Tetrahedron Vol. 41, No 8, pp. 1543 to 1554, 1985
Printed in Great Britain.

0040–4020/85 \$3.00 + .00
Pergamon Press Ltd.

SINGLET–TRIPLET INTERCONVERSION OF DIPHENYLMETHYLENE. ENERGETICS, DYNAMICS AND REACTIVITIES OF DIFFERENT SPIN STATES

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(*Received in USA* 25 *October* 1983)

Abstract—A combination of picosecond and nanosecond laser spectroscopy measurements, chemical quenching experiments and triplet sensitization experiments has allowed the determination of the rapid singlet to triplet and slower triplet to singlet intersystem crossing rates for diphenylmethylene in fluid solution at room temperature. It is shown that under the conditions of the kinetic measurements, singlet and triplet diphenylmethylene (^{1}DPM and ^{3}DPM, respectively) are in rapid equilibrium relative to reactions, so that knowledge of the values of k_{ST} and k_{TS} allows determination of the equilibrium constant and change in free energy for the ^{1}DPM $\rightleftarrows$ ^{3}DPM process. The absolute reactivity of ^{1}DPM toward a series of alcohols has been determined and is discussed in terms of other current investigations of carbene reactivity.

In recent years much theoretical and experimental work has centered on attempting to understand the chemical and physical properties of carbenes.[1] Of particular interest is the presence of an unshared pair of electrons which results in two low-lying electronic spin configurations, singlet and triplet. EPR spectroscopy has been extremely useful in establishing the ground state multiplicity of most aryl and alkyl carbenes to be the triplet.[2] Valuable structural information for these carbenes is also available from EPR and ENDOR experiments,[2] but little is known concerning the energetics and dynamics between the two spin states. An important and controversial aspect of this is the magnitude of the singlet–triplet energy gaps. Numerous calculations of the singlet–triplet energy splittings have appeared;[3] however, little quantitative experimental information is available. Recent reports of the experimental determination of the singlet–triplet energy gap in the parent methylene have placed the value at ~8 kcal/mol;[4] however the corresponding value for other carbenes has not been determined.

In addition to the dearth of experimental information concerning singlet–triplet energy gaps, little is known about the dynamics of the singlet–triplet interconversion. Generation of a ground state triplet carbene, either photochemically or thermally from an appropriate precursor is expected to lead initially to the singlet state because of spin conservation restrictions. The singlet may then undergo reaction or intersystem crossing to the ground state triplet which subsequently reacts. As a result, interpretation of carbene chemistry is often complicated by products originating from both spin states. It is important, therefore, to determine the rate(s) of interconversion of the spin states and in addition the rate constants for reaction of each with various substrates.[5]

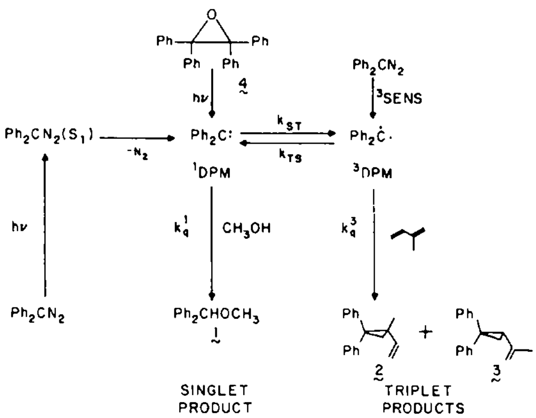
We have undertaken an in-depth study of diphenylmethylene (DPM) and wish to report the determination of the absolute rate constants for singlet–triplet interconversion, and the energy spacing between these two states for DPM, following the pioneering work of Closs and Rabinow.[6] DPM is a particularly attractive candidate for study because it should be prototypic of arylcarbenes and furthermore, it has been shown to be amenable to flash spectroscopic techniques.[6] EPR spectroscopy has conclusively established DPM to be a ground state triplet.[7] Previous work has provided evidence for the establishment of a rapid equilibrium between the singlet and triplet states of DPM relative to most reactions.[6,8] By combining competitive quenching experiments with a flash spectroscopy study, Closs and Rabinow were able to supply an estimate of the upper limit for the equilibrium constant in benzene.[6] However, the absolute rate constants for the interconversion of the two spin states could not be measured due to the ultrafast rate constant (k_{ST}) for the ^{1}DPM → ^{3}DPM process, which, however, was estimated to be of the order of 10^{10} s^{-1}. Lack of knowledge of the exact value for this rate constant permitted only estimates of the equilibrium constant (K_{eq}) and the free energy difference (ΔG_{ST}) between the spin states.

We have combined competitive quenching experiments, picosecond and nanosecond laser flash spectroscopy, and triplet sensitization experiments to evaluate the rates of singlet–triplet interconversion of DPM in fluid solution. From these rate constants, K_{eq} and ΔG_{ST} are determined for DPM.[9] In addition, the absolute rate constants for the reactions of ^{1}DPM and ^{3}DPM with a number of substrates are reported.

RESULTS

1. *Approach.* To obtain various relationships between the rate constants of interest, we have used spin state selective traps in competitive experiments similar to those of Closs and Rabinow[6] and Bethell *et al.*[8] DPM was photogenerated at room temperature from either diphenyldiazomethane or tetraphenyloxirane (4) in N_2-saturated acetonitrile in the presence of spin state selective traps (Scheme 1). We assume that direct irradiation at low light flux of either of these precursors leads initially to formation of ^{1}DPM. The experimental design and conditions that were chosen allow us to assume that only four processes are available to the carbene system: (a) singlet to triplet interconversion, (b) triplet to singlet interconversion, (c) singlet reaction with a singlet trap, or (d) triplet reaction with a triplet

trap. Kinetic analysis of such a system provides relationships between the rate constants k_{ST}, k_{TS}, k_1 and k_3, respectively. Of the four rate constants that characterize this system, two can be directly measured using time resolved spectroscopic methods. Picosecond spectroscopy was used to directly measure k_{ST} and nanosecond flash photolysis techniques were used to measure k_3. The rate constants k_1 and k_{TS} were obtained from competitive quenching experiments analyzed according to Scheme 1.



Scheme 1.

