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Divalent Carbon Intermediates: Laser Photolysis and Spectroscopy

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Summary. A brief review is given of the structures of an important class of reactive intermediates, divalent carbon species (carbenes). The electronic properties of carbenes force an unusual electronic character upon these species that, in turn, leads to intriguing physical and chemical properties. Because of the fleeting nature of carbenes, which are extraordinarily reactive, direct investigation of their structural and chemical behavior has presented a challenge to the experimentalist. The application of spectroscopic and ultrafast laser techniques has met this challenge. With the use of laser methods, along with conventional techniques, quantitative evaluation of the energetics, dynamics, and reactivities of a variety of carbenes has been possible.

In nature and in the laboratory, tetravalent carbon is the normal structural form that underlies the structure of organic molecules. The dominance of tetravalent carbon as a low-energy state of the carbon atom can be traced to the octet rule, which states that first row elements prefer to assume a rare-gas configuration of valence electrons. Since a carbon atom possesses four valence electrons, it can readily obey the octet rule by forming four covalent bonds with atoms capable of donating a total of four electrons.

This article is concerned with abnormal, high-energy, reactive forms of carbon. In contrast to conventional, tetravalent-carbon compounds, which can be put into bottles and whose properties and reactions can be measured on the time scale of minutes or days, we are concerned here with species of carbon that exist only as reactive intermediates and whose properties and reactions must be measured on the time scale of 10^{-6} to 10^{-12} seconds or less. These reactive transients are termed divalent carbon intermediates or, more commonly, carbenes (*1–4*).

Carbenes possess only six valence electrons and fully lack two valences. The high energy and reactivity implied by the carbene structure has challenged chemists over the past three decades. This article describes advances in carbene chemistry which have resulted mainly from the use of time-resolved laser spectroscopy. This technique has allowed the direct experimental observation of many divalent carbon species in fluid solution at or near room temperature (*5–7*).

Reactive Intermediates in Chemical Reactions

To fully understand and appreciate the nature of chemical change, the chemist must know more than the chemical species that exist at the beginning of a reaction and at the end of a reaction, because few chemical reactions proceed by a direct conversion of reactants to products.

If a reaction proceeds in more than one step, intermediates must be postulated in any reaction mechanism. Indeed, it is a standard tactic to postulate reactive intermediates whose existences are fleeting (*8, 9*).

A crucial task in the investigation of chemical reactions involves the identification and characterization of those intermediates. The scientific fascination and importance of observing species with lifetimes that are vanishingly small relative to conventional molecules has led chemists to a variety of chemical and spectroscopic techniques.

Methylene, the Simplest Carbene

In this article we focus attention on divalent carbon species or carbenes. In order to familiarize the reader with carbene chemistry, we consider some significant structural properties of methylene (CH_2), the parent molecule of the carbenes.

Methylene is a simple three atom system. It can be described in terms of a limiting linear structure possessing a center of symmetry or in terms of a bent structure (Fig. 1) (*10–12*). The contribution of the central carbon atom to the electronic character of the linear structure may be described in terms of four valence atomic orbitals: a $2s$ orbital and three $2p$ orbitals. The combination of two orbitals (the s and one p) produces two σ orbitals that are responsible for binding the carbon atom to the two hydrogen atoms. The remaining two p orbitals are labeled as p_x and p_y.

Methylene possesses six valence electrons. The way these six electrons distribute themselves depends on the geometry of the methylene molecule. For linear methylene refer to the molecular orbital scheme in Fig. 2A. The bonding σ_{CH} orbitals are of considerably lower energy than the nonbonding p_x or p_y orbitals. In accordance with both the Aufbau and Pauli Principles, four valence electrons, two from carbon and one from each hydrogen, will be placed pairwise in the two σ_{CH} orbitals. The remaining two electrons will go into the

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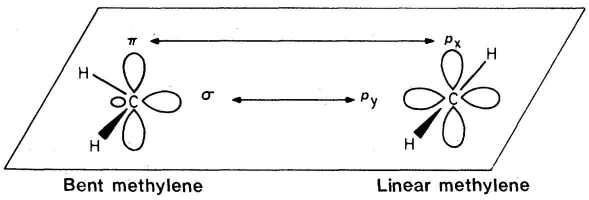


Fig. 1. Orbital representations for bent and linear methylenes. For bent methylene, the hydrogen atoms and the σ orbital are in the indicated plane; the π orbital is above and below it. For linear methylene, the hydrogen atoms and the p_y orbital are in the plane; the p_x orbital is above and below it.

remaining two p orbitals, p_x and p_y. Since the orbital energies of p_x and p_y for the linear methylene are equal by symmetry, one would predict that one electron would occupy p_x and the other p_y, with their spins parallel. This arrangement with parallel spins yields a triplet state; the energy advantage of this arrangement arises from the larger average separation of electrons in the triplet state relative to that of spin-paired electrons in what is called the singlet state (Fig. 2B) (*13, 14*).

