on the MP2 geometries at the QCISD and QCISD(T)[29,30] levels with the same 6-311++G** basis set; for reactions with two water molecules, additional CCSD and CCSD(T)[29,31,32] energy calculations were carried out. Justification for this choice of methodology can be found in previous studies on the electronic structure, singlet−triplet gaps, and gas phase reactions between water and substituted carbenes and nitrenium ions.[16,20,36] The IRC method of Gonzalez and Schlegel[33−35] computed within the framework of the MP2 formalism was used to verify that indeed the transition states are uniquely connected to the intermediates and products via the minimum energy path for each reaction. All geometry optimizations, frequencies, electronic structure, and IRC calculations on this project were performed using the *Gaussian 03* suite of programs.[28]

Classical transition-state theory with Eckart tunneling corrections was used to determine reaction rates (TST/Eckart). Within the TST framework, rate constans for unimolecular decomposition reactions ($A \rightarrow TS$) are determined by (for instance ref 37):

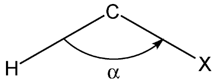
$$k(T) = \Gamma(T)\frac{k_B T}{h}\frac{Q^{\ddagger}}{Q_A}e^{-E_0/k_B T} \qquad (1)$$

where $Q^{\ddagger}$ is the partition function for the transition state in the $3N - 1$ degrees of freedom excluding motion along the reaction coordinate, whereas Q_A is the total partition function for reactants, which in the present study is taken as the intermediate leading to the transition state. $\Gamma(T)$ is the tunneling correction for the symmetrical Eckart barrier. E_0 is the energy needed to go from the reactants to the transition state.

3. Results and Discussion

Our calculations indicate that, when reacting with one water molecule, all studied species follow similar reaction paths that are best described by the general type ii mechanism (Figure 1). In all cases, the water molecule reacts with the carbene in a barrierless fashion to produce ylide-like stable intermediates,

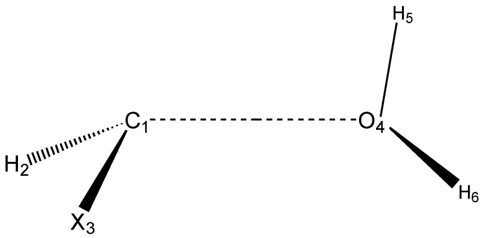
TABLE 1: MP2(full)/6-311++G** Optimized Geometries and CHelp Atomic Charges for a Series of Monosubstituted Singlet Carbenes[a]



X	R_{C-H}	R_{C-X}	α	Q_H	Q_C	Q_X[c]
Me	1.11	1.45	106	0.3	−0.8	0.9
CN	1.10	1.41	108	0.3	−0.5	0.7
H[b]	1.11	1.11	102	0.2	−0.5	0.2
Cl	1.11	1.69	103	0.3	−0.4	0.2
F	1.12	1.31	102	0.3	−0.4	0.1

[a] Bond distances in Å, bond angles in degrees, and charges in atomic units. [b] Virtually identical numbers were obtained from Gonzalez et al.[16] [c] For polyatomic substituents, Q_X is the charge on the atom directly bonded to the central carbon.

TABLE 2: MP2(full)/6-311++G** Optimized Geometries and CHelp Atomic Charges for the Intermediates in the $^1[XCH] + H_2O$ Reactions[a]



X	R_{12}	R_{13}	R_{14}	R_{15}	R_{45}	R_{46}	α_{213}	α_{546}
Me	1.10	1.50	1.91	2.23	0.96	0.96	106	104
CN	1.09	1.43	1.63	2.10	0.97	0.97	112	108
H[b]	1.10	1.10	1.76	2.12	0.96	0.97	104	105
Cl	1.10	1.71	2.37	2.55	0.96	0.96	103	104
F	1.11	1.32	2.41	2.68	0.96	0.96	103	104
	X	Q_{C_1}	Q_{H_2}	Q_{X_3}[c]	Q_{O_4}	Q_{H_5}[d]	Q_{H_6}	
	Me	−0.8	0.3	0.8	−0.5	0.4	0.4	
	CN	−0.9	0.3	0.7	−0.3	0.4	0.4	
	H	−0.8	0.2	0.2	−0.4	0.3	0.4	
	Cl	−0.5	0.3	0.1	−0.6	0.3	0.3	
	F	−0.4	0.3	0.0	−0.6	0.3	0.4	

