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Kinetic Studies on Diarylcarbenes[1]

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Received April 6, 1976

Abstract: Flash spectroscopic studies of diarylcarbenes have indicated optimal wavelength maxima for observation by kinetic spectrophotometry. In benzene solution at 25 °C, the second-order dimerization rate constants of diphenylcarbene, *p,p'*-dibromodiphenylcarbene, and *p,p'*-dimethyldiphenylcarbene were found to be 5.4, 3.5, and 1.1×10^9 M^{-1} s^{-1}, respectively. The absolute rate constants for reaction of 1,3-butadiene with the above carbenes are all 6.4×10^5 M^{-1} s^{-1}. The quotient of the absolute rate constant of reaction of singlet diphenylcarbene with methanol, k_{me}, and the singlet–triplet carbene equilibrium constant, K, has been determined to be $k_{me}/K = 6.8 \times 10^6$ M^{-1} s^{-1}. Steady-state competition experiments for the pairs oxygen–methanol, methanol–styrene, butadiene–styrene, and styrene–1,1-diphenylethylene were performed. These indicate the absolute rates of reaction of diphenylcarbene with styrene, 1,1-diphenylethylene, and oxygen to be 3.8×10^5, 4.8×10^5, and 1.0×10^9 M^{-1} s^{-1}, respectively. The results of the oxygen–methanol experiment, in conjunction with similar experiments performed under different conditions, suggest that k_{me} is near the diffusion limit. This fact, taken together with the experimental value of k_{me}/K, implies that $-\Delta H \approx 3$ kcal/mol, where $-\Delta H$ is the singlet–triplet energy splitting of diphenylcarbene.

During the last two decades much progress has been made in the chemistry of divalent carbon compounds. As an overview[3,4] of the literature will quickly show, most of the advances were made in the areas of structural information and in the exploration of new reactions involving carbenes. Despite the vast amount of data collected on relative reactivities of various carbenes with a great spectrum of substrates, relatively little quantitative kinetic information has been reported. To our knowledge not a single rate constant is known for a reaction of a carbene with an olefin in fluid solution, one of the most fundamental and useful carbene reactions.

Another topic of carbene chemistry that has drawn much attention follows from the close spacing of the lowest singlet and triplet states. Experimental efforts have been mostly directed toward establishing the spin multiplicity of the ground state of various substituted methylenes. Numerous theoretical calculations have reported energy differences for the spacing of the lowest states, but only few experiments[5-7] have been directed toward that problem. This information would be very useful because of relatively large discrepancies in the calculations for even the simple triatomic methylene, although recently the values tend to converge to 11 kcal.[8]

Of similar theoretical interest are the kinetics of interconversion between the triplet and singlet states of various carbenes. Indirect observations[9,10] made on several substituted methylenes point to a fast singlet–triplet intersystem crossing in both directions. For the case of diphenylmethylene it appears that the two states of different spin multiplicity convert so fast that they are in effective equilibrium during most reactions, thus preventing the separation of singlet and triplet chemistry. That this behavior is not characteristic for all carbenes has been demonstrated with fluorenylidene,[11,12] where slow reaction rates give predominantly triplet behavior, while in fast reactions the initially formed singlet state has a chance to compete.

To obtain better insight into the mechanistic detail of carbene reactions and to gather the facts necessary for answering some of the questions posed above, we decided to explore the feasibility of obtaining quantitative kinetic data of some simple carbene reactions in solution. In this paper we wish to report the results obtained from a flash photolysis study on some reactions of diphenylmethylene and some of its simple derivatives.[13] Although the reactions studied are by necessity simple and comprise only a tiny fraction of the known carbene reaction types, we believe the results when coupled with other data from relative rate measurements do enhance significantly our understanding of the chemistry of divalent carbon compounds. One other study of an arylmethylene by flash photolysis has been reported; however, no attempts were made to analyze the kinetics.[14]

Experimental Section

Flash Apparatus. The flash spectroscopic apparatus used was provided by Lehman and Berry.[15] Also modelled after their flash kinetic spectrophotometric apparatus, a similar device was built[16] with the following modifications. A Textronix RM503 oscilloscope, a Fairchild 453A oscilloscope recording camera using Polaroid type 47 film, a Beckman DU monochromator (*f*/10), and a Tobe Deutschmann capacitor with specifications of 5 nH, 8 μF, and maximum 25 kV, were used. Delay circuits, consisting of Amelco 342 Dual one shots and associated circuitry, were also employed.

The applicability of Beer's Law was guaranteed by keeping the slit width of the monochromator less than 0.05 mm, so that over the band width of light analyzed, the extinction coefficient of the absorbing carbene varied less than 1%. Also, the absorbance recorded by the optical detection system was linear with the concentration of added absorber (benzophenone) in the flash cell.

The unstable mercury arc analysis lamp did not distort the observed kinetic decay of light intensity because the latter phenomenon occurred on a time scale much shorter than the fluctuations of the lamp. However, the value of the absolute absorbance was in error if the arc lamp were used to measure sequentially the reference voltage, V_{ref} (see Appendix), and then, 2 h later, the transient kinetics. Therefore, prior to and immediately after flashing, a Cary 14 UV spectrophotometer was used to analyze the sample.

Negligible increase in absorbance occurred after flashing either pure benzene or 7.1×10^{-4} M methanol in benzene solution. However, solutions of 1,3-butadiene in benzene underwent a noticeable increase in absorbance after flashing. When correction was made for this self-reaction of butadiene, excellent agreement was observed between the values for the absolute absorbence after flashing a reaction mixture as determined by the Cary 14 and STEPIT optimization (as described in the Appendix).

Sample Preparation. Mallinckrodt reagent grade benzene was dried by refluxing over calcium hydride for 24 h, then distilled under nitrogen directly into the flash photolysis reaction vessel. In runs where methanol was the scavenger the reagent was added at this time. A glass ampule, containing a premeasured amount of a substituted diphenyldiazomethane, was broken and dropped into the reaction vessel, which was reassembled. The reaction vessel was connected to a vacuum line and several freeze-pump-thaw degassing cycles were performed. In runs where butadiene served as the substrate it was determined manometrically and then condensed in the reaction vessel from an attached cylinder. Gas chromatographic analysis of the resulting benzene solution at 25 °C showed that 95% of the butadiene in the reaction vessel resided in the liquid phase.

Steady-State Photolyses. Reaction mixtures of 10-ml volume were freeze-thaw degassed three times and the sealed 20-ml glass ampules were irradiated for 3 min at 22 °C with an Eimac 150-W xenon arc lamp. At the desired levels of methanol concentration, infrared analysis showed that an appreciable amount of the alcohol existed as hydrogen-bonded aggregates in hydrocarbon solvents. Acetonitrile was therefore selected as a solvent.

The competition reactions between methanol and oxygen for diphenylcarbene involved a sample preparation different from that followed in the case where the very condensable butadiene was used as reactant. After degassing an acetonitrile solution of diphenyldiazomethane and methanol, the liquid phase was magnetically stirred to facilitate equilibration with an atmosphere containing a desired pressure of oxygen. Knowledge of the Ostwald solubility coefficient of oxygen in acetonitrile permits determination of the oxygen concentration.[17]

Product Analyses. Stability of all products of the steady-state photolyses under the reaction conditions was verified. A Varian 1200 flame ionization gas chromatograph with a 5-ft stainless steel column of 3% SE-30 on varaport (120 °C) was used for product analyses of both steady-state and flash experiments.

