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The Chemistry of Carbenes: New Insights from the Gas Phase

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Abstract

This review describes insights obtained from recent studies of unimolecular and bimolecular reactions of small carbenes in the gas phase and cryogenic environments. Following a description of what determines the singlet-triplet gap in carbenes, we discuss the challenges involved in producing carbenes in concentrations sufficient for studying their reactions. We document the methods developed for their preparation and the array of spectroscopic techniques available for their characterization. The review emphasizes recent progress in studies of hydroxycarbenes and small alkyl carbenes that easily isomerize to more stable isomers. The studies of unimolecular reactions of hydroxycarbenes show how quantum mechanical tunneling determines their lifetimes. A new carbonyl-ene mechanism was demonstrated in the biomolecular reactions of hydroxymethylene and methylhydroxycarbenes. We evaluate the impact of the new results on chemical processes relevant to atmospheric, planetary, and interstellar environments, and highlight the importance of collaboration between theory and experiment in interpreting mechanisms.

1. INTRODUCTION

Carbenes are divalent organic molecules with six electrons surrounding the central carbon atom, exemplified by the simplest carbene, methylene (CH_2). Carbenes are key reactive intermediates in synthetic organic chemistry, combustion, catalysis, planetary atmospheres, and astrochemistry, and also function as ligands in organometallic chemistry (1). Due to their high reactivity, all early evidence of carbenes comes from reaction product observations that infer the existence of a carbene reactant. Later research (2) clarified that carbene substituents could dramatically

modulate reactivity, leading eventually to synthesis of isolable, or “stable” carbenes (3). A vast literature, summarized in many reviews, (4-7) documents transient carbenes in solution and isolable carbenes in both solution and solid phases. However, solvent can obscure and modify the chemistry of highly reactive species. As in free radicals (8-10) and zwitterions (11), studies of carbenes in the gas phase can isolate the fundamental nature of these reactive species. This review highlights recent advances that enable the study of a broader range of small, substituted carbenes in both the gas phase and in weakly-interacting cryogenic matrices and helium nanodroplets, focusing on hydroxycarbenes and small alkyl carbenes. After a brief overview of carbenes we focus on new insights provided by these solvent-free studies of carbene chemistry.

1.1. An Overview of Carbenes

In most carbenes, two of the central carbon’s valence electrons form bonds to substituents X and Y (see **Figure 1a**) with its two remaining valence electrons distributed among two orthogonal non-bonding orbitals. As described by Mulliken in 1932 (12), within C_{2v} symmetry the two lowest electronic states are 3B_1 ($\sigma^1\pi^1$) and 1A_1 ($\sigma^2\pi^0$). Within the framework of s - p hybridization, the out of plane π orbital is of pure p_π character, whereas the in-plane σ orbital is sp^2 . In methylene, where the substituents are H atoms, the ground state is $\tilde{X}^3B_1$ ($\sigma^1\pi^1$). The ($\sigma^1\pi^1$) occupation minimizes Coulomb repulsion between the two electrons due to their larger average spatial separation compared to ($\sigma^2\pi^0$) or ($\sigma^0\pi^2$). Furthermore, the parallel electron spins in 3B_1 ($\sigma^1\pi^1$) maximize the two-electron exchange integral relative to all the singlet states (13), which further stabilizes the 3B_1 ($\sigma^1\pi^1$) configuration. From the earliest effort by Dumas (14) in 1835 to study carbenes, chemists found that carbenes are highly reactive, transient species, and this description is apt for many but not all carbenes. The two singly occupied orbitals of triplet

carbenes result in reactivity that is similar to doublet free radicals (4; 7), which have a corresponding half-filled highest occupied molecular orbital (HOMO). By contrast, the reactivity of the 1A_1 configurations ($\sigma^2\pi^0$) and ($\sigma^0\pi^2$) is usually described as either electrophilic reactivity of the empty orbital—attacking an electron rich moiety such as a C=C bond—or nucleophilic reactivity initiated by the doubly occupied orbital (7). All but the 1B_1 state (see **Figure 1a**) can be the ground electronic state of a particular carbene (15), and hence determining the ground state and the singlet-triplet energy gap E_{ST} are key parameters in understanding the reactivity of carbenes. We note a recent report of the first ground state singlet ($\sigma^0\pi^2$) carbene (16).

1.2. Singlet-Triplet Splitting and Effect of the α Substituent

Because carbenes with a triplet ground state react differently than singlet carbenes, significant effort has been devoted to understanding the magnitude and sign of E_{ST} , which by convention is positive for a triplet ground state. There are several insightful summaries (15; 17) examining how substituents α to the carbenic carbon (X and Y in **Figure 1a**) affect the electronic structure of carbenes, and hence their spectroscopy and reactivity. To summarize, α -substituents that withdraw σ electron density increase the partial positive charge on the carbenic carbon. This more positive charge Coulombically stabilizes the carbenic σ orbital (which has partial s character and hence radial probability very close to the nucleus) more than the carbenic π orbital (which has pure p_π character and hence low electron density in the X-C-Y plane). Therefore the ($\sigma^2\pi^0$) singlet state is increasingly stabilized relative to the triplet as the electronegativity of the X or Y atom increases. There is also clear evidence that α substituents capable of donating π electron density to the carbenic π orbital stabilize the closed-shell singlet $\sigma^2\pi^0$ state, adding electron density to the otherwise empty π orbital, more closely approximating a full octet. By

contrast, such π electron donation destabilizes all three of the remaining configurations in **Figure 1** due to electron repulsion with the partially- ($\sigma^1\pi^1$) or fully- ($\sigma^0\pi^2$) occupied carbenic π orbital. An effective π donation substituent contains an out-of-plane lone pair (e.g., X = F or OH), a π orbital (e.g., X = C $\equiv$ N or C $\equiv$ CH), or is capable of hyperconjugation (e.g. X = CH₃) arising from an out-of-plane C-H bond.

For the base case of CH₂, $E_{ST} = 9.00 \pm 0.03$ kcal mol⁻¹ (18). There is a fascinating and instructive history (19) that led to this now-secure value, in which a very direct measurement of $E_{ST} = 19.5$ kcal mol⁻¹ (20), which was later proven incorrect, fueled intense efforts by many experimental and theoretical groups to accurately and precisely determine $E_{ST}(\text{CH}_2)$. The eventual convergence of theory (19) and experiment (21; 22) to the now accepted value of 9.00 ± 0.03 kcal mol⁻¹ underscores the value of repeated and independent inquiry within the scientific method.

Figure 1b displays the correlation between E_{ST} and the α substituents X and Y. One can see several trends consistent with the substituent effects described earlier. First, R-C-H carbenes (R = alkyl) have triplet ground states but with smaller E_{ST} than CH₂, consistent with hyperconjugation—the donation of electrons from a β C-H bond into the carbene π orbital—stabilizing the singlet. The combined hyperconjugation of X and Y in CH₃-C-CH₃ leads to a singlet ground state. Although one would expect π donation from the -C $\equiv$ CH groups in H-C-CCH and HCC-C-CCH to stabilize the singlet, in fact the triplet state becomes more stable than in CH₂. In this case the π carbene electron may delocalize along the conjugated backbone, lowering the energy of the triplet ($\sigma^1\pi^1$) state.

Carbenes with α substituents of increasing electronegativity yield a ground singlet ($\sigma^2\pi^0$) state with E_{ST} becoming increasingly negative, although electronegativity alone cannot explain

the comparison between H-C-F vs. H-C-OH. Finally, the carbenes vinylidene (H_2CC) and propadienylidene (H_2CCC) are qualitatively different from the other species (23; 24). In these two cases the X, Y substituents are replaced by a C= functionality with the carbenic carbon bonded to only a single C atom. This change results in two excited triplet states lying well above the singlet ground state. For reasons of these qualitative differences, we don't discuss carbenes in this class further.

In 1998, Igau et al. (25) prepared the first stable (isolable) carbene, followed in 1991 by Arduengo (3) synthesizing a stable, crystalline carbene using N atoms as σ -withdrawing, π -donating α substituents, combined with a ring-structure enabling 6-electron aromaticity decorated with bulky ligands for steric crowding. These achievements catalyzed an explosion of research and practical applications of these N-heterocyclic carbenes (26; 27) that we will not review here.

Drawing on previous literature one may classify carbene reaction types as follows (4). Carbenes with a triplet ground state react similarly to free radicals via abstraction or addition-elimination, generally involving only one of the carbene's unpaired electrons in an elementary step. By contrast, the evidence for singlet carbenes implies reactions involving both non-bonding carbene electrons via 1) insertion into C-H bonds, 2) 1,2-migration reactions forming more stable isomers, 3) dimerization of two singlet carbenes, 4) cycloaddition to a C=C or C $\equiv$ C bond forming a 3-member ring, 5) addition to the lone pair of oxygen atoms in carbonyl groups to form carbonyl ylides. We highlight in this review a less-explored "carbonyl-ene" addition mechanism of singlet carbenes via a pre-reactive complex through a pericyclic transition state.