[a] Bond distances in Å, bond and dihedral angles in degrees, atom charges in atomic units. [b] Virtually identical numbers were obtained in ref 16. [c] For polyatomic substituents, Q_{X_3} is the charge on the atom directly bonded to the central carbon. [d] H_5 is the proton to be transferred.

which in turn undergo structural transformations to form early transition states (resembling the intermediate) for the proton transfer; the reaction is finalized by simultaneous rearrangement and proton migration to produce the corresponding alcohols. For the reactions with two water molecules, all studied species follow similar reaction paths along the lines described by the general type iv mechanism (Figure 1). The first step is the barrierless spontaneous formation of stable intermediates with geometries closely resembling those of the next to be formed transitions states; the transformations from the intermediates to the transition states require very small intrinsic barriers but no overall barriers from the reactants. Double proton transfer accounts for the decomposition of the transition states, allowing formation of the corresponding alcohol and releasing one water molecule. Specific details concerning molecular geometries, mechanisms, and energetics are discussed next.

3.1. Molecular Geometries. ***3.1.1. Reactants.*** Table 1 lists the relevant geometrical parameters and atom charges for the series of reacting carbenes. With the exception of MeCH, all the other structures have been reported in previous studies at the same level of theory;[16,36] our own results are included here for completeness. The calculated geometries are in excellent agreement with theoretical and experimental studies done by others.[38−47] It can be seen that the C−X bond distance along the series increases as follows: C−H < C−F < C−CN < C−Me < C−Cl; this trend follows the same pattern as the size of the substituents, namely, the bulkier the group, the longer the bond.

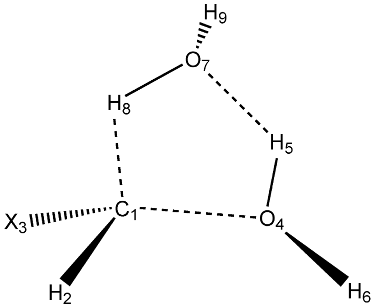
3.1.2. Intermediates. The most significant geometric parameters and atom charges for the intermediates formed in the $^1[XCH] + H_2O$ reactions are listed in Table 2; Table 3 shows equivalent information for the $^1[XCH] + 2H_2O$ reactions. In general, attractive long-range van der Waals interactions seem to be responsible for the formation of the intermediates. Support for this suggestion is provided by the following observations: (a) The interaction cannot be purely electrostatic because both C and O atoms bear negative charges, thus repelling each other (except possibly the case when FCH reacts with $2H_2O$ molecules, when the charge on the C atom is too small to make an impact; the small charge however reinforces the van der Waals argument). (b) Long C−O distances (except perhaps for X = CN) make for long separation of the molecules. (c) There is always a favorable orientation of the dipole moments of the moieties. (d) Only small variations on bond lengths and angles when compared to the isolated reactants are observed, such that the fragments retain their molecular structure to a high degree. (e) At the intermediate stage of the reaction, the soon to be transferred protons (H_5 for 1 water molecule cases and H_5 and H_8 for the two water molecules cases) remain well attached to the oxygen atoms and far away from the reaction center.

The somewhat short C−O distances for the cases of X = CN could be the result of the presence of resonance structures (:N≡C−:C−H → $^+$:N=C=:C$^-$−H) in the parent carbene similar to those reported for the reaction of the analogous nitrenium ion[20] and whose effect is to add extra stabilization to the adducts in both reactions (most stables intermediates in ref 20 and Tables 7 and 8).

3.1.3. Transition States. Tables 4 and 5 list the most relevant geometrical parameters for the calculated transition states and the assigned atom charges when the carbenes react with 1 and 2 water molecules, respectively. The three- and five-atom reaction centers seem to retain their basic structures no matter the nature of the substituent on the carbene; furthermore, the three-member ring transition states impose greater structural strains as can be inferred by comparing the bond distances and angles to those of the intermediates in the $XCH + 2H_2O$ reactions. For instance, for the reactions with 1 water molecule, the maximum difference in C−O distances between any two TSs is 0.27 Å, whereas for the intermediates that bond changes up to 0.779 Å; a similar trend is observed for the C−H_5 bond. Five-member ring transition states are less strained and resemble the intermediates much more than the corresponding three center cases, that is transition states for reactions with two water molecules happen earlier than for reactions with one water molecule. One important consequence of this observation is that reactions with two water molecules exhibit smaller activation energies (adduct → TS), leading to higher rate constants (below).