Flash photolysis reaction mixtures were concentrated and trimethylsilylated (Pierce Chemicals) to analyze for benzhydrol. Identification of products was determined by agreement of the GC peak retention times with those of authentic samples of the anticipated products. The report of product analyses on similar reaction mixtures using similar GC conditions justifies this procedure.[18]

Benzophenone azine, which decomposed under the GC conditions, was analyzed by alumina TLC using 1:9 benzene/pentane (v/v). The spots were extracted into ethanol and quantitatively analyzed by their absorption at 278 nm. The same internal standard used for the GC work, 9,10-dibromoanthracene, sufficed for the azine determination and was analyzed at 400 nm. The recovery of both the standard and azine was 65-75% by this procedure. Accurate comparisons between experimental and calculated flash reaction product analyses are precluded because only about 60% of the original diazo compound could be accounted for in terms of identifiable products. This recovery may be appreciated in view of the tiny amount of initial diazo compound, about 40 μg. The experimental product yield mirrored not only the carbene kinetics which occur during a flash, but also the thermal reactions of the residual unreacted diazo compound during work-up.

Table I. Product Analysis of Flash Photolysis Dimerization Reaction: 1.7×10^{-6} M Diphenyldiazomethane in Benzene[a]

	Yield
Compd, found[b]	
Tetraphenylethylene	0.36
Benzophenone	0.09
Benzhydrol	0.06
Benzophenone azine	0.08
Total found mole fraction	0.59
Compd, calcd	
First-order products	0.29
Tetraphenylethylene	0.44
Unreacted $(C_6H_5)_2CN_2$	0.26

[a] Both calculated and experimental yields are expressed in terms of mole fraction of initial diazo compound represented by the indicated product. [b] Tetraphenylethane was not detected.

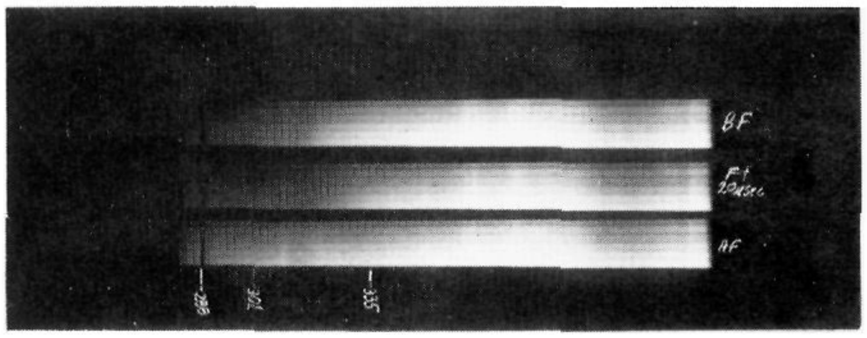


Figure 1. Plates of spectra of diphenyldiazomethane photolysis in benzene. See text for details.

The few percent azine found in the analyses justify the neglect of the azine forming reaction in the kinetic scheme, especially since it is probable that this trace amount was formed during workup.

The product analysis of a flash photolysis dimerization study of diphenyldiazomethane appears in Table I.

Materials. The following reagent-grade chemicals were used without further purification: Aldrich brand benzophenone, benzhydrol, tetraphenylethylene, and 9,10-dibromoanthracene; Baker absolute methanol; National Cylinder Gas Company oxygen; and Matheson Instrument grade 1,3-butadiene.

Aldrich styrene was purified by vacuum distillation at 46 °C (17 mm) from calcium hydride. The styrene distillate was stored at −30 °C.

Baker reagent-grade acetonitrile was further purified, following literature methods.[19] The purified acetonitrile was stored in a glass flask and protected against light.

Diphenyldiazomethane,[20] *p,p'*-dibromodiphenyldiazomethane,[21] and *p,p'*-dimethyldiphenyldiazomethane[22] were synthesized by the mercuric oxide oxidation of the respective benzophenone hydrazone, following standard procedures. Prior to use in an experiment, the diazo compounds were recrystallized from pentane, and the crystals dried in vacuo in the dark at 5 °C. The purity was monitored by UV absorbance.

The following were synthesized by published procedures: benzhydryl methyl ether,[23] 1,1,2,2-tetraphenylethane[24] (mp 208-209 °C). Benzhydryl ether[25] was recrystallized from ether, then pentane (mp 104-106 °C). 2-Vinyl-1,1-diphenylcyclopropane,[26] 1,1,2-triphenylcyclopropane,[27] and benzophenone azine,[28] were also synthesized by published procedures.

Results and Discussion

Diphenylmethylene (I) and its derivatives were chosen as the carbenes to study for several reasons. First, they are easy to generate by photolysis of the corresponding diazo compounds with high quantum yields. The electronic spectra have been determined by matrix isolation techniques and consist of

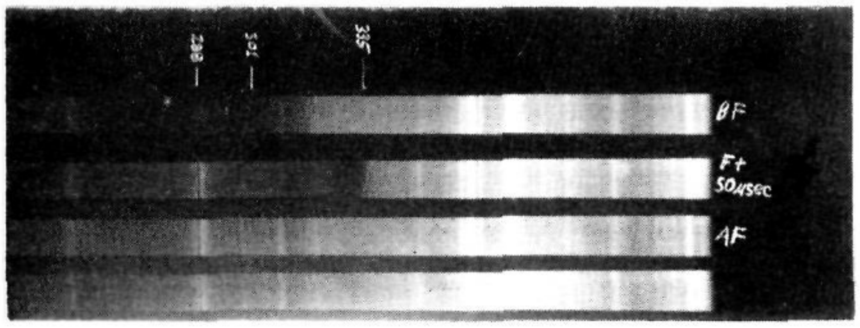


Figure 2. Plates of spectra of diphenyldiazomethane photolysis in cyclohexane. See text for details.

two bands, one in the visible region with low extinction coefficient and a strong absorption in the ultraviolet.[29-31] The structure[32,33] and reactivity[34] of diphenylmethylene have been much studied and are generally well understood. Finally, a more direct confirmation of the possibility of rapid interconversion between singlet and triplet states was highly desirable.