2. *Flash spectroscopic determination of* k_{ST} *and* k_3. Picosecond laser induced fluorescence spectroscopy was used to measure the rate of formation of ^{3}DPM upon photolysis of diphenyldiazomethane and hence the singlet-to-triplet interconversion rate constant (k_{ST}). The experiment consisted of photolyzing a vacuum degassed acetonitrile solution of diphenyldiazomethane (8×10^{-4} M) with a picosecond laser pulse at 266 nm from a passively mode-locked Nd:YAG laser (25–30 ps FWHM, <0.02 mJ). The formation rate of ^{3}DPM was monitored by laser induced fluorescence using a weak probe pulse at 266 nm at variable delays. The rise-time of ^{3}DPM was then obtained by computer simulation of the plot of the $^3\text{DPM}^* \rightarrow {}^3\text{DPM}$ integrated fluorescence intensity *versus* time separating the excitation and probe pulses.[11] The results are shown in Fig. 1. The rate constant of the formation of ^{3}DPM obtained in these experiments, $k_{ST} = (3.22 \pm 0.23) \times 10^9\ \text{s}^{-1}$, is equal to the rate of intersystem crossing process $^1\text{DPM} \rightarrow {}^3\text{DPM}$, since the lifetime of the excited diazo compound is $\leqslant 20$ ps.[11]

The absolute value of k_3 in degassed acetonitrile at room temperature was measured by nanosecond laser spectroscopy employing a Lambda Physik excimer laser as the excitation source ($\lambda = 308$ nm, pulse width 20 ns).[10] Nanosecond laser photolysis of diphenyldiazomethane (4×10^{-5} M) in argon purged acetonitrile at room temperature, results in transient absorption due to ^{3}DPM and bleaching due to diphenyldiazomethane in the spectral region studied, 280–320 nm. Following pulsed laser excitation a time-resolved absorption decay is observed at 295 nm due to the decay of ^{3}DPM. An overall bleaching is observed which is a measure of the extent of reaction occurring upon photolysis. Upon addition of isoprene the rate of decay of the triplet carbene absorption signal increases due to the reaction of these species. At sufficiently high quencher concentration the decay of the ^{3}DPM becomes pseudo-first order. The slope of the plot of τ^{-1} from the first order region, *versus* [IP] gave a value for $k_3 = (1.36 \pm 0.15) \times 10^6\ \text{M}^{-1}\ \text{s}^{-1}$. This value is similar to that obtained by Closs and Rabinow for the reaction of ^{3}DPM with butadiene in benzene ($k_3 = 6.5 \times 10^5\ \text{M}^{-1}\ \text{s}^{-1}$).

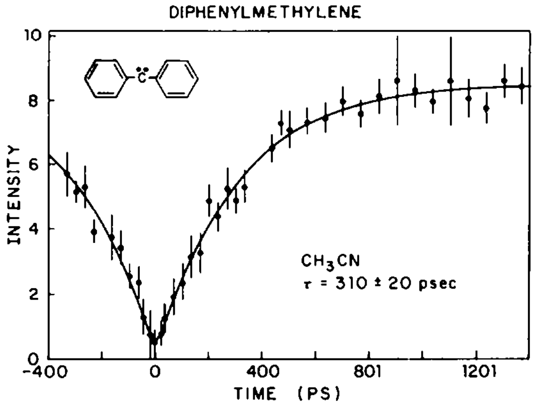


Fig. 1. Formation kinetics of ^{3}DPM in degassed acetonitrile. The laser-induced fluorescence signal as a function of time delay between excitation and probe laser pulses. The solid curve is a calculated fit.

Using the values of k_3 and k_{ST} obtained from flash spectroscopic techniques, it is possible to evaluate k_{TS} and k_1 from relationships obtained in the spin selective competition experiments.

3. *Choice of spin state selective scavengers.* Crucial to the design of the competitive quenching experiment is the choice of two DPM scavengers, since each must be very selective for one of the two spin states. We have chosen methanol as the singlet scavenger based on previous reports[1,6] that alcohols react efficiently and selectively with ^{1}DPM via insertion reactions, but that ^{3}DPM will react only slowly via H-abstraction reactions. The product resulting from photolysis of diphenyldiazomethane in methanol is benzhydryl methyl ether (**1**), Scheme 1. It arises from O—H insertion as opposed to C—H insertion, which would be expected from an abstraction recombination mechanism of a radical-like triplet state. The absence of reaction between triplet DPM and alcohols is further supported by the lack of CIDNP which would be expected to result from radical reactions.[6] The possibility of a single step insertion of the triplet carbene into the alcoholic O—H bond would lead to the formation of the excited triplet state of the ether product, however this reaction would not be considered likely due to the unfavorable energetics involved.[24b]

We have chosen isoprene as the triplet scavenger because dienes have been shown to be efficient triplet carbene traps, presumably because of the stabilization of the initially formed triplet 1,3-biradical.[12] As reported,[13] the generation of DPM in the presence of isoprene produces two isomeric cyclopropanes (**2** and **3**) as the only detectable products. The ratio **2**:**3** was determined to be 1.6 ± 0.3 in all cases regardless of the isoprene concentration and the DPM precursor used.

We have used the ratio **2**:**3** to define isoprene as selective for ^{3}DPM under the conditions of our experiments. We have done so by assuming that singlet reaction and triplet reaction with isoprene will lead to different ratios of the isomeric cyclopropanes and, therefore, any change in the relative extent of reaction from the spin states should lead to a change in **2**:**3**. Direct irradiation of diphenyldiazomethane in acetonitrile containing 10 M methanol and 0.5 M isoprene gave (**2**+**3**):**1** = 5.1×10^{-3} and **2**:**3** = 1.6. Photosensitized irradiation of diphenyldiazomethane under identical conditions leads to a large enhancement (~10 times) in the cyclopropanes relative to benzhydryl methyl ether (**2**+**3**):**1** = 3.4×10^{-2} and **2**:**3** = 1.5. This result may be explained by an increased yield of triplet product. It is significant that the ratio **2**:**3** for the photosensitized experiment is the same within experimental error (±10%) as the value obtained for the direct irradiation. These results are consistent with the conclusion that in the direct irradiation, the cyclopropanes are also arising solely via a triplet state reaction, barring some fortuity whereby the singlet and triplet reactions both give the same **2**:**3** ratio. The possibility that isoprene is not triplet state selective but it reacts such that singlet and triplet reactions would yield identical **2**:**3** product ratios is rendered improbable because of the enormous difference in reactivity of ^{1}DPM and ^{3}DPM toward reaction with methanol. It is unlikely that two species which show orders of magnitude difference in reactivity toward methanol would show no selectivity toward isoprene. Thus, the ratio **2**:**3** should be characteristic of selective triplet reaction and its invariancy for all our experiments indicates that no significant singlet reaction with isoprene is present under our conditions.