1.3. Opportunities and Challenges in Gas-Phase Studies of Carbenes

The solvent in a solution phase experiment can interact strongly—reactively or non-reactively—with the two non-bonding carbene orbitals. Studies free of solvent effects have focused on smaller carbenes in the gas phase and in cold, weakly interacting condensed phases. Much of this work centers on electronic and molecular structure revealed by spectroscopy in supersonic jets and cryogenic matrices. Except for CH₂ there is relatively less work on reactivity in weakly interacting environments. A major impediment to such studies is the difficulty producing clean and intense samples of carbenes. In this review we highlight methods of preparation and characterization of small carbenes. We describe recent results of their unimolecular and bimolecular chemistry, with specific emphasis on hydroxycarbenes, and discuss impacts this new knowledge provides in diverse areas of chemistry.

2. METHODS OF CARBENE PRODUCTION AND DETECTION

2.1. Methods of Carbene Production

As with other transient species, efficient and clean sources of carbenes are the key to success. Ideally, carbenes should be produced at concentrations sufficient to detect their kinetic time evolution, and results should be independent of precursor.

2.1.1. Pyrolysis

Pyrolysis has long been utilized to produce transient species. Some of the carbenes described here were produced by flash pyrolysis under carefully optimized conditions and trapped immediately in cryogenic matrices (28). Flash pyrolysis in the gas-phase is particularly useful when followed by cooling in supersonic expansion to simplify spectroscopy (29; 30). Recent designs make this technique more efficient and allow better characterization of flow in the pyrolysis tube (31). Diazirines and α -keto carboxylic acids and their esters have served as

precursors for several hydroxycarbenes, whereas HOCOH was generated from oxalic acid (32; 33).

Pyrolysis often generates high yields of carbenes, but when other low-energy thermodynamic pathways are open, a mixture of products is generated, which is hard to control. Also, vibrational degrees of freedom may be inefficiently cooled in a supersonic expansion and the rotational temperature is typically 50-100 K (34).

2.1.2. Photolysis

Photolytic methods have been used to generate gas-phase carbenes such as CH₂ (35), HCOH (36), CH₃COH (37), and other alkyl carbenes (38-40). For spectroscopic characterization, it is best to photolyze the precursor at the exit of a nozzle (often pulsed), which facilitates rotational cooling in supersonic expansion to < 10 K.

Optimally, the carbenes should be born with low internal energy, which may be achieved when the photon energy is only slightly above the heat of reaction of the carbene-generating process. Unfortunately, azo compounds and diazirenes—oft-chosen precursors in solution phase studies—tend to generate carbenes with internal energy sufficient for isomerization and/or dissociation. Efficient collisional energy removal can ameliorate this problem but is difficult to achieve in the dilute gas phase. Better gas-phase precursors are ketenes, acrolein, and α -keto carboxylic acids, which have lower energy excited states and more endothermic heats of reaction, enabling less energy deposition into the carbene. Internal conversion (IC) and intersystem crossing (ISC) in the excited precursor can lead to products in both spin states, reducing selectivity, but tuning the excitation energy can increase spin specificity, as seen in ketene photolysis (35).

Infrared Multiple Photon Dissociation (IRMPD) can be advantageous because it inherently limits product internal energy deposition due to competition between the photon absorption rate and the dissociation rate, as the latter increases rapidly with excess energy.

2.1.3. Electric Discharges

Pulsed discharges at the throat of a pulsed nozzle have been applied to create radicals and carbenes for spectroscopic studies (41; 42). Typically, a mixture of the precursor (~1%) in a rare gas (typically He or Ar) is subjected to a high-voltage pulse that generates electrons and excited metastable rare gas atoms, which react with the precursor to produce the carbene, among other products. This method is not highly selective, but when combined with selective detection it has been used for spectroscopic characterization; e.g., in producing HOCOH, which was characterized by Fourier Transform microwave spectroscopy (43).

2.1.4. Chemical Generation

Carbenes have been produced by chemical reaction with atomic reactants, either in gas cells or in a small tube attached to a pulsed nozzle. For example, $^3\text{CH}_2$ was generated for kinetic studies by the reaction $\text{O}(^3\text{P})$ (produced by microwave discharge) with ketene (44), and Cl atoms produced photolytically from Cl_2 reacted with methanol to produce CH_2OH , which was photolyzed to generate HCOH (36).

2.2 Detection and Characterization Techniques

The arsenal of detection and characterization techniques used in studying transient species also applies to carbenes. These techniques are well documented and/or described in a previous review on halocarbenes (5). Here we list those most useful for studying carbenes in the gas phase and cryogenic environments.

Matrix isolation was particularly useful in characterizing HCOH, HOCOH, and several of the alkyl hydroxycarbenes described in Section 3. In this technique, the carbenes, produced by flash pyrolysis, were transported quickly from the gas phase to a cold film, diluted with an inert gas, and frozen at 2-20 K (28). The cryogenic environment affords good spectroscopic resolution of vibrational levels, albeit with small shifts due to interactions with the matrix. A recent variant, used for HCOH (45) and HOCOH (46) is trapping in superfluid He nanodroplets.

Traditional absorption methods like microwave, infrared (IR), and UV absorption spectroscopies are commonly used (47-51). Laser based action spectroscopic techniques, in which a signal is detected only when a specific rovibrational transition to an electronic excited state coincides with the tunable radiation energy, are exploited mostly in gas phase studies. These include Laser Induced Fluorescence (LIF) and Resonance Enhanced Multiphoton Ionization (REMPI). The latter combines mass resolution with high spectral resolution and sensitivity.

Translational energy spectroscopy is used often to characterize reaction products. Here the kinetic energy release (KER) distribution of one product in a pair (detected by LIF or REMPI) is measured, and the internal energy distribution of the undetected product is inferred by using energy and angular momentum conservation. The most common variants of these methods are: (i) Time-of-Flight (TOF) Mass Spectrometry (52), and (ii) Velocity map imaging (VMI) (53).

More recent techniques include exploiting tunable VUV ionization to record photoionization spectra, which enables distinguishing isomers. Examples include the multiplexed photoionization mass spectrometer (MPIMS) developed by Osborn and coworkers, which combines tunable VUV radiation with very high mass resolution (54), and tabletop VUV sources developed by Davis and coworkers (55).

Photoelectron spectroscopy of mass-selected negative ions is exploited to reveal neutral carbene vibronic structure (56) encoded in the kinetic energy and angular distributions of the ejected electrons. For neutral carbenes the most powerful approach is Photoelectron Photoion Coincidence spectroscopy (PEPICO) (57), providing mass-selected photoelectron spectra of carbenes (58).

3. UNIMOLECULAR CHEMISTRY AND SPECTROSCOPY

3.1. Methylene and :CXY Halocarbenes

As the smallest carbene, the structure and spectroscopy of methylene ($^1\text{CH}_2$ and $^3\text{CH}_2$) have fascinated scientists for over 60 years (49; 59). CH_2 is also of interest as the intermediate in the $\text{C}(^3\text{P}) + \text{H}_2 \rightarrow \text{CH} + \text{H}$ reaction, which is of combustion and astrochemical relevance, and as a possible product of methane photolysis in interstellar and planetary atmospheres (60; 61).

In contrast to larger carbenes, methylene has no stable isomer, preventing the 1,2-H shift isomerization common in carbenes. A consequence of methylene's moderate $E_{\text{ST}} = 9.00 \pm 0.03$ kcal mol $^{-1}$ is that collision-induced intersystem crossing (CIISC) makes conversion between the lowest two electronic states relatively facile (62; 63), which in high-temperature environments blurs the distinction between the reactivities of each electronic state.

Low-energy excitation of ketene to S_1 followed by ISC to T_1 (35) produces $^3\text{CH}_2$ ($\tilde{X}^3\text{B}_1$). At higher photon energies ketene produces $^1\text{CH}_2$ ($\tilde{a}^1\text{A}_1$) exclusively (35), as does diazirine. $^1\text{CH}_2$ can be sensitively detected by LIF (64; 65) and cw-absorption spectroscopy (50) on the ($\tilde{b}^1\text{B}_1$) $\leftarrow$ ($\tilde{a}^1\text{A}_1$) transition. $^3\text{CH}_2$ does not fluoresce, and has been monitored by laser magnetic resonance (66), absorption spectroscopies (48; 67), and REMPI (68).