Now let us consider the consequences of bending a linear methylene in the *y,z*-plane (Fig. 2, C and D). The atomic orbital, p_y, will pick up *s* character and be lowered in energy. We classify this orbital as a σ orbital in a bent methylene. The atomic p_x orbital will not be significantly perturbed as a result of bending. We classify this orbital as a π orbital in a bent methylene.

How will the electrons distribute themselves in this molecular orbital scheme? Again, four electrons can be immediately placed pairwise in the two low-energy bonding σ_{CH} orbitals. The distribution of the two remaining electrons is determined by achieving the lowest sum of the orbital energies and electron-electron repulsion. To achieve the lowest orbital energy both electrons would occupy the lowest orbital, $(\sigma)^2$, whereas to achieve the smallest electron-electron repulsion the two electrons would occupy different orbitals, $(\sigma)^1(\pi)^1$. However, if placing an electron in the higher energy π orbital gives a lower sum of orbital energies and electron-electron repulsion than when both electrons occupy the σ orbital, the low-energy configuration will be $(\sigma)^1(\pi)^1$, a triplet state (Fig. 2C). Within the $(\sigma)^1(\pi)^1$ configuration, a singlet state is possible (Fig. 2E), but it has a much higher energy than any of the electron states considered here. Additionally, if the energy needed to occupy σ and π is larger than when both electrons occupy the σ orbital, then the electronic configuration will be $(\sigma)^2$, which is a singlet state (Fig. 2D). For methylene, as for many carbenes, the ground state has been found experimentally to be the triplet state, $(\sigma)^1(\pi)^1$, with a low-lying, neighboring singlet state σ^2. The geometries of the triplet and singlet are predicted to be different, with the singlet being more bent. The triplet and singlet geometries and the energy gap between the triplet and singlet will vary as the groups attached to the central carbon are changed. Despite this variation in bond angles and energies among different carbenes, useful generalizations about this class of chemical intermediates can be made. Now we can explore the key issues that relate the carbene structure and its reaction characteristics to the energies of the triplet and singlet states, to the dynamics of the triplet-singlet interconversion, and to their distinctive chemistries.

Chemistry of Carbenes

Because methylene possesses only six valence electrons, it is expected to seek two electrons for the central carbon atom and thereby achieve the stable octet structure. Reactions of methylene are known in which the CH_2 fragment is inserted into C–H bonds and added across C=C bonds.

Some chemistry of methylene, the prototype of substituted carbenes, is summarized in Fig. 3 in terms of a molecular orbital representation. The forms of methylene in which the two nonbonding electrons occupy different orbitals (symbolized by $\cdot\dot{C}H_2$) are expected to react with C–H bonds as shown in Fig. 3A. The radical character of this state is manifest in the radical-like abstraction of a hydrogen atom to lead to a radical pair, RP. As a result of the spin selection rules of chemical reactivity, the spin state of the methylene will determine the spin of the radical pair, and thus the reaction path in Fig. 3A (*15*). For example, the singlet-state radical fragments, ^{1}RP, produced by reaction of singlet-state $\cdot\dot{C}H_2$ with CH_3OH combine in the solvent cage to form a coupling product from the radical pair. On the other hand, triplet-state radical fragments, ^{3}RP, cannot combine because of spin restrictions; they escape from the solvent cage in which they were born and eventually combine with uncorrelated spin systems to form coupling products such as those shown in Fig. 3A.

The chemistry of methylene in which both nonbonding electrons occupy the same orbital (symbolized by $:CH_2$) is different from that of the states in which each of the nonbonding electrons occupies a different orbital. The two electrons from the oxygen atom of CH_3OH can overlap nicely with the empty π orbital of $:CH_2$ to form a C–O bond, the key step in formation of the eventual product, an ether (Fig. 3B). The singlet and triplet states of $\cdot\dot{C}H_2$ do not possess a low-lying empty orbital, and therefore, do not react with CH_3OH in this fashion.

One of the more fascinating reactions of carbenes is their addition to C=C bonds, that is, a [1 + 2] cycloaddition to form cyclopropanes. Both the singlet and triplet states of $\cdot\dot{C}H_2$ can be envisioned to yield diradical intermediates. Depending on spin state, the diradical will either close rapidly and with retention of configuration (the path for singlet $\cdot\dot{C}H_2$) or persist for many bond rotations and eventually close with some loss of configuration (the path for triplet $\cdot\dot{C}H_2$) (Fig. 3C). The reaction of $:CH_2$ with a C=C bond is expected to produce an intermediate which has both nonbonding electrons in the same orbital, and which, because further reaction is spin-allowed, should cyclize rapidly to yield a cyclopropane with retention of a configuration (Fig. 3D). Although the reactions of methylene are discussed as proceeding via intermediates, for the singlet states the reaction could be concerted and proceed directly to products without the occurrence of an intermediate (*16*).