4. *Direct irradiation of DPM precursors.* Kinetic analysis of Scheme 1, assuming that there is an equilibrium between the spin states predicts that the ratio of the yield of triplet products ($^3\phi$) to the yield of singlet products ($^1\phi$) will obey Eq. (1). A plot of $^3\phi/^1\phi$ *versus* the concentration of isoprene, [IP], at a fixed

$$^3\phi/^1\phi = \frac{k_3 k_{\mathrm{ST}}[\mathrm{IP}]}{k_1[\mathrm{CH_3OH}](k_{\mathrm{TS}} + k_3[\mathrm{IP}])} \tag{1}$$

concentration of methanol is expected to exhibit two regions of differing behavior. Under conditions where $k_{\mathrm{TS}} \gg k_3[\mathrm{IP}]$, Eq. (1) reduces to Eq. (2). In this domain, $^3\phi/^1\phi$ should exhibit a linear dependence on isoprene

$$^3\phi/^1\phi = \frac{k_{\mathrm{ST}} k_3[\mathrm{IP}]}{k_{\mathrm{TS}} k_1[\mathrm{CH_3OH}]} \tag{2}$$

concentration, at a fixed methanol concentration, with slope $k_{\mathrm{ST}}k_3/k_{\mathrm{TS}}k_1[\mathrm{CH_3OH}]$. In a region of isoprene such that $k_{\mathrm{TS}} \ll k_3[\mathrm{IP}]$ the $^3\phi/^1\phi$ should be independent of [IP] as given by Eq. (3).

$$^3\phi/^1\phi = \frac{k_{\mathrm{ST}}}{k_1[\mathrm{CH_3OH}]}. \tag{3}$$

It is to be noted that the kinetic scheme used in this work assumes rapid singlet–triplet equilibration. This leads to a nonlinear dependence of $^3\phi/^1\phi$ on isoprene concentration as given by Eq. (1), assuming that ^{3}DPM does not react with methanol. However, if there were no conversion from the triplet to the singlet, i.e. k_{TS} can be neglected compared to all other processes, then $^3\phi/^1\phi$ would be independent of isoprene concentration and would be determined solely by the competition between the singlet reaction with methanol and the singlet to triplet intersystem crossing. This latter model is contrary to our experimental observation that $^3\phi/^1\phi$ does indeed depend upon the isoprene concentration as given by Eq. (1).

Direct irradiation of diphenyldiazomethane ($2\text{–}3 \times 10^{-3}$ M) in nitrogen bubbled acetonitrile solutions at 273 K in the presence of a fixed amount of methanol (0.05 M) and varying amounts of isoprene (0.10–10 M) allowed an experimental test of Scheme 1. In all cases, steady state photolysis of diphenyldiazomethane leads to three major products (>95% yield) which could be detected by GLC: benzhydryl methyl ether, the singlet product, and the two isomeric cyclopropanes, the triplet products. In addition, relatively small amounts of diphenylmethane and benzophenone (<5%) from H-abstraction reactions and reaction with trace amounts of oxygen, were detected. Injection comparisons of authentic samples demonstrated that no detectable tetraphenylazine, tetraphenylethylene or tetraphenylethane were produced. These results justify a kinetic analysis incorporating only the four processes shown in Scheme 1.

Under the conditions of these experiments, the $^3\phi/^1\phi$ ratio may therefore be accurately estimated by the relative yields of cyclopropanes to benzhydryl methyl ether. The values of this ratio as a function of isoprene concentration at a fixed methanol concentration are given in Table 1. These data are plotted in Fig. 2 and show the behavior predicted by the kinetics for a system which has achieved a singlet–triplet equilibrium. The theoretical curve, obtained by fitting Eq. (1) to the experimentally observed values of $^3\phi/^1\phi$ via a nonlinear multiparameter least-squares search routine

Table 1. Product ratios under different experimental conditions. $^3\phi/^1\phi$ from the reaction of diphenylmethylene at fixed (0.05 M) concentration of methanol and variable concentrations of isoprene in acetonitrile, at 273 K. Diphenylmethylene generated from direct irradiation of diphenyldiazomethane and tetraphenyloxirane, and triplet photosensitized decomposition of diphenyldiazomethane

Experimental conditions	[IP], M	($^3\phi/^1\phi$)†
Diphenyldiazomethane precursor	0.10	0.1, 0.2
	0.50	0.70
	1.0	1.3, 1.1
	1.5	1.7
	2.0	2.4
	4.0	4.1
	5.0	4.7, 4.8
	7.0	5.3
	8.0	5.1
	10.0	5.1
Tetraphenyloxirane precursor	0.50	0.47
	1.5	1.6
	4.0	4.7
	10.0	4.7
Photosensitization	0.50	0.44‡
	0.50	0.84‡
	2.0	2.2§

† Yield of cyclopropanes relative to ether.

‡ Biacetyl sensitization of diphenyldiazomethane.

§ 4-Phenylbenzophenone sensitization of diphenyldiazomethane.