The two low-lying singlet states of CH₂—the ($\tilde{a}^1A_1$) and ($\tilde{b}^1B_1$) states—form a Renner-Teller pair (49; 59). The combination of Renner-Teller effects and spin-orbit coupling with ($\tilde{X}^3B_1$) makes assignment of the rovibrational ($\tilde{b}^1B_1$) $\leftarrow$ ($\tilde{a}^1A_1$) spectrum difficult, with many perturbations as reviewed earlier (5). Methylene serves also as a benchmark for high-level quantum calculations, with emphasis on the singlet-triplet gap and the molecular orbitals that control it (19; 69; 70).

Studies of :CXY (X, Y = H, F, Cl, I) halocarbenes, which all have singlet ground states (Section 1), proceeded concurrently with those of methylene (71). While studies of the photodissociation dynamics of carbenes are rare, ref. (5) describes several detailed studies of the photochemistry of :CXY carbenes from the $\tilde{A}^1A''$ state, which include product quantum state distributions. The vast volume of research on the spectroscopy, spin-orbit gap, photophysics, and photochemistry of the halocarbenes was summarized by Kable et al. (5), in a comprehensive review with 257 references where we direct the interested reader for an in-depth discussion.

3.2. Hydroxycarbenes

Small organic hydroxycarbenes (RCOH)—high-energy isomers of aldehydes and ketones—have been increasingly studied in the last 15 years. They all have singlet ground states and have become a testbed for understanding tunneling dynamics and unusual reaction mechanisms. Below, we describe recent research on hydroxymethylene (HCOH) and methylhydroxycarbene (CH₃COH) and summarize information on other small hydroxycarbenes.

3.2.1. Hydroxymethylene and Dihydroxymethylene

The simplest hydroxycarbene, HCOH, the high-energy isomer of H₂CO, has been implicated in combustion, reactions of organometallic compounds, and as an intermediate in the production of sugars (72; 73). It generated theoretical attention over 40 years ago as a possible participant in the photodissociation of formaldehyde (74-77), with renewed interest following the identification of a roaming mechanism as a pathway to the CO + H₂ channel (78). This discovery led to the generation of global PESs for H₂CO photodissociation that encompass HCOH, the CO + H₂ and H + HCO product channels, including S₀, S₁ and T₁ surfaces (79-81).

In 2004, Reisler et al. first reported gas phase HCOH(D) via photodissociation of Rydberg states of CH₂OH, monitored by KER of H(D) photofragments (36; 82; 83). Core-sampling TOF spectroscopy and time-sliced VMI showed that above the threshold of CH bond breaking in CH₂OH, the HCOH yield and internal energy increase with excitation energy. HCOH is produced mainly in the higher lying *cis*-isomer (84; 85). *trans*-HCOH lies $18,264 \pm 140 \text{ cm}^{-1}$ above H₂CO, and the *cis-trans* separation was measured at $1550 \pm 40 \text{ cm}^{-1}$ (84; 85), in good agreement with theory (86-88).

The experimental results show that the *cis*-HCOH yield increases sharply after the onset of absorption to the 3p_x Rydberg state and keeps rising with excitation energy. At the 3p_x absorption peak, the HCOH : H₂CO branching ratio is ~ 2:3 (36; 82; 89-91). Theoretical studies of the CH₂OH photodissociation mechanism from 3s and 3p_x show that separate conical intersections lead to H₂CO and *cis*-HCOH (92; 93). HCOH produced in this way is formed with internal energy—mainly in the CO stretch and bend (84; 85)—which can exceed its dissociation threshold. The ensuing secondary dissociation proceeds directly or via isomerization to formaldehyde (90).

The lowest energy isomer, *trans*-HCOH(D), was detected by Schreiner and coworkers who pyrolyzed glyoxylic acid and captured products in an 11 K Ar matrix (87). They characterized *trans*-HCOH by IR and UV absorption spectroscopy, with assignments aided by anharmonic vibrational energy calculations. The diffuse electronic absorption spectrum to S₁ peaks at ~427 nm (87), in good agreement with theory (75; 76; 94). HCOH was captured in superfluid He nanodroplets and analysis of its IR spectrum revealed the orientation of the transition dipole moment in the inertial frame (45).

Surprisingly, HCOH isolated in the cold Ar matrix isomerized to formaldehyde by tunneling through a narrow barrier of 29.7 kcal mol⁻¹ with a half-life of ~ 2 hours, whereas HCOD was essentially stable (94), supporting a tunneling mechanism. The tunneling rate was simulated by electronic structure and dynamical calculations using the WKB approximation. This result spurred a detailed set of unimolecular tunneling studies (33; 95-103) in a variety of carbenes (section 3.2.3).

Most recently, HCOH was detected in the gas phase in the 193 nm photolysis of methanol in a flow tube in 4 Torr He pressure (104). The fractional yield of HCOH was not reported but its concentration was sufficient to monitor its reaction with O₂ (see Section 4).

The calculated C–O bond length of HCOH, 1.311 Å, is shorter than the corresponding 1.427 Å distance in methanol, demonstrating π -donation stabilization of the electron-deficient carbon by the oxygen *p* lone pair (87). Calculations of the vibrational spectra of *trans*- and *cis*-HCOH showed that both fundamental and overtone transitions are strongly affected by anharmonic mode couplings (86; 87). The photoelectron spectra of the two conformers were also simulated, showing that ionization results in vibrational progressions in different modes for each conformer, which could be used for their distinction (105). In addition, excited valence and Rydberg states

of HCOH were calculated, including ionization energy, and several detection schemes based on photoionization and REMPI were proposed (88).

The related dihydroxymethylene (HOCOH) was studied in Ar matrix and He nanodroplets and characterized by IR and microwave spectroscopies (32; 33; 43; 46). See also Section 3.2.3.

3.2.2. Methylhydroxycarbene, CH₃COH

The simplest alkyl hydroxycarbene, methylhydroxycarbene (CH₃COH), attracted much attention because of its atmospheric relevance as a primary product in the sunlight-driven photolysis of pyruvic acid (106; 107). Unlike most volatile organic compounds in Earth's troposphere, which are principally consumed by OH radicals, pyruvic acid is destroyed mainly by photolysis (108), with a photodissociation quantum yield of $1_{-0.4}^{+0}$ at 351 nm (37). Vibrational or electronic excitation leads to decarboxylation following H-transfer from the OH group to the carbonyl (109). The hydrogen bond in the Tc conformer of S₀ aligns the bonds for facile H transfer, leading to chattering dynamics that ends in H-transfer and decarboxylation (109). In the gas-phase, fluorescence and phosphorescence are important near the S₁ ← S₀ origin, but at shorter wavelengths, light emission diminishes, indicating a shorter S₁ lifetime (110).

CH₃COH was first isolated in an 11 K Ar matrix by Schreiner and coworker following flash pyrolysis of pyruvic acid (103). Although its yield was low (~5%), it was characterized by IR and UV spectroscopies and high-level theoretical calculations. The IR spectrum, like in HCOH, shows strong anharmonic effects, and the UV absorption to S₁ has a maximum at 393 nm.

The most intriguing aspect concerning the CH₃COH lifetime is what the authors call “tunneling control of a chemical reaction.” **Figure 2** shows the intrinsic reaction coordinate for the two distinct 1,2-H shifts. Although the barrier to isomerization to vinyl alcohol (CH₂CHOH, 22.6 kcal mol⁻¹) is lower than to acetaldehyde (CH₃CHO, 28 kcal mol⁻¹), tunneling produces only

acetaldehyde, with a half-lifetime of about 1 hour (103). Tunneling through the two barriers was successfully simulated using the WKB approximation, revealing that the narrower barrier width to the acetaldehyde product makes this pathway dominant. CH_3COD does not decay by tunneling in observable times.

Samanta et al. first directly detected CH_3COH in the gas phase from 351 nm photodissociation of pyruvic acid highly diluted in helium (37). Tunable vacuum ultraviolet photoionization spectroscopy provided clear evidence for three $\text{C}_2\text{H}_4\text{O}$ isomers in this system: CH_3CHO , CH_2CHOH , and CH_3COH . The initial co-product of CO_2 is vibrationally excited CH_3COH where ~50% of the population can isomerize to acetaldehyde or vinyl alcohol, with the remaining population stabilized by collisions to CH_3COH that can undergo bimolecular reactions (37) (see Section 4).