Identification of Transient Carbenes. Before any kinetic studies could be undertaken it was necessary to establish that any transient intermediates detected by optical means did indeed correspond to the sought-after carbenes. This was accomplished by using flash absorption spectroscopy, recording the ultraviolet and visible spectra on photographic plates with various delay times between photolysis and analysis flash. Figure 1 shows representative examples of these experiments. The plates show the absorption spectra obtained from a 1.8×10^{-6} M solution of diphenyldiazomethane in benzene before the photolysis flash, 20 μs after the flash, and minutes after the flash. The features of interest are that the initial absorbance of the diphenyldiazomethane (λ_{max} 288 nm) before the flash is replaced by a very similar absorption centered around 300 nm immediately after the flash. This transient absorption has vanished in the third plate taken long after the flash. A densitometer reading of the plates confirmed the position of the ultraviolet band associated with the transient intermediate to be very close to the reported position of matrix isolated diphenylmethylene. To make sure that the transient absorption did not arise from benzhydryl radical, a separate experiment was performed in which this intermediate was deliberately produced by changing the solvent to cyclohexane. Under these conditions, the carbene abstracts a hydrogen atom from the solvent and is converted to benzhydryl radical. As shown in Figure 2 a new transient species is produced with an absorption maximum at 335 nm. This value is in good agreement with the published spectrum for benzhydryl.[35] Comparison of Figure 1 with 2 clearly shows that no abstraction takes place in benzene solution. It should be noted that under the conditions of the experiment the absorption in the visible region of the spectrum is too weak to appear. When more concentrated solutions are used the amount of residual diphenyldiazomethane is largely increased and interferes with an analysis of the carbene absorption band in the visible region. An apparent complication arises from the overlap of the ultraviolet absorptions of the carbene with that of the diazo precursor. This overlap is less pronounced in the *p,p′*-dibromo-substituted system. Figure 3 shows the absorption spectra obtained from flashing a 3.6×10^{-6} M solution of *p,p′*-dibromodiphenyldiazomethane in cyclohexane with 20, 50, and 300 μs delay times between photolysis and analysis flash. In this case the absorption of the diazo compound (λ_{max} 294 nm) is clearly separated from the carbene absorption (λ_{max} 335 nm), which in turn is different from the *p,p′*-dibromobenzhydryl radical (λ_{max} 350 nm). Comparison of the spectra with the increasing delay times shows a good conversion to the carbene and the replacement of the transient attributable to the carbene by a new transient feature originating from the radical.

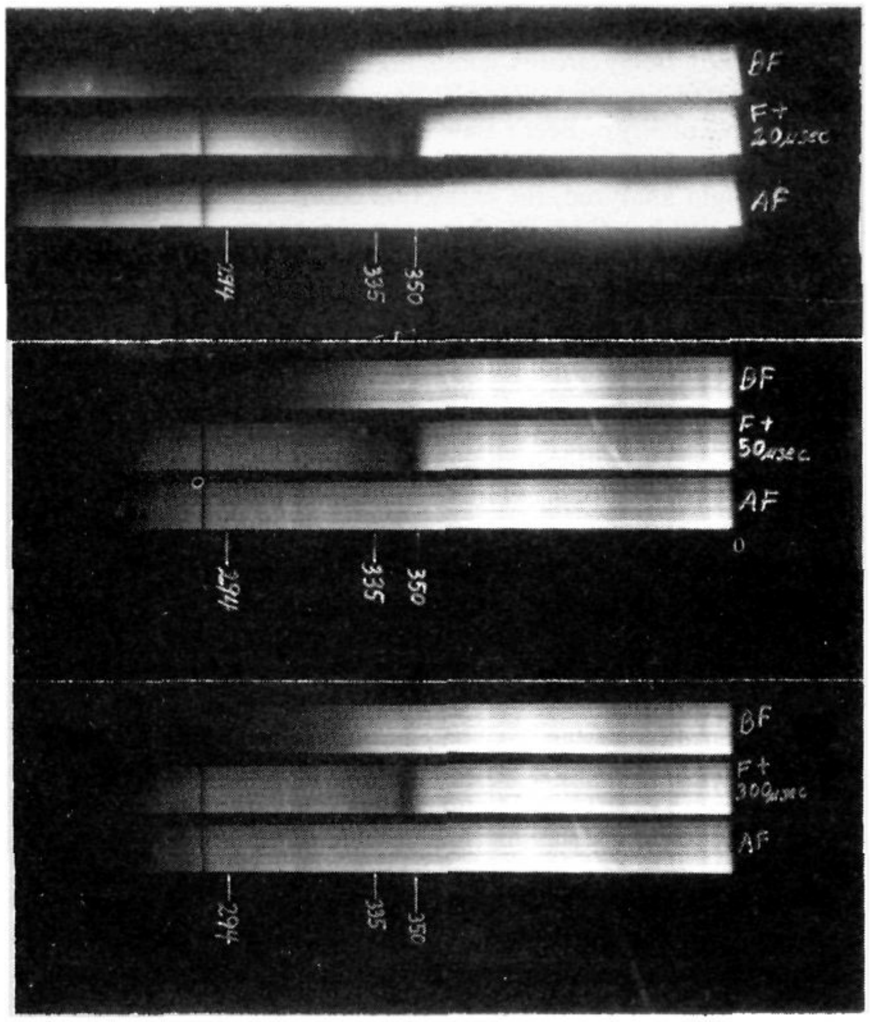


Figure 3. Plates of spectra of *p,p′*-dibromodiphenyldiazomethane photolysis in cyclohexane with various delay times. See text for details.

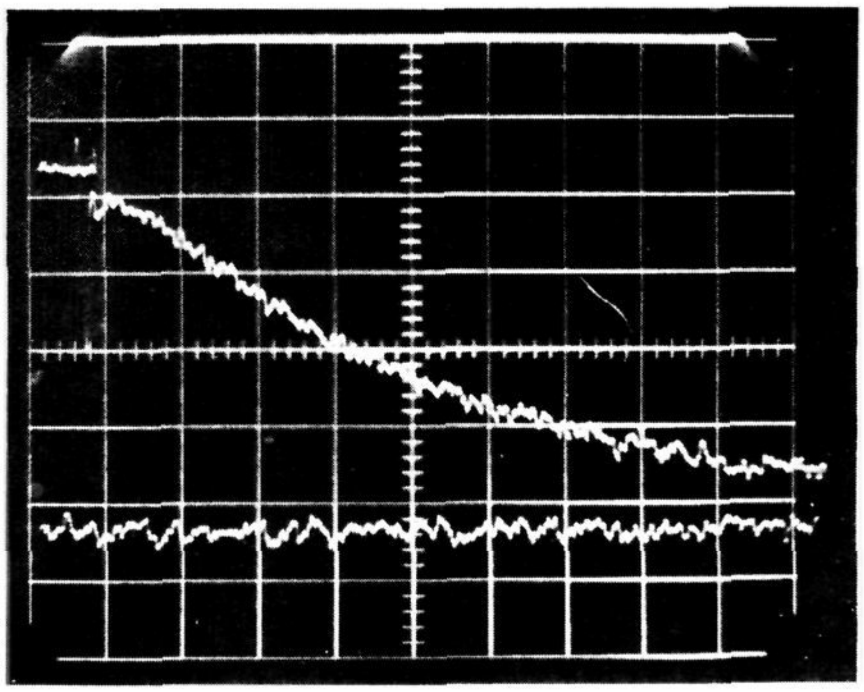


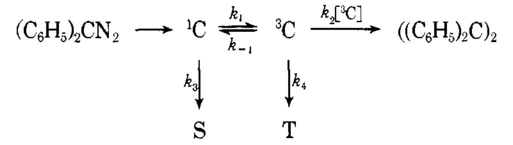
Figure 4. Typical flash photolysis oscillogram monitoring the absorption at 301 nm. Time axis: 50 μs per division.