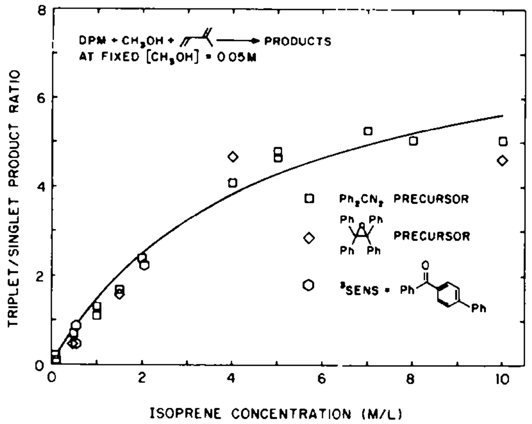


Fig. 2. Experimental behavior of $^3\phi/^1\phi$ as a function of the isoprene concentration at a fixed methanol concentration (0.05 M). The solid curve is calculated from Eq. (1) using $k_{ST} = 3.23 \times 10^9$ s^{-1}, $k_3 = 1.36 \times 10^6$ M^{-1} s^{-1}, $k_1 = 7.77 \times 10^9$ M^{-1} s^{-1} and $k_{TS} = 6.29 \times 10^6$ s^{-1}.

is shown in Fig. 2. The subroutine STEPIT, which was developed by Chandler,[14] was used to minimize the function χ^2 in which fixed values of

$$\chi^2 = \sum_{i=1}^{\text{all pts}} \left[(^3\phi/^1\phi)_i - \frac{k_3 k_{ST}[\mathrm{IP}]_i}{k_1[\mathrm{CH_3OH}](k_{TS}+k_3[\mathrm{IP}]_i)} \right] \tag{4}$$

$k_{ST} = 3.2 \times 10^9$ s^{-1} and $k_3 = 1.4 \times 10^6$ M^{-1} s^{-1} were taken and leaving k_1 and k_{TS} as the adjustable parameters. The results after minimization of χ^2 gave $k_1 = 7.8 \times 10^9$ M^{-1} s^{-1} and $k_{TS} = 6.3 \times 10^6$ M^{-1} s^{-1}. The value for k_1 evaluated from this data is close to the value calculated ($\sim 2 \times 10^{10}$ M^{-1} s^{-1}) for a diffusion controlled reaction in acetonitrile.

To determine whether we were measuring properties inherent to the DPM system and not those unique to the diazo precursor, we generated the carbene from a quite different precursor. Direct irradiation of tetraphenyloxirane, **4**, a well-documented method for DPM generation, under the same conditions showed identical behavior. Irradiations of **4** were carried out to low conversions (~20%) to avoid complications due to photoexcitation of the benzophenone fragment. The results of these experiments are also listed in Table 1 and plotted in Fig. 2 for comparison to the results obtained from the diazo precursor. The agreement with the results obtained from the photolysis of the diazo precursor confirms the hypothesis that the products result from the reactions of DPM and not an excited state precursor or other intermediate.

The validity of the kinetic model can also be tested by determining the relative yields of products for varying concentrations of methanol in the presence of a fixed concentration of isoprene. The measured $^3\phi/^1\phi$ ratio can then be related to the four rate constants of Scheme 1 by using the inverse of Eq. (1) for analysis:

$$^1\phi/^3\phi = \frac{k_1[\mathrm{CH_3OH}](k_{TS}+k_3[\mathrm{IP}])}{k_{ST}k_3[\mathrm{IP}]}. \tag{5}$$

The test was performed by the irradiation of diphenyldiazomethane at a constant isoprene concentration of 1 M, while varying the concentration of methanol from 0.01 to 0.5 M, at 273 K. The values for $^1\phi/^3\phi$ under these conditions are given in Table 2 and plotted in Fig. 3. According to Eq. (5) the ratio should follow a linear dependence on methanol concentration, as is observed experimentally. Use of STEPIT to optimize the values for k_1 and k_{TS} in the two parameter least squares fit of Eq. (5) to the observed values gave $k_1 = 6.9 \times 10^9$ M^{-1} s^{-1} and $k_{TS} = 1.0 \times 10^7$ s^{-1}. The k_1 and k_{TS} values are in quite good agreement with those values obtained from the competition experiment in which isoprene was varied at fixed methanol concentration. The reliability of these values is further tested by the results of the photosensitization experiments presented in the next section.

Table 2. $^1\phi/^3\phi$ from the irradiation of an acetonitrile solution of diphenyldiazomethane in the presence of a fixed concentration of isoprene (1.0 M) and varying concentrations of methanol at 273 K

[CH$_3$OH], M	$^1\phi/^3\phi$
0.50	9.1
0.40	6.7
0.30	5.6
0.050	0.77
0.010	0.17

The previous experiments were performed at 273 K, whereas the absolute rate constants k_{ST} and k_3 were determined at 298 K. Consequently, we repeated the competitive quenching experiment, holding methanol constant, at room temperature. The values of $^3\phi/^1\phi$ were determined for the steady-state irradiation of diphenyldiazomethane in the presence of fixed methanol (0.05 M) concentration and various isoprene concentrations. The results are given in Table 3. Analysis of the data as before, using the known values of k_{ST} and k_3 yields $k_{TS} = 1.1 \times 10^7$ s^{-1}, and $k_1 = 5.6 \times 10^9$

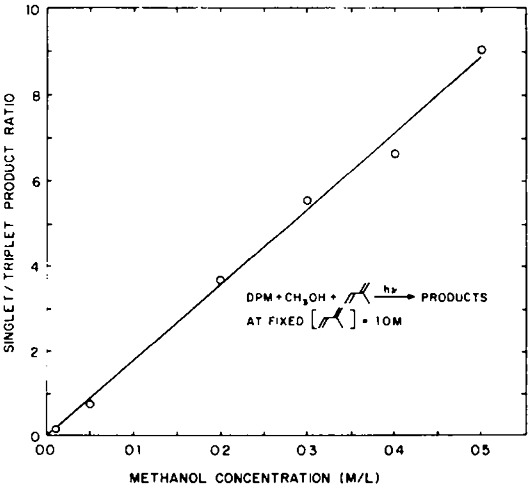


Fig. 3. Experimental behavior of $^1\phi/^3\phi$ as a function of the methanol concentration at a fixed isoprene concentration (1.0 M). The solid curve is calculated from Eq. (5) using $k_{ST} = 3.23 \times 10^9$ s^{-1}, $k_3 = 1.36 \times 10^6$ M^{-1} s^{-1}, $k_1 = 6.9 \times 10^9$ M^{-1} s^{-1} and $k_{TS} = 1.0 \times 10^7$ M^{-1} s^{-1}.