Recently, jet-cooled pyruvic acid was photodissociated at 369.74, 354.45, and 322.50 nm, monitoring CH_3COH with photoionization translational spectroscopy (111). The main product is ground singlet state $^1\text{CH}_3\text{COH}$ with a minor fraction of $^3\text{CH}_3\text{COH}$. At 369.74 and 354.45 nm, the CH_3COH population has internal energies below and above the isomerization energy to acetaldehyde and vinyl alcohol, whereas at 322.50 nm, all population lies above the isomerization energy. Theoretical studies of the dissociation mechanism on S_1 invoke H-transfer in the Tc conformer in the excited state, either via H-atom transfer (112) or proton coupled electron transfer (PCET) (113).

These studies show that pyruvic acid photolysis is a source of CH_3COH at wavelengths near the onset of excitation to S_1 , where its absorption lines are narrow (114). At these wavelengths, CH_3COH likely lives long enough in the atmosphere to participate in bimolecular reactions.

3.2.3. Other Hydroxycarbenes (RCOH) and Tunneling Dynamics

Recent work on small RCOH carbenes reveals common motifs that help rationalize their survival probability and predict reactivity. The investigations are summarized in a series of papers by Schreiner and coworkers, which combine experiments and theory to describe structure, lifetime, and IR and UV spectroscopy of RCOH (97; 115; 116); see also **Table 1**. Most of these small carbenes were produced by flash pyrolysis of α -ketocarboxylic acids or their esters, with products immediately trapped in Ar matrices. The *cis*-isomers have higher energies than the *trans*-isomers (88), and all have singlet ground states (117).

Their S_1 and T_1 states derive from promotion of an electron from the lone pair sp^2 hybridized carbon orbital to the C-O π^* orbital (88). These states show a change in the H-O-C-C(R) dihedral angles with respect to S_0 caused by interactions of the relevant molecular orbitals upon rotation about the CO bond axis (88). Like HCOH and CH₃COH, these carbenes exhibit a weak and broad $S_1 \leftarrow S_0$ absorption band around 390-500 nm, with long vibronic progressions. The singlet-triplet gap energies (**Table 1**) range between -20 to -35 kcal.mol⁻¹, depending on the specific interactions among molecular orbitals of the OH and RC groups.

As described above, tunneling through barriers that separate isomers shortens the lifetimes of the RCOH carbenes. The tunneling rate depends on barrier height and width, and this can lead to selectivity in product formation when more than one decay pathway is open (97).

The barrier heights to isomerization and the half-lives of a series of RCOH carbenes are summarized in Table 1. The barriers were determined by high-level electronic structure calculations and tunneling was simulated using the WKB approximation. However, the PESs of these organic carbenes are multidimensional and tunneling rates will depend on vibrational modes, temperature, etc.

The half-lives depend on the nature of the R- group in RCOH, sometimes in a subtle way. In electronic structure models, stability is determined by the nature and overlap of molecular orbitals (88). However, from an organic chemistry perspective, correlations are also useful. For example, the so-called push-pull interactions in carbenes (4) result from the combined action of electron donating and electron withdrawing substituents on the central carbon, known as the captodative effect (118). This interaction extends the half-lives of cyanohydroxycarbene (NC-C-OH) and trifluoromethylhydroxycarbene (F₃C-C-OH)(97) to 23.5 and 6 days, respectively, relative to the 1.1 hour half-life of methylhydroxycarbene (CH₃COH). In addition, π donating groups to the central carbon, as in t-butylhydroxycarbene, phenylhydroxycarbene and cyclopropylhydroxycarbene, increase the half-life through the so-called push-push stabilization of carbenes (see **Table 1**). Tunneling is completely suppressed when the carbene has a second heteroatom as a π -donating substituent with a lone pair, such as in HOCO[•]H and H₂NCO[•]H (33; 116).

The situation is more subtle when there are several pathways with different barrier heights open to unimolecular tunneling, with CH₃COH being the most striking example (103). Other examples are t-butylhydroxycarbene and cyclopropylhydroxycarbene that have barrier heights and widths that depend on their conformers or rotamers (100; 101) and ethynylhydroxycarbene where the *trans*-isomer decays by tunneling much faster than the higher lying *cis*-isomer (95).

3.3. New Insights into Alkyl Carbenes

One might naively assume that alkyl carbenes, R-C-H and R-C-R (R = CH₃ or C₂H₅), would be nearly as well studied as CH₂. However, the smallest alkyl carbene, ethylidene (CH₃-C-H), was first directly observed only in 2020 (38). That report was soon followed by studies on CH₃-C-CH₃ (39) and C₂H₅-C-H (40). Several aspects make studies of alkyl carbenes challenging in gas

and condensed phases. First, they may isomerize to alkenes via the 1,2-H-shift discussed previously. Furthermore, as **Figure 1** shows, their singlet-triplet splittings are less than 4 kcal mol⁻¹, increasing the likelihood of triplet conversion to the singlet PES, where the 1,2-H-shift isomerization is expected to be essentially barrierless and therefore fast and irreversible. These nearly isoenergetic singlet and triplet energies underscore the need for carbene production schemes that deposit minimal internal energy into the carbene to avoid isomerization.

The authors (38) formed a supersonic expansion of 2% methylketene (CH₃CH=CO) in helium and photodissociated this precursor with $\lambda = 355.1$ nm. The photoproducts were detected as $m/z = 28$ cations using either 8.8 or 9.9 eV single-photon ionization, sufficient to ionize ³CH₃CH (IE = 8.51 eV) but not cold H₂C=CH₂. The center-of-mass translational energy distributions of photofragments used to fit the measured $m/z = 28$ TOF data (**Figure 3c**) required only the blue component when using 8.8 eV ionization, but both blue and orange components for 9.9 eV ionization, providing evidence of two distinct species at this m/z . The higher energy (blue) component corresponds to ³CH₃CH, and the maximum translation energy $E_{\text{max}} = 36.8$ kJ mol⁻¹ (8.80 kcal mol⁻¹) is assigned to internally cold CO + ³CH₃CH products. This limit agrees within 0.5 kcal mol⁻¹ with the calculated available energy using reactant and product thermochemistry from ATcT (18), providing experimental support for ΔH_f° (0 K) (³CH₃CH) = 86.4 ± 0.1 kcal mol⁻¹.

Schematic PESs for photodissociation of methylketene (CH₃CH=CO) are shown in **Figure 3a**. Detection of ³CH₃CH implies that ISC from S₁ to T₁ must occur prior to dissociation. By contrast, the yellow distribution in **Figure 3c**, with $E_{\text{max}} \sim 20$ kJ mol⁻¹ (5 kcal mol⁻¹), is only observed with 9.9 eV ionization. The authors assign this signal to ¹CH₃CH produced by

methylketene dissociation on S_0 following IC. Considering the PESs for the 1,2-H-shift isomerization of ethylidene (**Figure 3b**), the negligible barrier on the singlet surface implies facile $^1\text{CH}_3\text{CH} \rightarrow ^1\text{H}_2\text{C}=\text{CH}_2$ isomerization with a large exothermicity of $\Delta H(0\text{ K}) = -75\text{ kcal mol}^{-1}$. However, the experimental E_{max} of only $\sim 5\text{ kcal mol}^{-1}$ means that the $^1\text{CH}_3\text{CH} \rightarrow ^1\text{H}_2\text{C}=\text{CH}_2$ isomerization energy is unavailable to product translation, and hence methylketene fragmentation to $^1\text{CH}_3\text{CH} + \text{CO}$ happens prior to, and independently of, the later isomerization to $^1\text{H}_2\text{C}=\text{CH}_2$. This result contradicts a previous hypothesis, known as Reaction in Excited State (RIES) (119), in which, during solution-phase experiments, isomerization to singlet ethene happens concurrently with (or prior to) CO ejection from methylketene. Despite the small $E_{\text{ST}} = 3.7\text{ kcal mol}^{-1}$ for ethylidene, the authors conclude that $^3\text{CH}_3\text{CH}$ is “indefinitely stable in the absence of collisions,” so long as it is formed with minimal internal energy, consistent with the large triplet surface isomerization barrier in **Figure 3b**.

In contrast, in a study of dimethylketene photodissociation (39) producing $^1\text{CH}_3\text{-C-CH}_3 + \text{CO}$, it was observed that a significant amount of the isomerization heat of reaction for $^1\text{CH}_3\text{-C-CH}_3 \rightarrow ^1\text{CH}_3\text{CH}=\text{CH}_2$ appears as translational energy in the separating photoproducts. This result implies that the RIES mechanism is active for dimethylcarbene in the isolated gas phase environment. It seems likely that larger carbene precursors may have longer dissociation lifetimes, and hence would be more susceptible to the RIES process, which may hinder the corresponding carbene production schemes.

