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Research paper

Bimolecular reactions of carbenes: Proton transfer mechanism

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ABSTRACT

Here we report the bimolecular reaction of trifluoromethylhydroxycarbene conformers and the water-mediated mechanism of the 1,2-proton shift for the unimolecular *trans*-conformer by using quantum chemical calculations. The CCSD(T)/cc-pVTZ//MP2/cc-pVDZ potential-energy profile of the bimolecular reaction of *cis*- and *trans*-trifluoromethylhydroxycarbene, shows the lowest gas-phase barrier height of 13 kJ mol^{-1} compared to the recently reported value of 128 kJ mol^{-1} for the unimolecular reaction. We expect bimolecular reactions of carbene's stereoisomers will open a valuable field for new and useful synthetic strategies.

1. Introduction

Carbene is a neutral organic compound featuring a divalent carbon atom, which bears a pair of nonbonding electrons. The molecular geometry of carbenes can be either quasi linear or bent depending on the carbon's hybridization. The two nonbonding electrons can be parallel (triplet state) or opposite (singlet state) spin. Typically, the electronic configurations of singlet and triplet carbenes can be assigned as σ^2 ($^1A_1$) and $\sigma^1 p_\pi^1$ ($^3B_1$), respectively, as depicted in Fig. 1. It is well-known that the singlet carbene has a bond angle less than 120°, while the triplet state has an angle greater than 120° [1,2].

Generally, carbenes in the singlet or triplet state are unstable intermediates and can only be detected either by ultrafast laser spectroscopy or under cryogenic conditions (i.e., matrix isolation spectroscopy) [3]. Nevertheless, several studies have been published on stable carbenes [4–10]. In particular, attaching carbenes to bulky groups including heteroatoms makes them more stable to some extent. Heteroatoms can stabilize carbenes through π-interactions, where the lone pair of the heteroatom interacts with the vacant p_π orbital of the carbene. For example, the well-known heterocarbenes, N-heterocyclic carbenes, are used as ligands in homogeneous catalysis [11,12], organometallic materials [13], metallopharmaceuticals [14], and coordination to surfaces [15,16]. On the other hand, oxygen-donor substituted carbenes are less stable. This is due to π-donation from the oxygen's lone pair to the carbene vacant orbital (p_π) which is an inferior donor compared to the nitrogen's lone pair [17]. Furthermore, oxygen-donor substituted carbenes have been less studied; this may refer to the deficiency of suitable synthetic precursors [18]. Hoffmann and Schaefer reported that *cis*- and *trans*-hydroxycarbene might be formed from protonated formaldehyde via a dissociative recombination process in interstellar clouds [19].

Schreiner and coworkers have successfully generated and captured by cryogenic matrix isolation dimethoxycarbene [20], hydroxymethylene [18], dihydroxycarbene [21,22], phenylhydroxycarbene [23], cyclopropylhydroxycarbene [24], and methylhydroxycarbene [25]. A recent study by Mardyukov et al. [26] on thermal generation of *cis*- and *trans*-trifluoromethylhydroxycarbene from 3,3,3-trifluoro-2-oxopropanoic acid suggested that 1,2-proton shift in unimolecular *trans*-trifluoromethylhydroxycarbene favorably rearranges through a hydrogen tunnelling pathway at a very low temperature (11 K). The energy barrier of the 1,2-proton shift in the unimolecular reaction is 128 kJ mol^{-1} (30.7 kcal mol^{-1}) at CCSD(T)/cc-pVTZ level of theory. However, the bimolecular approach of the carbene system has not been considered in their study.

2. Results and discussion

Both theoretical calculations and experimental studies were performed on carbene systems several decades ago. As of yet, the mechanistic details underlying the bimolecular reaction of carbene's stereoisomers remain neglected. To the extent of our knowledge, the bimolecular reaction of such organic reactive intermediates, tri fluoromethylhydroxycarbenes, has not been investigated. With the aid of high level quantum mechanical computational methods, this study discusses the theory of bimolecular reaction of

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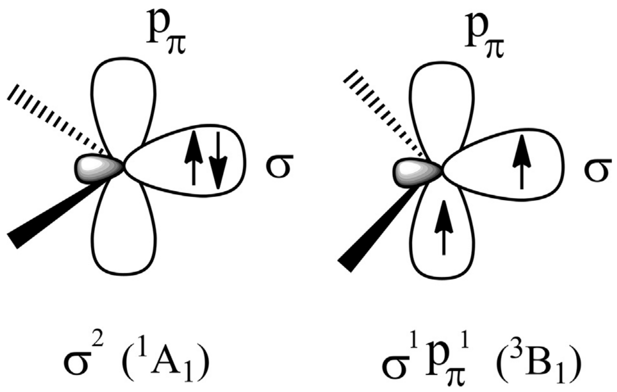


Fig. 1. Electronic configurations of singlet and triplet carbenes.

trifluoromethylhydroxycarbene conformers in the gas phase. Bimolecular reactions of carbenes focus not only on the chemistry of the carbenes themselves, but also on their wide applications to other chemical systems. Meanwhile, this approach provides insight into the detailed mechanisms of bimolecular chemical reactions of carbenes.