Table 3. ${}^3\phi/{}^1\phi$ obtained from the irradiation of an acetonitrile solution of diphenyldiazomethane in the presence of a fixed concentration of methanol (0.05 M) and varying concentrations of isoprene, at 298 K

[IP], M	${}^3\phi/{}^1\phi$
0.1	0.50
0.5	0.50
1.5	1.69
4.0	3.82
7.0	5.90
10.0	6.20

$M^{-1}\,s^{-1}$. Comparison of this data with that found for 273 K indicates that Scheme 1 is valid under these conditions and that for this small temperature range, as anticipated, a negligible temperature effect is observed on the derived values of k_{TS} and k_1.

5. *Photosensitized decomposition of diphenyldiazomethane.* If the two spin states of DPM are in rapid equilibrium relative to their reactions, then under appropriate conditions, identical results will be observed for the methanol–isoprene competitive quenching experiments regardless of whether the carbene is formed via direct (singlet precursor) or sensitized (triplet precursor) excitation. We have carried out a series of triplet sensitized decompositions of diphenyldiazomethane in the presence of methanol and isoprene to test these ideas.

A number of photosensitizers were employed in order to find a system which would efficiently triplet sensitize the diazo decomposition and be free of complicating side reactions. Benzophenone, which has been used as triplet sensitizer in a number of carbene studies,[16] could not be used because it interfered with the chemical analysis of the products by GLC. Initially, biacetyl was chosen as the sensitizer because its absorption spectrum is very convenient for selective excitation of the sensitizer in the presence of diphenyldiazomethane. However, the utility of biacetyl is severely hampered by side reactions which yielded complex product mixtures. In addition, because of the relatively long singlet lifetime of biacetyl ($\sim 10^{-8}$ s)[17] and at the concentration of diphenyldiazomethane used ($\sim 2.5 \times 10^{-3}$ M), it was difficult to rule out the presence of a significant amount of singlet excitation of the diazo compound.

4-Phenylbenzophenone, an established triplet sensitizer,[18] was tried because its lowest triplet state is π,π^* in nature. This latter feature makes H-abstraction by the sensitizer much less competitive with energy transfer to diphenyldiazomethane and thus reduces complications due to this photoreaction. 4-Phenylbenzophenone possesses an absorption band which is convenient for its selective excitation (λ 370 nm) in the presence of diphenyldiazomethane. Indeed, smooth photosensitized decomposition of diphenyldiazomethane is observed. Irradiations carried out under sensitized conditions without 4-phenylbenzophenone indicate that direct excitation of diphenyldiazomethane can account for no more than 20% of the observed diphenyldiazomethane disappearance. The actual percentage of direct absorption by diphenyldiazomethane (O.D. $^{370\,\mathrm{nm}} \sim 0.03$) is probably much less because of the internal filtering created by the use of concentration of the sensitizer (O.D.$^{370\,\mathrm{nm}} \sim 1.5$). These relative absorbances indicate that $\sim 2\%$ of the incident light is absorbed by diphenyldiazomethane under these conditions.

Evidence that the diphenyldiazomethane decomposition occurs via triplet photosensitization is necessarily indirect. Although the triplet state of 4-phenylbenzophenone is not known, the nature of its excited states, S (n,π) and T (π,π^*) suggests that intersystem crossing should be very rapid.[19] A typical intersystem crossing rate constant for such a ketone should be of the order of $10^{10}\,s^{-1}$.[19] This is consistent with the lack of fluorescence from 4-phenylbenzophenone and a quantum yield for intersystem crossing equal to one. With such a rapid intersystem crossing rate and low diphenyldiazomethane concentration (10^{-3} M), singlet sensitization should be unlikely. The arguments presented above suggest that the vast majority of the diphenyldiazomethane disappearance under these conditions is from triplet photosensitization.

4-Phenylbenzophenone sensitized decomposition of diphenyldiazomethane, like the direct photolysis, leads to three major observed products: benzhydryl methyl ether and the two cyclopropanes **2** and **3** (**2**:**3** = 1.7). In addition, trace amounts of diphenylmethane and benzophenone are formed.

6. *Evaluation of k_{TS} and k_1 from photosensitized competitive quenching.* Using the assumptions of the selective reaction of methanol (singlet scavenger) and isoprene (triplet scavenger), and equilibrium between the spin states, and that photosensitization leads initially to triplet DPM, it is possible, as before, to derive an expression for the ratio ${}^3\phi/{}^1\phi$ under steady state conditions (Eq. 6).

$$ {}^3\phi/{}^1\phi = \frac{k_3[\mathrm{IP}](k_{ST}+k_1[\mathrm{CH_3OH}])}{k_{TS}k_1[\mathrm{CH_3OH}]}. \tag{6} $$

Straightforward comparison of the photosensitized experiments to the data from the direct irradiation experiments is possible when the sensitized irradiation is performed at a constant concentration of methanol (0.05 M) and varying amounts of isoprene. At this concentration of methanol $k_{ST} > k_1[\mathrm{CH_3OH}]$ and Eq. (6) reduces to Eq. (2) and predicts the same behavior as observed from the direct irradiation of diphenyldiazomethane at low concentrations of isoprene.

Triplet sensitized decomposition of diphenyldiazomethane at a fixed methanol concentration (0.05 M), and two isoprene concentrations (0.05 M and 2.0 M) at 273 K, confirmed these expectations. The ${}^3\phi/{}^1\phi$ ratios for these experiments using 4-phenylbenzophenone as sensitizer is also given in Table 1 and plotted in Fig. 2. These results add still further support to the contention that a rapid equilibrium between the spin states of DPM is established prior to reaction.

