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NANOSECOND LASER FLASH PHOTOLYSIS OF SEVERAL DIARYLCARBENES

The Ohio State University

Ph.D. 1984

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NANOSECOND LASER FLASH PHOTOLYSIS OF SEVERAL DIARYLCARBENES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of the Ohio State University

By

Linda Michele Hadel, B.Sc., M.Sc.

The Ohio State University

1984

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1984
To Matt and Tito
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Lastly, I would like to thank my parents, Julius and Anna Marie Balbo Hadel, for their unending support and faith in me.
VITA

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I. INTRODUCTION

The reactivity of carbenes is a topic of ongoing interest to organic chemists. The identifying feature of carbenes is a divalent carbon atom which can have either a singlet or triplet spin configuration.¹

If the orbitals on the carbenic atom are degenerate then, according to Hund's rules, the electrons prefer to occupy different orbitals with parallel spins. For the nondegenerate case, if the difference between the energies of the nonbonding molecular orbitals (MOs) on the carbenic carbon is greater than the energy required to bring the two electrons together in a single molecular orbital, then both electrons will occupy the lower energy nonbonding MO. In this case, the spins must be paired, giving rise to a singlet electronic state. However, if the difference in MO energies is less than the increase in electron-electron repulsion energy when the nonbonding electrons are brought together in the same spatial orbital, then the nonbonding electrons will occupy different orbitals. For the lower excited-
levels of most organic molecules, the triplet state is observed to be lower in energy than the singlet state of the same molecular orbital configuration.\(^2\)

Generation of carbenes, either thermally or photochemically, from an appropriate singlet ground state precursor generally leads to the singlet state because of spin conservation restrictions. The singlet then undergoes reaction or intersystem crosses to the triplet, which subsequently reacts. Electron spin resonance (ESR) spectroscopy is useful in identifying the triplet ground state multiplicity of several aryl and alkyl carbenes.\(^3\)\(^-\)\(^5\) The energy separation between the lowest lying singlet and triplet states of most carbenes is small enough (3-5 kcal/mole) that it is possible to have a significant thermal population of both states at room temperature. As a result, both the singlet and triplet give rise to the chemistry observed.\(^6\)

A major stumbling block to explaining the experimental observations to date is the deduction of the spin state which is being captured chemically and the assignment of the proportions of the spin state(s) responsible for the observed reaction mixture. The widely referenced Skell's rules distinguish between the reactions of the different spin states with an olefin.\(^7\)\(^,\)\(^8\) The singlet state is expected to add in a concerted stereospecific manner to form the cyclopropane. The triplet, on the other hand, is expected to react in a stepwise manner to form a biradical intermediate whose rapid conformational isomerization generally leads to a mixture of cyclopropanes. The proportion of the various stereoisomers observed
in product analyses is expected to depend on the relative rates of rotation around the C-C bond of the biradical and of spin inversion and closure to the cyclopropane. However, the properties of the two spin states are not well-differentiated under many reaction conditions and a clean assignment of the reacting transients responsible for the observed product mixture is not possible. The expected reaction pathways of the singlet and triplet spin states of the simplest carbene, methylene, according to Skell's rules, are shown in Figure 1.
Figure 1. Methylene Cyclopropanation Pathways
Methylene is perhaps the most extensively studied carbene. There are several summaries of the available data for this species, experimental as well as theoretical, which focus mainly on the stereochemical nature of this species and not on the reactivities of the different spin states.\textsuperscript{6,9-12} The observation of the gas phase spectrum of methylene by Herzberg provided the first substantial experimental data on the the singlet and triplet states.\textsuperscript{13} Herzberg observed the two lowest-lying states of methylene on flash photolysis of diazomethane at low pressure, the ground state triplet absorption ($\lambda_{\text{max}}$ 141.5 nm) and the lowest lying singlet absorption ($\lambda_{\text{max}}$ 405 nm). Singlet methylene has an HCH bond angle of 102°.\textsuperscript{14} Theoretical calculations have shown that the energy of this state increases rapidly as the angle is increased due to the loss of s-character in the doubly occupied, in-plane orbital.\textsuperscript{14b,c} It was originally deduced that the triplet was nearly linear, although later work, including $^{13}\text{C}$ hyperfine\textsuperscript{15} and rotational\textsuperscript{16} studies, established a 138° bond angle.

\[
\begin{align*}
\text{Singlet} & \quad 102° \\
\text{Triplet} & \quad 138°
\end{align*}
\]

The energy of the triplet state does not climb as steeply as does the singlet with variation in angle.
Far IR laser magnetic resonance spectroscopy and photodetachment spectroscopy have been used to determine the singlet-triplet energy gap.\textsuperscript{17} An important and controversial aspect of carbene chemistry is the magnitude of the singlet-triplet energy splitting and its relation to carbene structure.\textsuperscript{6,17c,18} Although there appears to be growing consensus that the energy splitting for methylene, $\text{CH}_2$, is 8 kcal/mole, very little information exists for larger carbenes concerning the singlet-triplet energy gap and the dynamics of interconversion of the two spin states.\textsuperscript{19} A knowledge of the energy separation between the singlet and triplet carbenes and of their absolute reactivities is vital in deducing the mechanism of reactions and in explaining the observed products in terms of the correct precursor species.

Most of the work on larger carbenes of synthetic and mechanistic interest is typically carried out in the liquid or solid phase, where effects of the medium complicate the interpretation of experimentally observed phenomena. Low temperature matrix isolation ESR has been a useful tool for establishing the ground state multiplicity of several aryl carbenes.\textsuperscript{4} Unfortunately, solid state ESR experiments are not completely relevant to product studies of solution phase reactions. It appears to be more logical to perform spectroscopic and kinetic studies of carbenes in the same medium as the chemical analyses. The technique of UV-visible optical spectroscopy is ideally suited to this purpose.
Two species for which the triplet ground states are easily confirmed using ESR are the substituted methylenes, diphenylmethylene (DPC, 1) and fluorenylidene (Fl, 2).

Despite the structural similarities of these carbenes, widely differing chemical reactivities are reported for them.\textsuperscript{9,20}

Electron delocalization in these arylmethylenes is expected to be a function of the molecular conformation. The two unpaired electrons in the triplet ground state are in separate orbitals and will be delocalized to a different extent. For example, spin density measurements by Hutchison and others using electron nuclear double resonance spectroscopy (ENDOR) support a planar model for Fl in which one electron is delocalized over a pi orbital array which extends over the whole carbon skeleton, while the second unpaired electron is confined to an in-plane sigma orbital on the divalent carbon atom.\textsuperscript{9,20} ENDOR work on DPC defines a central bond angle of 148° and a dihedral angle of the phenyl groups of 34°. In this species, there is diminished delocalization of the pi electron and increased delocalization of the sigma electron. Another important difference between these carbenes is the fact that the pi electron of DPC is part of an odd, alternate hydrocarbon pi system, while Fl must be
classified as a non-alternate hydrocarbon. In general, odd alternate hydrocarbons are expected to show greater stability through pi-electron delocalization.

The geometry of fluorenylidene allows the singlet to have a small carbenic angle\(^9,20\), but the possible closed shell structures for this state indicate unfavorable electronic interactions for the singlet.

![Diagram of structures](image)

The structure on the left contains the antiaromatic cyclopentadienyl cation. The structure on the right has an empty orbital rich in s-character (\(\sim sp^2\)). The decreased amount of s-character in the orbital containing the electron pair destabilizes the singlet, reminiscent of vinyl and phenyl cations. Since fluorenylidene is accepted to have a much smaller singlet-triplet gap than diphenylcarbene (vide infra), the small angle factor must dominate over the electronic ones.

Due to steric hindrance between the two phenyl rings in diphenyl carbene, the singlet cannot have a small central angle. This results in a larger singlet triplet separation than in the case of fluorenylidene.
II. OBJECTIVES

The present work contains reports of spectral analyses of fluorenylidene (F1), diphenylcarbene (DPC) and several of its para-substituted derivatives, as well as other diaryl carbenes which have carbenic angles intermediate between those in F1 and DPC. Carbene 3 (10,10-dimethyl-9-anthrorylidene, DMA) is expected to have a small carbenic angle similar to that in F1, yet has no unfavorable electronic factors that might destabilize the singlet. For these reasons, it is hypothesized that this compound will have an even smaller S-T gap than fluorenylidene. Early product studies indicate a remarkable similarity in the observed reactivities for DPC and carbene 4 (10,11-dihydrodibenzo[a,d]cycloheptadienyldiene, DBS). Although the exact carbenic bond angles for 3 and 4 are not known, molecular models indicate that 4 can achieve a structure necessarily bent and easily twisted.
Those carbenes with a large (3-5 kcal/mole) S-T energy gap are observed to undergo mainly radical-like processes of the triplet, e.g. DBC, DPC, and several di-p-substituted derivatives of DPC. For DPC, the first absolute rate constants for a triplet carbene atom transfer reaction in solution are reported. For the carbenes expected to have a small singlet-triplet separation, a greater proportion of singlet reaction is observed, e.g. Fl, 1-naphthylcarbene, and DMA, 3. The reactivity observed for the latter group of carbenes is fairly rapid and is assumed to reflect a composite of singlet and triplet processes.

A large angle for the singlet carbene is typically accepted to result in a larger S-T gap than for those carbenes which have a small carbenic bond angle. Transient absorption spectra, absolute reaction rate constants, and Arrhenius parameters obtained using nanosecond laser flash photolysis are combined with product studies to determine whether a simple correlation actually exists between carbene angle and the energy separation of the singlet and triplet electronic states.
III. DIPHENYLCARBENE, DPC

DPC Introduction

Early product studies

Kirmse, Horner, and Hoffmann studied the decomposition of diphenyldiazomethane (DDM) in hydrocarbon solvents and found strong evidence of a hydrogen abstraction-recombination mechanism. These workers found that in cyclohexane the major reaction product was tetraphenylethane 9. This product was believed to have been formed via hydrogen abstraction by triplet DPC from solvent to give radical pair 7. The radicals can diffuse apart, whereupon dimers 8 and 9 are formed upon combination of like radicals, or recombine to form 6. The amount of 9 actually formed was seen to depend on the ability of solvent to lose hydrogen. Only in the event of a failure of the presumably initially formed singlet to intersystem cross to the triplet or a rapid singlet-triplet equilibrium coupled with a large difference in reactivity favoring the singlet would insertion have been the main reaction, leading to 6.
Closs examined the toluene-DPC system in considerable detail, using chemically induced nuclear spin polarization (CIDNP) as a tool for determining the spin multiplicities of the radical pair precursors. NMR emission or enhanced absorption displayed by organic compounds immediately after their formation from radical intermediates was concluded to be the consequence of a non-equilibrium population of nuclear spin states. Closs compared the products from the photolysis of DDM in toluene and the thermal or photolytic decomposition of azo compound 10.

$\text{Ph}_2\text{CH-N=N-CH}_2\text{Ph} \rightarrow^\text{10} \text{Ph}_2\text{CHN}=\text{NR} \xrightarrow{\text{hv, } \Delta} [\text{Ph}_2\text{CH} \cdot \text{-R}] + \text{N}_2$

Both reactions afforded the same products (triphenylethane 6b, bibenzyl 8b, and tetraphenylethane 9); but the ratio of unsymmetrical to symmetrical products $6/(8 + 9)$ was higher in the reaction of 10 (1.5/1) than in the DPC reaction (1:1). NMR spectra obtained from both reaction mixtures showed opposite polarizations, in confirmation of the theoretical predictions for radical pairs of different multiplicity. Since there was little doubt that acyclic azo compounds decompose through the singlet state, the results of this experiment were used to assign a triplet multiplicity to the radical pairs involved in the DPC reaction.

The chemistry of DPC with olefins also reflected hydrogen atom transfer processes. Closs found that the major pathway for reaction
tetraphenylazine, which resulted from reaction of the carbene with unreacted diphenyldiazomethane. Two rationalizations can be made of their observations. The first is that the latter was most likely a result of the higher diazo concentrations (\( \sim 10^{-4} \) M) used in the steady-state trials than in the solutions (\( \sim 10^{-6} \) M) used for flash photolysis. The second is that a higher transient concentration was formed with the flash photolysis technique than in the case of the steady state experiments and favored a reaction between carbenes with tetraphenyl ethylene as the product.

Turro et al. used a diene/alcohol competition approach similar to that of Closs and Rabinow but also measured the rate of singlet to triplet intersystem crossing (ISC) by picosecond laser induced fluorescence.\[^{50,51}\] These workers calculated a free energy gap (-\( \Delta G \)) of (5.1 ± 1) kcal/mole at 25°C and a rate constant for singlet quenching by methanol of (3.5 ± 0.5) \( \times 10^{10} \) M\(^{-1}\) s\(^{-1}\). Furthermore, the singlet carbene was postulated to behave as a zwitterion and the rate of triplet reaction with methanol was estimated to be < \( 10^4 \) M\(^{-1}\) s\(^{-1}\).\[^{50b}\] The kinetic models used to extract their rate constants were a steady-state treatment of the triplet for direct irradiation experiments and a steady-state assumption for the singlet in the case of triplet-sensitized irradiation.\[^{51}\]

Eisenthal et al. studied the kinetics of formation and decay of the excited triplet state of DPC in acetonitrile.\[^{52,53}\] The fluorescence rise time was less than 15 psec and the decay lifetime was 3.8 ns. Since the rate of ground state triplet formation was
N₂ Ph^Ph^Ph^Ph

\[ \text{Ph} = \text{cyclohexyl or benzyl} \]

5 (a) R = cyclohexyl
(b) R = benzyl
with cis- and trans-2-butene was H-abstraction from the allylic position, followed by recombination of the fragments to form the olefin $11.10$ Cyclopropanes accounted for only 10\% of the isolated products.

\[
\begin{align*}
\text{Ph} \quad \text{Ph} & \quad + \quad \text{CH}_3 \quad \text{CH}_3 \\
\downarrow & \\
\text{Ph}_2 \text{CH} + \quad \text{CH}_2 \quad \text{CH}_3 & \quad \longrightarrow
\end{align*}
\]

With cis-2-butene, the stereospecificity of addition increased with decreasing temperature: the cis/trans ratio was 3.2 at $-10^\circ$ C and 9.0 at $-66^\circ$ C. In the presence of oxygen, an assumed selective triplet trap, the ratio did not change, although the yield of cyclic and acyclic hydrocarbons approached zero for high oxygen concentrations. This ratio was found to be independent of olefin concentration over a 150-fold dilution with cyclohexane.

Closs postulated that intersystem crossing (ISC) is faster than any chemical reaction in the system and that the rate of singlet addition to olefin is much greater than that for the triplet carbene. It was further claimed that the temperature dependence of the cyclopropane ratio could be easily explained if the difference in free
energies of activation for the two addition reactions is larger than the free energy difference between the electronic states. Such a suggestion had been made earlier for DPC. \(^{32}\) Baron suggested that one need not postulate a greater rate of addition of singlet to olefins than triplet carbene addition to olefins, since the triplet may spend most of its time abstracting hydrogen in the butene system. \(^{20}\)

It may well be the case that at lower temperatures the triplet does abstract hydrogens in preference to cyclopropane formation, depending on the relative activation energies of the two processes. An alternative explanation could be that at lower temperatures bond rotation in the biradical intermediate, formed in the addition of triplet to olefin, is slowed relative to spin flip and closure. The latter would lead to an increased stereospecificity of triplet cyclopropanation reactions (Figure 1).

Baron et al. found that the ratio of H-abstraction to cycloaddition products was highly dependent on the substitution pattern of the olefin. \(^{33}\) Moss found that the ratio of olefins to cyclopropanes was markedly increased in neat polycrystalline matrices at \(-196^\circ\) C with DPC as well as with other carbenes. \(^{34}\) The product studies of Bethell\(^{35}\), Closs and Closs\(^{36}\), and Jones et al.\(^{37}\) have all been used to support a contention of rapid interconversion of DPC spin states, although alternative interpretations were not ruled out. \(^{35}\)

In 1963, Kirmse studied the reaction of DPC, produced by photolysis of diphenyldiazomethane, with alcohols to form the corresponding ether. \(^{38}\) The ability of alcohols to suppress the
oxidation of the intermediate carbene by molecular oxygen was found to increase with increasing acidity of the alcohol. In the presence of lithium azide (LiN₃), the oxidation was not affected and the major observed products were the azide and ether compounds. These results were interpreted as a nucleophilic attack of the carbene on the alcohol to form the cation through abstraction of a proton. This cation was postulated to then partition itself between the remaining nucleophilic species (A).

Bethell et al. studied the products obtained from the thermal decomposition of DPC in acetonitrile in the presence of a series of alcohols. They also found ether and benzophenone azine as the major reaction products, with diphenylmethane and diphenylmethanol as minor products. These authors tentatively ruled out Kirmse's mechanism (A) on the basis of an observation of a reaction of the cation with unreacted diazo to form the azine product. The dependence on alcohol concentration of the proportion of products was said to be consistent with the reversible interconversion of the singlet and triplet states of the intermediate DPC. Two reaction mechanisms were proposed to account for their findings: electrophilic attack of the carbene on the oxygen atom of the alcohol to form the ylide, which is then transformed into the ether product (B); and a direct insertion mechanism (C). However, their results were not sufficient to unequivocally distinguish between the proposed mechanisms.
Ph\(_{2} \text{C} + \text{ROH} \rightarrow \text{Ph} \text{CH}^{+} \text{RO}^{-} \rightarrow \text{Ph} \text{CH-OR} \quad (A)

\text{Ph}\text{C-O}\text{R} \quad (B)

\text{Ph}\text{C} \text{H} \quad (C)
Electron Spin Resonance Spectroscopy

As mentioned earlier, ESR has been useful in establishing that the ground state of diphenylcarbene is a triplet.\textsuperscript{3-5,40} Doetschmann and Hutchison followed the kinetics of the growth and decay of the ESR signal of this carbene in a single crystal of 1,1-diphenylethylene and observed a strong dependence of the rate on the observation temperature and initial diazo concentration.\textsuperscript{41} They were able to measure the rate constant for cyclopropanation and the associated Arrhenius parameters. This was the first report of a carbene reaction in a condensed phase.