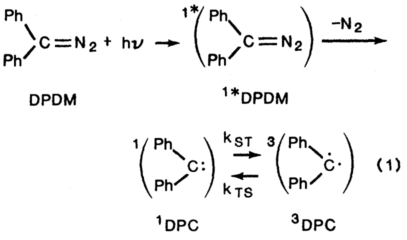
Experimental determination of the low-lying states of divalent carbon. One of the very first questions to be addressed in an investigation of carbenes concerns the nature of the low-lying state of the divalent carbon system under investigation. Prior to 1980 electron spin resonance spectroscopy (*17–19*), product analyses (*20–22*), and optical spectroscopy (*7, 23–25*) were the main experimental methods employed to probe carbene structures and energetics. These methods revealed that methylene possesses a triplet ground state, $(\sigma)^1(\pi)^1$, with a singlet state, $(\sigma)^2$, about 35 kJ/mol higher in energy (*26–28*). On the other hand, substantial evidence suggests that, although most derivatives of methylene possess triplet ground states, the singlet-triplet energy gap is on the order of only 5 to 20 kJ/mol (*1, 29*). Furthermore, some derivatives of methylene appear to possess singlet ground states (*30*).

Measurement of the dynamics of sin-

glet-triplet relaxation and the singlet-triplet energy gap in diphenylcarbene. We were encouraged to study diphenylcarbene by the pioneering theoretical and spectroscopic studies of the dynamics, structure, and chemistry of this aromatic carbene with a triplet ground state (*3, 17–19, 23, 24, 31*). The spectroscopic information on emission and absorption makes it possible to probe the chemical and physical aspects of carbene formation, intramolecular energy relaxation, chemical reactions, and excited electronic-state properties.

The way in which the carbene is generated can be important in unraveling its chemistry. If the carbene is produced in the excited, singlet state, it undergoes singlet reactions that compete with energy relaxation to the triplet ground state where different reactions occur. Similarly, producing the carbene in its triplet state can yield triplet reactions, or the carbene can undergo a thermal excitation to the singlet state, $(\sigma)^2$, where other reactions can occur. The observed chemistry of a carbene thus depends on the difference in energy and interactions between these two states of different spin multiplicity and on their rates of interconversion.

To elucidate the rapid dynamics of carbene formation, energy relaxation within the carbene itself, and reaction of the carbene with other molecules, a picosecond, ultraviolet laser pulse is used to generate the diphenylcarbene (DPC) from diphenyldiazomethane (DPDM) (Eq. 1) (*32, 33*). Photoexcitation of DPDM to an excited singlet state breaks the $C=N_2$ bond in the diazo compound releasing DPC in a singlet state. The sequence of energy decay steps following the laser photoexcitation of DPDM ultimately leading to DPC in its triplet ground state is given in Eq. 1, where Ph represents the phenyl group and the superscript * represents excited states. Earlier work showed that ^{3}DPC is generated in a subnanosecond time scale from the excited diazo precursor (*25*), and the calculated value of k_{ST} (the rate constant for the singlet-triplet transition) was based on the assumed diffusional quenching of the singlet state, ^{1}DPC, by methanol. It was for these reasons picosecond laser methods were necessary to follow the rapid steps of carbene generation and energy relaxation.



(1)

Our laser experiments revealed that the bond breaking step in the photoexcited diazo molecule occurred (*32*) in less than 5 psec. The k_{ST} value was measured using a laser-induced fluorescence technique (Fig. 4) (*32*). The experiment employs two laser pulses. One pulse is used for the excitation of the diazo compound; a second pulse is delayed with respect to the excitation pulse and is used for determining the formation rate of ^{3}DPC. In acetonitrile, CH_3CN, at room temperature the time it takes for ^{1}DPC to convert into ^{3}DPC, which is the inverse of the rate constant, k_{ST}, is 310 psec.

By measuring the rate constant, k_{TS}, for the reverse process, namely, triplet to singlet transition, in the same solvent we obtain the equilibrium constant of the singlet-triplet interconversion (Eq. 2) (*32, 33*).