Kinetic Spectrophotometric Analysis. After the spectral identification of the carbene intermediates had been successfully demonstrated it became desirable to follow the decay kinetics of the transients. The optical density of the solution was monitored at the mercury resonance line at 303 nm, close to the absorption maximum of I (301 nm). A typical oscillogram is shown in Figure 4. The evaluation of the raw data of the oscillogram was performed as detailed in the Appendix and yielded optical density as a function of time. Since the optical density is related to the species i by

$$A(t) = l \sum_i \epsilon_i [C_i(t)] \qquad (1)$$

it is necessary to discuss the data in terms of specific reaction schemes. The function $[C_i(t)]$ can then be evaluated in terms of initial concentrations and specific rate constants, the latter

Scheme I



$$\begin{tikzcd}(C_6H_5)_2CN_2 \arrow[r] & {}^1C \arrow[r, shift left, "k_1"] \arrow[d, "k_3"'] & {}^3C \arrow[l, shift left, "k_{-1}"] \arrow[r, "k_2[^3C]"] \arrow[d, "k_4"] & ((C_6H_5)_2C)_2 \\ & S & T & \end{tikzcd}$$

being fitted to the experimental data via a nonlinear multiparameter least-squares search routine. The routine used was the subroutine STEPIT developed by Chandler.[36] It should be pointed out that although the initial concentration of diphenyldiazomethane was known, the fraction (N) converted to the carbene varied from experiment to experiment and was treated as a variable parameter in the least-squares fit.[37]

The first series of experiments were concerned with the decay kinetics of the carbene in the "inert" solvent benzene. At high conversion fractions the predominant reaction should be the dimerization of the carbene yielding tetraphenylethylene. This is in contrast to steady-state photolysis where the major product is tetraphenylazine, resulting from the reaction of the carbene with unreacted diphenyldiazomethane. Product analysis of flashed dilute solutions of diphenyldiazomethane confirmed that tetraphenylethylene was the major product and only small amounts of azine were found (see Experimental Section). However, due to the fact that the experiments were carried out at extreme dilution (10^{-6} M) small amounts of benzophenone and benzhydrol were also detected. Presumably traces of oxygen and water were responsible for the formation of these products.

The kinetics of the disappearance of diphenylmethylene (C) in benzene were analyzed by the computer fitting of the data to the rate law

$$-\frac{d[C]}{dt} = k_2[C]^2 + k_f[C] \qquad (2)$$

where diphenyldiazomethane, diphenylcarbene, and tetraphenylethylene have been included as the absorbing species. The small amount of azine was not specifically taken into account because its neglect does not contribute much to the estimated errors.

The second-order component of the rate law is most reasonably attributed to the dimerization of the carbene. At this point it becomes necessary to propose a reaction scheme serving as the basis for discussion. It is reasonable to assume, though not proven, that the photolysis of diphenyldiazomethane initially yields the carbene in the singlet state. The next assumption to be made is that of a rapid equilibrium between the singlet and triplet. A suitably simplified sequence is shown in Scheme I, where ^1C and ^3C are the singlet and triplet carbene, respectively, k_1 and k_{-1} are the intersystem crossing rate constants, and k_2 is the triplet dimerization rate constant. The pseudo-first-order rate constants k_3 and k_4 describe the scavenging rates of the carbene to give singlet and triplet derived products S and T. Clearly this scheme does not include all possible reactions. For example, singlet–triplet and singlet–singlet dimerization steps are omitted. This simplification is justified by the following considerations. ESR studies have established the carbene to have a triplet ground state. With rapid intersystem crossing the concentration of the singlet state should be small at any given time, thus making dimerization via the singlet a minor pathway. Also, there is no spectroscopic evidence for any significant concentration of another transient, such as the singlet state of the carbene. The consequences of this simplification being in error are considered in the Appendix.

The observed first-order component of the decay kinetics is not readily attributed to any specific reaction in the absence of any scavengers. The most likely explanation is reaction with small amounts of impurities, such as oxygen and water. The concentrations required of impurities to give pseudo-first-order behavior are in the order 10^{-5} M.

Table II. Rate Constants of Carbene Dimerizations in Benzene Solution at 25 °C[a]

Carbene	k_2, $M^{-1}\,s^{-1} \times 10^{-9}$ [a]
$(C_6H_5)_2C$:	5.4 ± 1.6
$(p\text{-}BrC_6H_4)_2C$:	3.5 ± 1.1
$(p\text{-}CH_3C_6H_4)_2C$:	1.1 ± 0.3

[a] The rate constant k_2 is defined in accordance with the rate law for carbene C: $d[C]/dt = -k_2[C]^2$. [b] The error limits are estimates of the probable cumulative error.

Evaluation of the oscillograms (see Appendix for the analysis of the kinetics) gave second-order rate constants as shown in Table II. We equate these rate constants with the dimerization of the carbenes. As is apparent from the magnitude of the constants, the rates are near diffusion controlled. Since the dimerization occurs mainly from the triplet state, five-ninths of the encounters lead to quintet states and are presumably unproductive. One-third of the encounters give triplet states which are probably bound and lead to the triplet of tetraphenylethylene, which then decays to the ground state. One-ninth of the encounters lead directly to the singlet state of the product. There appears to be a small but real substituent effect on the rate of dimerization. A similar substituent effect has been noted previously for the dimerization of cumyl radicals.[38] Considering the experimental error attached to these measurements it is fair to say that dimerizations of diarylcarbenes are proceeding with rates comparable to the dimerization of diarylmethyl radicals and that both processes are near the diffusion limit.

The next set of experiments was concerned with determining the rate of cyclopropanation of a suitable olefin. Although diphenylmethylene does add to a large number of olefins, usually the yields of cyclopropanes are poor and therefore most additions are unsuitable for kinetic study. One of the few exceptions is the reaction of diphenylmethylene with butadiene, where almost quantitative conversion to 2-vinyl-1,1-diphenylcyclopropane can be realized. Presumably the easy and clean addition can be attributed to a high reactivity of the diene toward the triplet state of the carbene forming a resonance stabilized diradical with triplet spin multiplicity of the intermediate. Similar reasons have been cited for the clean addition to styrene.[27] For these reasons butadiene was chosen as a logical substrate for addition kinetics.

Again the oscillograms obtained from the flash photolysis of diphenyldiazomethane in benzene containing varying concentrations of butadiene were evaluated in terms of a composite second- and first-order reaction. In this case the first-order behavior is attributed in part to the pseudo-first-order scavenging of the carbene by the diene. The second-order component is due to the competing dimerization reaction. It should be noted that not all of the first-order reaction is due to the reaction with the diene, but part must be attributed to the inevitable reaction with impurities. By running at variable butadiene concentrations, it is possible to extract the second-order rate constant for the cyclopropanation step. The results are shown in Figure 5, where the nonzero intercept shows the presence of the side reactions. It should be pointed out that the butadiene is not completely inert to the photolysis flash and that the absorbance of the solution is changed due to these side reactions. Corrections had to be made and this accounts in part for the relatively large uncertainty of the determinations of the second-order rate constants.