Senthilnathan and Platz studied the nature of matrix effects on carbene reactions, finding it necessary to plot the ESR signal intensity as a function of $t^{1/2}$ for glasses and $t^{1/3}$ for polycrystals in order to obtain good kinetic fits over more than 50\% of the signal decay. The kinetics of DPC could be observed only in a temperature-viscosity window of 10 degrees near 100 K.\textsuperscript{42} This behavior was attributed to a distribution of site reactivities in the matrix resulting in non-exponential decays.\textsuperscript{42,44} These workers also demonstrated that the observed rate of carbene decay in matrices depends on the concentration of diazo precursor, length of photolysis time, and the chemical nature of the matrix.\textsuperscript{42} In a more recent work, Platz et al. studied DPC in various matrices and interpreted the reaction kinetics in terms of a quantum mechanical tunneling mechanism for atom transfer.\textsuperscript{45} The data were fitted to an asymmetric Eckart
barrier, which was assumed to represent the motion of the hydrogen atom along a linear path. The calculated barrier height for reaction of triplet DPC with toluene was reported as 12.9 kcal/mole. Assuming the loss of all zero point energy, the model predicted a classical activation energy of ca. 9 kcal/mole for this reaction in solution.

**Electronic Spectroscopy**

Closs et al. reported the electronic absorption spectrum of triplet DPC in a single crystal of 1,1-diphenylethylene. Through the use of an oriented sample and polarized light, these workers determined that only light polarized parallel to the line of phenyl ring centers was absorbed. Trozzolo and Gibbons obtained the absorption, excitation, and emission spectra of triplet DPC in a glass at 77 K. The absorption spectrum showed a strong band near 300 nm and a much weaker band in the visible range, with both attributed to the triplet state. The latter transition was said to be consistent with a $\pi-\pi^*$ assignment. In absorption experiments in which a known amount of diazo was destroyed, the workers calculated the following minimum extinction coefficients for DPC triplet: 25,000 ($\lambda_{\text{max}}$ 301 nm) and 300 ($\lambda_{\text{max}}$ 465 nm). The emission of DPC in 2-MTHF showed a broad band ($\lambda_{\text{max}}$ 480 nm) with a shoulder at longer wavelength. The same spectrum was obtained for all excitation wavelengths in the range 230-470 nm and all solute concentrations ($10^{-4}$ to $10^{-6}$ M). The
excitation spectrum was independent of emission wavelength in the range 475-550 nm. The latter indicated that the observed emission was that of only one species, diphenylcarbene.

Flash photolysis has been used extensively in the gas phase to study simple carbenes. The first application of flash photolysis to a diarylcarbene in solution was reported by Moritani in 1968. Through the use of a flash of approximately 1 microsecond duration, these workers obtained the absorption spectrum of DBS, and estimated its lifetime as 1-50 μs, but did not report any rate constants.

In a pioneering study, Closs and Rabinow obtained the first absolute rate constants for a carbene reaction in solution. They used an intense homemade flashlamp to generate DPC from diphenyldiazomethane in benzene solution. In this analysis, it was assumed that the optically invisible singlet state formed first and was in rapid equilibrium with the triplet state. Through a measurement of the decay of the absorption of triplet DPC at 301 nm, these workers determined the rate constants for triplet dimerization and reaction with 1,3-butadiene and for reaction of the singlet state with methanol. Since the triplet decay was followed in all cases and it was assumed that only the singlet reacts with methanol, the observed quenching rate in the presence of alcohol was $k_s/K_{eq}$. In this instance, $k_s$ is the rate constant for singlet reaction with methanol and $K_{eq}$ is the singlet-triplet equilibrium constant. Benzhydryl methyl ether was the major product obtained from photolysis
in methanol and was predicted to be a result of singlet insertion into
the OH bond of the alcohol. This product is not expected to result
from a hydrogen abstraction-recombination mechanism involving the
triplet (which should give an alcohol product).

\[
\begin{align*}
\text{Ph}_2\text{C} : \text{MeOH} & \rightarrow \text{Ph}_2\text{CHOCH}_3 \\
& \rightarrow \text{Ph}_2\text{CH} \text{ CH}_2\text{OH} \rightarrow \text{Ph}_2\text{CHCH}_2\text{OH}
\end{align*}
\]

A radical process involving the triplet state was discounted due to
the lack of CIDNP signals when the experiment was run in an NMR
spectrometer. With the assumption that methanol reacts with the
singlet at a diffusion-controlled rate, Closs and Rabinow set the
upper limit of the singlet-triplet gap (-\(\Delta H\)) as 2.5 kcal/mole.
Steady-state experiments were performed in acetonitrile solvent
(since IR analysis showed that methanol formed H-bonded aggregates in
benzene at 0.10 M) with a variety of quenchers and product analyses
were conducted. With the assumption that the singlet and triplet
states were in rapid equilibrium and that the ratio of products was
equal to the ratio of quenching rate constants, additional rate
constants were obtained. Product studies indicated that the major
product in solutions of the diazo compound photolyzed in benzene (an
"inert solvent") with flash photolysis techniques was
tetraphenylethylene, while that in the steady-state experiments was
found to be 110 psec, they concluded that the dominant pathway to its formation was through ISC from the lowest singlet state. The excited triplet was found to react with methanol with a rate constant of \((3.1 \pm 0.4) \times 10^8 \text{ M}^{-1} \text{s}^{-1}\). From the observation of increasing reactivity with increasing alcohol acidity and methanol-OD isotope effects of 1.5, these authors concluded that excited triplet DPC preferentially attacks the OH bond of the alcohol. They also reported a concave deviation from linear behavior for the rate as a function of methanol concentration (>3M); but other alcohols gave linear behavior. This nonlinear behavior had been noted earlier by Bethell for DPC and Scaiano et al. for phenyl chloro carbene, which has a singlet ground state. The effect was attributed to the aggregation of quencher molecules.

Griller, Nazran, and Scaiano report activation energies for the methanol quenching of DPC in a variety of solvents that are inconsistent with the typically accepted mechanism of exclusive reaction of the singlet state with methanol. Their argument involves the relation

\[ E_{\text{obsd}} = -\Delta H_{\text{eq}} + E_s \]

where \(E_{\text{obsd}}\) is the activation energy calculated from a simple Arrhenius treatment of methanol quenching rates, \(-\Delta H_{\text{eq}}\) is the singlet-triplet energy separation in the corresponding solvent, and \(E_s\) is the activation energy for singlet reaction with methanol. The
values of $E_s$ of $(1.66 \pm 0.20)$ kcal/mole\(^{55}\) and $(-\Delta H_{eq})$ of 3 kcal/mole\(^{49}\) indicate a negative activation energy for singlet quenching by methanol according to Scheme 1.

Scheme 1

$$\begin{align*}
1\text{DPC} & \xrightleftharpoons[k_{TS}]{k_{ST}} 3\text{DPC} \\
\text{MeOH} & \downarrow k_s \\
\text{Ph}_2\text{CHOCH}_3 & \text{singlet ether}
\end{align*}$$

In general, if the reaction of the singlet with methanol is diffusion controlled, then an activation energy of 1-2 kcal/mole and an $E_{obsd}$ value of 4-6 kcal/mole are expected. In hydrogen bonded systems, the activation energy is approximately 5 kcal/mole and an $E_{obsd}$ of 8 kcal/mole is predicted. The authors claim that if the available data on the reaction of diphenylcarbene are correct, then their results require that the triplet state react with methanol to give the corresponding ether (Scheme 2).

Scheme 2

$$\begin{align*}
1\text{DPC} & \xrightleftharpoons[k_t]{k_{ST}} 3\text{DPC} \\
\text{MeOH} & \downarrow k_s \\
\text{Ph}_2\text{CHOCH}_3 & \text{singlet ether}
\end{align*}$$

Such a process appears to require a substantial lowering of the singlet-triplet energy gap in the presence of methanol and/or a
surface crossing at some point along the reaction path in order to obtain the ground state singlet ether product.\textsuperscript{55}

They further claim that if the reported value for S-T ISC is in error, being too high, then their data is consistent with a mechanism involving thermal equilibration between the triplet and singlet states, followed by reaction of the singlet with methanol to give ether. This explanation follows from the fact that a lower $k_{ST}$ value would result in a smaller S-T equilibrium constant ($K_{eq}$) and thus a singlet-triplet gap less than the presently reported values. If such were the case, then the $E_{obsd}$ values could be hypothesized to more adequately account for both the energy separation between the states and the activation energy for reaction of singlet DPC with methanol, as required by Scheme 1.

Scaiano et al. found that diphenyl carbene (DPC, 1) reacts with oxygen with a rate constant of $5 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ in acetonitrile solvent at 300 K.\textsuperscript{56} Closs and Rabinow earlier obtained a rate constant of $1 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ for oxygen quenching of DPC under steady state conditions.\textsuperscript{49} The latter rate is expected to be lower due to the nature of the monitoring technique. The 410 nm transient has been assigned as the ylide 12, "benzophenone oxide".
Quenching rate constants for the reaction of 12 with diethyl fumarate and diphenyl diazomethane were measured to be $1.5 \times 10^6$ and $4 \times 10^5$ M$^{-1}$ s$^{-1}$, respectively. Oxygen pressures up to 1 atmosphere did not lead to detectable transient quenching.

**DPC Experimental Procedure**

Diphenyldiazomethane (DDM) was prepared according to a literature procedure and was purified by sublimation under vacuum. The solvents were used as received when spectral quality was commercially available. Benzene and chlorobenzene were washed with sulfuric acid and distilled water, dried over calcium chloride, then refluxed for 6 hours and distilled over calcium hydride. Fisher HPLC grade acetonitrile was refluxed and distilled over calcium hydride under an atmosphere of nitrogen. Styrene was bulb-to-bulb distilled in a vacuum line.

Samples, deaerated by oxygen-free nitrogen bubbling for the flash photolysis experiments, were either contained in or flowed through cells made of 7mm x 7 mm Suprasil tubing. The temperature of the cell was controlled by a constant-temperature nitrogen flow in a manner similar to that normally employed in EPR spectrometers. A Suprasil vacuum jacket provided adequate windows and thermal insulation. The temperature was measured with a copper-constantan thermocouple, whose output was amplified and measured directly by the computer via a
DEC-ADV11-A A/D interface. An excimer laser (Lumonics model TE-860-2) operated with Xe/HCl/He mixtures was used for excitation at 308 nm (4 ns, up to 80 mJ/pulse). A pulsed 200-W Xenon lamp served as the monitoring light source. The detection system employed a 7A16A plug-in unit of a R-7912 Tektronix digitizer to capture the signals from the photomultiplier tube. The traces were then displayed on a Tektronix 607 storage monitor, and the data was transferred to a PDP 11/23 computer which controlled the experiment and provided suitable processing, storage, and hardcopy facilities. DEC-Fortran IV extension routines were used to process the data. Further details of the NRCC laser system of Dr. Scaiano have been given elsewhere. The laser flash photolysis system in our laboratory at the Ohio State University is controlled by an Apple II Plus microcomputer as described previously.
Reactions with Solvent

When a dilute sample of diphenyldiazomethane, typically $10^{-4}$ M, is excited with the 308 nm laser pulses, we observe the instantaneous (< 5 ns) formation of DPC, 1, at 314 nm. Close indicated the $\lambda_{\text{max}}$ of the carbene to be 300 nm$^{49}$; however, we are unable to monitor at this wavelength due to bleaching of the diazo precursor ($\lambda_{\text{max}}$ 288 nm).

The absorption spectrum in benzene shows a maximum at 325 nm for a time window of 0-300 ns after laser photolysis (Figure 2). Figure 3 shows the signals obtained as a function of wavelength. The individual traces indicate the transient absorbance or optical density as a function of time after the laser strikes the sample. The weak transient absorptions in the 400-500 nm region are believed to belong to ylide 12, which results from the reaction of DPC with residual oxygen. The measured growth lifetime at 400 nm is equal to the decay lifetime at 314 nm, further implicating 1 as a precursor to the 400 nm transient.

In hydrogen donor solvents such as cyclohexane, as the 314 nm signal decays (frequently in the microsecond range) a new species is formed which shows a remarkably strong absorption with $\lambda_{\text{max}}$ 334 nm. This signal is attributed to the diphenylmethyl radical 13, whose spectrum has been previously characterized.$^{61}$
Figure 2. Absorption Spectrum of DPC in Benzene at 0-300 ns After 308 nm Photolysis at 300 K.
Figure 3. Transient Absorptions at Various Wavelengths for DPC in Benzene Solvent.
Figure 4. Diphenylmethyl Radical Absorption Spectrum in Cyclohexane Solvent at 300 K at 6 - 12 μs After Photolysis.
Figure 5. Carbene and Radical Absorptions for DPC in Cyclohexane at 300 K.
Figure 6. Three Dimensional Plot of Absorptions of DPC and 13 in Cyclohexane With a Time Window of 15.72 $\mu$s.
High extinction coefficients (and thus strong signals) are not uncommon for resonance stabilized radicals such as 13. Figure 4 shows the transient spectra obtained after the decay of the carbene is complete (6–12 μsec); the inserts show the decay of the carbene at 314 nm and the formation of the radical 13 at 334 nm. Closs and Rabinow also observed the spectrum of 13, but did not resolve the growth of this species. Figure 5 shows the time evolution of the spectra obtained and the overlap of the carbene and radical absorptions. A weak signal is again seen at long wavelengths with a growth lifetime similar to that of the radical but with a much longer decay lifetime. Figure 6 shows a three-dimensional plot of the optical density of the sample as a function of time and wavelength for decay of the carbene absorption and subsequent growth of the radical 13. The total time window is 15.72 μs. The depression observed at 3.1 μs in Figure 6 corresponds to fluorescence or scattering of the laser light and that at 11 μs is assumed to be an instrumental artifact. Figure 6 is a composite of the transient signals (such as those in Figure 3) recorded at the individual wavelengths with the specified time window.

\[
\text{RH} \rightarrow \begin{array}{c}
\text{H} \\
\text{334 nm}
\end{array} + R^*
\]
In chloroform solvent, the long wavelength component is seen in a spectrum taken 0-8 ns after the laser flash, but it has decayed by the time a spectrum was recorded with a 330-500 ns time window. The observed signal at 365-445 nm has an essentially instantaneous growth on the time scale of our detection system (i.e. < 5 ns).

In principle, kinetic studies can be performed on the decay of the signal at 314 nm or the growth at 334 nm. In practice, the latter is more suited for our studies in which the radical is produced. In these systems the increased separation between excitation and monitoring wavelengths (which should be > 8-10 nm) as well as the decreased overlap between the radical and carbene absorptions facilitate the experiment considerably. The apparent decay of the 314 nm band (10-20 \( \mu \)sec) is usually substantially longer than the growth at 334 nm (∼2 \( \mu \)sec). Since the radical 13 also absorbs strongly at 314 nm, decay signals measured at 314 nm reflect a composite of three processes: (1) decay of triplet DPC, via first or second order reactions; (2) growth of radical 13; and (3) decay of 13. The radical absorption at 334 nm can be cleanly fitted to first order growth kinetics and is thus assumed to be free of significant contributions from carbene absorption. The results are summarized in Table 1 for measurements of this type in several solvents. In some systems, e.g. toluene, the presence of underlying signals is evident (benzyl absorbs at 317 nm). The carbene decay at 320 nm in benzene, chlorobenzene, and acetonitrile appears to be first order even though no reaction is expected with these solvents. The predicted decay pathways in these
solvents are carbone dimerization, azine formation, and reaction with adventitious oxygen. The Arrhenius parameters for radical growth in some of the solvents are given in Table 2.
Table 1. First Order Kinetics for the Decay of Diphenylcarbene in Several Solvents at 300 K.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( k \times 10^5 \text{ s}^{-1} )</th>
<th>( \lambda_{\text{obsd}} )</th>
<th>( k_R/k_D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexane</td>
<td>5.7</td>
<td>334 nm</td>
<td>2.6</td>
</tr>
<tr>
<td>toluene</td>
<td>4.8</td>
<td></td>
<td>6.5</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cyclohexene</td>
<td>40</td>
<td>334 nm</td>
<td>1.5</td>
</tr>
<tr>
<td>methylcyclohexane</td>
<td>7</td>
<td>330 nm</td>
<td></td>
</tr>
<tr>
<td>2-methyltetrahydrofuran</td>
<td>38</td>
<td>330 nm</td>
<td></td>
</tr>
<tr>
<td>triethylamine</td>
<td>25</td>
<td>330 nm</td>
<td></td>
</tr>
<tr>
<td>cyclopentane</td>
<td>22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>6</td>
<td>320 nm</td>
<td></td>
</tr>
<tr>
<td>benzene</td>
<td>5</td>
<td>320 nm</td>
<td></td>
</tr>
<tr>
<td>acetonitrile</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( ^a \text{measured in a flow system, monitored at 334 nm unless designated otherwise, typically } \pm 20\%. \)

\( ^b \text{in static cells, should be regarded as a lower limit.} \)

\( ^c k_D \text{refers to the perdeuterated substrate.} \)
Table 2. Arrhenius Parameters for the Decay of Diphenylcarbene in Various Solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>T-range (K)</th>
<th>$E_a$, kcal/mole</th>
<th>log (A /s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene</td>
<td>264 - 343</td>
<td>3.2 ± 0.7</td>
<td>8.0 ± 0.5</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>276 - 327</td>
<td>2.5 ± 0.4</td>
<td>7.5 ± 0.3</td>
</tr>
<tr>
<td>cyclohexene</td>
<td>267 - 339</td>
<td>3.0 ± 0.3</td>
<td>8.7 ± 0.2</td>
</tr>
<tr>
<td>cyclopentane</td>
<td>234 - 317</td>
<td>2.9 ± 0.3</td>
<td>7.9 ± 0.2</td>
</tr>
</tbody>
</table>
Laser flash photolysis studies which monitor the growth of radicals derived from carbenes give the sum of the absolute rate constants for all first order reactions that the triplet carbene may undergo with substrates in the solvents. Dimerization is assumed to be an insignificant decay pathway due to the low sample concentrations used and the low intensity of the excitation light. For example, the highest radical first order growth rate in Table 1 is observed for cyclohexene solvent and may include addition reactions of carbene to the double bond as well as allylic hydrogen abstractions and reaction with diazo compound and impurities in the system. It is also possible that the observed rate of radical growth in an alkane solvent is a composite of both triplet carbene abstractions and singlet carbene processes (such as C-H insertion) if triplet-singlet equilibration is rapid. Studies with fluorenylidene and 1-naphthylcarbene in alkanes indicate that the singlet decay route is dominant in these systems; thus the observed rate constants for these two carbenes cannot be associated with elementary triplet reaction rate constants. Based on the product studies of Kirmse and Closs which indicate predominantly triplet-derived products, we are assuming that the observed growth rates for reaction of triplet DPC with hydrogen atom donors reflect pure triplet processes (Scheme 3).
SCHEME 3