In a manner completely analogous to the direct irradiation experiments, it should be possible, from a kinetic treatment, to extract relationships between the various rate constants for the triplet sensitized formation of DPM. A simple inversion of Eq. (6) gives Eq. (7), which predicts that ${}^1\phi/{}^3\phi$ for photosensitized irradiation of diphenyldiazomethane at a fixed isoprene concentration and varying amounts of

$$ {}^1\phi/{}^3\phi = \frac{k_{TS}k_1[\mathrm{CH_3OH}]}{k_3[\mathrm{IP}](k_{ST}+k_1[\mathrm{CH_3OH}])} \tag{7} $$

Table 4. $^1\phi/^3\phi$ obtained from the photosensitized (4-phenylbenzophenone) decomposition in N_2. Saturated acetonitrile in the presence of a fixed isoprene (0.10 M) concentration and varying amounts of methanol, at 273 K

$[CH_3OH]$, M	$^1\phi/^3\phi$
0.010	1.7
0.020	3.9
0.030	6.7
0.050	11.0
0.10	18.0
0.50	75.0
1.0	110.0
2.5	130.0
5.0	130.0
10.0	130.0

Table 5. $^3\phi/^1\phi$ obtained from an isooctane solution of diphenyldiazomethane in the presence of a fixed concentration of methanol (0.05 M) and varying concentrations of isoprene, at 298 K

[IP], M	$^3\phi/^1\phi$
0.1	0.24
0.5	1.79
1.0	3.24, 4.42
1.5	7.59
2.0	10.6
2.5	10.7
3.0	9.0, 9.77
4.0	8.9

methanol should give two regions of differing behavior. When $k_1[CH_3OH] \ll k_{ST}$, then Eq. (7) should be approximated by Eq. (8):

$$^1\phi/^3\phi = \frac{k_{TS}k_1[CH_3OH]}{k_{ST}k_3[IP]}. \tag{8}$$

At the other extreme, when $k_1[CH_3OH] \gg k_{ST}$, then $^1\phi/^3\phi$ should be independent of methanol concentration (Eq. 9).

$$^1\phi/^3\phi = \frac{k_{TS}}{k_3[IP]}. \tag{9}$$

As expected from Eqs (8) and (9), triplet sensitized decomposition of diphenyldiazomethane at a fixed isoprene concentration (0.1 M) and varying amounts of methanol (0.01–10.0 M) does show two distinct domains. The data are listed in Table 4 and shown graphically in Fig. 4.

Fitting Eq. (7) by the method of least squares to the data gives $k_{TS} = 1.97 \times 10^7$ s^{-1} and $k_1 = 7.4 \times 10^9$ M^{-1} s^{-1}. These results are in good agreement with the corresponding rate constants evaluated from the direct irradiation experiments.

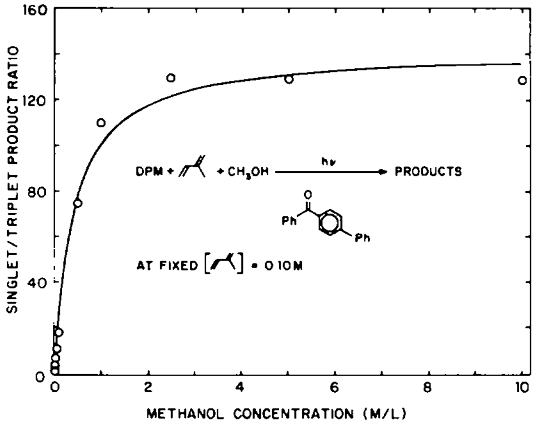


Fig. 4. Experimental behavior of $^1\phi/^3\phi$ as a function of the methanol concentration at a fixed isoprene concentration (0.10 M) obtained from the photosensitized decomposition of diphenyldiazomethane. The solid curve is calculated from Eq. (6) using $k_{ST} = 3.23 \times 10^9$ s^{-1}, $k_3 = 1.36 \times 10^6$ M^{-1} s^{-1}, $k_1 = 7.43 \times 10^9$ M^{-1} s^{-1} and $k_{TS} = 1.97 \times 10^7$ s^{-1}.

7. *The effect of solvent.* The results of the two experiments in which either the methanol or the isoprene concentration were fixed are completely consistent with the concept of rapid equilibrium between the two spin states of the carbene. In view of the large concentrations of isoprene that are required in the experiment with fixed methanol (>4 M) we have examined the effect of solvent on the equilibrium constant. We have chosen to use the non-polar isooctane since this solvent should have a similar medium effect on the kinetics as that of isoprene itself.

The values of $^3\phi/^1\phi$ for experiments in which a methanol concentration of 0.05 M was fixed and the isoprene concentration was varied, and the values of $^3\phi/^1\phi$ for a fixed isoprene concentration and various methanol concentrations were measured and are given in Tables 5 and 6. Additionally the values of k_{ST} (1.05×10^{10} s^{-1}) and k_3 (1.52×10^6 M^{-1} s^{-1}) were determined in isooctane in a manner identical to that previously described for acetonitrile. Analysis of the quantum yield data, using the STEPIT program as before, yields values of $k_1 = 1.23 \times 10^{10}$ M^{-1} s^{-1} and $k_{TS} = 3.47 \times 10^6$ s^{-1} for the fixed methanol experiment and $k_1 = 1.62 \times 10^{10}$ M^{-1}s^{-1} and $k_{TS} = 5.70 \times 10^6$s^{-1} for the fixed isoprene experiment. These results demonstrate a small but significant solvent effect on the kinetics of the intersystem crossing process of the carbene system. Although we note that for the solvents used, the kinetic model given by Scheme 1 yields good agreement with experiment, it is apparent that the solvent does influence the dynamics of the intersystem

Table 6. $^1\phi/^3\phi$ obtained from irradiation of an isooctane solution of diphenyldiazomethane in the presence of a fixed concentration of isoprene (1.0 M) and varying amounts of methanol, at 298 K

$[CH_3OH]$, M	$^1\phi/^3\phi$
0.01	0.023
0.05	0.36
0.20	1.60
0.30	2.30
0.40	2.80, 2.90

crossing process of the carbene and thus the product ratios. This is an especially important consideration in experiments using high concentrations of either methanol or isoprene, in which case the quenchers themselves could affect the nature of the solvent. For example, the observed differences between the experimental ${}^3\phi/{}^1\phi$ ratios, and those calculated using the rate constants derived from the curve fitting analysis, particularly in systems with high concentrations of methanol, may be due to solvent effects. The rate constants derived from the nonlinear least squares analysis represent values evaluated from relative quantum yield data determined over a wide range of quencher concentrations, with equal weighting given to each data point.