In all cases, the H atom to be transferred to the carbene (H_5 for reactions with 1 H_2O, H_8 for reactions with 2 H_2O) is closer to the carbon atom in the transition state than to that in the intermediate, and the corresponding O−H distances are larger than the O−H bonds not participating in the chemical transformation, which essentially retain their O−H character; charges for the nonparticipating H atoms also remain virtually unchanged during the reaction.

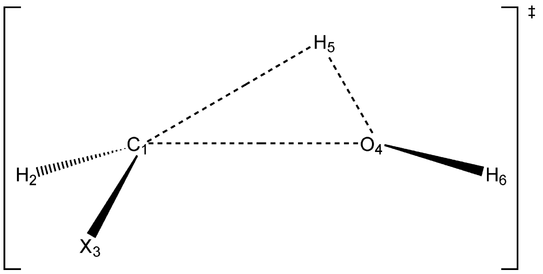
TABLE 3: MP2(full)/6-311++G Optimized Geometries and CHelp Atomic Charges for the Intermediates in the ^{1}[XCH] + $2H_2O$ Reactions[a]**



X	R_{12}	R_{13}	R_{14}	R_{45}	R_{46}	R_{18}	R_{57}	R_{78}	α_{213}	α_{546}	α_{879}
CN	1.09	1.43	1.56	1.02	0.97	1.95	1.54	1.00	112	112	107
Cl	1.10	1.77	1.65	1.01	0.97	1.80	1.58	1.02	105	108	107
F	1.11	1.35	1.81	0.99	0.96	1.92	1.71	1.00	104	107	106
	X	Q_{C_1}	Q_{H_2}	Q_{X_3}[b]	Q_{O_4}	Q_{H_5}[c]	Q_{H_6}	Q_{O_7}	Q_{H_8}[c]	Q_{H_9}	
	CN	−0.5	0.2	0.5	−0.5	0.4	0.4	−0.7	0.3	0.4	
	Cl	−0.2	0.1	−0.1	−0.4	0.4	0.4	−0.8	0.2	0.4	
	F	0.0	0.1	−0.2	−0.4	0.4	0.3	−0.7	0.2	0.4	

[a] Bond distances in Å, bond and dihedral angles in degrees, atom charges in atomic units. [b] For polyatomic substituents, Q_{X_3} is the charge on the atom directly bonded to the central carbon. [c] H_5 and H_8 are the protons to be transferred.

TABLE 4: MP2(full)/6-311++G Optimized Geometries and CHelp Atomic Charges for the Transition States in the ^{1}[XCH] + H_2O Reactions[a]**



X	R_{12}	R_{13}	R_{14}	R_{15}	R_{45}	R_{46}	α_{213}	α_{546}
Me	1.10	1.49	1.99	1.52	1.03	0.97	109	103
CN	1.09	1.42	1.72	1.45	1.06	0.97	114	106
H[b]	1.10	1.10	1.81	1.54	1.02	0.97	107	104
Cl	1.09	1.72	1.95	1.39	1.09	0.97	108	102
F	1.10	1.33	1.94	1.35	1.11	0.97	107	102
	X	Q_{C_1}	Q_{H_2}	Q_{X_3}[c]	Q_{O_4}	Q_{H_5}[d]	Q_{H_6}	
	Me	−0.6	0.3	0.5	−0.5	0.2	0.4	
	CN	−0.9	0.3	0.7	−0.3	0.3	0.4	
	H	−0.6	0.2	0.2	−0.4	0.2	0.4	
	Cl	−0.4	0.3	0.0	−0.5	0.2	0.4	
	F	−0.4	0.3	0.0	−0.6	0.3	0.4	

[a] Bond distances in Å, bond and dihedral angles in degrees, atom charges in atomic units. [b] Virtually identical numbers were obtained in ref 16. [c] For polyatomic substituents, Q_{X_3} is the charge on the atom directly bonded to the central carbon. [d] H_5 is the proton to be transferred.