We have chosen to interpret the reaction as proceeding entirely through the triplet state and therefore the pseudo-first-order rate constant corresponds to k_4 in the reaction

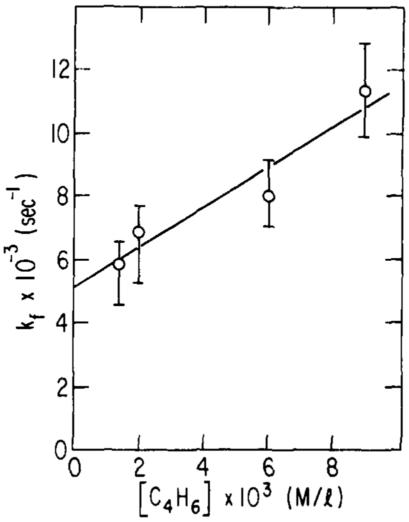


Figure 5. Pseudo-first-order rate constant for the disappearance of diphenylmethylene as a function of butadiene concentration.

Table III. Second-Order Rate Constants for Reaction of Diarylcarbenes with Scavengers

Scavenger: 1,3-Butadiene Carbene	k_{bu}, $M^{-1}\ s^{-1} \times 10^{-5}$ [b]
$(C_6H_5)_2C$:	6.5 ± 2.0
$(p\text{-}BrC_6H_4)_2C$:	6.3 ± 2.0
$(p\text{-}CH_3C_6H_4)_2C$:	6.2 ± 2.0
Scavenger: Methanol Carbene	**k_{me}/K, $M^{-1}\ s^{-1} \times 10^{-6}$ [a]**
$(C_6H_5)_2C$:	6.8 ± 2.1

[a] See text for explanation of parameter. [b] The error limits are estimates based on combined random and systematic errors.

scheme.

The corresponding second-order rate constants, k_{bu}, measuring the addition rate to the diene are given in Table III. Within the rather large error limit there is no noticeable substituent effect. This is perhaps to be expected because the rate-limiting attack on the diene occurs via the σ orbital on the carbene, which is largely orthogonal to the π system.

The next series of experiments involved trapping with methanol. Based on previous work in our and other laboratories there is good reason to believe that diphenylmethylene reacts with alcohols via the singlet state. Triplet state reactions in general resemble free-radical reactions and one would expect hydrogen abstraction at the α position. This is not observed; instead, a clean insertion occurs into the OH bond, yielding the corresponding ether. The absence of a radical reaction is further indicated by the total lack of CIDNP signals when the reaction was run in an NMR spectrometer probe.

Again the reaction kinetics could be fitted to a rate law of simultaneous first- and second-order decay. The second-order component is attributed to the dimerization of the carbene, while the first-order parts are the pseudo-first-order reactions with methanol and a small amount of impurities. Variation of the methanol concentration permits extraction of a second-order rate parameter for the reaction of the carbene with methanol (Figure 6). Since the carbene is assumed to react from the singlet state, this rate parameter corresponds to k_{me}/K, where $K = k_1/k_{-1}$ in terms of Scheme I and k_{me} is the second-order rate constant for reaction of I with methanol. The value is listed in Table III. The intercept of the plot of the first-order rate constant against methanol concentrations,

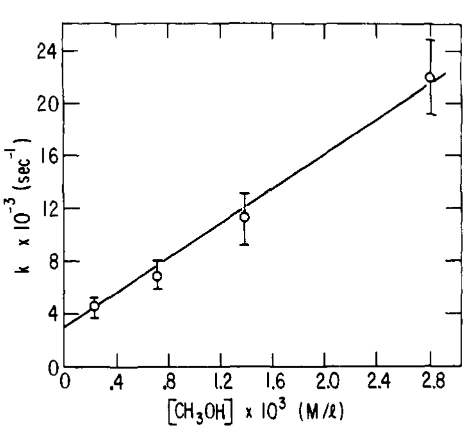


Figure 6. Pseudo-first-order rate constant for the disappearance of diphenylmethylene as a function of methanol concentration.

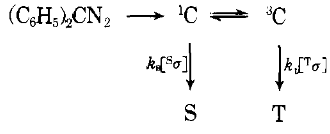
while still larger than zero, is smaller than in the butadiene experiments. This is presumably due to the more efficient degassing that is possible in the methanol trapping experiments.

The experiments with methanol as a singlet scavenger have some bearing on the magnitude of the carbene singlet–triplet equilibrium constant. If the reaction followed does indeed correspond to Scheme I, then an upper limit can be set for K by assuming k_{me} to be no larger than the diffusion-controlled rate constant of $5 \times 10^9\ M^{-1}\ s^{-1}$. This yields a value for $K < 10^3$. The competition and relative rate measurements described below lend support to this assumption and we believe this upper limit to be quite firm. Before these findings are put in perspective it is necessary to discuss some relative rate measurements with other scavengers and to relate these data to the absolute rate measurements.

Relative Rate Measurements. Two series of steady-state photolyses of diphenyldiazomethane were devised. In one set the relative rates of the triplet scavenger oxygen and the singlet scavenger methanol were determined under conditions of variable oxygen concentrations. The second set is characterized by methanol scavenging in the presence of variable concentrations of styrene. Finally, the relative rates of carbene addition to styrene, butadiene, and 1,1-diphenylethylene were determined by standard competition experiments. In both steady-state photolysis experiments involving the methanol–oxygen pair and the methanol–styrene pair the relative reactivities of both members of a pair were found to be invariant with respect to the ratio of the reactants. From the relative rates listed in Table IV and the absolute rates determined for butadiene and methanol the absolute rate constants for the triplet scavengers styrene, diphenylethylene, and oxygen can be determined and they are listed in Table V. Comparison of the relative rates of carbene reaction with methanol and butadiene determined from the steady-state photolysis with the values obtained from flash photolysis shows consistency within a factor of 1.4. This disagreement is well within the error limits estimated for flash photolysis.

Another interesting result regarding the magnitude of the intersystem crossing rate constants can be deduced from these steady-state scavenging experiments, assuming the reactions can be expressed with Scheme II, where $[^S\sigma]$ and $[^T\sigma]$ are the singlet and triplet scavenger concentrations and S and T are the singlet and triplet derived products as before. The product

Scheme II



$$\begin{tikzcd} (C_6H_5)_2CN_2 \arrow[r] & {}^1C \arrow[r, shift left] \arrow[d, "k_s[^S\sigma]"'] & {}^3C \arrow[l, shift left] \arrow[d, "k_t[^T\sigma]"] \\ & S & T \end{tikzcd}$$

Table IV. Steady-State Photolyses of Acetonitrile Solutions of Diphenyldiazomethane and Competing Scavengers

Scavengers: Methanol and Oxygen

Reaction no.	CH_3OH, M	$(C_6H_5)_2CN_2$, M	Oxygen pressure, mmHg	$[O_2]$ calcd, M	$\frac{[(C_6H_5)_2CHOCH_3]}{[(C_6H_5)_2CO]}$	$\frac{[(C_6H_5)_2CHOCH_3][O_2]}{[(C_6H_5)_2CO][CH_3OH]}$
1	0.110	2.74×10^{-4}	130	1.41×10^{-3}	0.735	0.0094
2	0.110	2.74×10^{-4}	130	1.41×10^{-3}	0.780	0.0100
3	0.110	2.74×10^{-4}	206	2.23×10^{-3}	0.408	0.0083
4	0.110	2.74×10^{-4}	206	2.23×10^{-3}	0.431	0.0088
5	0.110	2.74×10^{-4}	442	4.79×10^{-3}	0.213	0.0093
6	0.110	2.74×10^{-4}	442	4.79×10^{-3}	0.191	0.0083
7	0.110	2.74×10^{-4}	712	7.72×10^{-3}	0.149	0.0104
8	0.110	2.74×10^{-4}	710	7.70×10^{-3}	0.146	0.0102
						Av 0.0093