Pathways Monitored

\[
\begin{align*}
\text{DDM} & \xrightarrow{\text{hv}} \text{olefin} \\
\text{RH} & \xrightarrow{\text{RCI}} \text{olefin} \\
\text{RH} & \xrightarrow{\text{olefin}} \text{insertion/addition reactions}
\end{align*}
\]

Side Reactions

\[
\begin{align*}
\text{DPC} & \xrightarrow{\text{DDM}} \text{Azine} \\
\text{DPC} & \xrightarrow{\text{O}_2} \text{O}^+ \\
\text{DPC} & \xrightarrow{\text{PhC=CPh}} \text{O}^-
\end{align*}
\]
Solvent Isotope Effects

Isotope effects on the radical growth rate are measured using techniques similar to those mentioned previously. The high cost of several of the deuterated solvents limit the studies to static samples and to measurements at room temperature only. Rate constants for static samples are seen to be typically about 40% larger than those for samples in flow systems and are considered to be less accurate. Furthermore, in the deuterated solvents the rate of atom transfer should be slowed for a pure abstraction mechanism, whereas other competitive processes, such as azine formation, reactions with water, oxygen or other impurities, or underlying second-order processes, may contribute more significantly to the observed rate than in the unmodified solvent. The maximum transient absorption for deuterated samples are seen to decrease faster than those in protonated solvents with an increasing number of laser pulses. The isotope effects reported in Table 1 are those for matched static cells of protonated and deuterated solvents.
Reactions with Various Solutes

The monitoring techniques for these experiments are the same as indicated above. The experimental pseudo-first order rate constant, \( k_{\text{expt}} \), is measured at a series of quencher concentrations, then plotted as a function of the concentration of quencher in order to obtain \( k_q \), according to the relation:

\[
    k_{\text{expt}} = k_0 + k_q [\text{quencher}].
\]

The quenching rate constant \( k_q \) includes all possible sites and modes of attack by the quencher or its adventitious impurities. As a result, it is not assumed that just because the species monitored is the radical that other modes of attack are excluded. This is a common situation in laser flash studies of this type, where all reactions with quencher are included regardless of the path actually monitored.\(^6\) Scheme 3 indicates the reactions expected for the carbene with solvent, impurities, and added quencher. For example, in the case of styrene the expected reaction path is addition, not abstraction; nevertheless, the kinetic technique does not differentiate between these, but simply measures molecular reactivity. In this case, the growth of the benzhydryl radical is used as a probe, but the signal is derived from reaction with the solvent, not with the added styrene quencher. Also, in the presence of carbon tetrachloride, \( \text{CCl}_4 \), the carbene reacts with quencher to form the diphenylchloromethyl radical, thus providing the carbene with extra decay channels as the concentration of \( \text{CCl}_4 \) quencher is increased.
The mathematical justification for using the radical signal to gauge all first order reactions of the carbene in cases where the quencher does not necessarily lead to the signal being followed is given in Appendix 1 for the triplet/styrene/cyclohexane/impurity system.

The chloro radical is observed to have a much shorter growth lifetime than the hydrogen radical. Fast and slow signal growth components are observed in neat CCl$_4$. For quenching studies with CCl$_4$ and DPC in cyclohexane, there appears to be only one growth component, assigned to be that of the diphenylmethyl radical. The two growth components noted in CCl$_4$ solvent could be due to two precursors to the absorbing species, which would be expected to react with significantly different rates; or the two components could be due to the overlapping absorptions of transients, such as those of the chloro radical and the carbene 1 and/or ylide 12.

In some cases, it is possible that the process being followed is only an insignificant fraction of all reaction pathways but that the absorbing species has a much higher extinction coefficient than the major products. This phenomenon serves to emphasize the importance of combining spectroscopic results with those based on product studies using conventional techniques such as gas chromatography (GC) or GC-mass spectroscopy, so that one does not rely too heavily on spectral kinetic studies (especially if the correct identity has not been assigned to the absorbing or fluorescing species being monitored).
In a plot of $k_{\text{expt}}$ as a function of quencher concentration, the intercept $k_0$ includes all first order reactions which DPC may undergo in the solvent in the absence of added quencher. Possible reactions include hydrogen abstraction from and/or addition to solvent or quenching by adventitious solvent impurities. For quenching trials performed in cyclohexane solvent, the diazo solution is degassed by nitrogen bubbling until the radical signal has a growth lifetime of $\sim 2 \text{ ms}$ in order for all samples to be consistent. For the subsequent quenching plots, the values of $k_0$ are typically $5 \text{ to } 7 \times 10^5 \text{ s}^{-1}$.

For solute quenching studies in cyclohexane solvent, measurements of the first order rate are made using the radical signal at 334 nm as a probe. For quenching trials in other solvents the decay of the carbene signal at 320 nm is followed. The results are summarized in Table 3. The temperature dependence of the rate of methanol quenching of DPC in acetonitrile and chlorobenzene yields the Arrhenius parameters in Table 4.
Table 3. Bimolecular Rate Constants for the Reaction of Diphenylcarbene with Various Substrates at 300 K.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Solvent</th>
<th>( k_r / 10^5 \text{ M}^{-1} \text{ s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon tetrachloride</td>
<td>cyclohexane</td>
<td>3.6 ± 0.4</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>cyclohexane</td>
<td>2.0 ± 0.3</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>benzene</td>
<td>1.4 ± 0.2</td>
</tr>
<tr>
<td>cyclohexene</td>
<td>cyclohexane</td>
<td>2.8 ± 0.1</td>
</tr>
<tr>
<td>cyclohexene- ( d_{10} )</td>
<td>cyclohexane</td>
<td>2.6 ± 0.5</td>
</tr>
<tr>
<td>cyclooctene</td>
<td>cyclohexane</td>
<td>3.3 ± 0.3</td>
</tr>
<tr>
<td>1-octene</td>
<td>cyclohexane</td>
<td>10 ± 1</td>
</tr>
<tr>
<td>2,3-dimethyl-2-butene</td>
<td>cyclohexane</td>
<td>2.1 ± 0.3</td>
</tr>
<tr>
<td>styrene</td>
<td>cyclohexane</td>
<td>14 ± 3</td>
</tr>
<tr>
<td>1,4-cyclohexadiene</td>
<td>cyclohexane</td>
<td>100 ± 10</td>
</tr>
<tr>
<td>1,3-cyclohexadiene</td>
<td>cyclohexane</td>
<td>26 ± 2</td>
</tr>
<tr>
<td>1,5-cyclooctadiene</td>
<td>cyclohexane</td>
<td>20 ± 12</td>
</tr>
<tr>
<td>1,3-cyclooctadiene</td>
<td>cyclohexane</td>
<td>2.8 ± 0.1</td>
</tr>
<tr>
<td>1,3-octadiene</td>
<td>cyclohexane</td>
<td>15 ± 1</td>
</tr>
<tr>
<td>chloroform</td>
<td>cyclohexane</td>
<td>8.4 ± 0.9</td>
</tr>
<tr>
<td>triethylamine</td>
<td>cyclohexane</td>
<td>3.4 ± 1.4</td>
</tr>
<tr>
<td>methanol</td>
<td>cyclohexane</td>
<td>120 ± 10</td>
</tr>
<tr>
<td>methanol</td>
<td>benzene</td>
<td>180 ± 20</td>
</tr>
<tr>
<td>methanol</td>
<td>chlorobenzene</td>
<td>170 ± 30</td>
</tr>
<tr>
<td>methanol</td>
<td>acetonitrile</td>
<td>200 ± 20</td>
</tr>
</tbody>
</table>
Table 4. Arrhenius Parameters for the Methanol Quenching of Diphenylcarbene.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>T-range, K</th>
<th>$E_a$ (kcal/mole)</th>
<th>log ($A / M^{-1} s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>chlorobenzene</td>
<td>255 - 317</td>
<td>1.44 ± 0.46</td>
<td>8.34 ± 0.36</td>
</tr>
<tr>
<td></td>
<td>255 - 320</td>
<td>2.48 ± 0.44</td>
<td>9.30 ± 0.34</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>241 - 326</td>
<td>1.45 ± 0.60</td>
<td>8.35 ± 0.47</td>
</tr>
<tr>
<td></td>
<td>242 - 336</td>
<td>1.66 ± 0.20</td>
<td>8.62 ± 0.16</td>
</tr>
</tbody>
</table>

* Taken from reference 55 for comparison purposes.
DPC Discussion

The results given in Tables 1 to 3, when coupled with the product studies of DPC\textsuperscript{24,25}, confirm the radical-like nature of the carbene reactions observed. However, the reactivity is at first sight substantially greater than expected; the reactivity of DPC is much larger than that of the diphenylmethyl radical 13. While DPC abstracts hydrogen atoms from cyclohexane with a lifetime of ca. 2 $\mu$s at 300 K, the lifetime of the radical produced is measured to be at least 10 times longer and is assumed to be controlled by radical-radical reactions (self-reaction and reaction with cyclo C\textsubscript{6}H\textsubscript{11}.), not by reaction with the solvent. Diphenylmethyl radicals are at the very least 100 times less reactive than DPC in atom transfer reactions. The reactivity of DPC exceeds that of alkyl radicals; for example, the rate of reaction of DPC with cyclohexane has been measured here as $6.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and with THF as $1.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. The reported rate for reaction of methyl radicals with cyclohexane\textsuperscript{65} is $10^3 \text{ M}^{-1} \text{ s}^{-1}$, which is about one order of magnitude faster than comparable reactions of methyl with ethers and only about 30 times slower than the reaction of phenyl radicals with THF ($4.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$).\textsuperscript{65} Thus, DPC has a reactivity towards hydrogen abstraction intermediate between those of methyl and phenyl radicals. The relative reactivity of DPC with the various substrates parallels that seen for the reaction of benzophenone triplets with allylic hydrogens,
although rates for the former are slower by about 2 to 3 orders of magnitude.\textsuperscript{66}

It is possible to rationalize the enhanced reactivity of triplet DPC relative to the diphenylmethyl radical based on either of the following assumptions\textsuperscript{67}: (a) One of the singly-occupied carbene orbitals is pure $p$ and the other singly-occupied orbital is a hybrid containing substantial $s$-character, roughly $sp^2$; or (b) both singly-occupied MOs have the same hybridization (roughly $sp^3$), each having poor overlap with the aromatic ring. The latter explanation is similar to that encountered in silicon centered radicals. Radical 14 is pyramidal; the odd electron is essentially localized on silicon, and consequently there is almost no difference in the kinetic behavior and spectroscopy of radicals such as $\text{RSiH}_2$ and $\text{PhSiH}_2$.\textsuperscript{68}

\begin{center}
\includegraphics[width=0.5\textwidth]{radical14.png}
\end{center}

Explanation (a) accounts for the enhanced reactivity of triplet DPC by the larger amount of $s$ character present in the in-plane orbital. In this view, triplet DPC is similar to the phenyl radical. For a high sigma character in the reacting orbital one would expect very small DPC substituent effects, as observed (vide infra). This explanation also requires that triplet DPC and diphenylmethyl radical 13 have very similar pi systems. Thus similar absorption spectra are expected for these transients. The 20 nm shift in $\lambda_{\text{max}}$ between triplet DPC and 13 suggests at least some differences in their
electronic structures. However, there is also a 30 nm shift in absorption maxima between 2 and the fluorenyl radical\textsuperscript{62}, whose pi systems must be similar as a result of enforced planar geometry.
Skell et al. suggested that the unpaired electrons in DPC are in different orbitals which are nearly equivalent in stabilization, proposing a central sp carbon (with orthogonal p-orbitals) and orthogonal aromatic nuclei. This rationalization has the virtue of permitting each benzene ring to interact with a different electron. The two benzene nuclei are insulated from one another, thus leading to a structure which might be described as two resonance stabilized radicals. However, this interpretation is not consistent with an observed dihedral angle of 34° between the benzyl rings seen in a presumably solid matrix. (It is possible that irradiation leads to a softening of the matrix, although this possibility is typically not considered.) The structure of DPC observed in the crystal may not be the same as that of DPC in solution due to crystal packing forces in the solid and solute-solvent interactions in the liquid state at room temperature. These interactions may influence the possible conformations of the reactants in the separate media. The Skell view also does not explain the large radical reactivity of DPC.

The results in Table 1 clearly show that attack at the allylic hydrogens plays an important role in the reaction of DPC with olefins, a fact that was recognized earlier in reports based on product studies. In the case of 1,4-cyclohexadiene hydrogen abstraction is clearly the dominant process, even if truly quantitative evaluations of the yield are difficult based on signal size due to spectral overlap between Ph₂CH* and cyclo-C₆H₇* radicals. The cyclohexadienyl radical also absorbs at 334 nm. The excellent
hydrogen donor properties of 1,4-cyclohexadiene are demonstrated by its interaction with benzophenone triplets, where abstraction accounts for 94% of the quenching events.\textsuperscript{66}

Isotope effects of 1.5-6.5 on the rate of radical formation are observed and indicate carbon-hydrogen bond breaking in the transition structure. These findings are rather different from those in the case of fluorenylidene\textsuperscript{62} and 1-naphthylcarbene\textsuperscript{63} where low isotope effects, low radical yields, and indications of predominantly singlet insertion (from product studies) all combine to support the assumption of composite rate constants involving singlet as well as triplet reactions. These problems do not seem to be present in the case of DPC where we suggest that the kinetic and spectroscopic data reflect predominantly, or even exclusively, triplet behavior.\textsuperscript{67}

The activation energies of Table 2 are much smaller than those predicted from low temperature ESR kinetic data.\textsuperscript{45} One may be looking at reaction trajectories or steric interferences to reaction in the matrix that are not the same as those in solution. This is expected to result in a larger activation barrier for the matrix reaction than for the solution process. The latter could also result from: (1) reactions from different carbene levels; (2) the existence of different structural intermediates in the reactions in the various media; and (3) a limited applicability of the rapid singlet-triplet equilibrium assumption in the solid and liquid phases. Higher diazo concentrations are typically used in low temperature ESR studies ($10^{-2}$ M) than in flash photolysis experiments at 300 K. When the matrix is
formed, the diazo has a chance of being located next to a molecule of solvent, diazo, or other solute. This increases the number of reactions which the matrix carbene may undergo, e.g. azine formation. In such events, a simple comparison or correlation between the solution and matrix data cannot be made. The solution Arrhenius parameters (particularly the pre-exponential factors) are much smaller than expected and may reflect a change in mechanism over the temperature interval studied or may be a composite of those for parallel first order reactions. The predominant mechanism in operation at a given temperature depends on the relative activation entropies and enthalpies for the various reaction pathways (e.g. intersystem crossing, hydrogen abstraction, addition to double bonds, and insertion). To gain further insight into this matter, it is necessary to monitor the kinetics for and the product mixtures obtained from the various pathways as a function of temperature. It is also possible that the assumption of a thermal equilibrium between the singlet and triplet spin states is applicable only within a restricted (1/T) range in each of the two regimes (i.e. in the restricted low temperature window within which the kinetics are measurable and in one at room temperature). The limits of the room temperature observation window should be determined by: (a) the melting point and decomposition temperature of the diazo; and (b) the melting and boiling points of the solvents and added substrates.

The Arrhenius parameters for methanol quenching of DPC given in Table 4 are in good agreement with those reported previously. They
Indicate no obvious solvent effect on the rate of quenching, seen also in Table 3 for studies in several solvents. The log A values are higher and the activation energies are lower for methanol quenching studies than those in Table 2 for first order decay of DPC in pure solvent (if both are expressed in the same units). A direct comparison between the two cases or interpretation of such in terms of a conclusive mechanism is at present not possible.

For the reaction of DPC with pure solvent, one is looking at the probability of a DPC molecule colliding with any second body, as well as its reacting, e.g. via dimerization, azine formation, H-abstraction, or insertion. These collisions could result in a transfer of excess vibrational energy from the carbene to the solvent and reaction from a single level; whereas in the solid such collisions are not expected to occur. Dimerization is a second order process and could be differentiated from the first order processes through a concentration variation. For the case of methanol reacting with DPC in the presence of solvent, an additional variable is introduced. In the latter system, the carbene is capable of reacting with added quencher, either directly from the triplet state or after reversion to the singlet, as well as with solvent, with itself, or with unreacted diazo compound. Depending on the nature of the quencher, it is also possible to change the involved equilibria through solvation (e.g. between singlet and triplet states and/or in other reversible steps in the reaction mechanism). At high quencher concentrations, the primary solvating species of the carbene could change from the initial solvent
to the quencher. A simple interpretation of the observed $E_a$ and log $A$ values as the composite of those for the individual reaction pathways requires that both the mechanism for reaction of DPC with a given substrate and the differences in activation energies for the various processes remain constant over the observed temperature range. The likelihood of this occurring is not known at present and requires further experimentation.

The mechanism for reaction of DPC with methanol remains a matter for speculation. Bethell tentatively ruled out the carbonium ion mechanism (A) based on the observation of reaction of the cation with diaryldiazomethanes to form tetra-arylethylenes only.\(^7\) It has been suggested\(^2\) that the diazo and alcohol form a hydrogen bonded complex which promotes the reaction of the photolytically produced carbene with the alcohol.\(^1\) Such a model is favored by increasing acidity of the alcohol and is consistent with the findings of Eisenthal for excited triplet DPC reactions with methanol.\(^5\) If a complex is formed prior to generation of the carbene then no energy contribution for diffusion is expected. Pople et al. performed ab initio calculations for reactions of simple carbenes with water and found that the ylide (B) is not a stable intermediate for reaction of the singlet carbene and that there is no barrier for the reaction of singlet methylene with methanol.\(^5\)

It has been suggested that methanol may change the energy separation between the singlet and triplet forms of DPC.\(^5\) This behavior would be difficult to separate from DPC reactivity toward
methanol using only kinetic measurements of the disappearance of one species. However, the presently available data do not allow one to assign the unequivocally correct mechanism nor to eliminate alternative reaction pathways proposed by earlier workers. It is best here to just present the data as obtained and not speculate on their implications until further experiments are performed.
IV. SUBSTITUTED DIPHENYLCARBENES

Substituted Diphenylcarbene Introduction

Organic chemists traditionally use substituent effects to answer questions regarding structure and reactivity. This is certainly true in the area of carbene chemistry. In the preceding section several alternatives for the mechanism of reaction of DPC with methanol are discussed. In order to attempt to distinguish between these alternatives, kinetic studies are performed on a series of substituted diphenylcarbenes. There are four kinetic and spectroscopic studies using substituted diphenylcarbenes available in the literature.