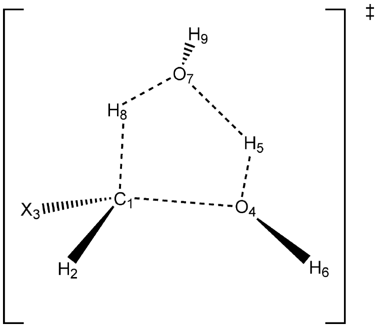
3.1.4. Products. The geometries of all the alcohols reported here are well-known and are included in this report (Table 6) for completeness. A sensible shortening on the C−O bond length is observed when comparing to the corresponding intermediates and transition states. The charge on the transferred H atoms experience severe changes in all cases in going from the TS to the alcohol, transforming a highly electron-deficient H atom into a one in a typical C−H bond.

It is important to notice that the product geometries reported here are the stationary points found by the IRC without further global minimum search; they were characterized as minima by frequency calculations. Because the geometries of the products were taken directly from the IRC, they may not be the lowest-energy isomer with respect to internal rotations; which is the reason for disparity in the charges on the hydrogen atoms for the X = H and X = Me cases. This procedure does not change the overall results concerning the mechanism and the nature of the species involved in the chemical transformation; it might however predict products that are a few kcal/mol higher in energy than the lowest isomer, but all of the predicted alcohols are already more than 70 kcal/mol lower in energy than the reactants, so that difference is irrelevant.

3.2. Energetics. Table 7 summarizes the relative energies for all of the species involved in the XCH + H_2O reactions, and Table 8 relates similar results for the XCH + $2H_2O$ cases. MP2 calculations consistently overestimate the stability relative to reactants of all of the species when compared to the more sophisticated QCISD(T) and CCSD(T) results. An extreme case is the predicted profile for the reaction HCCN + $2H_2O$ in which MP2 places the intermediate 29.03 kcal/mol below the reactants, whereas QCISD(T) predicts a relative stabilization of 21.41 kcal/mol (a 7.62 kcal/mol difference); this particular case is probably a direct result of the better ability of the QCISD(T) and CCSD(T) formalisms to handle contributions from different configurations (resonant structures) to the ground states. The previous results stress the importance of electron correlation and cast serious doubts on the applicability of MP2 to predict relative energies on this type of reactions. On the other hand, application of the QCISD and CCSD formalisms to study the energetics of the title reactions yield inconclusive results as there are over- and underestimations of the relative energies when compared to QCISD(T) and CCSD(T), in some cases even suggesting overall positive barriers while QCISD(T), CCSD(T) place the transition states below the reactants. Such results reaffirm the need to include triple excitations to accurately describe the energetics involved in the reactions between carbenes and water. As an example of the influence of the level of theory on the reaction profile, Figure 2 depicts the calculated paths at various levels of theory for the NC−:CH + H_2O → $NCCH_2OH$ gas-phase reaction.

A fact worth noticing is that, for the reactions with two water molecules, all ZPE uncorrected intrinsic barriers are positive, thus placing the TS barely above the intermediate; however, after ZPE corrections, those barriers become negative. With the

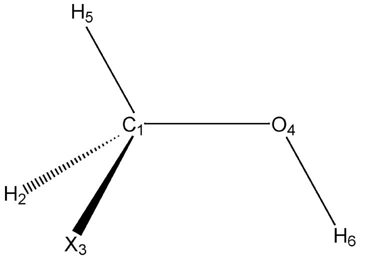
TABLE 5: MP2(full)/6-311++G Optimized Geometries and CHelp Atomic Charges for the Transition States in the ^{1}[XCH] + $2H_2O$ Reactions[a]**