Scavengers: Methanol and Styrene

Reaction no.	CH_3OH, M	$(C_6H_5)_2CN_2$, M	Styrene, M	$\frac{[(C_6H_5)_2CHOCH_3]}{[(C_6H_5)_2C_3H_3C_6H_5)]}$	$\frac{[(C_6H_5)_2CHOCH_3][\text{Styrene}]}{[(C_6H_5)_2C_3H_3C_6H_5][CH_3OH]}$
9	0.0200	5.66×10^{-4}	0.0697	7.58	26.5
10	0.0200	5.66×10^{-4}	0.0697	7.58	26.5
11	0.0200	5.66×10^{-4}	0.879	0.555	24.4
12	0.0200	5.66×10^{-4}	0.879	0.531	23.4
					Av 25.2

Scavengers: Styrene and 1,3-Butadiene

Reaction no.	1,3-Butadiene, mol	$(C_6H_5)_2CN_2$, mol	Styrene, mol	$\frac{[(C_6H_4)_2C_3H_3C_2H_3]}{[(C_6H_5)_2C_3H_3(C_6H_5)]}$	$\frac{[(C_6H_5)_2C_3H_3C_2H_3][\text{Styrene}]}{[(C_6H_5)_2C_3H_3(C_6H_5)][C_4H_6]}$
13	0.0141	4.3×10^{-5}	0.00863	2.72	1.67
14	0.0141	4.3×10^{-5}	0.00863	2.71	1.66
15	0.00307	4.3×10^{-5}	0.00863	0.600	1.66
16	0.00307	4.3×10^{-5}	0.00863	0.625	1.75
					Av 1.69

Scavengers: Styrene and 1,1-Diphenylethylene

Reaction no.	Styrene, M	$(C_6H_5)_2CN_2$, M	1,1-Diphenylethylene, M	$\frac{[(C_6H_5)_2C_3H_3(C_6H_5)]}{[(C_6H_5)_2C_3H_2(C_6H_5)_2]}$	$\frac{[(C_6H_5)_2C_3H_3(C_6H_5)][(C_6H_5)_2C{=}CH_2]}{[(C_6H_5)_2C_3H_2(C_6H_5)_2][(C_6H_5)CH{=}CH_2]}$
17	0.876	2.96×10^{-3}	0.572	1.22	0.80

Table V. Absolute Rate Constants for Reaction of Diphenylmethylene with Triplet Scavengers

Scavenger	Rate constant, $M^{-1}\,s^{-1}$ [a]
1,3-Butadiene	6.5×10^5
Styrene	3.8×10^5
1,1-Diphenylethylene	4.8×10^5
Oxygen	1.0×10^9

[a] Estimated error: ±30%.

ratio is given by

$$\frac{[S]}{[T]} = \frac{k_s[^{S}\sigma][^{1}C]}{k_t[^{T}\sigma][^{3}C]}$$

and the ratio of singlet to triplet carbene concentration in the steady state is

$$[^{1}C]/[^{3}C] = (k_{-1} + k_t[^{T}\sigma])/k_1 \tag{3}$$

Substitution yields

$$\frac{[S][^{T}\sigma]}{[T][^{S}\sigma]} = \frac{k_s k_{-1}}{k_t k_1} + \frac{k_s}{k_1}[^{T}\sigma] \tag{4}$$

As mentioned above, when the quantity on the left side of the equation is plotted against the triplet scavenger concentration the slope of the line is zero within experimental error in both the styrene-methanol as well as the oxygen-methanol experiments. In the latter experiment the oxygen concentration was varied more than fivefold. This, of course, means that even at the highest oxygen concentrations

$$(k_s k_{-1}/k_t k_1) \gg (k_s/k_1)[^{T}\sigma] \tag{5}$$

With the inequality (eq 5) having been established and using the experimentally determined value for $[S][^{T}\sigma]/[T][^{S}\sigma] = 10^{-2}$, it follows from eq 4 that

$$k_1/k_{-1} = K \simeq 10^2(k_s/k_t) \tag{6}$$

The only unknown in this equation is k_s, the bimolecular rate constant of the singlet carbene reaction with methanol. Presumably the maximum value that the rate constant can assume is the diffusion-controlled limit of $5 \times 10^9\ M^{-1}\ s^{-1}$. These numbers are of significance in two ways. First, they show that the concept of the carbene being in a rapid equilibrium between the singlet and triplet state is a valid one. Under all reaction conditions established in this work, by far the fastest reaction is intersystem crossing in either direction. Second, they establish an upper limit for the magnitude of the equilibrium constant of 5×10^2. After making the appropriate correction for the entropy term arising from the triple degeneracy of the triplet state, it follows that the maximum energy difference between the singlet and triplet state of diphenylmethylene is 3 kcal/mol. Finally, it is possible to set a lower limit on k_1.

Since the inequality (eq 5) was shown to hold up to oxygen concentrations of $\sim 10^{-2}$ M and the left side of eq 5 was determined as 10^{-2}, it follows that $k_1 \geq 10^{10}\ \mathrm{s}^{-1}$ if k_s is taken at the diffusion limit.

Conclusion

The results of the measurements reported in this paper are of significance to several areas of carbene chemistry. The dimerization of arylcarbenes, and presumably therefore carbenes that are at least as reactive as diphenylmethylene, proceed with rate constants which are near the diffusion limit.

In general, the triplet state of diphenylmethylene is found to resemble free radicals in reactivity. The rate of the reaction with oxygen is again nearly diffusion controlled. The increased reactivity of diaryl carbenes toward conjugated olefins relative to isolated double bonds is consistent with a two-step mechanism involving a biradical intermediate.

The rate constant for the rate-determining first step is similar to that found for the addition of methyl radical to 1,3-butadiene. Combining the value of $6.5 \times 10^5\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ (Table III) with the range of Arrhenius pre-exponential factors ($10^{7.5}$–$10^{8.5}$) observed for similar addition reactions of radicals to dienes,[39,40] an activation energy of 2.3–3.7 kcal/mol is indicated for this reaction. This is somewhat lower than the 4.5 kcal/mol value for the addition of simple alkyl radicals to butadiene.[39] However, less energy is required to deform the two carbene bonds by a smaller angular displacement (subject to a smaller force constant) than is involved in the three-bond deformation of a trivalent radical at the transition state of addition. The small activation energy of 3.35 kcal/mol for the addition of vinyl radical to ethylene[41] may be relevant to the discussion of small energies attendant with minimal rehybridization processes.