4. BIMOLECULAR CHEMISTRY

4.1 Triatomic carbenes

The bimolecular reactions of methylene ($^1\text{CH}_2$ and $^3\text{CH}_2$) are the most studied of all carbene reactions in the gas phase (120). Its well-documented reactivity provides a baseline against which substituted carbenes may be compared. As discussed in Section 1, $^3\text{CH}_2$ has reaction kinetics similar to low-reactivity free radicals (e.g., resonance-stabilized radicals). Specifically, $^3\text{CH}_2$ reacts rapidly with free radicals such as NO and NO_2 ($k(\text{NO}) = 2.91 \times 10^{-11}$, $k(\text{NO}_2) = 6.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), more slowly with $^3\text{O}_2$ ($k(\text{O}_2) = 3.24 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), and very slowly ($k < 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) with most closed-shell singlet molecules including alkanes, alkenes, aromatics, and carbonyls (44; 121). Mechanistically, reactions of $^3\text{CH}_2$ occur via addition elimination ($^3\text{CH}_2 + \text{NO} \rightarrow \text{HCNO} + \text{H}$, $\text{HCN} + \text{OH}$). Although abstraction of H atoms from organic molecules by $^3\text{CH}_2$ is generally exothermic—due to the strong C-H bond that would form in the CH_3 product ($D_0(\text{H}_2\text{C-H}) = 109.3 \text{ kcal mol}^{-1}$)—the kinetics of such reactions are generally very slow and hence unimportant (121).

By contrast, $^1\text{CH}_2$ is extremely reactive with all classes of organic molecules, proceeding by insertion into C-H bonds (but not insertion into C-C bonds) and cycloaddition to C=C and C $\equiv$ C bonds forming 3-member rings (122). In early work, Doering et al. (123) found from end-product analysis that $^1\text{CH}_2$ inserts at equal rates to 1° , 2° , 3° , allylic, and vinylic C-H bonds, leading him to label it the “most indiscriminate reagent known in organic chemistry.” Motivated by photochemical production of $^1\text{CH}_2$ from CH_4 at $\lambda = 121.6 \text{ nm}$ in the atmosphere of Saturn’s moon Titan, Douglas et al. (60; 61) recently measured the kinetics of $^1\text{CH}_2$ with CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , N_2 , H_2 , and O_2 over the unprecedented range of $T = 43 - 298 \text{ K}$. Removal of $^1\text{CH}_2$ may arise from both CIISC and chemical reaction, with the achieved low temperatures providing insight to the reaction mechanism. These experiments show a negative temperature dependence (i.e., $k(T)$ that increases with decreasing temperature) in all reactions of $^1\text{CH}_2$, reaching large

magnitudes as in $^1\text{CH}_2 + \text{C}_2\text{H}_2$, where $k(43\text{ K}) = 7.81 \pm 0.77 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Another key insight is that the branching fraction for CIISC increases as temperature decreases. Therefore, a significant portion of the negative temperature dependence is comprised of increasing quenching to $^3\text{CH}_2$, with consequent changes to downstream chemistry on Titan due to the distinctly different reactivities of $^1\text{CH}_2$ vs. $^3\text{CH}_2$. Mechanistically, Douglas et al. propose the formation of long-lived collision complexes in the entrance channel of the PES, increasing the time for ISC to occur.

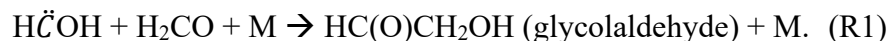
Many gas phase studies of methylene's reactivity have been motivated by its role in combustion (124; 125) where the $^1\text{CH}_2 + \text{C}_2\text{H}_2$ reaction produces the propargyl radical (H_2CCCH), a key precursor to soot (126). Davis et al. (127) explored the dynamics of this reaction using crossed molecular beams, producing $^1\text{CH}_2$ by 308 nm photolysis of CH_2CO and using soft photoionization of the propargyl product with 9.6 eV synchrotron radiation. The isotropic product angular distribution and small KER observed are the fingerprints of a long-lived C_3H_4 collision complex that decays statistically without an exit barrier to the propargyl + H products. Both insertion into a C-H bond yielding propyne (H_3CCCH) and cycloaddition to the $\text{C}\equiv\text{C}$ bond of acetylene yielding cyclopropene are feasible pathways to either an allene (H_2CCCH_2) or propyne intermediate, although this dynamics experiment could not differentiate between the entrance pathways. High-level electronic structure and kinetics calculations (122) for $^1\text{CH}_2$ reacting with unsaturated hydrocarbons containing 2 – 6 carbon atoms concluded that the insertion pathway is negligible for reaction with acetylene, but becomes increasingly competitive with cycloaddition for larger unsaturated reactants, both due to a more attractive barrierless entrance channel PES and as the number of C-H bonds increases. In the case of $^1\text{CH}_2 + \text{benzene}$, insertion dominates over cycloaddition at room temperature. This work provides an

experimentally validated benchmark that state-of-the-art theoretical approaches can provide new insights to the reaction mechanisms.

There is a substantial body of work on bimolecular reactions of triatomic halocarbenes such as HCF (128-131) and CCl₂ (132-134) that we will not review here. Although these halocarbenes have singlet ground states of the same $\sigma^2\pi^0$ configuration as ¹CH₂, they are significantly less reactive due to the σ -withdrawing α -halogen atom(s) that also donate π electron density into the empty carbene π orbital.

4.2 Hydroxycarbenes

Because of the difficulty in developing clean carbene sources, there has been little exploration of gas phase bimolecular chemistry in carbenes other than the triatomics mentioned above, in stark contrast to the substantial literature for reactions in solution. However, in recent years hydroxycarbene production methods have advanced, as discussed in Sections 2 and 3. Both HCOH and CH₃COH have been generated and have $\sigma^2\pi^0$ singlet ground states well separated from the excited triplet state (18), (87; 103). Motivated by previous evidence that hydroxycarbenes + aldehyde chemistry might contribute to prebiotic sugar formation (135; 136), Eckhardt et al. (137) studied the bimolecular reactions of HCOH and CH₃COH with small aldehydes. The goal in these experiments was to test the hypothesis that the simplest sugar, glycolaldehyde, could be formed in the following reaction,



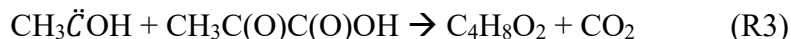
In a gas phase flow pyrolysis experiment they produced HCOH from glyoxylic acid in the presence of H₂CO and collected a colorless polymer on a cold trap, which they analyzed using NMR and gas-chromatography / mass spectrometry. Although these experiments provided evidence for R1, the most convincing support for this mechanistic class came from high vacuum

flash pyrolysis studies, in which the analogous CH₃COH was formed from pyruvic acid in the presence of H₂CO, with these co-flowing gases deposited into a $T = 3$ K inert gas matrix. They assigned IR spectral peaks to hydroxyacetone, interpreted as evidence for the gas phase reaction



Notably, upon warming the matrix to 28 K for 5 minutes, enabling faster diffusion of guest molecules, the signals of hydroxyacetone increased, providing good evidence that R2 can occur not only in the gas phase, but also in ices at 28 K. This result implies there are no barriers above the energy of the reactants for R2 and, by analogy, R1.

As detailed in Section 3, CH₃COH has been produced by 350 – 370 nm photolysis from pyruvic acid (37; 111). Using this precursor, Samanta et al. observed that CH₃COH reacts in the gas phase with pyruvic acid:



yielding CO₂ and a C₄H₈O₂ molecule of unidentified isomeric nature. Very recently, Osborn et al. (138) applied the same source of CH₃COH to enable the time-resolved investigation of a hydroxycarbene + aldehyde reaction in the gas phase. For technical reasons, the reaction of methylhydroxycarbene with *d*₄-acetaldehyde was chosen



As depicted in **Figure 4**, the authors considered these possible mechanisms for R4: insertion of CH₃COH into a formyl C-D bond of CD₃CDO (cyan path), insertion into the methyl C-D bond (red path), or a carbonyl-ene mechanism (135-137) involving a deeply submerged five-member peri-cyclic transition state (blue path). Both pathways on the right in **Figure 4** lead to acetoin, whereas the path on the left leads to 3-hydroxybutanal.

The photoionization spectrum of the product of R4 was a perfect match to the isomer acetoin, with no evidence for the insertion product 3-hydroxybutanal. The authors used a relative rate method to examine the reaction kinetics via the competing reactions R3 and R4, where the rate of R3 remains fixed while the rate of R4 increases as a function of increasing [CD₃CDO]. Combined with high-level electronic structure calculations and a two-transition state master equation kinetics model, the theory/experiment comparison showed that kinetics of R4 via the carbonyl-ene pathway have a negative temperature dependence with $k(300\text{ K}) = 1.4 \times 10^{-10}$ rising to $k(28\text{ K}) = 9.3 \times 10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$. Together with the results from Eckhardt et al. (137), this work confirms that singlet hydroxycarbenes reacts rapidly with aldehydes, but via a carbonyl-ene mechanism that has seldom been invoked in carbene chemistry.