X	R_{12}	R_{13}	R_{14}	R_{45}	R_{46}	R_{18}	R_{57}	R_{78}	α_{213}	α_{546}	α_{879}
CN	1.09	1.43	1.54	1.09	0.97	1.67	1.36	1.07	112	115	108
Cl	1.09	1.77	1.61	1.04	0.97	1.65	1.47	1.06	106	110	108
F	1.10	1.37	1.63	1.04	0.97	1.61	1.47	1.08	105	111	109
	X	Q_{C_1}	Q_{H_2}	Q_{X_3}[b]	Q_{O_4}	Q_{H_5}[c]	Q_{H_6}	Q_{O_7}	Q_{H_8}[c]	Q_{H_9}	
	CN	−0.5	0.2	0.5	−0.5	0.4	0.4	−0.7	0.3	0.4	
	Cl	−0.2	0.1	−0.1	−0.4	0.4	0.4	−0.8	0.2	0.4	
	F	0.0	0.1	−0.2	−0.4	0.4	0.3	−0.7	0.2	0.4	

[a] Bond distances in Å, bond and dihedral angles in degrees, atom charges in atomic units. [b] For polyatomic substituents, Q_{X_3} is the charge on the atom directly bonded to the central carbon. [c] H_5 and H_8 are the protons to be transferred.

TABLE 6: MP2(full)/6-311++G Optimized Geometries and CHelp Atomic Charges for the Products in the Reactions of Singlet Carbenes with Water[a]**



X	R_{12}	R_{15}	R_{13}	R_{14}	R_{46}	α_{213}
Me	1.09	1.10	1.52	1.42	0.96	111
CN	1.09	1.10	1.47	1.41	0.96	109
H	1.10	1.09	1.10	1.42	0.96	109
Cl	1.09	1.09	1.78	1.39	0.96	107
F	1.09	1.09	1.39	1.38	0.96	108
X	Q_{C_1}	Q_{H_2}	Q_{X_3}[b]	Q_{O_4}	Q_{H_5}	Q_{H_6}
Me	0.4	0.0	−0.2	−0.7	−0.0	0.4
CN	−0.1	0.2	0.4	−0.5	0.1	0.4
H	0.5	0.0	−0.1	−0.7	−0.1	0.4
Cl	0.1	0.1	−0.2	−0.6	0.1	0.4
F	0.3	0.1	−0.3	−0.6	0.0	0.4

[a] Bond distances in Å, bond and dihedral angles in degrees, atom charges in atomic units. [b] For polyatomic substituents, Q_{X_3} is the charge on the atom directly bonded to the central carbon.

TABLE 7: Relative Energies in kcal/mol for the ^{1}[HCX] + H_2O → XCH_2OH Gas-Phase Reactions[a] and Rate Constants in s^{-1} for the Elementary Intermediate → TS steps

species	MP2	QCISD	QCISD(T)
	MeCH		
reactants	0.00	0.00	0.00
intermediate	−2.46	−0.91	−1.83
TS	−2.36	0.13	−1.78
alcohol	−87.26	−82.04	−82.68
barrier[b]	0.10	1.04	0.05
k[d]	4×10^{12}		
	NCCH		
reactants	0.00	0.00	0.00
intermediate	−13.57	−6.71	−7.41
TS	−7.58	0.97	−1.20
alcohol	−85.57	−78.03	−77.88
barrier[b]	5.99	7.69	6.20
k[d]	2×10^{9}		
	HCH[c]		
reactants	0.00	0.00	0.00
intermediate	−9.50	−4.83	−6.32
TS	−8.10	−2.55	−4.82
alcohol	−94.74	−87.07	−88.20
barrier[b]	1.40	2.27	1.50
k[d]	1×10^{12}		
	ClCH		
reactants	0.00	0.00	0.00
intermediate	−3.01	−1.93	−2.29
TS	2.49	8.44	5.70
alcohol	−80.75	−73.55	−73.86
barrier[b]	5.50	10.37	7.98
k[d]	3×10^{8}		
	FCH		
reactants	0.00	0.00	0.00
intermediate	−2.93	−2.10	−2.48
TS	5.37	11.06	7.93
alcohol	−80.10	−73.62	−74.16
barrier[b]	8.30	13.17	10.41
k[d]	6×10^{6}		

[a] All calculations using the MP2/6-311++G** geometries and unscaled ZPE corrections. [b] Intrinsic barriers: Intermediate → TS. [c] Very similar results obtained in ref 16. [d] TST/Eckart MP2/6-311++G** rate constant (intermediate → TS) at 298.15 K, 1 atm.

exception of methylcarbene, the computed intrinsic barriers for carbene reactions with one water molecule (intermediate → TS) are higher than the barrier for singlet methylene and are high enough in all cases as to allow direct experimental gas-phase characterization under the right conditions of those intermediates that have not been observed yet.