Carbene and biradical intersystem crossing (ISC) can be visualized to occur via spin orbit, hyperfine, or uncorrelated spin relaxation. Using CIDEP, Doetschmann showed that DPC intersystem crosses via spin orbit coupling in oriented crystals. Closs explained the origin of biradical derived CIDNP as the hyperfine induced mixing of spin states. Uncorrelated spin relaxation is similar to a $T_1$ process in a free radical and is the only relaxation mechanism of the three which should be sensitive to temperature and
viscosity. Halogen substitution is expected to ensure a spin-orbit ISC mechanism via an internal heavy atom effect. To a first approximation, halogenation is assumed to not change the spin distribution significantly and is expected to be most effective at those sites carrying the largest spin density.

Thermal Decomposition Studies

Bethell et al. studied the thermal decomposition of 4,4'-dichlorodiphenyl diazomethane at 85°C in acetonitrile (ACN) containing methyl, isopropyl, isobutyl, t-butyl, 2,2,2-trifluoroethyl, and benzyl alcohols. They deduced that 4,4'-dichloro DPC was formed as an intermediate and reacted with alcohol to yield the corresponding diarylmethyl ether as the principal product (≈70%). They reported that, unlike diphenyl diazomethane (DDM), the thermal decomposition of the dichloro compound in ACN yielded complex product mixtures even in the presence of added alcohols. Accordingly, the reactivities of different alcohols had to be compared by competition experiments in which the diazoalkane was allowed to decompose in the presence of a large excess of a mixture of two alcohols. Methanol was used in excess, at a concentration of 0.4 M. The observed reactivities of the alcohols increased with increasing acidity of the alcohol. Trifluoroethanol caused the rate of disappearance of diazo compound to be increased substantially over that observed in anhydrous ACN. The authors suggested that this was due to a direct reaction between the
alcohol and diazoalkane, perhaps via proton transfer from alcohol to diazo compound.

Bethell et al. later studied the thermal decomposition of DDM and its 4,4'-dichloro, dimethoxy, and dimethyl analogs at 85°C in ACN with methanol and t-butanol. The major product was again the alkyl diarylmethyl ether. Some dimeric olefin was formed in amounts which increased with increasing electron repulsion by the p-substituent (OMe > Me > H) or when t-butanol rather than methanol was present. Methanol was found to be more reactive than t-butanol in all cases, but the difference in reactivity between the alcohols was found to decrease with increasing electron release by the para substituents. Through the use of tritiated alcohols and a measurement of the radioactivity of the product ethers, they observed substantial isotope effects for the formation of t-butyl ethers and small, if any, effects for methyl ethers. The authors concluded that the most likely route of ether formation was that in which the carbene attacked the oxygen atom of the alcohol to form an ylide, which was subsequently transformed by a prototropic rearrangement into the ether.

They suggested that the proton transfer capability of the oxonium part of the ylide reflected the acidity of the precursor alcohol.
Shechter et al. determined unimolecular rate constants for the thermolyses of

\[
\begin{align*}
4\text{-}X\text{C}_6\text{H}_4 & \xrightarrow{\text{C=N}_2} \\
4\text{-}Z\text{C}_6\text{H}_4 &
\end{align*}
\]

to form diphenylcarbenes in water/1,2-dimethoxyethane. Their results indicated that incorporation of any single para substituent, electron withdrawing or electron donating, facilitated the decomposition relative to DDM. Di-substituted compounds with X as an electron donating group (e.g. CH\(_3\)) and Z as an electron withdrawing group (e.g. NO\(_2\)) decayed more rapidly than either of the corresponding monosubstituted derivatives. Symmetrically p-substituted (chloro and nitro) DDMs thermolyzed more slowly than their monosubstituted analogs. For the case of the dinitro substituted DDM, thermolysis was observed to be slightly slower than for the parent DDM. Comparison of ground state \(^{13}\text{C} \text{NMR}\) substituent effects in the substituted DDMs with kinetic results indicated that the observed rate behavior was determined almost exclusively within the reaction transition state (TS). The authors interpreted their kinetic results on the basis of a tetrahedral-like TS for loss of nitrogen in which the aryl groups interacted with electron deficient and electron rich orbitals developing on the carbenic atom. Kinetic substituent effects were correlated by a quantitative free-energy relationship in terms of independent, simultaneous interactions with developing carbenic orbitals. This work indicated that the singlet state of the substituted DPCs has a closed-shell configuration, with one filled and one empty carbone orbital.
Photochemical Studies

Gibbons and Trozzolo reported the emission and absorption maxima for several monosubstituted (chloro, bromo, methyl, methoxy, nitro, phenyl) and for di-p-methoxy substituted DPCs matrix isolated in 2-methyl tetrahydrofuran (2-MTHF) at 77 K. Their results are reproduced below.

<table>
<thead>
<tr>
<th>R</th>
<th>Absorption maxima, µm</th>
<th>Emission maximum, µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>H; H</td>
<td>300; 465</td>
<td>480</td>
</tr>
<tr>
<td>Cl; H</td>
<td>311; 475</td>
<td>487</td>
</tr>
<tr>
<td>Br; H</td>
<td>316; 475</td>
<td>488</td>
</tr>
<tr>
<td>CH₃; H</td>
<td>301; 472</td>
<td>487</td>
</tr>
<tr>
<td>OCH₃; H</td>
<td>335-345*</td>
<td>495</td>
</tr>
<tr>
<td>NO₂; H</td>
<td>265; 370, 555</td>
<td>No emission</td>
</tr>
<tr>
<td>C₆H₅; H</td>
<td>355*</td>
<td>555</td>
</tr>
<tr>
<td>OCH₃; OCH₃</td>
<td>335-345*</td>
<td>507</td>
</tr>
</tbody>
</table>

* Obtained from the fluorescence excitation spectrum rather than the absorption spectrum.

They observed anomalous results for the mono and disubstituted methoxy derivatives. At low concentration (10⁻⁶ M) of 4,4'-bismethoxy DDM, the corresponding ground state triplet methylene was detected neither by fluorescence studies nor by ESR spectroscopy. In absorption studies, the spectrum of the diazo precursor disappeared upon photolysis in a Rayonet photochemical reactor (maximum output 350 nm) and was replaced by that of a species X which absorbed at 294 and 390 nm. Photolysis of more highly concentrated (10⁻⁴ M) solutions of diazo gave intermediate X as well as ESR and fluorescence spectra of the ground state triplet Y. The latter emitted at 507 nm and its fluorescence excitation spectrum exhibited a maximum at 330-350 nm.
The authors indicated that the excitation spectrum was of doubtful reliability since the principal absorbing species was the unknown intermediate X at all concentrations. Attempts to photolyze X in order to demonstrate that it is a precursor of Y led to inconclusive results.

Photolysis of 4-methoxyphenyl phenyl diazomethane yielded results that were very similar to that of the disubstituted compound. Absorption studies showed an unstable intermediate Z (λmax 379 nm) as the principal photolysis product. However, the fluorescence excitation spectrum of emission at 495 nm (assumed to be that of the triplet in analogy to the disubstituted case) was vastly different from the absorption of Z. ESR studies showed that Z was not the ground state triplet 4-methoxyphenyl phenyl methylene nor was it a free radical.

Closs and Rabinow obtained the absorption spectrum of 4,4'-dibromo DDM in cyclohexane at 25°C. The absorption maxima observed were as follows: diazo, 294 nm; carbene, 335 nm; and radical, 350 nm. They also performed quenching studies on DPC and its dibromo and dimethyl substituted analogs. The second order rate constant for reaction of all three carbenes with 1,3-butadiene was found to be (6 ± 2) x 10^5 M^-1 s^-1. This was rationalized as due to the rate-limiting attack on the diene via the carbene sigma orbital. This orbital was assumed to be orthogonal to the pi-system. The rates of dimerization of triplet DPC, dibromo DPC, and dimethyl DPC were 5.4, 3.5, and 1.1 x 10^9 M^-1 s^-1, respectively. There was a small but
real substituent effect on the rate of dimerization. A similar
substituent effect was noted previously for the dimerization of cumyl
radicals. Closs and Rabinow claimed that, in light of the
experimental error attached to these measurements, dimerizations of
diarylcarbenes proceeded with rates comparable to the dimerization of
diarylmethyl radicals and that these processes were near the diffusion
limit.
Substituted Diphenylcarbene Experimental Procedure

The substituted diphenyldiazomethane (DDM) samples were prepared and purified according to literature procedures. All solutions were contained in a flow system reservoir and degassed at 300 K for approximately 30 minutes prior to laser photolysis. The diazo concentration was typically 0.05 mM. The monitoring procedures used were similar to those described previously for DPC.

Substituted Diphenylcarbene Results

Reactions with Solvent

Absorption spectra are given for a series of substituted diphenylcarbenes in cyclohexane solvent. The observed absorption maxima and lifetimes for the carbene and radical intermediates are shown in Table 5. There is at least a 20 nm separation between the absorption maxima of the transients as was seen also for DPC and other diaryl carbenes. It is possible that the carbene absorption maxima reported here are approximately 10 nm higher than the actual absorption maxima. This is due to the overlap of this band with that for bleaching of the precursor diazo and with the excitation wavelength (308 nm). The lifetime for carbene decay is substantially
larger than the value for radical growth for di-p-tolyl diazomethane. This is attributed to overlap of the carbene and radical absorptions, in analogy to the observations for DPC. For cases in which the absorbing species can not be assigned with reasonable certainty the observed maxima and corresponding measured transient lifetimes are given in Table 6.
Table 5. Spectral Parameters for Substituted Diphenyldiazomethane Photolysis in Cyclohexane Solvent.

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>Carbene</th>
<th></th>
<th>Radical</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\lambda_{\text{max}}$</td>
<td>$\tau_D$</td>
<td>$\lambda_{\text{max}}$</td>
<td>$\tau_G$</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>314 nm</td>
<td>20 ys</td>
<td>334 nm</td>
<td>1.5 ys</td>
</tr>
<tr>
<td>H</td>
<td>Br</td>
<td>321 nm</td>
<td></td>
<td>340 nm</td>
<td>2.1 ys</td>
</tr>
<tr>
<td>Br</td>
<td>Br</td>
<td>330 nm</td>
<td>5.6 ys</td>
<td>350 nm</td>
<td>1.6 ys</td>
</tr>
<tr>
<td>H</td>
<td>Cl</td>
<td>321 nm</td>
<td></td>
<td>338 nm</td>
<td>2.0 ys</td>
</tr>
<tr>
<td>Cl</td>
<td>Cl</td>
<td>322 nm</td>
<td>9.4 ys</td>
<td>345 nm</td>
<td>2.1 ys</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>CH$_3$</td>
<td>323 nm</td>
<td>22 ys</td>
<td>340 nm</td>
<td>1.2 ys</td>
</tr>
</tbody>
</table>
Table 6. Unknown Absorbing Transients in the Laser Photolysis of Some Di-p-substituted Diphenyldiazomethanes in Cyclohexane Solvent.

<table>
<thead>
<tr>
<th></th>
<th>Decaying Intermediate</th>
<th>Growing Intermediate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$</td>
<td>$\tau_D$</td>
</tr>
<tr>
<td>OCH$_3$</td>
<td>390 nm</td>
<td>600 ns</td>
</tr>
<tr>
<td>OCH$_3$</td>
<td>324 nm</td>
<td>5.4 ns</td>
</tr>
<tr>
<td>N(CH$_3$)$_2$</td>
<td>440 nm</td>
<td>282 ns</td>
</tr>
<tr>
<td>N(CH$_3$)$_2$</td>
<td>330 nm $^a$</td>
<td>143 ns</td>
</tr>
</tbody>
</table>

$^a$ In benzene solvent.

$^b$ Lifetime was measured at 360 nm and could include a contribution from the 330 nm signal.
Photolysis of 4,4'-dibromo DDM in cyclohexane produces an absorption spectrum with a maximum at 330 nm and weaker bands at 335 and 350 nm at short (0-470 ns) times after photolysis (Figure 7). At times longer than 1 μs, the maximum is at 350 nm with a weaker absorption at 335 nm. The first detected species is assumed to be the carbene, which abstracts a hydrogen atom from the solvent to form the corresponding diarylmethyl radical. Closs indicated that the absorption maxima of the dibromo carbene and radical are 335 and 350 nm, respectively, in good agreement with this work.
Figure 7. Carbene and Radical Absorptions for the Laser Photolysis of 4,4'-Dibromo DDM in Cyclohexane.
4-Bromodiphenyl Carbene

For the 4-bromo DDM photolysis, the main absorption bands at 0-864 ns after photolysis are seen at 320, 330 and 345 nm, with relative signal intensities decreasing in that order. An additional weak absorption band is observed at 380 nm. The time evolution of the spectrum is represented by Figure 8. Again, the short wavelength band is attributed to the carbene and the absorption observed in the 330-345 nm region is assigned to the radical. Trozzolo found carbene maxima at 316 and 475 nm for the photolysis of p-bromo DPC at 77 K in 2-MTHF. The long wavelength band is believed to result from the ylide formed through reaction of the carbene with adventitious oxygen, in analogy to DPC. For the spectra of dibromo and p-bromo DPC, there are two apparent growth components to the signals in the 360-375 nm region (possibly overlapping absorptions). Growths measured at 350 and 340 nm have the same lifetimes as the weaker (√1/10 in optical density) signals at 450 and 430 nm, respectively.
Figure 8. Carbene and Radical Absorption Spectra for the Photolysis of 4-Bromo DDM in Cyclohexane.
4,4'-Dichlorodiphenyl Carbene

For 4,4'-dichloro DDM in cyclohexane, detection at times less than 500 ns after photolysis reveals overlapping absorptions of approximately equal magnitude with maxima at 315 and 330 nm and a weaker band at 345 nm (Figure 9). At 3 μs, the band at 330 nm remains unchanged in optical density, while the species absorbing at 315 nm has decayed and that at 345 nm has increased in relative magnitude. The short wavelength band is due to the triplet carbene and that at longer wavelength is associated with radical formation through hydrogen abstraction from solvent. A relatively clean first order growth is seen for the radical only at 346-350 nm. A sharp spike is seen in the sample trace at all wavelengths immediately after photolysis. It is not presently known whether this spike is an instrumental artifact or is due to an additional intermediate. The maximum absorption recorded for dichloro DPC is about 1/3 as intense as those measured for mono- and dibromo DDM and for the parent diazo solutions of comparable concentration (0.05 mM). This is due either to differences in extinction coefficients of the absorbing species in the different cases or to a variation in laser output in the separate trials.
Figure 9. Carbene and Radical Absorptions After Laser Photolysis of 4,4'-Dichloro DDM in Cyclohexane.
4-Chlorodiphenyl Carbene

Photolysis of 4-chloro DDM results in the spectra shown in Figure 10. Two overlapping absorption bands of approximately equal magnitude are observed at 320 and 340 nm at 0-1.65 µs after sample photolysis, with a much weaker absorption band at 425 nm. For a delay time of 5 µs the absorption maximum appears to be at 335 nm with a shoulder at 345 nm. In analogy with previous assignments, the short wavelength band is attributed to the carbene and that centered at 340 nm to the radical. Trozzolo\(^4\) noted an absorption maximum for the triplet carbene of 311 nm which is in reasonable agreement with our assignments. We were unable to monitor the signal at 311 nm due to the proximity to the laser line (308 nm) and to diazo precursor bleaching.
Figure 10. Carbene and Radical Absorptions After Laser Photolysis of 4-Chloro DDM in Cyclohexane.
Di-p-tolyl Diazomethane (dimethyl DDM) in cyclohexane produces the spectra in Figure 11 on photolysis with 308 nm excitation. An initially absorbing transient is seen at 325 nm and decays to form a transient with $\lambda_{\text{max}}$ 340 nm. The former species is assigned as the carbene and the latter as the diarylmethyl radical. The lifetime for radical growth at 340 nm is 1.2 $\mu$s and that for carbene decay at 325 nm is 22 $\mu$s. In analogy to DPC, this discrepancy is attributed to overlapping carbene and radical absorptions with radical decay making a significant contribution to the signal measured at 325 nm. For the region of 350-450 nm two growth components are apparent in the traces recorded on a 500 ns time scale (39.3 ns per indicated point). This might result from overlapping absorptions of the carbene and radical or of either of these with an unidentified intermediate (e.g. an oxygen ylide or an azine).
Figure 11. Carbene and Radical Absorptions After Laser Photolysis of Di-p-tolyl DDM in Cyclohexane.
Photolysis of di-p-methoxy DDM in cyclohexane produces rather anomalous results. For a "fresh" diazo sample the spectra shown in Figure 12 are obtained. At 80 ns after photolysis, absorption bands are seen at 330, 350, 375 and 390 nm. The relative intensity of the bands decreases with increasing wavelength. At 1 \mu s after the flash, the $\lambda_{\text{max}}$ is 350 nm and weak absorptions are seen at the other noted wavelengths. A sample prepared at a later date with the same "diazo" concentration exhibits slightly different spectra (Figure 13). The initial (0-39 ns) absorbing species have $\lambda_{\text{max}}$ at 330 and 385 nm and decay to yield a transient absorbing at 350 nm. The signal sizes are lower in the latter trial and the relative intensities of the various transients have changed. This phenomenon is attributed to decomposition of the diazo compound with time and different absorbing transients on the different dates, even though the diazo samples were stored in the freezer in a light-tight air-tight vial. Figure 14 gives a three dimensional plot of the absorption spectra of the latter sample. The total time window for the 3D plot is 3.93 \mu s. Signals at 300-330 nm exhibit an essentially instantaneous growth and a decay lifetime (measured at 325 nm) of 6 \mu s. The decay lifetime at 390 nm is 600 ns and the growth lifetime at 350 nm is 270 ns. Trozzolo reported that dimethoxy DPC triplet has a maximum at 335-345 nm in its fluorescence excitation spectrum. Our results indicate an intermediate absorbing in this region which has a significantly longer
growth lifetime than does the DPC triplet. The growth of the former is exponential whereas that of the latter is instantaneous on the time scale of our detection system. One might be inclined to assign the 390 nm band (X) as the precursor to the 350 nm species (Y), although Trozzolo's results indicate that photolysis of X does not lead to Y. If the 390 nm band is hypothesized as the di-p-methoxy triplet and the 350 nm band as the corresponding radical, this situation is again unusual in that the radical is at shorter wavelengths than the carbene. The present data is insufficient to unequivocally establish the identities of all the observed transients.
Figure 12. Absorption Spectra Obtained on Laser Photolysis of "Fresh" Di-p-methoxy DDM in Cyclohexane.
Absorption Spectra Obtained on Laser Photolysis of "Impure" Di-p-methoxy DDM in Cyclohexane.
Figure 14. 3D Absorption Spectra Obtained on Laser Photolysis of Di-p-methoxy DDM in Cyclohexane.
Bis(p-dimethylamino)diphenyl Carbene

Laser photolysis of bis(p-dimethylamino) DDM in cyclohexane solvent results in the spectra given in Figures 15 and 16. Figure 15 displays the sample absorption as a function of wavelength for selected delay times. The first detected intermediate has a \( \lambda_{\text{max}} \) of 440-445 nm and decays to give a transient absorbing at 390 nm. Unlike the previously reported compounds, we could not detect an absorption in the region where a carbene signal is expected (320-340 nm) due to bleaching of the diazo precursor. The lifetimes of decay at 444 nm and signal growth at 395 nm are the same within experimental error (280 vs. 210 ns) and the decay measured at 350 nm is approximately 100 times as long. A 3D representation of this sample after laser photolysis is given in Figure 16. The total time window for these spectra is 3.93 \( \mu \)s.