$$K = \frac{k_{ST}}{k_{TS}} \qquad (2)$$

This equilibrium constant, for which an upper limit had been obtained in earlier

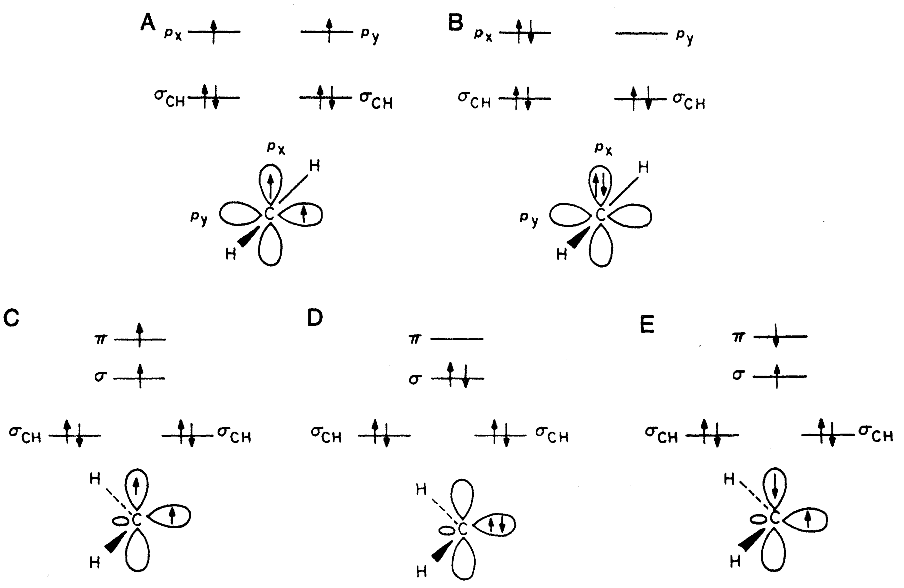


Fig. 2. Energy level and orbital representations for bent and linear geometries of methylene. (A) Linear methylene, the triplet state. (B) Linear methylene, the singlet state. (C) Bent methylene, the triplet state, $(\sigma)^1(\pi)^1$. (D) Bent methylene, the singlet state, $(\sigma)^2$. (E) Bent methylene, the high-energy singlet state, $(\sigma)^1(\pi)^1$.

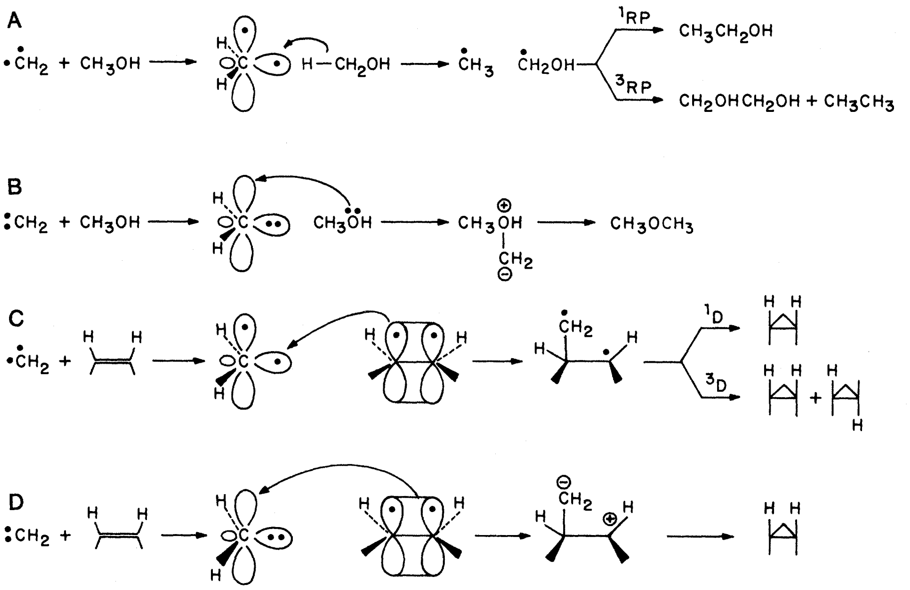


Fig. 3. Some prototypical reactions of divalent carbon with methylene as an example. RP and D represent radical pairs and diradicals, respectively. A superscript 1 stands for a singlet state; a superscript 3, a triplet state.

studies (*25*), can then be used to calculate the free energy difference between singlet and triplet states (Eq. 3).

$$\Delta G = -RT \ln K \qquad (3)$$

However, the measurement of k_{TS} (^{3}DPC → ^{1}DPC) is not straightforward (*25, 33*). Clean and rapid production of ^{3}DPC is difficult. As a result, k_{TS} is determined by a procedure that is indirect, because of the required coordination of conventional product analysis, triplet photosensitization, photochemical kinetics, and time resolved methods.

On combining the measured k_{ST} and k_{TS} values for DPC in acetonitrile at room temperature, we obtain an equilibrium constant $K = 290$ and the free energy difference given in Eq. 4.

$$\begin{aligned}\Delta G = G_{\mathrm{T}} - G_{\mathrm{S}} &= -RT \ln K \\ &= -14 \text{ kJ/mol} \qquad (4)\end{aligned}$$

An estimate of the energy difference between the singlet and triplet states can now be made from the thermodynamic relation $\Delta G = \Delta H - T\Delta S$. Since the entropy difference, ΔS, is expected to be primarily due to the multiplicity difference between the singlet and triplet states ($\Delta S = R \ln 3$) and since the enthalpy difference, ΔH, and the energy gap, ΔE, are approximately equal in liquids, we obtain Eq. 5 (*25*).

$$\Delta G = \Delta H - T\Delta S = \Delta E - RT \ln 3 \quad (5)$$

Therefore, for DPC in acetonitrile at room temperature we obtain the singlet-triplet energy gap in Eq. 6.

$$\begin{aligned}\Delta E &= E_{\mathrm{T}} - E_{\mathrm{S}} \\ &= -11 \text{ kJ/mol} = -950 \text{ cm}^{-1} \qquad (6)\end{aligned}$$

Solvent Effects on Singlet-Triplet Relaxation

After obtaining these kinetic and thermodynamic results for DPC in acetonitrile, the question of how applicable these findings are to other solvent environments arose. That is, to what extent does the solvent affect the dynamics of the intramolecular spin conversion in carbenes? Prior to this work, the effect of the solvent on intersystem crossing in carbenes was not considered.