In another recent discovery, Hockey et al. (104) found that 193 nm photodissociation of CH₃OH (CH₃OD) produces small amounts of HCOH (HCO), presumably accompanied by H₂ as the coproduct, as later explored by Houston (139). HCOH was identified from its ionization onset and shape, well below the 10.889 eV ionization energy of formaldehyde. In the presence of only He, CH₃OH, and minor amounts of reaction products, HCOH decayed with a 1/e lifetime of 4.3 ms, whereas H₂CO was stable. Adding increasing concentrations of O₂ produced monotonically shorter HCOH lifetimes, with a lifetime of 1.8 ms observed at [O₂] = $1.2 \times 10^{16}\text{ molecules cm}^{-3}$. Although insufficient data was available to measure a rigorous rate coefficient, clearly $k(^1\text{HCOH} + \text{O}_2, 300\text{ K})$ is several orders of magnitude smaller than $k(^1\text{CH}_2 + \text{O}_2, 295\text{ K}) = 7.4 \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (50). Note that for ¹HCF, another carbene stabilized by a strong σ-withdrawing / π-donating α substituent, $k(^1\text{HCF} + \text{O}_2, 295\text{ K})$ has only an upper bound of $< 5 \times 10^{-16}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (129).

In another sign of the growing interest in gas phase hydroxycarbene reactions in atmospheric chemistry, Mondal et al. (140) reported calculations on the reactions of CH₃COH with N₂, O₂, and H₂O. Pyruvic acid's primary destruction by photolysis in Earth's atmosphere (108) implies a significant tropospheric source of CH₃COH, underscoring interest in its atmospheric fate. Mondal's calculations find that the CH₃COH + N₂ reaction is negligible, whereas reaction with O₂ is impeded by a 6 kcal mol⁻¹ barrier, resulting in $k(\text{CH}_3\text{COH} + \text{O}_2 \rightarrow \text{CH}_3\text{CO} + \text{HO}_2, 298 \text{ K}) = 1.03 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, consistent with the small rate coefficient implied for HCOH + O₂ (104). However, they conclude that by far the dominant tropospheric fate of CH₃COH is reaction with H₂O, characterized by a relatively large $k(\text{CH}_3\text{COH} + \text{H}_2\text{O}, 298 \text{ K}) = 2.70 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and a negative temperature dependence, similar to previous work (141). The mechanism Mondal extracts is of a water-catalyzed H-atom shuttle, in which a pre-reactive hydrogen-bonded CH₃COH---H₂O complex forms, after which the water oxygen accepts the H atom from the OH group of methylhydroxycarbene and donates an H atom to the carbene carbon, resulting in the traditional 1,2-H-shift isomerization of carbenes, but with a much-reduced barrier.

5. OUTLOOK

New approaches to production and detection of carbenes in the last 15 years have enabled spectroscopy, kinetics, and dynamics studies beyond triatomic carbenes, and advancement in theoretical calculations have been crucial in identifying reaction products and mechanisms when several pathways are thermochemically possible. Studies over wider temperature ranges, most importantly below room temperature and in cold molecular beams, have changed our understanding of carbene chemistry. For example, increasingly fast consumption of ¹CH₂ in

bimolecular collisions as temperature decreases is now known to mainly arise from quenching to $^3\text{CH}_2$, not reaction, and hence $^3\text{CH}_2$ reactions have gained importance for planetary atmospheres (61). Quantum mechanical tunneling is now recognized (116) as a major loss pathway for carbenes in ices of astrochemical interest. Augmenting canonical reaction mechanisms (4), recent work on the reactivity of hydroxycarbenes has confirmed early reports (135; 136) of a carbonyl-ene mechanism (137; 138) that is enabled both by the singlet ground state of hydroxycarbenes and the hydrogen bonding possible between the -COH group of hydroxycarbenes and carbonyl groups, with the labile H atom enabling facile chemistry. In Earth's atmosphere we now expect (140; 141) the major loss channels of hydroxycarbenes will not be reaction with O_2 , but instead reaction with water and water clusters via 1,2-H shift isomerization forming aldehydes. For CH_3COH , this bimolecular reaction implies an additional source of acetaldehyde in Earth's atmosphere that is not currently included in atmospheric models, and further implies that negligible CH_3COH reacts with O_2 , which should lower the amount of acetyl (CH_3CO) radicals in tropospheric budgets.

The importance of hydroxycarbenes continues to expand. For example, HCOH has been implicated (142) as an important intermediate in liquid hydrocarbon synthesis via the Fischer-Tropsch reaction, in which $\text{CO} + \text{H}_2$ are the feedstock. Direct monitoring of this intermediate could provide new insights into this industrially important reaction. Hydroxycarbenes have been shown to be viable candidates as a source of pre-biotic sugars (137; 138) in their reactions with aldehydes even in cold, dry environments, but one must ask the question of how these hydroxycarbenes could be formed in space. Recent laboratory simulations of photochemistry on cold ices revealed the formation of pyruvic acid—a precursor of CH_3COH —when acetaldehyde / CO_2 ices are irradiated (143). Furthermore, the simplest sugar, glycolaldehyde, has been

observed in laboratory irradiation of ices composed of methanol and methanol / CO mixtures (144; 145). Together, this evidence increases the plausibility that hydroxycarbenes chemistry may be involved in synthesis of simple sugars that are known to have been delivered to Earth by meteorite impacts (146). New experimental and theoretical investigations will be needed to critically evaluate and expand upon these findings. We expect that soon even crossed molecular beam studies with larger carbenes will be possible, and further insights from solvent-free gas phase studies will continue to surprise us.

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TERMS AND DEFINITIONS LIST

Kinetic Energy Release (KER): The kinetic energy, measured in the center-of-mass frame of reference, of two products recoiling from each other in a photodissociation or a bimolecular collision.

Internal Conversion (IC): a non-radiative transition between two electronic states of the same spin multiplicity, in which electronic energy is converted to vibrational energy

Intersystem Crossing (ISC): a non-radiative transition between electronic states of different spin multiplicity (here triplet to singlet or singlet to triplet) that converts electronic to vibrational energy.

Collision Induced Intersystem Crossing (CIISC): intersystem crossing induced by a non-reactive collision with another atom or molecule.

Multiplexed Photoionization Mass Spectrometer (MPIMS): a photolysis-initiated chemical reactor connected to an orthogonal acceleration mass spectrometer using single-photon ionization of neutral species.

REFERENCE ANNOTATIONS:

- (5) Kable et al.: In-depth review on halocarbenes described in the Sidebar.
- (54) Osborn et al.: A detailed description of the MPIMS instrument and modes of operation.
- (57) Fischer: Perspective article focusing on advances in photoelectron spectroscopy which includes reactive intermediates in different environments.
- (56) Herzberg: Classic book on spectroscopy of polyatomic molecules. Also parts I and II in the series.
- (66) Apeloig: This article includes many references to previous theoretical articles on CH₂.

(67) Schaefer: Article describing the initial disagreement between experiment and theory on the singlet-triplet gap in CH₂.

(105) Schreiner: Perspective Article describing proposing tunneling control as a new reactivity paradigm in hydroxycarbenes.

(97) Eckhardt: This article explains the influence of the captodative effect on the stability of hydroxycarbenes.

(121) Darwin: Kinetics of ³CH₂ with a variety of co-reactants.

SIDEBAR

Except for methylene, the most detailed and comprehensive studies concern the halocarbenes. The studies are described in a 2009 review by Kable et al. (5), which emphasizes their spectroscopy and photochemistry. The structure and spectroscopy of the halocarbenes have much in common with CH₂. Their spectra display strong perturbations in rovibrational levels, which were assigned using absorption and fluorescence excitation spectroscopic techniques. They exhibit the Renner-Teller effect, and in addition, have larger spin-orbit interactions than CH₂, especially for the heavier halogens. Their $\tilde{A}^1A'' \leftarrow \tilde{X}^1A'$ spectra display extended progressions in the bending vibrational mode reflecting the different geometries of the ground and excited states. The review includes an in-depth discussion of theoretical and experimental studies of the singlet-triplet gap in halocarbons, which have a singlet ground state. Single vibronic level (SVL) emission spectroscopy and stimulated emission pumping (SEP) techniques were exploited to achieve accurate values of the gap. While studies of the photodissociation dynamics of carbenes are rare, ref. (5) describes several detailed studies of the photodissociation dynamics of :CXY carbenes from the $\tilde{A}^1A''$ state, which include couplings between singlet and triplet states, product quantum state distributions, and comparisons with theory.