For bis(p-dimethylamino) DDM in benzene, a \( \lambda_{\text{max}} \) of 320 nm and several weaker signals in the 390-650 nm region are observed for a time window of 0-353 ns (Figure 17). At 2 \( \mu \)s after photolysis the 320 nm transient is no longer seen and the absorption maximum is 390 nm. The magnitude of the optical density of this band does not increase with time (or concurrently through decay of the short wavelength species) although absorptions at longer wavelengths are decreased in relative size. Signals observed with a total time window of 3.9 \( \mu \)s show carbene-like signals at 300-340 nm, a relatively clean first-order growth at 360-370 nm, and instantaneous growths with
decays of differing rates and large amounts of residual absorption in the 440-650 nm region. Again, no attempt is made at present to assign identities to the absorbing transients.

Photolysis of Michler's ketone, 4,4'-bis(dimethylamino)benzophenone, in benzene can be used to determine whether this species is present as an impurity in the sample of bis-p-dimethylamino DDM. For a time window of 0.9 to 1.4 μs after photolysis of the ketone, absorptions at 410-440 nm, 460 nm and a broad absorption band at 490-560 nm are seen. After 2.1-2.6 μs the maximum is at 410 nm (absorption band 400-460 nm) and a weaker band is seen at 480-560 nm. These bands are observed also in the photolysis of bis(p-dimethylamino) DDM in benzene. The structure in the ketone spectrum is not as pronounced for the long wavelength component as for the case of the diazo compound. At 430 nm for the ketone photolysis, there appear to be two decay components with the decay of the 430 nm transient slower than that at longer wavelengths. For the transient at wavelengths greater than 450 nm, the observed decay lifetime is 10 μs. For transients observed in the photolysis of the diazo compound in benzene, decay lifetimes at 420 nm of 19 μs and at 490 nm of 1.5 μs are measured. This indicates the presence of an impurity in the photolyzed diazo compound.
Figure 15. Absorption Spectra Obtained on Laser Photolysis of Bis (p-dimethylamino) DDM in Cyclohexane.
Figure 16. 3D Absorption Spectra Obtained on Laser Photolysis of Bis (p-dimethylamino) DDM in Cyclohexane.
Figure 17. Absorption Spectra Obtained on Laser Photolysis of Bis (p-dimethylamino) DDM in Benzene.
Reactions with Methanol

Methanol quenching of the substituted diphenylcarbenes is examined by following both the changes in carbene decay and radical growth as a function of added concentration of methanol. The room temperature results are given in Table 7. In cyclohexane solvent, the halogenated carbenes all appear to react more slowly with methanol than does the parent DPC by a factor of 2-5. For quenching studies in cyclohexane, the rates measured for the dihalogenated compounds are slower than the rates for their monosubstituted analogs, if the rates measured for the same transient are compared (e.g. the radical). In isooctane solvent, a faster reaction for the di-halogenated carbenes is indicated, although the difference of a factor of two is not outside the realm of possible artifacts of the measurement technique.

Di-p-methyl DPC reacts about 10 times as rapidly as does DPC when the corresponding quenching rate constants are obtained by following the radical growth. However, a difference of a factor of 5 is seen in the quenching rates for the dimethyl compound if the rate obtained following the radical growth in cyclohexane is compared to that from measurement of the carbene decay in isooctane. The latter is slower and could result from inherent interferences by the overlapping carbene and radical decays.

Methanol quenching trials monitoring dimethoxy DPC at 320 nm in isooctane provide rather anomalous results. The rate constant for methanol quenching given in Table 7 must thus be taken only as a rough
approximation to the rapid rate of reaction. The signal observed at the carbene maximum changes as a function of time after addition of the quencher. It is not at present certain whether this is due to the limited solubility of methanol in isooctane or to the formation of secondary absorbing transients.

The Arrhenius parameters for methanol quenching of DPC, dibromo DPC, and dimethyl DPC in acetonitrile are determined by monitoring the decay of the carbene signals as a function of temperature. The results are presented in Table 8. Using these data, the predicted rates for carbene reaction with methanol are in good agreement with the values in Table 7. Dibromo DPC reacts 2.7 times as slowly as does DPC, while dimethyl DPC reacts 13 times as rapidly as DPC. The activation energies are hypothesized to be the same, complicating the interpretation of the lower reaction rates consistently observed for the halogenated DPCs. The much greater reactivity for dimethyl DPC is predicted to result from its higher log A value.
### Table 7. Bimolecular Rate Constants for the Reaction of Several p-Substituted Diphenylcarbenes with Methanol at 300 K.

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>Solvent</th>
<th>$k_q$</th>
<th>$k_o$</th>
<th>$\lambda_{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>cyclohexane</td>
<td>12 ± 1</td>
<td>$5.5 \pm 0.2$</td>
<td>340 nm</td>
</tr>
<tr>
<td>H</td>
<td>Br</td>
<td>cyclohexane</td>
<td>3.6 ± 0.8</td>
<td>5.1 ± 0.6 $^a$</td>
<td>340 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>cyclohexane</td>
<td>2.4 ± 0.2</td>
<td>1.0 ± 0.1</td>
<td>321 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>cyclohexane</td>
<td>3.0 ± 0.2 $^a$</td>
<td>1.1 ± 0.2</td>
<td>321 nm</td>
</tr>
<tr>
<td>H</td>
<td>Br</td>
<td>isooctane</td>
<td>3.4 ± 0.5</td>
<td>1.7 ± 0.2</td>
<td>321 nm</td>
</tr>
<tr>
<td>Br</td>
<td>Br</td>
<td>cyclohexane</td>
<td>2.0 ± 0.8</td>
<td>6.1 ± 0.2</td>
<td>350 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>isooctane</td>
<td>2.3 ± 0.2</td>
<td>0.9 ± 0.2</td>
<td>321 nm</td>
</tr>
<tr>
<td>Br</td>
<td>Br</td>
<td>isooctane</td>
<td>6.5 ± 1.4</td>
<td>1.2 ± 0.4</td>
<td>330 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>isooctane</td>
<td>4.5 ± 1.4</td>
<td>1.7 ± 1.4</td>
<td>321 nm</td>
</tr>
<tr>
<td>H</td>
<td>Cl</td>
<td>cyclohexane</td>
<td>6.9 ± 0.8</td>
<td>5.3 ± 0.3</td>
<td>338 nm</td>
</tr>
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<td></td>
<td></td>
<td>isooctane</td>
<td>2.5 ± 0.7</td>
<td>1.0 ± 0.3</td>
<td>321 nm</td>
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<tr>
<td>H</td>
<td>Cl</td>
<td>isooctane</td>
<td>2.8 ± 0.4</td>
<td>2.1 ± 0.1</td>
<td>321 nm</td>
</tr>
<tr>
<td>Cl</td>
<td>Cl</td>
<td>cyclohexane</td>
<td>2.9 ± 0.3</td>
<td>5.2 ± 0.3</td>
<td>340 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>isooctane</td>
<td>8.1 ± 0.8</td>
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<td>322 nm</td>
</tr>
<tr>
<td>CH₃</td>
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<td>cyclohexane</td>
<td>104 ± 7</td>
<td>7.8 ± 7</td>
<td>340 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>isooctane</td>
<td>23 ± 3</td>
<td>2.1 ± 0.8</td>
<td>323 nm</td>
</tr>
<tr>
<td>OCH₃</td>
<td>OCH₃</td>
<td>cyclohexane</td>
<td>87 $^b$</td>
<td>$-$</td>
<td>320 nm</td>
</tr>
</tbody>
</table>

$^a$ Data for second trial is thought to be more reliable than the first, due to a better quality of the data.

$^b$ Data was rather poor; this number is the rate obtained from 3 points.
Table 8. Arrhenius Parameters for Methanol Quenching of the Triplet State of p-Substituted Diphenylcarbenes in Acetonitrile Solvent.

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>$E_a$ (kcal/mole)</th>
<th>$\log (A / M^{-1} s^{-1})$</th>
<th>T-range, K</th>
<th>$k_{300 K}$ ($M^{-1} s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>1.45 ± 0.60</td>
<td>8.35 ± 0.47</td>
<td>241-326</td>
<td>1.97 x 10^7</td>
</tr>
<tr>
<td>Br</td>
<td>Br</td>
<td>2.02 ± 0.28</td>
<td>8.33 ± 0.24</td>
<td>234-324</td>
<td>7.20 x 10^6</td>
</tr>
<tr>
<td>CH₃</td>
<td>CH₃</td>
<td>1.52 ± 0.23</td>
<td>9.51 ± 0.19</td>
<td>236-328</td>
<td>2.52 x 10^8</td>
</tr>
</tbody>
</table>
Substituted Diphenylcarbene Discussion

The spectral parameters given in Table 5 indicate similarities between DPC and its substituted analogs. The observed carbene and radical maxima for the p-substituted species are all at longer wavelengths than the absorptions for the corresponding DPC carbene and radical. The dihalogenated radicals absorb at longer wavelengths than their monohalogenated analogs (by 7-10 nm). The radical growth lifetimes are also similar to the case of DPC thus indicating comparable reactivities of the carbenes in hydrogen abstraction reactions. The measured radical growth rate is in all cases faster than the corresponding carbene rate of decay in cyclohexane solvent. As in the case of DPC, this is attributed to overlapping carbene and radical absorptions and a resultant contribution of radical decay to that measured at the observed carbene absorption maximum. The carbene peak absorption is less than that of the radical (1/4 to 1/2 when measured at the respective maxima). The negligible substituent effects on the reaction of the carbene to form the radical indicate that the reactive center has a high sigma character. This is consistent with our observation that DPC and the phenyl radical exhibit similar reactivities.

The methanol quenching experiments were begun in order to ascertain the mechanism of reaction of the carbene with methanol and to assess the validity of previously suggested interpretations. If the reaction proceeds via a surface crossing mechanism as suggested by
Scaiano et al., then incorporation of a heavy atom into the system might be expected to facilitate the intersystem crossing rate and consequently to increase the reaction rate with methanol (if ISC is a rate determining step in the reaction sequence). Our results show that the inclusion of a heavy atom in the para position of the DPC aromatic system decreases the apparent rate of carbene reaction with methanol. The observed rates are opposite to what might be expected for the heavy atom enhancement of the intersystem crossing rate if the triplet carbene reacts with methanol concurrent with intersystem crossing to form the singlet ether product. On the other hand, the di-p-methyl substituted DPC has an enhanced reactivity relative to DPC.

In order to compare the observed methanol quenching rate constants, activation energies, and log A values for the unsubstituted and p-substituted DPCs a number of assumptions must be made. At a given temperature (e.g. room temperature) the mechanism for reaction of the various species with methanol must be the same. Further, the mechanism must not change over the observed temperature range in order for the $E_a$ and log A values to have a simple interpretation in terms of the steps of the reaction mechanism.

If it can be assumed that in all cases reaction of the carbene with methanol occurs only from the singlet state (as has been traditionally accepted and as indicated in Scheme 1) and that the observed quenching rate constants are a composite of the singlet-triplet equilibrium constant and the rate constant for
methanol quenching of the singlet carbene, then the results in Tables 7 and 8 require some of the following rationalizations:

(a) Halogenation increases the singlet-triplet separation (through destabilization of the singlet or stabilization of the triplet carbene).

(b) Halogenation increases the activation energy for singlet reaction with methanol.

(c) Para-substitution by an electron withdrawing group decreases the basicity of the reacting carbene and by an electron donating group increases the carbene basicity. This interpretation is consistent with the works of Bethell and Eisenthal where the carbene reactivity was found to increase with increasing acidity of the alcohol.

(d) Methyl substitution increases the efficiency of reaction as reflected in the larger A factor in this case than observed for DPC, while halogen substitution doesn't affect the efficiency of reaction. This is opposite to what would be expected for the latter if a surface crossing mechanism were operative but appears to be necessary in order to explain the experimentally observed Arrhenius parameters given in Table 8.

It is difficult to separate possibilities (a) and (b) using the above described techniques if either or both phenomena are applicable to the present situation. If (c) is in operation, this tends to rule out the ylide mechanism proposed by Bethell in which the carbene undergoes electrophilic attack on the oxygen atom of the alcohol. The highest
reaction rates are seen for dimethyl DPC, in which the carbenic carbon is expected to possess an excess electron density if resonance delocalization is operative. It should thus be less inclined to undergo electrophilic attack on oxygen than an electron deficient carbon. The latter is expected for the halogenated carbenes. It is not known whether substitution changes the hybridization of the carbene center; although this is a possible rationalization of the di-methyl DPC data if, in this case, more orbitals are available for reaction than for other DPC derivatives. Additional factors which should be taken into consideration are changes in the hydrogen bonding ability of the alcohol or in the solvation of the carbene or transition state with a change in the para substituents on DPC. Such phenomena are difficult to prove with the presently available techniques.

The temperature dependence of the experimental rate data are usually well represented by the commonly used form of the Arrhenius equation,

\[ k = A \exp \left( -\frac{E_a}{RT} \right) \]

Here, \( k \) is the measured reaction rate constant, \( A \) is the pre-exponential or frequency factor, \( E_a \) is the activation energy, \( T \) is the absolute temperature, and \( R \) is the gas constant. Reaction rate theories, such as collision theory and transition state theory, give theoretical significance to the various terms in the above equation. These are described briefly in Appendix 2.

If \( E_a \) is temperature independent, then a plot of \( \log k \) as a function of the inverse absolute temperature provides \( E_a \) from its slope and \( \log A \) as its intercept. This is the form of the equation commonly used by
physical organic chemists to explain the data in terms of a single, simple rate determining step. The present data is insufficient for an adequate simple explanation. It is possible that $E_a$ is not independent of temperature, in which case the $A$ value calculated from the experimental results concurrently changes with the variation in the activation energy. If different mechanisms are operative over the observed temperature range, then the calculated Arrhenius parameters are a composite of those for the various processes. It is more likely that the mechanism for reaction of the various carbenes changes with the substituents, as evidenced by Bethell's findings of more complex product mixtures for the thermolytic reaction of dichloro DDM with methanol than for the unsubstituted compound.
V. DIHYDRODIBENZOCYCLOHEPTADIENYLIDENE, DBS

DBS Introduction

In order to investigate the origin of the differences between the predominantly singlet reactivity observed for fluorenylidene and the triplet reactivity of diphenylcarbene (DPC) and several of its para substituted analogs, we have examined various alkyl bridged derivatives of DPC. This section deals with the nanosecond laser flash photolysis of 15, 5-diazo-10,11-dihydro-5H-dibenzo[a,d]cycloheptene, which leads to the carbene 4 (DBS).

\[ \text{DBS} \]

This system was studied previously by Moritani et al. who obtained matrix UV and ESR spectra of the triplet ground state of 4. These workers also studied the conventional flash photolysis of 15 in liquid paraffin. Triplet 4 was found to have a lifetime of a few \( \mu s \). Radical 16 was formed in liquid paraffin, and the eventual product was the radical-radical dimer 17. However, no carbenic rate constants were determined by Moritani.
Diazo compound 15 was prepared as described by Moritani. 10,11-Dihydro-5H-dibenz[a,d]cycloheptene (Aldrich) was used as received. Di-tert-butyl peroxide, triethylamine, and tetrahydrofuran were purified by passage through alumina. Benzene (Aldrich, Gold Label) was purified by washing with sulfuric acid and distilled water, stirred over calcium chloride, then refluxed for 4 hours and distilled over calcium hydride. Fisher HPLC grade acetonitrile was refluxed and distilled over calcium hydride under an atmosphere of nitrogen. Other solvents were of the highest purity commercially available and were used as received.

Diazo solutions were deaerated by bubbling with oxygen-free nitrogen, typically 1/2 hour degassing for a flow system reservoir containing 50 ml of 4 x 10^-5 M diazo. Samples for the majority of the laser experiments were flowed through a cell constructed of 7 mm x 7 mm Suprasil tubing. The laser system used the pulses of a nitrogen laser (Molelectron model UV 24; 337.1 nm, ~8 ns, up to 10 mJ/pulse) or of an excimer laser (Lumonics model TE-860-2) operated with Xe/HCl/He mixtures (308 nm, ~4 ns, up to 80 mJ/pulse). The data acquisition and processing procedures were the same as those described previously.
Laser flash photolysis of diazo compound 15 in benzene gives the transient spectrum shown in Figure 18. The two main bands observed at 328 and 340 nm are assigned to triplet carbene 4 in accord with the findings of Moritani. The triplet carbene lifetime in benzene (measured at 324 and 350 nm) is 15–30 $\mu$s; the growth of the carbene is too fast to be resolved with our detection system (i.e. < 5 ns). A weak band is observed around 410 nm which is not attributable to the carbene due to its very long lifetime (>> 200 $\mu$s) and short growth lifetime (several $\mu$s). This band is tentatively assigned as the ylide formed through reaction reaction DBS with oxygen, in analogy to the case of DPC.$^{56}$

Laser flash photolysis of 15 in toluene or cyclohexane gives transient spectra similar to that observed in benzene, with observed absorption maxima of 330 and 350 nm. However, the relative intensities of the two bands are time dependent (Figure 19). This indicates that the absorption spectra of triplet carbene 4 and radical 16 are very similar, with at least two components present in the absorption envelope for both the carbene and radical. This is illustrated in Figure 19, where the carbene to decay completely by 13 $\mu$s after the laser flash. Apparently the carbene has a larger extinction coefficient than the radical at 328 nm, whereas the radical absorbs more strongly than the carbene at 350 nm. The time evolution
Figure 18. Absorption Spectrum Obtained at 0–39 ns After 308 nm Laser Photolysis of 15 in Benzene.
Figure 19. Time Evolution of the Absorption Spectrum Obtained on Laser Photolysis of 15 in Toluene.
of signals at various wavelengths is shown in Figure 20. The weak 410 nm band is also observed following laser photolysis of 15 in toluene. This transient has a growth lifetime similar to that of the radical but a much longer decay lifetime, indicating that the intermediates arise from the same precursor but that they are not identical.