We found that the singlet to triplet conversion depends strongly on the choice of solvent (Fig. 4) (*34*). In isooctane, a hydrocarbon solvent, the time of intersystem crossing, k_{ST}^{-1}, is 95 psec, three times faster than in acetonitrile. There is a clear relation between the speed of singlet to triplet conversion and the polarity of the solvent, the conversion being faster in the less polar solvents. No correlation was seen with other solvent parameters that would be related to possible carbene-solvent complexes or parameters, such as viscosity, that could influence the dynamics of the structural change associated with the singlet to triplet conversion.

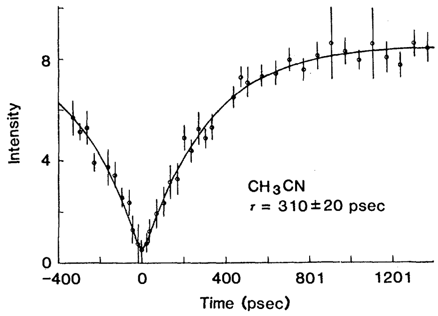


Fig. 4. Laser-induced fluorescence as a function of time delay between excitation and probe pulses yielding ^{1}DPC → ^{3}DPC for diphenylcarbene in acetonitrile.

To understand how solvent polarity could affect spin conversion, consider the electronic nature of the singlet and triplet states. The singlet state, $(\sigma)^2$, with both unshared electrons in the same orbital, localized on the central carbon, is more polar than the triplet state, $(\sigma)^1(\pi)^1$ (Fig. 2C). Therefore, the polar singlet will be more stabilized in the polar solvents than the triplet. This differential stabilization results in a decrease of the singlet-triplet energy gap as the solvent polarity increases. That the energy gap is smaller in a polar solvent than a nonpolar solvent was confirmed experimentally. We found the energy gap in nonpolar isooctane to be 17 kJ/mol compared to 11 kJ/mol in polar acetonitrile.

Why then does the rate of intersystem crossing increase as the energy gap increases, a seeming contradiction? Upon crossing from the singlet to the triplet state, the excess energy is taken up by the vibrational motions of the triplet. This conversion of electronic energy in the singlet state to vibrational energy in the triplet state is necessary to satisfy energy conservation: the sum of the electronic and vibrational energies in the triplet must equal the electronic energy of the singlet. This is the key. In aromatic carbenes, as the relatively small energy gap increases in magnitude with decreasing solvent polarity, there are more triplet vibrational states approximately equal to the singlet electronic energy, so more triplet vibrations can accept the excess energy from the singlet. Therefore, the carbene chemistry, which is dependent on these relaxation processes, can, in principle, lead to different product distributions in different solvent environments.

Photochemistry of Transient Chemical Intermediates

Although the chemistry of the low-energy electronic states of carbenes—the ground triplet and neighboring singlet—has been extensively studied, the chemistry and general properties of the higher energy electronic states remain unknown. Studies of the photochemistry of carbenes, or more generally the photochemistry of transient chemical intermediates, are just beginning. The transitory nature of reactive ground-state intermediates makes it difficult to generate their excited states in sufficient concentration to observe their chemical properties. Reactions of the thermally accessible states can destroy the chemical intermediate before it is elevated to excited electronic states with light. What is needed is the means to generate the excited intermediate in a time shorter than the reaction time of lower states. One can, of course, extend the reaction time of the lower states by keeping them away from other reactive molecules in the environment. However, if there are few reactive molecules around, then it is not possible to study the reactions of excited state intermediates before they decay back to the ground state, either by the emission of light or by nonradiative processes.

Our approach to this situation is to use picosecond laser methods first to generate the carbene and then to excite the carbene to higher electronic states (*35, 36*). For the case of diphenylcarbene, a picosecond, ultraviolet laser pulse was used to split the diphenyldiazomethane precursor, as discussed earlier. A second laser pulse arrives shortly after the reaction pulse and excites the triplet ground-state carbene to an excited triplet-state carbene. With these methods we were able to explore the interactions of alcohols with the excited triplet diphenylcarbene, ^{3*}DPC; and the result is a simple model to account for the different reactivity patterns of the singlet, triplet, and excited triplet states of diphenylcarbene. The model is an orbital filling scheme with nonbonding molecular orbitals, σ and π, and an antibonding orbital, π^*, of the carbene.

The key point in this model is the presence of an empty, low-lying nonbonding orbital for both ^{1}DPC and ^{3*}DPC (Fig. 5). ^{3}DPC possesses a half-filled, not an empty, π orbital, whereas ^{3*}DPC does possess an empty π orbital. Since the ^{3}DPC has both σ and π orbitals singly occupied, it is expected to behave like a free radical in its reactions. This expectation is borne out experimentally by the hydrogen abstraction reactions ^{3}DPC undergoes and its stepwise addition to olefins. On the other hand, because ^{1}DPC has a $(\sigma)^2(\pi)^0$ electron configuration, it can accept a pair of electrons into its empty π orbital. This means the singlet undergoes O–H insertion reactions with alcohols to form ethers (as in Fig. 2B) via the donation of a pair of electrons from the oxygen of the alcohol into the vacant π-orbital of the carbene. In a similar way, ^{3*}DPC, with a $(\sigma)^1(\pi)^0(\pi^*)^1$ configuration, also has an empty π orbital and could, therefore, undergo reactions resembling ^{1}DPC. This model not only accounts for the observed difference between the reactions of the ground triplet and lowest singlet state of the carbene but also predicts that the triplet excited should undergo certain reactions that the ground triplet would not.