3.3. Mechanism. Type ii reaction paths are predicted for all reactions with one water molecule, and type iv mechanisms are predicted for the reactions with two waters. A sensible stabilization of the intermediates and transition states is observed in the reaction profiles for the two water molecule cases when compared to the reactions with one water. The extra stabilization acts simultaneously with a lowering of the intrinsic barrier to afford a higher rate constant for the intermediate → TS step, and the net result is that the type iv mechanism is favored by both thermodynamics and kinetics in all cases. The mechanistic preference probably has its roots in the not-too-strained five-atom centers present in both the intermediates and the transition

TABLE 8: Relative Energies in kcal/mol for the ^{1}[HCX] + $2H_2O$ → XCH_2OH Gas-Phase Reactions[a] and Rate Constants in s^{-1} for the Elementary Intermediate → TS Steps

species	MP2	QCISD	CCSD	QCISD(T)	CCSD(T)
		NCCH			
reactants	0.00	0.00	0.00	0.00	0.00
intermediate	−29.03	−19.58	−19.71	−21.41	−21.45
TS	−30.66	−19.34	−19.44	−21.95	−21.97
alcohol	−89.73	−81.72	−81.93	−81.90	−82.00
ZPE barrier[b]	−1.63	0.24	0.27	−0.54	−0.52
barrier[c]	0.60	2.46	1.68	2.49	1.71
k[d]	3×10^{12}				
		ClCH			
reactants	0.00	0.00	0.00	0.00	0.00
intermediate	−14.72	−6.77	−6.98	−9.24	−9.33
TS	−15.84	−6.58	−6.80	−9.45	−9.53
alcohol	−84.83	−77.20	−77.60	−77.84	−78.04
ZPE Barrier[b]	−1.12	0.19	0.18	−0.21	−0.20
barrier[c]	0.12	1.42	1.41	1.03	1.03
k[d]	3×10^{12}				
		FCH			
reactants	0.00	0.00	0.00	0.00	0.00
intermediate	−10.77	−5.44	−5.46	−7.74	−7.66
TS	−11.32	−3.03	−3.13	−6.18	−6.14
alcohol	−83.67	−76.85	−77.21	−77.67	−77.76
ZPE barrier[b]	−0.55	2.41	2.32	1.55	1.53
barrier[c]	0.76	3.71	3.63	2.86	2.83
k[d]	1×10^{12}				

[a] All calculations using the MP2/6-311++G** geometries and unscaled ZPE corrections. [b] ZPE-corrected intrinsic barriers: Intermediate → TS. [c] ZPE-uncorrected intrinsic barriers. [d] TST/Eckart MP2/6-311++G** rate constant (intermediate → TS) at 298.15 K, 1 atm.

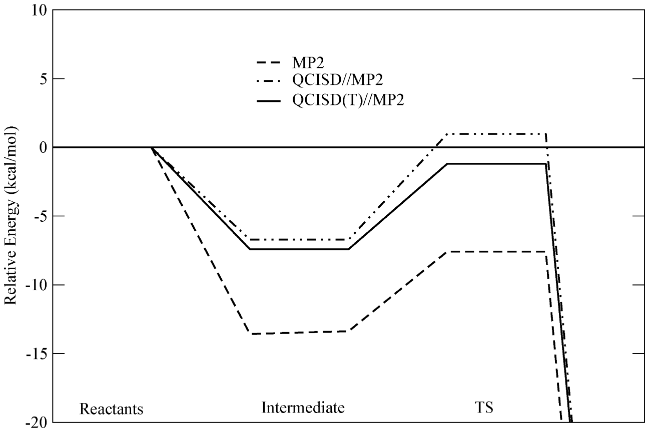


Figure 2. Effect of the level of theory on the calculated reaction path for the reaction NC−:CH + H_2O → $NCCH_2OH$. The alcohol is not shown.

states for the reactions with two water molecules; in such cases, the TSs are very early (Hammond's postulate: structurally close to the intermediates → smaller activation energies → larger rate constants). For the reactions with one water molecule, the transition states happen later in the reaction coordinate as the intermediates undergo larger geometrical changes to place the H atoms in the right position to allow their transfer; in addition, the three atom centers are structurally more strained.