The absorption spectrum of radical 16 was generated independently. When irradiated with light of an appropriate wavelength, di-tert-butyl peroxide cleaves to form the t-butoxy radical, which has been found to readily undergo hydrogen abstraction reactions.

\[
\text{t-BuO-} \quad \text{hv} \quad \rightarrow \quad 2\text{t-BuO}^-. 
\]

Photolysis of a 1 mM solution of 18 in 5% (V/V) di-tert-butyl peroxide/benzene gives the transient spectrum seen in Figure 21 at 8.8-12.4 \( \mu \)s after photolysis. For times up to 3 \( \mu \)s after the flash, the absorption at 350 nm is seen to be greater than that seen at 325 and 338 nm (i.e. optical density decreases with decreasing wavelength). The absorption magnitude at all wavelengths is observed to increase as a function of time. The origin of the fine structure for the radical absorption is not certain, but it could be due to CH stretching vibrations or to radical 19 which forms through intramolecular hydrogen abstraction.
Figure 20. Transient Absorptions at Different Wavelengths for Laser Photolysis of 15 in Toluene.
Figure 21. Radical Spectrum Obtained on Photolysis of 18 and Di-t-butyl Peroxide in Benzene at 8.8 to 12.4 μs After Laser Excitation.
The 410 nm band is not seen in the radical spectrum. This further indicates that the 410 nm band cannot be due to radical 16.

For quantitative work the growth of the radical at 350 nm is used, where overlap with the carbene spectrum is assumed to be negligible. The latter is evidenced by a relatively clean exponential growth for the signal measured at this wavelength and is shown in Figure 20. The growth lifetimes of 16 in various solvents are: toluene 4.5 μs; triethylamine 1.2 μs; tetrahydrofuran 1 μs; and cyclohexane 2 μs. The growth lifetimes observed upon photolysis of 15 are very similar to those seen with diphenyldiazomethane.

Isotope effects of 6.7 to radical formation in cyclohexane/cyclohexane d_{12} at 300 K and 3.0 in toluene/toluene d_{8} are observed. This compares to isotope effects of 2.6 and 6.5 for the same respective solvents with DPC. These studies are necessarily performed in static cells due to the high cost of the deuterated material. The isotope effects measured are assumed to be lower limits, as competing processes (e.g. impurity quenching, azine formation and dimerization) are expected to make a larger contribution to the kinetics in the less reactive deuterated solvent.

The spectrum obtained for the photolysis of 15 in carbon tetrachloride (CCl₄) shows a strong absorption band at 345-350 nm which drops off sharply to a weaker, broad shoulder on the short wavelength side (Figure 22). The major chromophore in this region is assigned to be the chloro radical formed through chlorine abstraction.
Figure 22. Absorption Spectrum Obtained at 0.82 - 1.45 μs After Laser Photolysis of 15 in Carbon Tetrachloride.
by 4 from the solvent. The growth of the signal at 345 nm is instantaneous and the observed decay lifetime is 120 μs. At 350 nm, 2 components to the transient growth are observed with a jump making the largest contribution to the total sample optical density. This is due to the presence of overlapping absorptions (e.g. chloro radical and carbene) or to two precursors to the chloro radical which react with the solvent with significantly different rates. There is at present insufficient experimental evidence to either confirm or disprove the latter. For spectra recorded on the same day with identical diazo concentrations, the peak sample absorption at 350 nm is consistently seen to be lower by a factor of 4 to 6 for solutions in CCl₄ than for those in different mixtures (v/v) of benzene and CCl₄ or in pure benzene. For example, solutions of 0, 25, 50, and 75% CCl₄ have chloro radical optical densities of 0.03 (no systematic variation with solvent) while that in neat CCl₄ has a peak absorption intensity of ~0.08. The reason for this occurrence seen for several trials is unknown at present.

The results of an Arrhenius treatment of the carbene first order decay (as monitored by radical growth) in a few solvents are given in Table 9. The parameters for toluene and cyclohexane are essentially the same as those reported in Table 2 for diphenylcarbene (DPC). At ambient temperatures, the predominant mechanism of carbene decay is assumed to be hydrogen or chlorine atom abstraction. If this remains valid throughout the temperature range an unusually low pre-exponential value is implied, a feature previously observed in
Table 9. Arrhenius Parameters for the First Order Decay of IBS, 4, in Various Solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>T Range</th>
<th>$\lambda_{obed}$</th>
<th>$E_a$ (kcal/mole)</th>
<th>log ($A/s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene</td>
<td>253-336</td>
<td>400</td>
<td>2.7 ± 0.6</td>
<td>7.4 ± 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>350</td>
<td>1.8 ± 0.5</td>
<td>6.8 ± 0.4</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>278-343</td>
<td>350</td>
<td>2.7 ± 0.6</td>
<td>7.4 ± 0.4</td>
</tr>
<tr>
<td>$\text{CCl}_4$</td>
<td>288-338</td>
<td>350</td>
<td>1.9 ± 0.6</td>
<td>8.5 ± 0.4</td>
</tr>
</tbody>
</table>
other carbene abstractions. Experiments are currently in progress to establish the importance of abstraction reactions at the various temperatures, since a partial change of mechanism (that cannot be ruled out at present) could affect the Arrhenius parameters.

The effect of quencher concentration on the growth of radical 16 as well as on the decay of carbene 4 is used to determine the reactivity of 4 toward various substrates. The experiments are carried out at several reagent concentrations and the first order rate constant, $k_{\text{expt}}$, is plotted as a function of the substrate concentration to yield the substrate quenching rate constant $k_s$ according to

$$k_{\text{expt}} = k_o + k_s (\text{substrate}).$$

Here, $k_o$ includes all first order reactions which carbene 4 may undergo in the absence of quencher. As mentioned in earlier sections, $k_o$ typically includes contributions from hydrogen abstraction from solvent as well as impurity quenching. The rate constant $k_s$ includes all possible modes and sites of attack on the substrate. It is important to again note that while the kinetic method uses radical 16 as a probe, it is valid even for quenchers which do not give 16 as a reaction product (e.g. methanol and styrene: see Appendix 1). Quenching rate constants are listed in Table 10. The rate constants for carbene 4 are generally a factor of 2-40 lower than those obtained with DPC.$^{63}$
Table 10. Kinetics of the Reaction of 4 with Various Substrates at 298 K.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Solvent</th>
<th>( \lambda ) \text{ nm}</th>
<th>G/D</th>
<th>( k_q ) \text{ } \times 10^5 \text{ M}^{-1} \text{ s}^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-cyclohexadiene</td>
<td>cyclohexane</td>
<td>350</td>
<td>G</td>
<td>30 ± 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>44 ± 5(^b)</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>benzene</td>
<td>350</td>
<td>G</td>
<td>0.88 ± 0.08</td>
</tr>
<tr>
<td>styrene</td>
<td>benzene</td>
<td>330</td>
<td>D</td>
<td>0.83 ± 0.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>340</td>
<td>D</td>
<td>0.94 ± 0.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>G</td>
<td>2.4 ± 0.3(^c)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>420</td>
<td>D</td>
<td>0.15 ± 0.04(^d),(^h)</td>
</tr>
<tr>
<td></td>
<td>cyclohexane</td>
<td>350</td>
<td>G</td>
<td>11.0 ± 3.0(^e)</td>
</tr>
<tr>
<td>methanol</td>
<td>cyclohexane</td>
<td>350</td>
<td>G</td>
<td>19 ± 2</td>
</tr>
<tr>
<td>toluene</td>
<td>350</td>
<td>G</td>
<td>25  ± 2.0</td>
<td></td>
</tr>
<tr>
<td>acetonitrile</td>
<td>330</td>
<td>D</td>
<td>3.1 ± 0.2</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Monitoring signal growth (G) or decay (D) at the specified wavelength.

\(^b\) Excitation by 337 nm laser; all other data was obtained using 308 nm excimer laser excitation.

\(^c\) Large magnitude could be due to overlapping signals at this wavelength; see text.

\(^d\) Experimental plot levels off for styrene concentration greater than 1.5 M.

\(^e\) See text for discussion of large discrepancy between rate constants obtained monitoring radical growth in cyclohexane versus that from the carbene decay in benzene.
The temperature dependence of the methanol reaction rate constant was examined by this technique in acetonitrile. The Arrhenius parameters obtained are given in Table 11, along with the corresponding values for DPC. In Table 11 a difference of a factor of $\sim 100$ is seen in the calculated methanol rate constants at 300 K for reaction of DBS and DPC using the experimental Arrhenius parameters. The large difference is due to the significantly larger activation energy for the reaction of DBS, 4. This larger reaction barrier is easily explicable if a greater carbenic angle for DBS than for DPC is invoked, leading to a larger singlet-triplet gap. This increased angle is hypothesized to result from the ethano linkage serving as a rigid separator (spacer) of the phenyl rings perhaps resulting in particular enforced geometries which are capable of reacting. In DPC only steric hindrance by the phenyl rings is proposed to determine the magnitude of the carbenic angle.

Laser flash photolysis of diazofluorene or 1-naphthyl diazomethane in solvents such as acetonitrile and pyridine leads to readily detected ylide-type species.\textsuperscript{62d,63,84} Photolysis of 15 in pyridine gives rise to a new band at 470 nm. This band grows in with a time constant of 2.8 $\mu$s and has a lifetime of approximately 120 $\mu$s. There is no measurable quenching of this species in the presence of 0.26 M diethyl fumarate. The 470 nm band is tentatively assigned to ylide 20.
Table 11. Arrhenius Parameters for the Methanol Quenching of DBS and DPC in Acetonitrile.

<table>
<thead>
<tr>
<th>Carbone</th>
<th>T Range</th>
<th>$E_a$</th>
<th>log ($A/M^{-1}s^{-1}$)</th>
<th>$k_{300K}$ $10^5 M^{-1}s^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBS</td>
<td>251-339</td>
<td>5.0 ± 1.0</td>
<td>9.1 ± 0.8</td>
<td>3.09</td>
</tr>
<tr>
<td>DPC</td>
<td>241-326</td>
<td>1.4 ± 0.6</td>
<td>8.4 ± 0.5</td>
<td>197</td>
</tr>
</tbody>
</table>
Photolysis of 15 in acetonitrile gives a weak band at 410 nm which is attributed to the ylide 21. The exponential growth lifetime measured at 410 nm is the same as that for a radical-like signal at 355 nm. This species reacts with diethylfumarate with a rate constant of $(1.0 \pm 0.1) \times 10^4 \text{ M}^{-1} \text{s}^{-1}$. As mentioned previously, photolysis of 15 in benzene also gives a 410 nm band which is again assumed to be ylide 21 and is formed through reaction of DBS with oxygen. In benzene 21 reacts with styrene with a rate constant of $(1.4 \pm 0.3) \times 10^4 \text{ M}^{-1} \text{s}^{-1}$.

\[\text{}\begin{array}{c}
\text{O} \\
\text{O}
\end{array} \quad 21 \quad \begin{array}{c}
\text{O} \\
\text{O}
\end{array}\]
Laser flash photolysis studies which monitor the growth of radicals derived from carbenes give absolute rate constants for carbenic reaction with solvents. It is possible that the observed rate of radical growth in an alkane solvent is a composite of both triplet carbene abstraction and singlet carbene insertion rate constants if triplet-singlet equilibration is rapid. Studies with fluorenylidene and 1-naphthylcarbene in alkanes demonstrate that the singlet decay route is dominant in these systems. Thus the observed rate constants for these two carbenes cannot be associated with elementary triplet reaction rate constants. Product studies of DPC in toluene and cyclohexane indicate that triplet chemistry is the exclusive mode of carbene decay. We believe that the kinetics of 4 in hydrocarbons also reflect predominantly triplet processes due to the similarity of rate constants for DPC and DBS. Further evidence is provided by the product studies of Moritani which indicate an 81% yield of radical dimer 17 and a 6% yield of 18 upon photolysis of diazo compound 15 in cis-2-butene.

The 410 nm absorption band is most likely attributable to the DBS-oxygen ylide 21, in analogy to the observations for DPC.
An alternative assignment of the 410 nm band is xylylene 22. This species would be formed by intramolecular hydrogen abstraction in triplet carbene 4 followed by spin inversion. The parent ortho xylylene 23 absorbs at 370 nm and the phenyl derivative 22 should absorb at even longer wavelengths. This assignment would explain why the 410 nm band grows in with the same time constant as radical 16 in alkane solvents and why the 410 nm band reacts with dienophiles.

Triplet carbenes are not expected to react directly with substrates like pyridine to give singlet ylides in a spin forbidden process. A possible mechanism for ylide formation is singlet-triplet equilibration followed by rapid reaction of the invisible singlet carbene. The reluctance of DPC and 4 to form ylides relative to fluorenylidene and 1-naphthylcarbene is taken as evidence for a larger singlet-triplet energy separation in DPC and DBS relative to the other carbenes. The singlet-triplet splitting in carbenes is assumed to be a function of the central carbene bond angle. The large known angle (148°) in DPC and presumably in DBS destabilizes the singlet state. This view is reinforced by a study of the reaction of triplet 4 with methanol (Table 11). The methanol reaction may also proceed with the involvement of the low lying singlet. The reaction of triplet 4 is much slower than the corresponding reaction of triplet DPC with methanol10,49,50b,67 and much slower than the reactions of 1-naphthylcarbene and fluorenylidene with alcohols.
In Table 10, a large discrepancy is observed in the rate constants obtained for styrene quenching of DBS following the decay of the carbene at 330 nm in benzene versus that for the growth of the radical at 350 nm in cyclohexane. However, the rate calculated for the latter is similar to that observed for the reaction of DPC with styrene in cyclohexane using the 334 nm benzhydryl radical as a probe. This observation could be due to the fact that as the styrene concentration is increased an increasingly larger contribution to the measured absorption signal from a "fast" growth component (a.k.a. "jump") to the signal is observed at 350 nm in cyclohexane. This is most likely due to overlapping carbene and radical signals, with the result that attempted first order fits to the recorded signal growth yield artificially high $k_q$ values. It is unlikely that the large change in $k_q$ with solvent and monitored transient is due to solvent effects alone.

This type of variation in rates for reaction of presumably the same species is seen also for methanol quenching of the radical growth at 350 nm in toluene and cyclohexane and the carbene decay at 320 nm in acetonitrile. In neat toluene and cyclohexane there are 2 growth components to the signal at 350 nm, a jump and a slower exponential growth. The latter makes the largest contribution to the measured signal. On the first addition of methanol, the slow growth component disappears, introducing a large amount of uncertainty into the first order rate measured for the decreased radical yield.

For spectral signals at 390-400 nm for photolysis of a $5 \times 10^{-5}$ M diazo solution in a 0.43 M styrene/ benzene mixture, a jump and a slow
component appear in the recorded transient signal. The slow growth component makes a decreasing contribution to the signal as one approaches lower wavelength values. The detected signal is probably comprised of overlapping absorptions of the carbene (320-330 nm) and ylide (400 nm). It should be noted that no radical signals are observed at 350 nm, indicating that reaction of the carbene with styrene does not occur to an appreciable extent through hydrogen abstraction by DBS, 4, to form the radical 16.

For further studies on styrene quenching, the rates are obtained following the decays of the 340 and 420 nm species in benzene as a function of styrene concentration. This provides rate constants of $(9.4 \pm 1.2)$ and $(1.5 \pm 0.4) \times 10^4 \text{ M}^{-1} \text{s}^{-1}$. Monitoring the growth of the 400 nm species yields a rate constant for styrene quenching of $(2.4 \pm 0.3) \times 10^5 \text{ M}^{-1} \text{s}^{-1}$, which is in good agreement with the rate for quenching of the carbene at 340 nm.

Attempts to determine the Arrhenius parameters for hydrogen abstraction by the DBS carbene in Aldrich Gold Label cyclopentane provide inconclusive results. Following the decay at 320 nm, no systematic change in the rate or maximum signal intensity with temperature is observed. The measured decay lifetime fluctuates randomly between the values of 3 and 25 ms over the temperature range 187 to 308 K. This is again assumed to be due to the overlap of carbene and radical absorptions and to the difficulty of separating the fast carbene decay from the apparently slower radical decay.
Monitoring the 350 nm radical growth signal, an increasing signal contribution by a "jump" is observed as the temperature is lowered although the total signal size does not change. There is no apparent change in the measurable growth component with temperature; uncertainty in estimating the exponential rate for the slow component increases with decreasing temperature due to the progressively smaller optical density contribution by the species of interest. It is assumed that less radical is formed and the major absorbing species at this wavelength is the carbene.

The relative contributions to the signals observed at 320 and 350 nm as a function of temperature depend on the corresponding values of the:

(1) extinction coefficients of carbene 4 and radical 16 at the various wavelengths;

(2) growth and decay lifetimes of 4 and 16; and

(3) concentrations of the absorbing species as a function of time.

These factors are not independent of one another and must be simultaneously considered in the description or explanation of observed composite signals.