FIGURE CAPTIONS

Figure 1: (a) Structure of the four lowest energy electronic states of XCY carbenes, with term symbols in the C_{2v} symmetry limit of X = Y, orbital occupations, and characters given below. XCY carbenes with X ≠ Y have C_s symmetry, where B₁ terms reduce to A'', and A₁ terms reduce to A'. (b) Singlet-triplet splitting

$E_{ST} = E_S - E_T$ for small carbenes with substituents X and Y. By IUPAC convention, E_{ST} is positive for carbenes with a triplet ground state, and negative for carbenes with a singlet ground state.

Figure 2: Potential energy surface of C_2H_4O at the AE-CCSD(T)/cc-pCVQZ level of theory, showing methylhydroxycarbene in the center. The abscissa is the mass-weighted Cartesian intrinsic reaction coordinate. The 1,2-H shift isomerization pathway to vinyl alcohol (left) has a lower but wider barrier compared to the 1,2-H shift isomerization to acetaldehyde (right). Despite the higher barrier energy, isomerization by tunneling is only observed to acetaldehyde. Reproduced with permission from Reference 103.

Figure 3: (a) Schematic cut through the PES for the photodissociation of methylketene, showing triplet (T_1) and singlet (S_0) product channels producing ethylidene. (b) PES for the 1,2-H-shift isomerization of ethylidene on the triplet (blue) and singlet (orange) surfaces. (c) Center-of-mass translational energy distributions of $m/z = 28$ from methylketene photodissociation providing evidence of 3CH_3CH and 1CH_3CH production. Figure adapted from Reference 38 with permission.

Figure 4: Stationary points and geometries on the ZPE-inclusive potential energy surface of the reaction $CH_3-C-OH + CH_3CHO$, with these reactants at the zero of potential energy. The dominant carbonyl-ene mechanism is in dark blue, whereas the two non-competitive insertion mechanisms that might be expected of singlet carbene reactivity are shown in red and cyan. Figure adapted from Reference 138 with permission.

TABLES

Table 1: Barrier heights, half-lives and E_{ST} of hydroxycarbenes (energy values in kcal mol^{-1})

Carbene	Barrier Height	Half-Life	E_{ST}
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H-C-OH ^a	29.7	2.1 h	-25.5
CH ₃ -C-OH ^b	28.0	1.1 h	-30.5
(CH ₃) ₃ -C-OH ^c	28.5	1.8 h	--
C ₆ H ₅ -C-OH ^d	28.8	2.5 h	-22.3
cyc-C ₃ H ₅ -C-OH ^e	30.4	17.8 h	-35.4
HC≡C-C-OH ^f	31.8	3 d	--
F ₃ C-C-OH ^g	30.7	6 d	-26.8
NC-C-OH ^h	33.3	23.5 d	-20.4
HO-C-OH ⁱ	34.1	None	-61.7
HO-C-NH ₂ ^j	34.4	None	--

References: a) (87) b) (103) c) (100) d) (99) e) (101) f) (95) g) (102) h) (97) i) (33) j) (116)

FIGURES

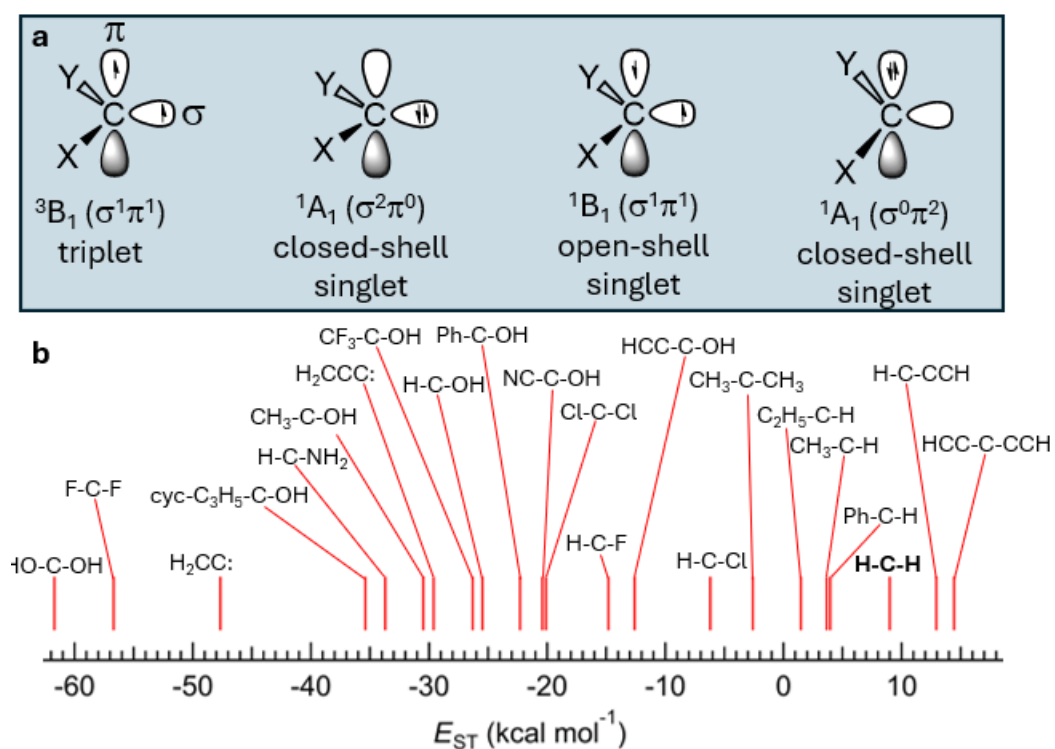


Figure 1

(a) Structure of the four lowest energy electronic states of XCY carbenes, with term symbols in the C_{2v} symmetry limit of $X = Y$, orbital occupations, and characters given below. XCY carbenes with $X \neq Y$ have C_s symmetry, where B_1 terms reduce to A'' , and A_1 terms reduce to A' . (b) Singlet-triplet splitting $E_{ST} = E_S - E_T$ for small carbenes with substituents X and Y. By IUPAC convention, E_{ST} is positive for carbenes with a triplet ground state, and negative for carbenes with a singlet ground state.