Reactions of Excited Triplet Carbenes with Alcohols

By observing the behavior of ^{3*}DPC in the presence of a series of alcohols, we can determine whether the mode of reaction for the excited triplet follows the singlet mechanism (attack at the O–H bond), the triplet mechanism (attack at the C–H bond), or some other mechanism. The rate constants, $^{3*}k$, for the reactions of ^{3*}DPC with alcohols (Eq. 7)

$$^{3*}\text{DPC} + \text{reactant} \xrightarrow{^{3*}k} \text{product} \qquad (7)$$

were obtained from an analysis of the lifetime of ^{3*}DPC in the presence of different concentrations of alcohols.

The rate constants for methanol, isopropanol, and *t*-butanol show that methanol is the most reactive, whereas *t*-butanol is the least. The observed order of alcohol reactivities closely parallels the relative lability and acidity of the alcohols. This observation supports the mechanism that ^{3*}DPC reacts with the O–H bond of the alcohol. If the C–H bond of the alcohol were attacked by ^{3*}DPC, as in the ground triplet state reaction, then one would not expect to see the observed trend in the rates. The interpretation that ^{3*}DPC attacks the O–H bond, rather than the C–H bond, of the alcohols is consistent with its observed kinetic behavior with other electron donors, such as amines and olefins (*36*). An overall pattern that systematizes the ability of an arbitrary electron donor (an alcohol, amine, or olefin) to quench ^{3*}DPC involves two factors: the electron donor's ability to share electrons [a property related to the donor's ionization potential (IP)], and the strength (and reactivity) of the bonds in the donor's structure. When the donor possesses a relatively low ionization potential (IP < 9 eV), for example, amines, a charge transfer quenching mechanism will dominate (Eq. 8).

$$^{3*}\text{DPC} + \text{amine} \rightarrow (\text{DPC}^- \cdots \text{amine}^+) \rightarrow \text{products} \qquad (8)$$

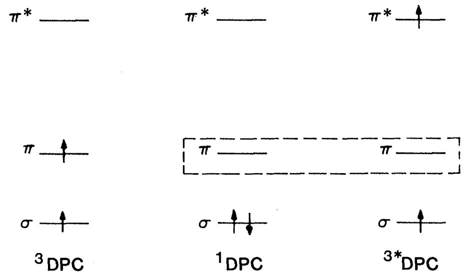


Fig. 5. Orbital occupancy for ^{3}DPC (ground state), ^{1}DPC (low-energy singlet state), and ^{3*}DPC (excited state of ^{3}DPC). Note the empty, low-energy π orbital common to ^{1}DPC and ^{3*}DPC.

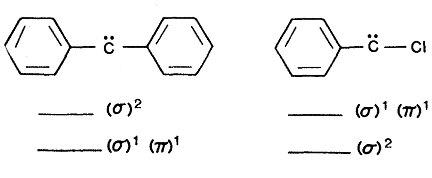
For donors possessing a relatively high ionization potential (IP > 9 eV), for example, alcohols, the charge transfer quenching mechanism becomes energetically disfavored and the breaking of bonds in the donor becomes the dominant quenching mechanism (Eq. 9).

$$^{3*}\text{DPC} + \text{alcohol} \rightarrow \text{ethers} \qquad (9)$$

In comparing the reactivities of ^{3}DPC, ^{1}DPC, and ^{3*}DPC with bimolecular quenchers, the common characteristic of an empty low-energy orbital that can accept a pair of electrons produces a similarity in the reactivity of ^{1}DPC and ^{3*}DPC toward electron donors. Thus, ^{3*}DPC, although formally a triplet, acts more like ^{1}DPC than ^{3}DPC.

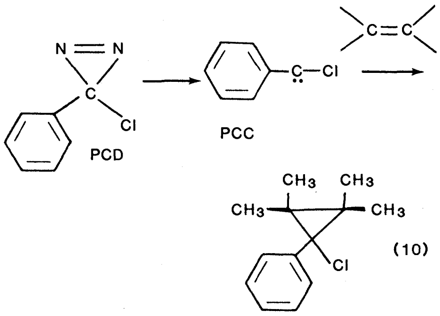
Arylhalocarbenes: Reaction Dynamics of Carbenes with Singlet Ground States

As we have said, diaryl carbenes typically possess triplet ground states with low-energy, thermally accessible singlet states. However, appropriate variations of carbene structure lead to such stabilization of the singlet state, $(\sigma)^2$, relative to the triplet state, $(\sigma)^1(\pi)^1$, that the singlet state becomes the ground state. For example, replacing a phenyl substituent with a halogen atom achieves the switch.