The reactivity of substituted carbenes can be determined by their spin multiplicity [27]. The relative stabilities for the lowest singlet and triplet states of the carbene system are given by the singlet-triplet energy gap (ΔE_{ST}). The conformers of *cis*- and *trans*-trifluoromethylhydroxycarbene are likely to possess a singlet ground state lying around 112 kJ mol^{-1} below the lowest triplet state, calculated at CCSD(T)/cc-pVTZ level of theory [26]. This large ΔE_{ST} gap confirms the singlet ground-state nature of trifluoromethylhydroxycarbene. As a result, the carbene's frontier molecular orbitals explain that the energy gap is influenced by both σ-donation and π-backbonding as shown in Fig. 2. The MP2/cc-pVTZ level of theory was used to calculate charge distribution (Mulliken definition) in the ground state of the singlet carbene's conformers. The Mulliken charge of the carbene's carbon of *cis*- and *trans*-trifluoromethylhydroxycarbene conformers is −0.038 and −0.097, respectively. As a result, the dipole moment (μ) of *cis*- and *trans*-trifluoromethylhydroxycarbene conformers is 2.213 and 3.088 Debye, respectively. The negative charge on the carbene's carbon means that the carbene's conformers have a nucleophilic behavior. The large dipole moment of the *cis*- and *trans*- conformers, results from the almost unsymmetrical distribution of charge within the molecular frame. The calculated Mulliken charges for both conformers are given in the Supporting Information (Fig. S1).

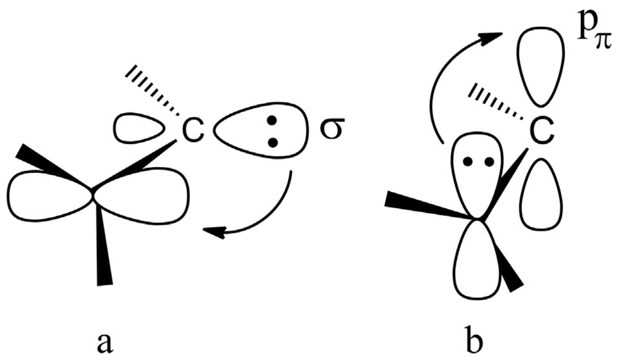
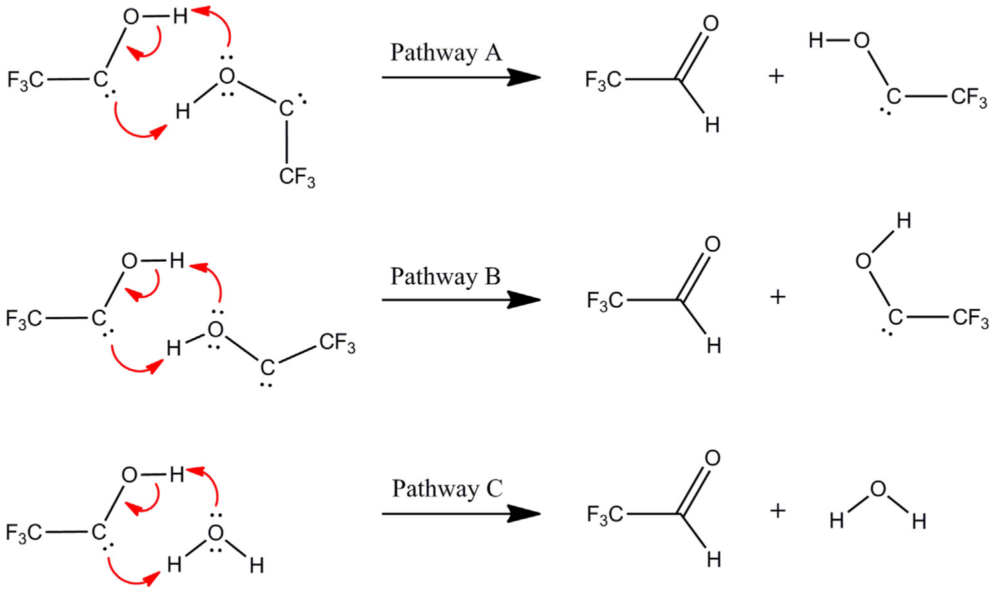


Fig. 2. Frontier molecular orbitals of carbenes. (a) Interaction of carbene σ-orbital with π-acceptor orbital. (b) Interaction of π-donor with carbene empty π-orbital.

All three proposed mechanisms (pathways A, B, and C) were considered and characterized in the gas phase by utilizing quantum chemical methods, as depicted in Scheme 1. Unless otherwise stated, all optimized structures of complexes and transition states given in the Figures were computed at the MP2/cc-pVDZ level of theory. For more details, Cartesian coordinates (in Å) of MP2/cc-pVDZ optimized structures are available in the Supporting Information (Table S1). The color codes of the optimized structures depicted in the figures are: light blue, fluorine; gray, carbon; red, oxygen; white, hydrogen. The overall activation energies for each reaction pathway investigated at different levels of theory are summarized in Table 1. Final potential energy curves for these pathways were then constructed from the CCSD(T)/cc-pVTZ single point energies. Furthermore, the thermodynamic parameters (ΔH and ΔG) were also calculated for each reaction investigated, and these are listed in the Supporting Information (Table S2). Details on the quantum chemical computation are provided in the Supporting Information.



Scheme 1. Bimolecular reactions of *cis*- and *trans*- (Pathway A), *trans*- and *trans*- (Pathway B), and *trans*-trifluoromethylhydroxycarbene with water (Pathway C).