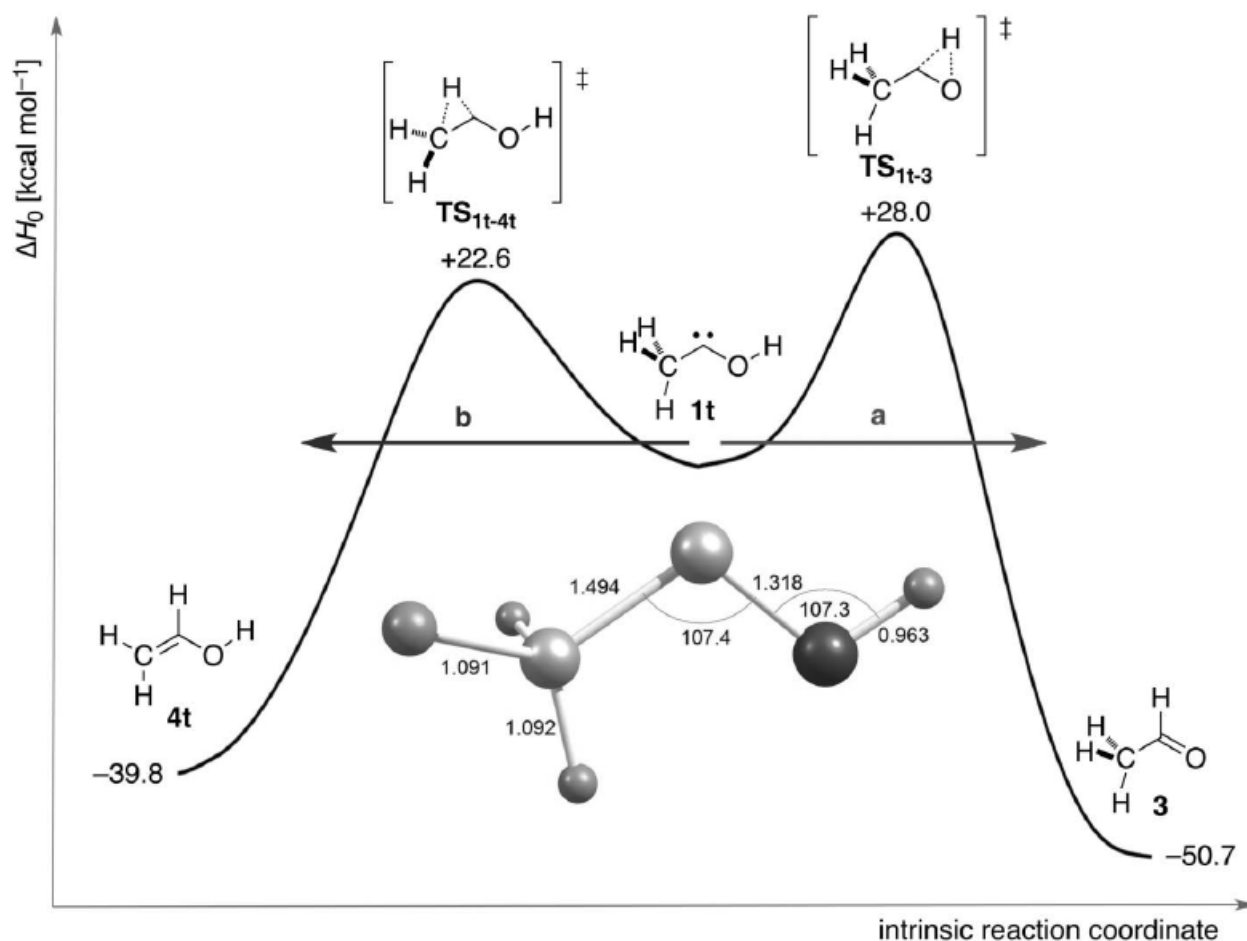


Figure 2

Potential energy surface of $\text{C}_2\text{H}_4\text{O}$ at the AE-CCSD(T)/cc-pCVQZ level of theory, showing methylhydroxycarbene in the center. The abscissa is the mass-weighted Cartesian intrinsic reaction coordinate. The 1,2-H shift isomerization pathway to vinyl alcohol (left) has a lower but wider barrier compared to the 1,2-H shift isomerization to acetaldehyde (right). Despite the higher barrier energy, isomerization by tunneling is only observed to acetaldehyde. Reproduced with permission from Reference 103.

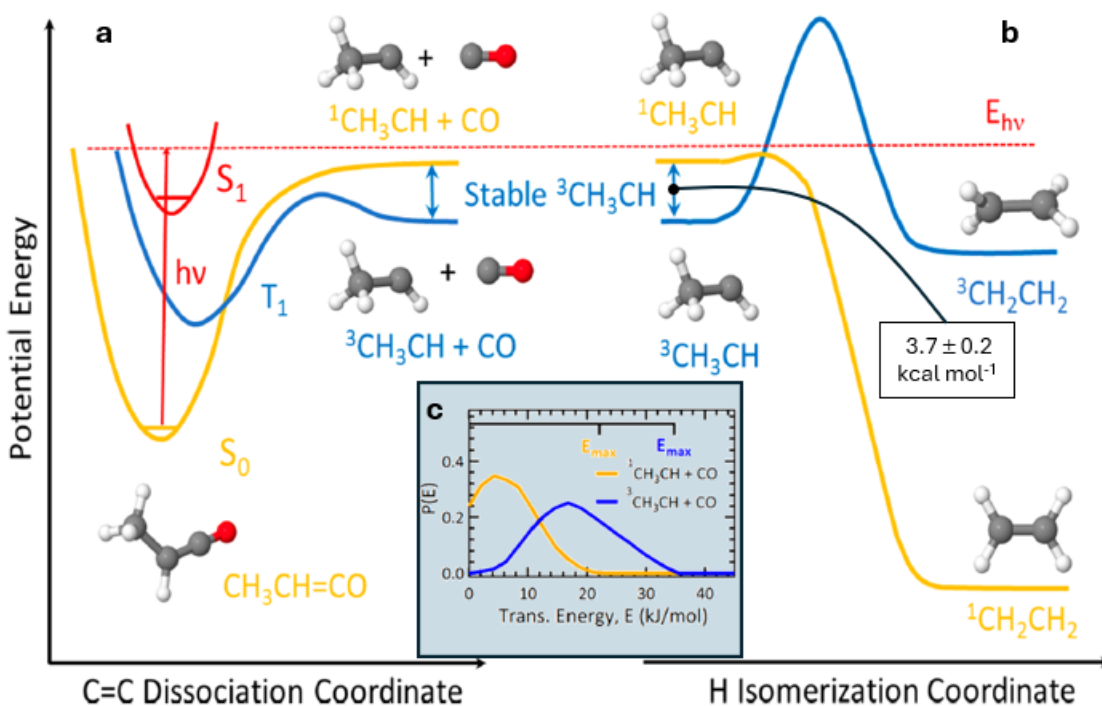


Figure 3

(a) Schematic cut through the PES for the photodissociation of methylketene, showing triplet (T_1) and singlet (S_0) product channels producing ethylidene. (b) PES for the 1,2-H-shift isomerization of ethylidene on the triplet (blue) and singlet (orange) surfaces. (c) Center-of-mass translational energy distributions of $m/z = 28$ from methylketene photodissociation providing evidence of $^3\text{CH}_3\text{CH}$ and $^1\text{CH}_3\text{CH}$ production. Figure adapted from Reference 38 with permission.

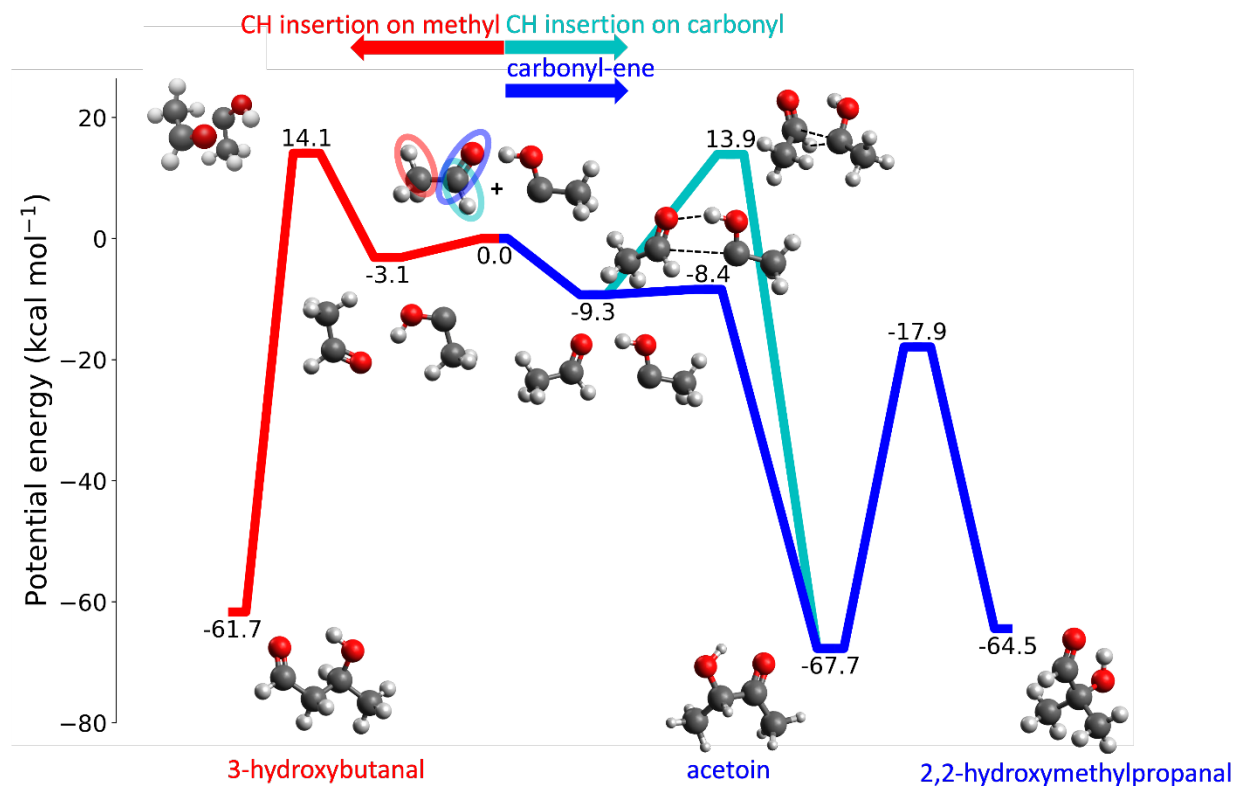


Figure 4

Stationary points and geometries on the ZPE-inclusive potential energy surface of the reaction $\text{CH}_3\text{-C-OH} + \text{CH}_3\text{CHO}$, with these reactants at the zero of potential energy. The dominant carbonyl-ene mechanism is in dark blue, whereas the two non-competitive insertion mechanisms that might be expected of singlet carbene reactivity are shown in red and cyan. Figure adapted from Reference 138 with permission.