The stabilization of the $(\sigma)^2$ state is so great for phenylhalocarbenes that only the $(\sigma)^2$ state is involved in the chemistry of such species. This simplifies the measurement and interpretation of the reaction dynamics for this class of carbenes, and it presents an opportunity to determine the nature of the relation between reactivity and structure for an exceedingly reactive species.

We have generated phenylchlorocarbene (PCC) by photolysis of phenylchlorodiazirine (PCD) (*37–39*). When the photolysis is conducted in the presence of olefins, clean production of cyclopropanes is observed (Eq. 10).



(10)

The absorption spectrum of PCC produced by laser flash photolysis of PCD at room temperature in fluid solution is experimentally identical to the spectrum of PCC in a solid matrix at 77 K (conditions under which the carbene is indefinitely stable). The decay of the absorption of PCC can be monitored by time-resolved spectroscopy. Upon addition of tetramethylethylene (or any olefin), the reaction shown in Eq. 10 occurs, and the PCC absorption decreases more rapidly with time as a result of the reaction of the carbene with the olefin. Analysis of the decay of PCC absorption as a function of olefin concentration allows evaluation of the absolute rate constant (k_{abs}) for reaction of PCC with an olefin.

Relative reactivity experiments have played an important role in developing an understanding of organic reaction mechanisms. The data from kinetic competition experiments have established the electrophilic nature of the selectivity of many carbenes toward reagents such as olefins, and a quantitative selectivity index has been created to standardize relative reactivity parameters (*37*). Selectivity refers to the ratio of rate constants for two related reactions of a carbene toward two substrates or two different carbenes toward the same substrate. These selectivity parameters have been assumed to imply reactivity parameters: high selectivity implies low reactivity, and low selectivity implies high reactivity. The advent of time-resolved laser spectroscopy allowed a direct test of the implied selectivity-reactivity relationship, because direct measurement of the absolute rate constants for reactions of carbenes became possible by this technique.

The absolute rate constants for the reactions of PCC and some of its derivatives with tetramethylethylene (a relatively reactive olefin) and with 1-hexene (a relatively unreactive olefin) in isooctane have been determined (*40–42*). For even the most reactive systems, the rate constant ($\sim 1.5 \times 10^9 M^{-1}$ sec^{-1}) is slightly below the diffusion control limit for isooctane ($\sim 1 \times 10^{10} M^{-1}$ sec^{-1}). However, even though carbenes are enormously reactive, their reactivity is a strong function of their structure and of the structure of the other reactant. For example, the rate constant for reaction of 1-hexene and a 4-methoxyl–substituted carbene is on $1.3 \times 10^5 M^{-1}$ sec^{-1}.

Thus, a highly reactive species can be, nonetheless, quite selective. Such a result suggests caution in the application of conventional selectivity-reactivity relationships to the chemistry of carbenes and other highly reactive intermediates.

The activation energy, E_a, for the rate limiting step in a reaction mechanism is conventionally obtained by measuring the absolute rate constant for the reaction (k_{abs}) as a function of temperature and then employing the Arrhenius expression (Eq. 11).

$$\log k_{abs} = \log A - E_a/2.3RT \qquad (11)$$

Chemical reactions are expected to proceed via mechanisms involving an energy barrier for the rate limiting step, and as a result, E_a is generally a positive quantity. This means that a graph of log k_{abs} versus T^{-1} will generally possess a negative slope. For the reaction given in Eq. 10, in toluene or acetonitrile, the slope of the plot is positive for temperatures of 225 K and above (*20*). A positive slope implies a negative activation energy. Investigation of other carbene reactions have revealed that they fall into three categories (*21*): (i) those that possess negative activation energies on the order of several kilojoules per mole; (ii) those that possess activation energies equal to zero within experimental error; and (iii) those that possess positive activation energies on the order of several kilojoules per mole.

There are at least two general (somewhat related) interpretations of the observation of a negative activation energy. Both seek escape from the apparent dilemma that theory does not allow the occurrence of anything other than a zero or positive energy barrier in a single step.

The first solution challenges the assumption that the rate constant, k_{abs}, corresponds to a single reaction step. For example, if the reaction of carbenes and olefins proceeded in two steps, neither of which was uniquely rate determining, the dependence of k_{abs} on temperature could be complex. In the simplest case, a reversibly formed complex between carbene and olefin might form (Eq. 12). As the temperature varies,

$$\begin{gathered}\text{carbene} + \text{olefin} \rightleftarrows \text{complex} \\ \text{complex} \rightarrow \text{product} \end{gathered} \qquad (12)$$

the complex can either dissociate to starting materials (slowing down the rate of reaction) or collapse to product (increasing the rate of reaction). Stating that a reaction has a negative activation energy is equivalent to stating that the rate of reaction increases as the temperature decreases. Such would be the case if the carbene complex were stabilized with respect to dissociation as the temperature decreased and, as a result of this stabilization, it proceeded more efficiently to product than it did at higher temperature. Such a condition could exist until the reaction became diffusion controlled; at that point the reaction of the complex would be 100 percent efficient and the reaction rate would be equal to and limited by the diffusion of reactants together. Indeed, below ~250 K in toluene the slope of log k_{abs} versus T^{-1} for the reaction of PCC and tetramethylethylene corresponds to a positive activation energy; that is, the reaction becomes diffusion controlled below 250 K, and the activation energy corresponds to the energy of diffusion.