In conclusion, laser flash photolysis of diazo compound 15 produces carbene 4 which can be readily detected at 328 nm. In hydrocarbon solvents, 4 decays by hydrogen atom abstraction within a few microseconds to form the radical 16 which is detected in its absorption at 350 nm. The absorption envelopes of 4 and 16 each have two bands, with one band of each overlapping with a band of the other. The kinetics of 4 are very
similar to DPC, thus implying a similarity in electronic structure. Diphenylcarbene has a rather large central angle of 148° due to repulsions between the ortho hydrogens of the different aromatic rings. Carbene 4 is also predicted to have a large central angle due to the ethano linkage. The large angles in DPC and 4 relative to that in fluorenylidene are probably responsible for the differences in the observed behavior of these species.
VI. 10,10-DIMETHYL-9-ANTHRONYLIDENE, DMA

DMA Introduction

Carbene 3 is expected to have a small carbenic angle but no unfavorable electronic factors in the singlet as does fluorenylidene.

As indicated previously, singlet carbenes are generally assumed to prefer small dihedral bond angles and large angles favor the triplet. The diazo precursor to 3 was prepared by Wright from the corresponding ketone as shown.

When ESR and product studies were carried out at low temperature in methanol, DMA was extremely reactive and gave almost exclusively singlet products. A Curie plot obtained by irradiation of crystals of 9-diazo-10,10-dimethyl-9,10-dihydroanthracene, 24, indicated that DMA is a ground state triplet. Curvature in the plot suggested a low lying, thermally accessible singlet state. We therefore
121

anticipated and observed a high reactivity for the carbene generated on laser photolysis. A very large methanol constant observed for quenching studies in benzene also indicated an easily accessible singlet state for carbene 3.

DNA Experimental Procedure

The DMA samples were prepared by Wright and purified according to literature procedure. All solutions were contained in a flow system reservoir and degassed by nitrogen bubbling at 300 K for 30 minutes prior to laser photolysis. The diazo concentration was typically $5 \times 10^{-4}$ M. The monitoring and data treatment procedures were similar to those described previously for DPC.
DMA Results and Discussion

Photolysis of 24 in benzene with 308 nm excitation leads to the spectrum seen in Figure 23. The $\lambda_{\text{max}}$ is observed to be 350 nm with a broad weaker shoulder (370-410 nm) at 1.5 $\mu$s after the flash. The transient at 350 nm has a decay lifetime of $\approx$150 ns in benzene, while the much weaker signal at 400 nm has an extremely long lifetime. The 350 nm species is assigned as the triplet carbene 3 and that at 400 nm as an ylide formed through carbene reaction with oxygen.

Methanol quenching studies of the carbene at 350 nm in benzene leads to a calculated reaction rate constant, $k_{\text{a}}$, of $(4.6 \pm 0.5) \times 10^9$ M$^{-1}$ s$^{-1}$ at 298 K. The procedure for the determination of $k_{\text{a}}$ is the same as that described in earlier sections where a plot of the experimental rate constant $k_{\text{expt}}$ as a function of the methanol concentration yields the quenching rate constant $k_{\text{a}}$ (Figure 24). The magnitude of the methanol reaction rate constant is very close to the value typically expected for diffusion-controlled reactions$^{49,50}$, implying a very small energy separation between the triplet and singlet states. This follows from the assumption that only the singlet reacts with methanol and that the triplet intersystem crosses back to the singlet before reaction with methanol occurs. The assumption of a small gap is consistent with ESR results which indicate a very weak, short-lived triplet signal and predominantly singlet OH insertion products at 77 K.$^{86}$
Figure 23. Absorption Spectrum at 0.27 - 1.12 \( \mu \text{s} \) Following 308 nm Laser Photolysis of 24 in Benzene.
**Figure 24.** Least Square Fit and Plot of First Order Rate of Decay of Carbene 3 at 350 nm as a Function of Methanol Concentration at 298 K.\(^a\)

\(^a\)Error in rates is twice the standard deviation.
Excimer laser photolysis of 24 in cyclohexane produces the spectra in Figure 25. For times to 16 ns after photolysis the absorption maximum is at 350 nm, a smaller band is present at 365 nm, and a band of unknown origin is seen at 410 nm. The carbene has an observed decay lifetime of 195 ns at 360 nm. On the short wavelength side of the maximum, a very weak shoulder is observed. For longer times (1.0-1.5 μs), the absorption maximum is still at 350 nm, the 360 nm bands are gone, and a weak absorption band appears with its maximum at 315 nm. From the first order growth observed for the signal at 315 nm, one is at first inclined to assign this transient as the radical 25 (Figure 26).

This is opposite to the observations for several other aryl carbenes in this work where the radical is observed to absorb at wavelengths 20 to 30 nm longer than its corresponding carbene, but is consistent with the case of di-p-methoxy DPC. The 350 nm species in cyclohexane on 337 nm photolysis of 24 is shown in Figure 27.
Figure 25. Absorption Spectra Obtained on 308 nm Laser Photolysis of 24 in Cyclohexane.
Figure 26. Transient Signals Observed at Various Wavelengths With a Time Window of 1.5 μs After 308 nm Laser Photolysis of 24 in Cyclohexane.
Figure 27. Absorption Spectrum Obtained on 337 nm Laser Photolysis of 24 in Cyclohexane.\textsuperscript{a}

\textsuperscript{a} The vertical markers on the upper trace indicate the time window for the lower spectrum.
For photolysis of 24 in carbon tetrachloride the observed spectra are invariant with time (Figure 28). The transient signals as a function of wavelength with a 3.93 µs observation window are seen in Figure 29. The 355 nm band is assigned as due to the chloro radical 26, with a measured growth lifetime of 60 ns and a decay lifetime of 150 µs.

![Structure of 26]

The carbene is expected to absorb at shorter wavelengths, and its decay is apparent in the 330 nm signal. The trace at 310 nm is a composite of diazo bleaching, fluorescence, carbene decay and an absorption growth. A weak signal with an essentially instantaneous growth and a lifetime of several microseconds is again seen at 410 nm; the species responsible for absorption at this wavelength is at present unknown but could be a DMA-oxygen ylide in analogy to the case of DPC. 56
Figure 28. Absorption Spectra Obtained After Laser Photolysis of 24 in Carbon Tetrachloride.
Figure 29. Transient Signals observed with a Time Window of 3.93 μs after laser photolysis of 24 in carbon tetrachloride.
Photolysis in other solvents gives rise to weak signals. In pyridine, the spectra don't change much with time, indicating one absorbing species (Figure 30). The pyridine ylide 27 is assigned as the source of the 510 nm band.

\[
\text{\includegraphics[width=0.2\textwidth]{27.png}}
\]

The decay lifetime measured at 520 nm is 20 $\mu$s and the growth is instantaneous. At 410 nm, there are 2 apparent components to the decay. This is probably due to overlap of the absorptions of 27 and the 410 nm transient.

For photolysis of 24 in pivalonitrile, a weak (0.002 optical density) broad absorption is seen from 380 to 500 nm immediately after photolysis (0-39 ns). For microsecond times, the spectrum structure does not change, although the broad band decreases and an absorption at 360 nm increases in intensity. For the transient observed at 400 nm, the measured growth lifetime is 175 ns and that for decay is 4 $\mu$s.

Photolysis of 24 in acetonitrile results in a weak broad absorption in the 370-500 nm region for times to 825 ns. The observed maximum is at 380-410 nm with the absorption magnitude decreasing with increasing wavelength. The structure of the absorption envelope indicates perhaps two different absorbers in the 350-525 nm region.
The latter can not be adequately investigated due to the extremely weak signals in this solvent. The signal at 420 nm exhibits an instantaneous growth (i.e. $< 5 \text{ ns}$) and a decay lifetime of 1.5 ms. In pivalonitrile and acetonitrile, the transients at 500 nm can be hypothesized as the ylides formed through the addition of 3 to the corresponding solvents, although the present experimental evidence is insufficient to definitively confirm or disprove such assignments.
Figure 30. Time Evolution of DMA Ylide Spectrum After Laser Photolysis of 24 in Pyridine.
VII. MISCELLANEOUS RESULTS

1-NAPHTHYL CARBENE

Reactions with Solvent

Nitrogen laser photolysis of 1-naphthyl diazomethane, 28 (1-NDM), in acetonitrile at 300 K produces a strongly absorbing transient with \( \lambda_{\text{max}} \) 390 nm and a lifetime of 100 \( \mu s \) (Figure 31). This band is assigned as that of the nitrile ylide 30.60,63

\[
\begin{align*}
\text{28} & \xrightarrow{\text{hv}} \text{29} \xrightarrow{\text{CH}_3\text{CN}} \text{30}
\end{align*}
\]

The reaction of carbene 29 with acetonitrile in benzene is observed to proceed with a rate constant of \( 4.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \). Based on the work of Huisgen87, Padwa88, and Schmid89, the nitrile ylide is expected to undergo dipolar addition reactions with electron poor olefins. The 390 nm transient is found to react with electron deficient olefins
such as acrylonitrile, fumaronitrile and diethyl fumarate with rates of $10^6$ to $10^8$ M$^{-1}$ s$^{-1}$.

Padwa$^{88}$ and Schmid$^{89}$ report that photolysis of azirines also produces nitrile ylides. Barcus et al.$^{84}$ claim that 308 nm photolysis of 31 in acetonitrile produces a transient spectrum identical to that for the 337 nm photolysis of 1-NDM in the same solvent (Figure 31).

It is necessary to use 308 nm excitation for 31 since the azirine does not absorb appreciably at 337 nm. Quenching of the transient seen on photolysis of 31 with acrylonitrile and diethyl fumarate$^{84}$ proceeds with the same rate constants as those for the 390 nm band on photolysis of 28 in acetonitrile.

Chemical evidence in support of the ylide assignment exists.$^{84}$ Photolysis of 28 (0.18 gm, 20 ml acrylonitrile, 150 ml benzene; 450 W Hanovia-corex filter; 30 min) gives heterocycles 32 and 33 which are formed from the ylide. As expected from Scheme 4, the ratio of carbene derived products (cyclopropanes 35 and 36) to ylide derived products (heterocycles 32 and 33) depends on the acrylonitrile concentration. High concentrations of acrylonitrile favor carbene chemistry, while low concentrations lead to larger yields of ylide products. Diazirine 34 is used for product studies as 1-NDM, 28, reacts rapidly with acrylonitrile to form pyrazolines 37 and 38. The pyrazolines are used to synthesize cyclopropanes 35 and 36.
Figure 31. Transient Absorption Spectra Obtained on Laser Flash Photolysis of 1-Naphthylazo methane (337 nm, top) and of Azirine 31 (308 nm Excitation) in Acetonitrile.
Scheme 4

(Np = 1-Naphthyl)

\[ \text{Scheme 4} \]

\[ \text{(Np = 1-Naphthyl)} \]

\[ \begin{align*}
\text{Np} & \equiv \text{N=C-N} \\
\text{37, 38} & \rightarrow \\
\text{Np} & \equiv \text{N=C-N} \\
\text{35} & + \\
\text{Np} & \equiv \text{N=C-N} \\
\text{36} & \\
\end{align*} \]

\[ \begin{align*}
\text{Np} & \equiv \text{N=C-N} \\
\text{34} & \rightarrow \\
\text{Np} & \equiv \text{N=C-N} \\
\text{37} & + \\
\text{Np} & \equiv \text{N=C-N} \\
\text{38} & \\
\end{align*} \]

\[ \begin{align*}
\text{Np} & \equiv \text{N=C-N} \\
\text{31} & \rightarrow \\
\text{Np} & \equiv \text{N=C-N} \\
\text{32} & + \\
\text{Np} & \equiv \text{N=C-N} \\
\text{33} & \\
\end{align*} \]
The reaction of a carbene with a nitrile to form an ylide is well preceded. This type of process was first suggested by Magee and Shechter and later by Sheppard and Kende and coworkers. Our laser flash photolysis data for 1-NDM in acetonitrile is very similar to Schuster's data with 9-diazofluorene (DAF) in the same solvent. In collaboration with Drs. J. C. Scaiano and David Griller of NRCC we report results of a reinvestigation of the laser flash photolysis of DAF in acetonitrile (Scheme 5). The band at 400 nm which was originally attributed to triplet fluorenylidene is actually the nitrile ylide. The 470 nm band, originally assigned as singlet fluorenylidene, is now accepted to be triplet fluorenylidene. The 500 nm band was earlier shown to be due to the fluorenyl radical by Scaiano et al. The low lying singlet state of fluorenylidene has not yet been detected in absorption. The revised assignments are in good agreement with recent work from Schuster's laboratory.

Nitriles are not the only functional group that can react with carbenes to form unstable ylides. Flash photolysis of 28 in acetone gives rise to a transient absorption with $\lambda_{\text{max}}$ 520 nm and a lifetime of 2 $\mu$s. In pyridine solvent, a transient is observed with $\lambda_{\text{max}}$ 535 nm and a lifetime longer than 100 $\mu$s. Photolysis of 28 in triethylamine leads to an absorption maximum at 363 nm and a weaker band at 483 nm (Figure 32). The measured lifetimes of these transients are 1.2 $\mu$s and 300 ns, respectively. The long wavelength bands in all solvents are assumed to be the ylides 40-42, respectively.
Scheme 5

\[
\begin{align*}
&\text{N}_2 \quad \text{hv} \quad \text{CH}_3\text{CN} \\
&\text{Not yet observed} \\
&\text{400 nm} \\
&\text{470 nm} \\
&\text{500 nm} \\
\end{align*}
\]
Figure 32. Absorption Spectra Obtained as a Function of Time After Nitrogen Laser Photolysis of 1-NDM, 28, in Triethylamine.
Ylides 40 and 41 are observed to react with electron deficient olefins with absolute rate constants between $10^4$ and $10^8$ M$^{-1}$ s$^{-1}$. Product studies analogous to those for the nitrile ylides derived from acetonitrile are in progress.$^{94}$ The spectroscopic assignments cannot be considered secure until the product studies are completed.

Nitrogen laser flash photolysis of 28 in cyclohexane produces a sharp absorption band at 363 nm (Figure 33). This species is assigned as the 1-naphthylmethyl radical 43, in good agreement with the spectrum of this radical reported by Porter.$^{95}$ A growth lifetime of 175 ns is measured and decay occurs by apparently clean second order kinetics.

Excimer (308 nm) photolysis of 28 in cyclohexane provides anomalous results. For a $5 \times 10^{-4}$ M diazo solution, the spectra shown in Figure 34 are obtained. The upper trace shows the signal at 370 nm, with the vertical markers indicating the time window for the corresponding spectra. The spectra are similar to those observed for 337 nm laser photolysis of 28 with $\lambda_{\text{max}} = 363$ nm and a weaker band at 420 nm. Excimer photolysis of a $5 \times 10^{-6}$ M solution leads to the
Figure 33. Radical 43 Absorption Spectrum Obtained After 337 nm Laser Photolysis of 28 in Cyclohexane.
Figure 34. Absorption Spectra Seen on 308 nm Photolysis of 28 in Cyclohexane.\textsuperscript{a}

\textsuperscript{a} The vertical markers in upper traces denote the spectral windows for the corresponding spectra.
observation of a transient at 4 to 8 µs after photolysis with a $\lambda_{\text{max}}$ of 420 nm (Figure 35). The signals obtained as a function of wavelength with a total time window of 78 µs are given in Figure 36. The growth and decay characteristics of the signals are the same at most wavelengths and are assumed to be due to secondary photolysis products. The identity of the 420 nm transient is assumed to be the ylide formed through carbene reaction with oxygen, in analogy to the findings for DPC.56

Nitrogen laser photolysis of 1-NDM, 28, in Freon 113 (1,1,2-trichloro-1,2,2-trifluoro ethane) gives spectra with weak absorptions at $\lambda_{\text{max}}$ 380, 410, and 510 nm (Figure 37). The growth lifetimes measured at 375 and 420 nm are the same as the decay lifetime at 530 nm (1 µs). This implicates the 530 nm transient as the precursor to those at shorter wavelengths. It is possible that this is a weak band of the triplet carbene 29, as this band disappears on the addition of 38 mM of methyl styrene. Trozzolo reports a strong absorption band at $\sim$ 300 nm and a weaker visible band for several diaryl carbenes, as well as similar absorption spectra for triplet carbenes and their corresponding radicals.5,47 As triplet carbenes generally absorb at 30 nm shorter wavelength than their radicals49,62g,63, we expect the $\lambda_{\text{max}}$ for carbene 29 to be at 333 nm

\begin{center}
\begin{tikzpicture}
\begin{scope}[scale=0.5]
\node at (0,0) {};
\end{scope}
\end{tikzpicture}
\end{center}
(radical 43 has an observed $\lambda_{\text{max}}$ of 363 nm). The strong band proposed for the triplet carbene overlaps severely with the laser line (337 nm) and with an absorption maximum of the diazo precursor. The latter effect is assumed to be the main source of the severe sample bleaching observed. Consequently the triplet carbene is not detected in our experiments.
Figure 35. Transient Spectrum for the 308 nm Laser Photolysis of a $5 \times 10^{-6}$ M Solution of 28 in Cyclohexane.
Figure 36. Transient Signals Seen on 308 nm Laser Photolysis of 1-NDM, 28, in Cyclohexane.
Figure 37. Absorption Spectrum Seen on 337 nm Photolysis of 28 in Freon 113.\textsuperscript{a}

\textsuperscript{a}Vertical markers on upper trace indicate time window for spectrum.
Reactions with Aromatic Organometallic Compounds

The addition of tetraphenyl silane (Ph₄Si) to a solution of 1-NDM in Freon 113 leads to an instantaneous transient growth at 410 nm. The signal decay appears to be second order. The overall spectral parameters are not changed from those seen in Freon 113 in the absence of the organometallics. In the presence of tetraphenyl lead and tetraphenyl tin, laser photolysis leads to a sharp absorption with λ_max 380 nm and a broad band from 390 to 500 nm (Figure 38). The former band is assumed to be the transient formed through reaction of the carbene with Freon 113, either the chloro radical shown below or an ylide.