In the gas phase, the studied monosubstituted singlet carbenes readily react in a barrierless fashion with one or two water molecules to produce ylide-like intermediates that are stabilized by long-range van der Waals attractive interactions. Internal rearrangements of the intermediates lead to transition states for the subsequent hydrogen shifts. Transition states feature three- or five-atom ring reaction centers, remaining somewhat structurally unaffected by the nature of the substituent on the carbene.

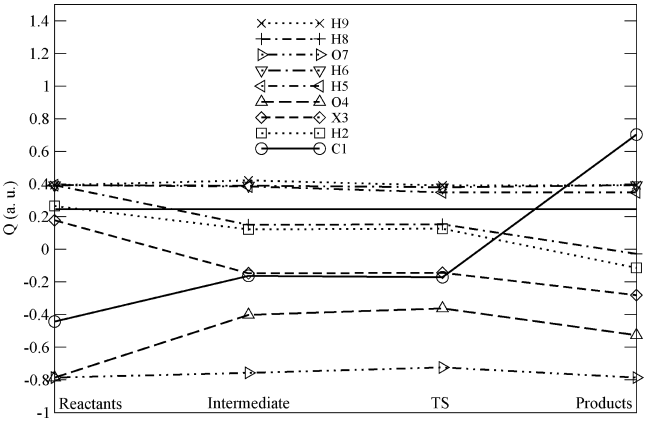


Figure 3. Evolution of the atom charges in the reaction Cl:CH + $2H_2O$ → $ClCH_2OH$ + H_2O.

The transition states undergo proton transfer and further rearrangement to produce the respective alcohols.

Because the central carbon atom in the carbene is electron-deficient, the atom from the substituent X that is directly bonded to the carbon starts the reaction with a net positive charge (in the case of X = F, a very electronegative group, the positive charge is very small); then as the reaction proceeds, X gains electron density finally becoming negative by the time the alcohol has formed (except for X = CN). The carbon atom shows just the opposite behavior; it starts out as a very negative center and ends up positive (again except for the X = CN). The soon-to-be-transferred hydrogens begin the chemical transformation as positive centers in the water molecules (charges not listed on tables are: $Q_O = -0.786$, $Q_H = +0.393$) and gradually lose their positive character to become part of a typical covalent C−H bond. Figure 3 shows the charge evolution on the atomic centers in one of the calculated reactions.

The charge analysis indicates that in the XCH + H_2O mechanisms a gain in electron density on the transferred H atom is observed as the reactions proceed. For the XCH + $2H_2O$ cases, the H atom gaining electron density is the one transferred to the catalyst water.

4. Conclusions

Highly correlated molecular orbital calculations predict the reactions between a series of monosubstituted carbene radicals (XCH, X = Me, CN, H, Cl, F) and one water molecule in the gas phase to abide by the rules of the type ii mechanism of Figure 1. For reactions with two water molecules, the preferred mechanism is type iv. Type iv paths are preferred both thermodynamically and kinetically. The general transformation goes as reactants → intermediate → TS → alcohol. For all of the cases studied, the intermediate was present, van der Waals long-range attractive forces being responsible for its net stabilization when compared to the reactants. The transition states are predicted to feature three- and five-member ring reaction centers for the reactions with one and two water molecules, respectively. Transition states seem to be mostly structurally unaffected by the nature of the substituent bonded to the central carbon atom in the parent carbene. With the exception of methylcarbene, intermediates in the reactions with one water molecule were found to have intrinsic barriers toward alcohol formation high enough to speculate that they could be isolated and studied under the right experimental conditions. MP2/6-311++g** significantly overestimates relative energies within the reaction paths. It is necessary to include single, double, and triple excitations in the QCI and CC formalisms to calculate good quality relative energies and intrinsic barriers for the title reactions.

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