8. *Calculation of the equilibrium constant and free energy gap between singlet and triplet diphenylmethylene.* Using the appropriate values of k_{ST} and k_{TS} as given in Table 7, one can calculate the equilibrium constant, K_{eq}, between the singlet and triplet states of DPM from Eq. (10). The free energy difference between these two spin states follows directly

$$K_{eq} = \frac{k_{ST}}{k_{TS}} \tag{10}$$

from K_{eq} by use of Eq. (11). The derived values of $-\Delta G_{ST}$ in acetonitrile obtained from the four competitive quenching experiments (Table 7) are the same within experimental error. The average value is 3.2 ± 0.3 kcal/mol.

$$\Delta G_{ST} = -RT \ln K_{eq}. \tag{11}$$

We calculate ΔS_{ST} between the two spin states due only to their different spin multiplicity to be R ln 3, or 2.2 eu. Thus, the enthalpy difference between the lowest singlet and triplet states is $-\Delta H_{ST} = 2.5 \pm 0.3$ kcal/mol.

The average values of $-\Delta G_{ST}$ and $-\Delta H_{ST}$ determined in isooctane are 4.6 ± 0.3 kcal/mol and 4.0 ± 0.3 kcal/mol, respectively. These results imply that ^{3}DPM is more stable than ^{1}DPM by 1.5 kcal/mol in isooctane than in acetonitrile.[20]

As discussed in the introduction, the only previous experimental data relevant to the magnitude of the energy gap between the spin states in DPM was an estimate by Closs and Rabinow.[6] In competitive experiments which served as a model for our own, they used methanol as a selective scavenger and either styrene or oxygen as a selective triplet trap. From styrene–methanol competitive experiments and knowledge of k_3 for sytrene, measured by independent experiments, they obtained a value for $(k_1/K_{eq}) = 6.8 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$ in benzene. We obtained a similar relationship from isoprene–methanol competitive experiments involving either direct or photosensitized irradiation of DPM precursors and find an average value of $(k_1/K_{eq}) = 2 \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$ in acetonitrile and $6.4 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$ in isooctane.

9. *Measurement of singlet diphenylmethylene rate constants.* At the initiation of this work, the absolute rate constants for the reaction of DPM with several substrates had been measured.[6] However, no values for the rate of ^{1}DPM reactions were known. Since the ^{1}DPM has not been directly observed spectroscopically, we have chosen a steady-state method and an alternative time-resolved method to study the relative reactivity of the DPM toward a series of quenchers which would be expected to react selectively with the singlet state.

As discussed earlier, it is generally accepted that arylmethylenes react with alcohols selectively via the singlet state. We have measured the competitive rates of reaction for methanol, isopropanol and t-butanol with DPM. Steady-state photolysis of diphenyldiazo-

Table 7. Kinetic and thermodynamic parameters obtained from competitive quenching experiments analyzed according to the kinetics given in Scheme 1

Solvent: ACETONITRILE $k_{ST} = 3.23 \times 10^9\ \mathrm{s^{-1}}$ $k_3 = 1.36 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$

Method	Quencher conditions	$k_1(\mathrm{M^{-1}s^{-1}}) \times 10^{-9}$	$k_{TS}(\mathrm{s^{-1}}) \times 10^{-6}$	K_{eq}	$-\Delta G_{ST}$ (kcal/mol)	$-\Delta H_{ST}$ (kcal/mol)	T (K)
Direct Irradiation	vary [IP] fix [MeOH]	5.56	11.1	291	3.36	2.7	298
Direct Irradiation	vary [IP] fix [MeOH]	7.77	6.29	512	3.38	2.8	273
Direct Irradiation	fix [IP] vary [MeOH]	6.9	10.0	321	3.13	2.5	273
Sensitized Irradiation	fix [IP] vary [MeOH]	7.43	19.7	164	2.77	2.2	273

Solvent: ISOOCTANE $k_{ST} = 1.05 \times 10^{10}\ \mathrm{s^{-1}}$ $k_3 = 1.52 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$

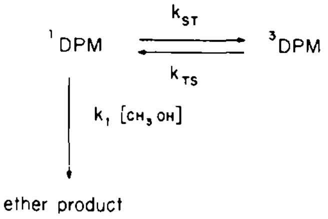
Method	Quencher conditions	$k_1(\mathrm{M^{-1}s^{-1}}) \times 10^{-9}$	$k_{TS}(\mathrm{s^{-1}}) \times 10^{-6}$	K_{eq}	$-\Delta G_{ST}$ (kcal/mol)	$-\Delta H_{ST}$ (kcal/mol)	T (K)
Direct Irradiation	vary [IP] fix [MeOH]	12.3	3.5	3031	4.75	4.1	298
Direct Irradiation	fix [IP] vary [MeOH]	16.2	5.7	1845	4.45	3.8	298

Table 8. Relative yield of the corresponding ether to benzhydryl methyl ether from the photolysis of diphenyldiazomethane in N_2 saturated acetonitrile containing methanol and either isopropanol or t-butanol

CH_3OH vs $R(CH_3)_2COH$	$Ph_2CHOCH_3/Ph_2CHOC(CH_3)_2R$†
R = H	1.6, 1.7
R = CH_3	3.1, 3.6, 3.6,‡ 3.4 (avg. 3.4 ± 0.2)

† Relative yield of the corresponding ether to benzhydryl methyl ether from the photolysis of diphenyldiazomethane in N_2 saturated acetonitrile containing methanol and either isopropanol or t-butanol.

‡ O_2 bubbled solution.



Scheme 2.

methane in the presence of equimolar methanol and one of the other alcohols leads to two major products, 1 and 7 (Eq. 12). The ratios of 1 : 7 which are assumed to be equal to the relative rates of reaction for the alcohols are listed in Table 8 for R = H, CH_3.

$$Ph_2CN_2 + CH_3OH + RC(CH_3)_2OH \rightarrow \underset{(1)}{Ph_2CHOCH_3} + \underset{(7)}{Ph_2CHO(CH_3)_2R} \quad (12)$$

$$R = H, CH_3.$$

Nanosecond laser flash photolysis of diphenyldiazomethane leads to rapid formation of DPM as described previously. As shown in Scheme 2 ^{3}DPM must crossover into the singlet manifold in order for a reaction with a singlet quencher to occur. Under the conditions of a rapid carbene spin state equilibrium the triplet state decay will be a simple function of the singlet quencher concentration.