The addition of I, substitutionally incorporated in a singlet crystal of 1,1-diphenylethylene, to its host has been studied.[32] Because of proximity and ideal juxtaposition of reactants, the addition could be treated as a unimolecular reaction involving the reaction partners. The high pre-exponential factor of $10^{15}\ \mathrm{s}^{-1}$ found has no comparative value for the bimolecular analogue of the same reaction under liquid solution conditions. Similarly, the activation energy of 7.8 kcal/mol found for the crystal work furnishes few guidelines for the reaction in the liquid phase because of the complexity of the vibrational constraint in the crystal.

As pointed out above, the magnitude of the singlet–triplet equilibrium constant, K, remains undetermined because the rate constant of the reaction of the singlet state of I with methanol, k_{me}, is unknown. A lower limit of $2 \times 10^7\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ is obtained for k_{me} upon substituting the lower limit of K into the experimental value found for k_{me}/K. However, this reaction may very well be diffusion controlled. This follows from the minimal variation in the relative reactivity ratios of I with methanol and oxygen, $k_{\mathrm{ox}}K/k_{\mathrm{me}}$, attendant with temperature and solvent change. In acetonitrile solution a temperature change from 25 to 85 °C only doubles this value.[10,42-44] Similarly, a solvent change from benzene to methanol again leads to a change by a factor of less than 2.[45] Since the near diffusion-controlled reaction between I and oxygen should be minimally sensitive to solvent effects, the constancy of $k_{\mathrm{ox}}K/k_{\mathrm{me}}$ in the face of changing solvents requires a similar insensitivity of k_{me}. Of course, this is expected for a diffusion-controlled reaction. As a consequence it is possible to state that the singlet–triplet splitting is ≤ 3 kcal/mol, with the most probable value at the upper limit.

This energy gap between two electronic states requires that a high density of states exist near the bottom of the respective potential wells to assure rapid intersystem crossing. That is, the required near continuum of states cannot be guaranteed by the high vibrational quantum numbers attendant with a large electronic energy difference. At the same time, a small force constant for the scissoring vibration of the two carbenic bonds would facilitate rapid transition between the disparate geometries of the two states, associated with rehybridization at the carbenic center. Both prerequisites for rapid intersystem crossing may well operate in diarylcarbene systems, characterized by many torsional modes of phenyl rings[46] and unhindered bending vibration at the carbene carbon. Neither of these qualities functions in fluorenylidene, which appears to have a lower intersystem crossing rate.

It is tempting to speculate that dibenzo[*a,d*]cycloheptatrienylidene may also undergo rapid intersystem crossing. This offers an alternative explanation of Moritani's observation that neither benzophenone sensitization nor dilution with cyclohexane affects the observed product distribution.[47,48]

Appendix

Kinetic Analysis. Knowledge of the observed transmittance, obtained from the oscillogram, and the requisite reference transmittance value yield the absorbance:

$$A(t) = \log\left(V_{\mathrm{ref}}/V(t)\right) \qquad \text{(A1)}$$

where $A(t)$ is the optical density at time t, $V(t)$ the voltage at time t, and V_{ref} the voltage in the absence of the species of interest, but in the presence of solvent.

Analysis lamp instability precludes accurate determination of V_{ref}. The voltage at the end of the reaction, V_∞, provides an alternative reference:

$$A(\infty) = \log\left(V_{\mathrm{ref}}/V_\infty\right) \qquad \text{(A2)}$$

Hence,

$$V(t) = V_\infty 10^{(A(\infty)-A(t))} \qquad \text{(A3)}$$

The absorbance $A(t)$ is given by Beer's Law, eq 1.

Analytical expressions for $C_i(t)$ are calculable for all moieties of Scheme I.

After the photolysis flash, diphenyldiazomethane (D) is no longer being photolyzed to yield ^{1}C. Then adding the differential rate equations for ^{1}C and ^{3}C, and substituting $[^1\mathrm{C}] = 1/K[^3\mathrm{C}]$, where $K = k_1/k_{-1}$, one obtains

$$\frac{\mathrm{d}[^3\mathrm{C}]}{\mathrm{d}t}\left(1 + (1/K)\right) = -\frac{k_3[^3\mathrm{C}]}{K} - k_4[^3\mathrm{C}] - k_2[^3\mathrm{C}]^2 \qquad \text{(A4)}$$

Integrating from time 0 → t yields

$$[^3\mathrm{C}]_t = \frac{(k_4 + (k_3/K))}{k_2\left[\dfrac{k_2[^3\mathrm{C}]_0 + (k_4 + (k_3/K))}{k_2[^3\mathrm{C}]_0}\exp\left(\dfrac{(k_4 + (k_3/K))t}{(1 + (1/K))}\right) - 1\right]} \qquad \text{(A5)}$$

The concentration of T at time t is obtained by integrating $[^3\mathrm{C}]$ with respect to time;

$$[\mathrm{T}]_t = \frac{k_4 b}{k_2}\left\{\frac{(1 + (1/K))}{b} \times \ln\left[\frac{(k_2 + (b/[^3\mathrm{C}]_0))\exp\left(\dfrac{bt}{1 + (1/K)}\right) - k_2}{b/[^3\mathrm{C}]_0}\right] - t\right\} \qquad \text{(A6)}$$

where

$$b = (k_4 + (k_3/K))$$

Similarly,

$$[\mathrm{S}]_t = (k_3/k_4K)\int_0^t k_4[^3\mathrm{C}]_t\,\mathrm{d}t = (k_3/k_4K)[\mathrm{T}]_t \qquad \text{(A7)}$$

Only a fraction N of the initial diazo concentration $[D]_0$ is photolyzed to produce carbene. Since $[^3C]_t \gg [^1C]_t$,

$$[^3C]_0 = N[D]_0$$

By material balance, the concentration of tetraphenylethylene (E) is given by

$$[E]_t = \tfrac{1}{2}([D]_0 - [^3C]_t - [S]_t - [T]_t - (1 - N)[D]_0) \tag{A8}$$

The concentration at infinite time, i.e., the product yield, of S, T, and E may also be calculated

$$[T]_\infty = \frac{k_4 b}{k_2}\left\{\frac{(1 + (1/K))}{b} \times \ln\left[\frac{(k_2 + (b/[^3C]_0))\, e^{bt/(1+(1/K))} - k_2}{b/[^3C]_0}\right] - t\right\}_{t=\infty} \tag{A9}$$

Similarly,

$$[S]_\infty = \frac{k_3(1 + (1/K))}{k_2 K} \ln\left(\frac{k_2[^3C]_0}{b} + 1\right) \tag{A10}$$

$$[E]_\infty = \tfrac{1}{2}(N[D]_0 - [S]_\infty - [T]_\infty) \tag{A11}$$

because $K \gg 1$, $1 + (1/K)$ may be replaced by unity. Substitution of the above analytical expressions for $C_i(t)$ and $C_i(\infty)$ in eq 1 and substitution of eq 1 in eq A3 complete the theoretical derivation of $V(t)$.

The parameter k_3 appears throughout the kinetic equations as only a factor in the ubiquitous quotient k_3/K. An optimized value of K itself cannot be obtained because the factor $1 + (1/K)$ varies only from 1 to 1.33; function optimization is thus insensitive to the parameter K. Therefore, $1 + (1/K)$ was set equal to one. The consequences of $1/K$ assuming its maximum value of one-third are considered later.