A second interpretation of negative activation energies focuses on the balance between enthalpy and entropy as the system proceeds along the reaction coordinate, and does not require any complex other than the conventional encounter complex required for bimolecular reactions of freely diffusing species in fluid solutions (*43*).

Whatever interpretation is applied, it is clear that conventional enthalpy control is not dominant in many of the carbene reactions investigated. Indeed, in all of the carbene reactions studied, the entropies of activation exert a strong influence on k_{abs} (*44*).

The application of fast spectroscopic and kinetic techniques to carbene chemistry has stimulated important research on reactive intermediates. In spite of the high reactivity of carbenes, which results in a short lifetime, their dynamics and chemistry can be investigated directly via time-resolved laser spectroscopy. In addition to the conventional features of structure-reactivity and the applicability to structure-selectivity relationships, we have been able to use kinetic measurements to obtain information about the singlet-triplet-energy gap, the effects of solvent interactions on the dynamics of singlet-triplet interconversions, and the nature of excited-state carbene reactions from picosecond spectroscopy. This information should be useful to theoretical and experimental chemists as well as to biological chemists who are involved with methods which allow controlled labeling of biological molecules (*45*).

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New Crops for Arid Lands

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Recent decades have witnessed an apparent increase in the rate of desertification of agricultural land. In the United States alone there are now over 200,000 million hectares of arid and semiarid range land, and there are even larger areas in Africa, Australia, and South America (*1*). More than one-third of our planet's land is now arid. Water for humans and their crops is rapidly becoming a critically short commodity.

Summary. Five plants are described that could be grown commercially under arid conditions. Once the most valuable component has been obtained from each plant (rubber from guayule; seed oil from jojoba, buffalo gourd, and bladderpod; and resin from gumweed), the remaining material holds potential for useful products as well as fuel. It is difficult to realize the full potential of arid land plants, however, because of the complexities of developing the necessary agricultural and industrial infrastructure simultaneously. To do so, multicompany efforts or cooperative efforts between government and the private sector will be required.

The two most important reasons usually given for desertification are denuding of the land through deforestation in ancient times and overgrazing in modern times, but many other factors may contribute. Farmers have tapped many aquifers to sustain their crops, and in some cases have depleted these nonrenewable underground reservoirs to such an extent that it is no longer economical to use them. Heavy irrigation over long periods has increased soil salinity in many areas, further diminishing the land's crop-carrying potential. Tilling and baring the thin topsoils of these delicate ecosystems has caused widespread erosion. As a result of these compounded problems, the deserts advance and farming of cotton and food crops becomes increasingly expensive, energy-intensive, and unproductive; indeed, growing conventional crops in arid regions is proving to be a self-limiting endeavor.

Of the approximately 350,000 plant species described by botanists, only about 3000 have been tried as sources of food and other useful materials (*1*). We cultivate only about 100 plant species on a large scale, with about 90 percent of our food coming from a dozen crops. Of the significant crops grown today, none is xerophytic. Thus, there is a need to identify usable xeric plants that can be made to produce abundantly in arid regions.

As Epstein (*2*) has explained in detail, plants in arid and semiarid regions face severe problems of water economy because the salinity of the soil causes osmotic withdrawal of water and because hot, dry atmospheric conditions cause excessive loss of water to transpiration. But Epstein also saw potential in the desert (*2*):

> Despite these precarious conditions, the arid and semiarid regions are among the most promising ones to turn to in our quest to increase the production of food, fiber, chemicals, and biomass for energy. The relatively unleached soils of these regions are often inherently fertile, the growing season is long, temperature and light intensity are high, and the atmospheric humidity is low, reducing disease problems. All these features favor agricultural productivity if water and salinity problems can be solved.

Some plants have amazing adaptive powers. One such plant, commonly found as a highway planting in California, is the shrub oleander. It is found from desert regions to mountains, and seems to thrive on neglect. Clones of oleander flourish at temperatures as high as 49°C and as low as 15°C, and mature plants can adjust rapidly and completely to dramatic temperature changes (*3*). The plant has an inherent ability to change its photosynthetic rate according to its environment.

Although few plants can be expected to be as hardy as oleander, the search for xerophytes of economic value has hardly started. Of the score or so that have been identified so far, I have selected five for discussion in this article: jojoba, guayule, buffalo gourd, bladderpod, and gumweed. The five offer a variety of useful products, and their development status ranges from research curiosity to near-commercial.

Jojoba

Jojoba (*Simmondsia chinensis*) has already received much publicity. Among the five plants it has closest to true commercial status, for a number of commercial jojoba plantations are already in existence.

Jojoba grows naturally as a shrub in

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