For 28 with the latter two compounds in benzene, the absorption spectrum seen on laser photolysis exhibits only a weak, broad band from 480 to 350 nm and bleaching at lower wavelengths (Figure 38). For UV spectra of the organometallics alone in benzene, only the silyl sample absorbs significantly at 337 nm. This indicates that the radiation is absorbed only by the diazo compound and that the carbene reacts with the ground state of the organometallic compound, if at all.
Figure 28. Absorption Spectrum Obtained on 337 nm Photolysis of 1-NDM, \textsuperscript{28} and Tetraphenyl Lead in Freon Solvent and in Benzene.
Reactions with Substituted Benzonitriles

Photolysis of 28 in benzonitrile produces a strong ylide absorption at 390 nm, with a growth lifetime of 111 ns (Figure 39). For an examination of the effect of substituents on benzonitrile on the rate of the reaction with carbene 29 to form a nitrile ylide, absorption spectra are obtained from the photolysis of the substituted benzonitriles and 1-NDM in benzene solvent. The substrates used are the 2-chloro, 3-chloro, 2-bromo, and 3-bromo derivatives of benzonitrile. In these trials 0.1 g of substituted benzonitrile is placed into a 3 mm x 7 mm quartz sample cell along with 1 ml of 0.1 mM diazo in benzene solution. The static cells are deaerated through bubbling with nitrogen. Photolysis leads to the spectra labeled A in Figures 40-45. The are observed to be the same for the substituted nitrile ylides as for the unsubstituted case. This indicates an insensitivity of the position of the observed chromophore absorption to the nature of the nitrile group substituents. The same was noted earlier in spectra of the ylides formed from the photolysis of 1-NDM in acetonitrile, benzonitrile and pivalonitrile.

Spectra are also presented for the photolysis of 28 in benzene to which aliquots of stock solutions of the benzonitrile derivatives are added. Several of the compounds used in the preparation of stock solutions are noted to be impure. The results are given in the B spectra of Figures 40-45. The ylide band is decreased in intensity or
missing completely, and the numerous new absorptions are attributed to
transients formed through reaction with impurities. The traces at 540
and 590 nm for the 3-chloro benzonitrile samples (B series) indicate a
growth and decay of the absorption on similar time scales (Figure 42).
It is not known whether the traces result from overlapping absorptions
or to a single absorbing transient. No further data exists for these
systems at present.
Figure 39. Absorption Spectrum of Ylide Formed on Photolysis (337 nm) of 1-NDM, 28, in Benzonitrile Solvent.
Figure 40. Absorption Spectrum Obtained on 337 nm Photolysis of 28 and 0.1 g of 2-Chloro Benzonitrile in Benzene Solvent.
Figure 41. Absorption Spectra Obtained on 337 nm Photolysis of 1-NDM and 3-Chloro Benzonitrile in Benzene Solvent. &

&See text for explanation of A and B spectral labels.
Figure 42. Transient Absorptions Observed on 337 nm Photolysis of 1-NDM, 28, and 3-Chlorobenzonitrile in Benzene.³

³These transients could result from impurities in the added benzonitrile salt (see text).
Figure 43. Absorption Spectra Observed on 337 nm Photolysis of 28 and 2-Bromobenzonitrile in Benzene.
Figure 44. Absorption Spectra Obtained on 337 nm Photolysis of 28 and 3-Bromo Benzonitrile in Benzene.

See text for explanations of A and B spectral designations.
Figure 45. Absorption Spectrum Obtained on 337 nm Laser Photolysis of 1-NDM and Impure 4-Bromo Benzonitrile in Benzene.
2-NAPHTHYL CARBENE

Nitrogen laser photolysis of 2-naphthyl diazomethane, 44, in acetonitrile gives rise to absorptions at 370 and 390 nm (Figure 46). The absorbing transient, which has a measured growth lifetime of 90 ns, is again assumed to be the ylide formed through reaction of carbene with solvent in analogy to the case of 29 and 30.

\[
\begin{align*}
 &
\end{align*}
\]

1-NAPHTHYL ETHYL CARBENE

Photolysis of 1-naphthyl diazoethane (45, 1-NDE, 2.4 mM) in cyclohexane yields an absorption at \( \lambda_{\text{max}} \) 380 nm (Figure 47). This band is assumed to be due to the radical formed through hydrogen atom abstraction from the solvent. The observed growth lifetime of 1.8 \( \mu \)s is considerably longer than the 143 ns lifetime measured for the 1-naphthylmethyl radical 43. Photolysis of a \( 6 \times 10^{-4} \) M solution of 45 in acetonitrile gives no detectable ylide absorption bands.

\[
\begin{align*}
 &
\end{align*}
\]
Figure 46. Absorption Spectrum Seen on Nitrogen Laser Photolysis of 2-NDM, \( \text{\textsuperscript{44}} \), in Acetonitrile.
Figure 47. Absorption Spectra Obtained on Nitrogen Laser Photolysis of 1-NDE, 45, in Benzene and Cyclohexane Solvents.
1-METHYL (4-BROMONAPHTHYL) CARBENE

Photolysis of 1-(4-bromonaphthyl) diazoethane (6 x 10^{-4} M, 46) in acetonitrile leads to absorptions with \( \lambda_{\text{max}} \) at 430 and 460 nm. The spectrum obtained for photolysis in cyclohexane indicates a \( \lambda_{\text{max}} \) of 420 nm and a weaker broad shoulder extending to 455 nm (Figure 48). The preliminary results obtained in these trials are insufficient to definitively establish the identity of the absorbing transients.

![Chemical Structure 46](image)

9-ANTHRYL CARBENE

Photolysis of a 6 x 10^{-4} M solution of 9-anthryl diazomethane, 47, in acetonitrile yields the spectrum seen in Figure 49. The \( \lambda_{\text{max}} \) is at 430 nm and a weaker shoulder extends from this band to 480 nm. A weak signal is also observed at 390 nm. Bleaching at 370-390 nm corresponds to the UV absorption maximum of the diazo precursor sample. No rate constants are available for these transients.

![Chemical Structure 47](image)
Figure 48. Absorption Spectra Seen on Photolysis of 1-(4-Bromo-naphthyl) Diazoethane, $46_2$ in Cyclohexane (top) and Acetonitrile Solvents.
Figure 49. Absorption Spectrum Obtained on 337 nm Laser Photolysis of 9-Anthryl Diazomethane, $\text{^A}_2$, in Acetonitrile.
1-PYRENYL CARBENE

Nitrogen laser photolysis of 1-pyrenyl diazomethane, 48, in cyclohexane gives rise to the spectrum in Figure 50. The $\lambda_{\text{max}}$ is located at 420 nm and weaker absorptions are seen at 595 and 635 nm. No transient lifetimes are available nor are any transient assignments proposed, as further spectroscopic and product studies are required.
Figure 50. Absorption Spectrum Obtained on 337 nm Laser Photolysis of 1-Pyrenyl Diazomethane, 48, in Cyclohexane.
VIII. SUMMARY

Nanosecond flash photolysis techniques are used to study the reactivities of several diarylcarbenes in solution at room temperature. Photolysis of diaryl diazo precursors yields transients whose absorption spectra can be recorded in various solute/solvent systems and conclusions derived about the nature of the reactive transients.

Excimer laser (308 nm) photolysis of diphenyl diazomethane yields the absorption spectrum of the triplet carbene which decays in about 1 microsecond. In the presence of hydrogen or chlorine donor solvents the absorption of the benzhydryl or chloro diphenylmethyl radical is easily detected at 330-340 nm. Quenching studies with various olefins, hydrogen donor species, and methanol using the 334 nm benzhydryl as a probe indicate predominantly triplet reactivity for diphenylcarbene. These findings are in agreement with those of early product studies.24,25

Photolysis studies of a series of para substituted diphenyl diazomethanes indicate similar radical like behavior for diphenyl carbene and its chloro, bromo, and methyl derivatives. Spectra obtained in hydrogen donor solvents are similar to those for the benzhydryl radical, indicating a large sigma character to the reactive
An Arrhenius treatment of the data for the methanol quenching of the carbenes reveals a significantly larger log A value for di-p-tolyl carbene than for the parent DPC. Photolysis of di-p-substituted methoxy and dimethylamino DDM leads to unusual spectra, the origin of which cannot be assigned with reasonable certainty at present.

Results for the photolysis of 5-diazo-10,11-dihydro-5H-dibenzo[a,d]cycloheptene lead to the assignment of largely triplet reactivity for carbene 4. Spectra are given for the carbene and for radicals formed through hydrogen and chlorine abstractions from solvent, as well as for radical 16 formed through reaction of 18 and t-butoxy radical. The rates for carbene quenching of 4 with various hydrogen donors are 2 to 40 times slower than the corresponding rates for diphenylcarbene. The conclusions from our kinetic studies are in good agreement with earlier spectroscopic and product analyses. 48, 82

The generation of 10,10-dimethyl-9-anthrorylidene, 3, from its diazo precursor leads to complex spectra in different solvents. The carbene reacts with methanol with a rate constant of $4 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$. This large reactivity is attributed to a small singlet-triplet splitting in the carbene and reaction primarily from the singlet state. This can result either from the small carbenic angle or to effects due to the presence of the methyl groups. The chloro radical is observed in carbon tetrachloride and an ylide formed in pyridine.

Laser photolysis of 1-naphthyl diazo methane generates the corresponding carbene, whose triplet absorption spectrum is not observed on the time scale of our experiments. In acetonitrile solvent an ylide
absorption is observed at 390 nm. The ylide assignment is easily
confirmed through quenching studies of the carbene in benzene and of
the ylide in different solvents by electron deficient olefins and
through generation of the ylide from the corresponding azirine
compound. The observed reactivity of the 1-naphthyl carbene leads
to the assignment of principally singlet reactivity or of a composite
of singlet and triplet processes.

Since 1-naphthyl carbene is not expected to have a small carbenic
angle yet exhibits singlet reactivity similar to fluorenylidene and
DMA, it is unlikely that a simple correlation exists between bond angle
and singlet-triplet splitting. It is more likely that the S-T gap and
the reactivities observed in the different diazos is dictated by the
hybridization of the carbene and the possible mixing of the different
spin states, which is expected to depend on structural as well as
substituent effects. Figure 51 shows the separation of the carbenes
into spin state categories based on their observed reactivities with
methanol.
Triplet Reactions

\[ \text{苯} \Rightarrow \text{苯} \]
\[ \text{芴} \Rightarrow \text{芴} \]
\[ \text{R, R'} = \text{CH}_3, \text{OCH}_3, \text{N(CH}_3)_2 \]

Singlet Reactions

\[ \text{二苯甲基} \Rightarrow \text{二苯甲基} \]
\[ \text{二苯甲基} \Rightarrow \text{二苯甲基} \]
\[ \text{R, R'} = \text{CH}_3, \text{OCH}_3, \text{N(CH}_3)_2 \]

Singlet GS

\[ \text{苯} \Rightarrow \text{Cl} \]

Figure 51. Reaction Pathways for Several Carbenes
APPENDIXES

Appendix 1

For concurrent first order reactions of the triplet carbene (T) with solvent cyclohexane (CH) to form the radical (R) and with added quencher styrene (Sty) to form the biradical, the following mechanism is proposed:

\[ T + CH \overset{k_1}{\rightarrow} \text{Radical} \]
\[ T + \text{Sty} \overset{k_2}{\rightarrow} \text{Biradical} \]
\[ T \overset{k^*}{\rightarrow} \text{products} \]

In this scheme, it is assumed that reactions occur primarily from the triplet state of DPC, and not by intersystem crossing back to the singlet. The latter is expected to give an addition or insertion product with styrene. It is further assumed that triplet dimerization, azine formation, and reactions with adventitious impurities are not significant decay pathways and can be included in the first order rate constant \( k^* \).

The rate of disappearance of the triplet state can be expressed as:

\[
(A.1) \quad - \frac{d(T)}{dt} = \left\{ k_1 (CH) + k_2 (Sty) + k^* \right\} (T) - k(T)
\]

with \( k \) equal to the experimentally determined rate constant. Integration of (A.1) leads to the first order rate expression for the triplet concentration:

\[
(A.2) \quad (T) = T_0 \exp(-kt).
\]
From (A.2) it is expected that $T_0$ is zero.

Similarly, the rate of formation of the diphenylmethyl radical (R) is given by

$$\frac{d[R]}{dt} = k_1 (CH) (T)$$

which when combined with (A.2) leads to (A.3).

(A.3) \[ \frac{d[R]}{dt} = k_1 (CH) T_0 \exp (-kt). \]

Integration of (A.3) between 0 and $t$, with the assumption that $R_0$ is zero, leads to

(A.4) \[ R_t = \frac{T_0 k_1 (CH)}{k} \left\{ 1 - \exp (-kt) \right\}. \]

The maximum amount of radical formed is expected at "infinite" times after photolysis, i.e. when the decay of the triplet is complete.

(A.5) \[ R_\infty = \frac{k_1 (CH)}{k} T_0 \]

Rearrangement of (A.5) leads to an expression for $T_0$, which cannot be easily determined experimentally since its extinction coefficient is unknown.

(A.6) \[ T_0 = \frac{R_\infty}{k_1 (CH)} \]

Subtracting (A.4) from (A.5) and using (A.6) for the initial triplet concentration leads to

$$R_\infty - R_t = R_\infty \exp (-kt)$$

or, on rearranging,

(A.7) \[ \log \left\{ \frac{R_\infty}{R_\infty - R_t} \right\} = 0.4343 \text{kt}. \]
If Beer's law is applicable to the radical absorption at 334 nm and only the radical absorbs at this wavelength, equation (A.7) can be alternatively expressed as:

\[
(A.8) \quad \log \left( \frac{A_t}{A_0 - A_t} \right) = 0.4343 t.
\]

Here, \( A_t \) is the optical density of the sample measured at 334 nm at time \( t \) after the laser pulse and \( A_0 \) is the radical absorption when its growth is complete and before decay has begun. A plot of the left-hand side of (A.8) as a function of time yields the expression for the experimental rate constant \( k \) which includes all possible first order reactions of the triplet, according to:

\[
k = k_1 (CH) + k_2 (Sty) + k'.
\]

In order to determine \( k_2 \), the rate constant for reaction of the carbene with styrene, \( k \) is measured as a function of styrene concentration. Assuming that the concentrations of cyclohexane and impurities remain constant, the following relation holds:

\[
(A.10) \quad k = k_2 (Sty) + k_0
\]

The slope of a plot of the experimentally determined rate as a function of the corresponding concentration of styrene is \( k_2 \) and the intercept is \( k_0 \) (equal to \( k' + k_1 (CH) \)).
Thus, although the growth of the radical formed through hydrogen abstraction by the carbene from the solvent cyclohexane is monitored, the measured growth lifetime at 334 nm is used to determine the rate constant for styrene quenching of the triplet carbene. The latter reaction is expected to form biradical $B$.

\[
\begin{array}{c}
\text{Ph}_2\text{CH} \\
\sim \\
\text{B}
\end{array}
\]

The relation between the product ratio and the ratio of the rates for the corresponding reactions is the following:

\[
\frac{\text{Radical Yield, } R}{\text{Biradical Yield, } B} = \frac{k_1(\text{CH})}{k_2(\text{Sty})}.
\]

It is important to note here that although the relative yields of the products are proportional to the relative rates of formation of each, the observed rate of formation of one of the products (i.e., the radical) is the **total** first order rate constant for carbene reaction.
Appendix 2

It has been observed that the temperature dependence of the rate constant of an elementary reaction in most cases is adequately described by the Arrhenius equation and is represented as

(B.1) \[ k = A \exp \left( -\frac{E_a}{RT} \right) \]

or alternatively as

(B.2) \[ \ln k = \ln A - \frac{E_a}{RT}. \]

If this equation is applicable to the observed reaction kinetics, then a plot of \( \ln k \) as a function of the inverse absolute temperature yields the Arrhenius activation energy from its slope and \( \ln A \) as its intercept. The formulation proposed by Arrhenius\(^6\) is

(B.3) \[ \frac{d \ln k}{dT} = \frac{E_a}{R T^2}. \]

If \( E_a \) is independent of temperature then integration yields equation (B.1), where \( A \) is merely the constant of integration and is prone to a large degree of uncertainty. This is the form of the relation used by physical organic chemists, with the derived parameters assumed to be those associated with a single simple process. Reaction rate theories such as collision theory and transition state theory define the various parameters in (B.1).

It is also possible that \( E_a \) is not independent of temperature (e.g. if the reaction mechanism changes over the observed temperature
range), in which case the A value calculated from the experimental results concurrently changes with the variation in the activation energy. More often, A is dependent on temperature and temperature.

\[(B.4) \quad k = A^* T^n \exp \left( -\frac{E_a}{RT} \right) \]

is used. Here \( n \) can have any value dictated by experiment.97

According to collision theory, the pre-exponential factor \( A \) is the product of two terms, the collision number \( Z \) and the steric factor \( P \). The \( P \) factor is related to the effectiveness of the collisions through the entropy changes associated with the formation of the activated complex. This term is dependent on the molecular orientation of the reactants on collision, as well as on many other factors (e.g. the degree of rotation of the various parts of the complex, etc). The rate can be expressed as98

\[(B.5) \quad k = P Z \exp \left( -\frac{E_a}{RT} \right). \]

The \( Z \) factor can itself be temperature dependent.

According to transition state theory, the reaction rate constant is defined as98

\[(B.6) \quad k^* = \left( \frac{k T}{\hbar} \right) \exp \left( \frac{\Delta S^\pi}{R} \right) \exp \left( -\frac{\Delta H^\pi}{RT} \right). \]

where \( k^* \) is the observed rate constant, \( \Delta S^\pi \) and \( \Delta H^\pi \) are the reaction activation parameters, \( k \) is the Boltzmann constant, and \( \hbar \) is the transmission coefficient over the reaction barrier. If relation (B.6) is applicable and \( A \) varies as a function of temperature, a plot of \( \ln (k/T) \) as a function of the inverse temperature is necessary in the determination of the enthalpy of activation for the reaction.
In this viewpoint, the rate of reaction is determined by the enthalpy and entropy changes involved in the formation of the transition state. \( H \) is related to the potential energy barrier for the reaction. In the transition state interpretation of the pre-exponential factor,

\[
A = \left( k T \frac{h}{b} \right) \exp \left( \frac{\Delta S^\pm}{R} \right).
\]

A small \( A \) factor indicates an improbable complex (\( \Delta S^\pm \) is negative), while a large \( A \) factor is indicative of a very probable or "loose" complex (\( \Delta S^\pm \) is positive).

An alternative representation of (B.6) is

\[
\frac{d \ln k'}{dT} = \frac{\Delta H^\circ}{R T^2} + \frac{R T}{R T^2}
\]

where \( \Delta H^\circ \) is the standard enthalpy of activation for the reaction.\(^{98}\)

The use of a free-energy function in a time-dependent system implies that the time scale for the reaction is long compared with that required for the molecules to come into statistical equilibrium with respect to the degrees of freedom determining the thermodynamic state. This is predicted to be true for all reactions except a few which may occur at "extraordinary" speeds.\(^{98}\)
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