The adjustable parameters were optimized so as to minimize the function

$$\chi^2 = \sum_{i=1}^{20} (1/\sigma_i^2)\,(V(i)_{\text{calcd}} - V(i)_{\text{obsd}})^2 \tag{A12}$$

where $V(i)_{\text{obsd}}$ is the observed voltage, measured from oscillogram, at time t_i, σ_i the error in determination of $V(i)_{\text{obsd}}$, and $V(i)_{\text{calcd}}$ the voltage, calculated by STEPIT, at time t_i. Regardless of experimental type, whether butadiene scavenging, methanol scavenging, or pure dimerization, the same computer program was used. For all three types, therefore, a pseudo-first-order rate constant, a second-order dimerization constant, and the fractional value N were subjected to optimization. The pseudo-first-order constant evaluated equals k_4 if a butadiene experiment is involved, and k_3/K if it is a methanol experiment which is under consideration. That is, the pseudo-first-order decay channels available for the carbene are considered to involve only the triplet state in the presence of butadiene, and only the singlet state in the presence of methanol.

Estimation of Confidence Limits. For the rest of this section, the optimized pseudo-first-order rate constant will be called k_f, it being understood to equal either k_4 or k_3/K, depending upon the nature of the scavenger. The small values of k_f found for the dimerization runs are not used in any subsequent analysis.

Time zero was taken to occur midway through the flash duration, or 10 μs after the start of the flash. This averaging procedure is adequate because altering the input constant t_0 by ±10 μs in the program affects the resultant optimized k_f by less than 5%.

Several observations common to all the error analyses emerge. The value of k_f undergoes comparatively little alteration as each error is, in turn, turned on. The value of k_2 varies by as much as 50%. This is expected because the first-order decay channels account for the major fraction of the disappearance rate of the carbene in the scavenging experiments. Hence, the smaller k_2 pathway may sustain computer simulated fluctuations large relative to the value of k_2, yet small compared to the magnitude of k_f and the overall disappearance rate. As k_2 is fairly constant in the pure dimerization studies, where the first-order processes have been minimized, k_2 was estimated from these experiments alone.

A study of the correlation between k_2 and k_f demonstrates that k_f is altered about ±20% if k_2 is constrained to values deviating as much as 200% from the actual best fit value of k_2 in a particular oscillogram. The correlation varies inversely with scavenger concentration. A detailed correlation analysis for each oscillogram imparts the asymmetry observed in the error bars of Figures 5 and 6.

A value of 2.5×10^4 was employed for the molar extinction coefficients of diphenylcarbene and dimethyldiphenylcarbene.[49] A larger value of 3.0×10^4 was used for dibromodiphenylcarbene, because lower values resulted in N exceeding unity for some scavenging experiments. For a variation in extinction coefficient of $\Delta\epsilon = \pm 5 \times 10^3$, k_f is affected by at most 5%, raising the value of k_f if ϵ 2×10^4, and lowering it if ϵ 3×10^4. The values of k_2 for the dimerization cases undergo larger variations of about 20%. These results are anticipated, since the spectroscopically determined rate constant of a simple first-order decay is independent of extinction coefficient, while that for a second-order decay is dependent upon the extinction coefficient of the diminishing species.

The effects of random error in the measurement of $V(t)$ from the oscillogram were considered by choosing the data values $V(t)$ randomly for each point from a Gaussian distribution centered at the best guessed value of $V(t)$ and having a half-width equal to the estimated error in measurement of the $V(t)$. For $\sigma_i = \Delta V(t)_{\text{obsd}}$ = width of the trace, the deviation in k_f is less than 7% for the scavenging experiments, and the deviation in k_2 is less than 20% for the dimerization runs.

Although the actual measurement of V is subject to a random error, its subsequent use as a constant in the computations makes for a systematic error. For a $\Delta V_\infty = \Delta V(t)_{\text{obsd}}$, k_f is determined to within 7%, and k_2, for the dimerization studies, to within 2%.

There is also an error in the optimized parameters incurred by the random selection of the starting point of the optimization procedure, the choice of the initial parametric vector. By evaluating the same set of data, using a different starting vector 27 times, it was found that this uncertainty in k_f is about 7%.

The effects of the possibly observable singlet carbene UV absorption and the increased importance of the singlet carbene's undergoing dimerization become manifest to the extent that the singlet carbene is present in much larger concentration than that implied by the usage of $1 + (1/K) = 1.00$. Furthermore, a larger concentration of ^1C increases the side reactions of the singlet, which affects k_f for a butadiene scavenging experiment. Because ^1C and ^3C are in rapid equilibrium, an increase in pseudo-first-order loss from ^1C is offset by a decrease in k_4, so as to maintain the sum of $k_4 + (k_3/K)$ constant. The sum must remain constant in order to account for the total pseudo-first-order decay of a given oscillogram. It is apparent that the incursion of pseudo-first-order side reactions is minimal in the dimerization experiments, where the calculated k_f is small although finite, and also in the methanol scavenging experiments, as evidenced by the near zero intercept in Figure 6. In these systems k_3/K is therefore small, since the sum $k_4 + (k_3/K)$ is small. That oxygen scavenging of ^3C explains the large intercept in Figure 5 has been mentioned in the Results.

Changing only $1 + (1/K)$ from 1.00 to 1.33 increases the evaluated parameter k_4 by the same factor, 1.33. Here, k_4 increases to maintain constant product of $k_4[^3C]$ in order to account for the observed experimental decay. In the dimerization studies, increasing $1 + (1/K)$ from 1.00 to 1.33 causes k_2 to decrease by the same factor of 1.33. This occurs because in addition to the ${}^3C + {}^3C$ dimerization, the ${}^3C + {}^1C$ dimerization requires consideration, resulting in the rate equation

$$d[{}^3C]/dt = -k_2(1 + (1/K))[{}^3C]^2 \qquad (A13)$$

For a constant observed rate, k_2 will be diminished by the same factor to which $1 + (1/K)$ is increased.

If the extinction coefficients of triplet and singlet are altered such that the sum

$$[{}^1C]\epsilon({}^1C) + [{}^3C]\epsilon({}^3C)$$

is constant, the evaluated parameters undergo negligible change. Because singlet and triplet are in rapid equilibrium, the effective observed extinction coefficient of the sum of carbenes is the same as the case where only the triplet absorbs. The effects of other combinations of extinction coefficients which have a weighted (by concentration of carbene) sum different from 2.5×10^4 has already been considered in connection with systematic errors arising from assumptions of the absolute extinction coefficients of carbenes.

To the extent that all of the random errors considered above are independent, the total random error in the evaluation of k_f for each experiment is given by the square root of the sum of squares of the errors. The error bars in Figures 5 and 6 reflect these independent random errors, as well as correlation error. Uncertainty about the molar extinction coefficient and simplifying kinetic assumptions are systematic errors which would affect all points in Figures 5 and 6 in similar fashion, with virtually no effect upon the slopes of the graphs, which are of primary interest.

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(1) Supported by National Science Foundation Grant No. NSF MPS73-08517.

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