In the presence of a sufficient concentration of quencher the decay becomes pseudo-first order as for the case of the triplet quencher isoprene. A plot of τ^{-1} *versus* quencher concentration yields an apparent triplet quenching constant (k^{t}_{app}). Assuming steady state conditions this rate constant (k^{t}_{app}) is given by k_1/K_{eq}.

The values of k^{t}_{app} are given in Table 9 for five hydroxylic quenchers. It is observed that the value of $k^{t}_{app} = 2.1 \times 10^7$ M^{-1} s^{-1} for methanol agrees well with the value of $k_1/K_{eq} = 2 \times 10^7$ which is obtained from the steady-state experiment.

Since the value of k^{t}_{app} for all of the quenchers depends only upon k_1 and K_{eq}, and since K_{eq} is the same for each of the quenchers, then the apparent triplet quenching values are a direct measure of the relative reactivity of the ^{1}DPM toward each substrate. In Table 9 is given the values of the relative rates for the various quenchers derived from the steady-state and time-resolved experiments. Good agreement is observed where the data overlap. Using the value of $k_1 = 5.6 \times 10^9$ M^{-1} s^{-1} for methanol, the absolute values of k_1 for the other quenchers can be calculated (Table 9). It appears that the reaction of ^{1}DPM with alcohols is very fast and is at or near the diffusion controlled rate expected for a bimolecular reaction under the conditions employed.

Bethell *et al.* have measured the relative reactivity of thermally generated DPM towards methanol and t-butanol to be 8.0 ± 0.5.[21] Direct comparison to our results is not possible, however, because their value was obtained via thermal decomposition of diphenyldiazomethane at 85° in acetonitrile. Nonetheless, their measurements confirm the trend which is also observed by us, i.e. that alcohol reactivity with the carbene increases with its acidity.

There has been a considerable amount of study done on the mechanism of heteroatom–hydrogen insertion reactions of diarylcarbenes.[1,21] Kirmse found a parallel between the relative reactivities of alcohols towards DPM and their acidity.[22,23] He interpreted this to indicate that the carbene abstracts a proton from the alcohol forming the diphenylmethyl cation (Eq. 13). Bethell *et al.* have studied the reaction of DPM with

$$Ph_2C\!: + ROH \rightarrow Ph_2CH^+ \ {}^-OR \rightarrow Ph_2CHOR \quad (13)$$

water and have provided results consistent with an electrophilic attack of the carbene on the oxygen atom as being the rate determining step.[21b] The initially formed ylide would subsequently undergo a proton

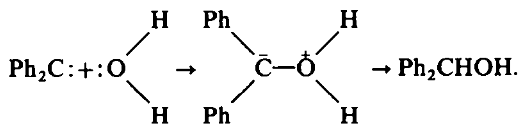
Table 9. Relative rate values for reaction of singlet diphenylmethylene with hydroxylic quenchers from time-resolved and steady-state studies

Quencher	Product yield ratio (1 : 7)	k^{t}_{app}, s^{-1}	Ratio† of k^{t}_{app}	k_1, M^{-1} s^{-1}‡
Water	—	2.1×10^7	1.14	4.9×10^9
Methanol	1.0	2.4×10^7	1.00	5.6×10^9
i-Propanol	1.65	1.5×10^7	1.60	3.5×10^9
t-Butanol	3.40	6.1×10^6	3.93	1.5×10^9
t-Amyl alcohol	—	6.6×10^6	3.64	1.5×10^9

† Ratio obtained by dividing by the value of k^{t}_{app} found for methanol.

‡ Determined from $k_1 = 5.6 \times 10^9$ M^{-1} s^{-1} for methanol together with the (average) relative rate values from the time-resolved and steady-state experiments where applicable, see text.

shift to form the product (Eq. 14).



(14)

They also favor this mechanism for the reaction with alcohols, but they too have noted a correlation between the reactivity of alcohols toward diarylmethylenes and their acidity.[21a]

Our results for the relative reactivities of the alcohols show a qualitative correlation with relative acidity of these substrates.

Upon addition of the alcoholic quenchers in the nanosecond flash experiments it is observed that both ^{3}DPM and the state(s) preceding it are quenched. The former effect is observed as a decrease in the lifetime of the triplet carbene, the latter as an increase in the transmitted light intensity at the end of the laser pulse due to the generation of a smaller triplet population. This is to be expected if the precursor state is the singlet state of the carbene and is intercepted by the quencher prior to intersystem crossing. Under these conditions a plot of the yield of the triplet carbene, immediately following nanosecond laser photolysis, *versus* methanol concentration should yield the Stern–Volmer constant for the singlet quenching directly, as given by Eq. (15). The quantity $(\mathrm{OD_o})$ is the optical density of

$$\frac{(\mathrm{OD_o})}{(\mathrm{OD})} = 1+(k_1/k_{\mathrm{ST}})[\mathrm{CH_3OH}] \qquad (15)$$

^{3}DPM in the absence of quencher at the end of the laser pulse and (OD) is the optical density in the presence of quencher.

However it is observed that there is a considerable laser intensity effect on the ground triplet carbene yield in the presence of a singlet quencher. As the laser intensity increases the extent of quenching increases. Furthermore, the extent of this quenching is smaller for experiments performed using 248 nm excitation light compared to those using 308 nm. These effects can be explained[24] as arising from reactions of the photoexcited triplet carbene (^{3}DPM*) which is formed within the 20 ns laser pulse. Since ^{3}DPM is formed within 0.3 ns, and this species has a high extinction coefficient at the excitation wavelength ($\varepsilon > 10^4$), then population of the excited triplet state manifold is an efficient process. Decay of ^{3}DPM* and intersystem crossing from ^{1}DPM determine the yield of ^{3}DPM at the end of the laser pulse. ^{3}DPM* has been shown to be extremely reactive toward alcoholic species,[24] and thus these substrates can quench two precursors (^{1}DPM and ^{3}DPM*) to the ground state triplet species. Under these conditions Eq. (14) is not valid. Analysis of the triplet yield as a function of isoprene, which is an efficient quencher of ^{3}DPM* but not of ^{1}DPM, confirms these conclusions. Using isoprene as the quencher, the triplet yield initially decreases and then levels off above 1 M. At an isoprene concentration of 1 M more than 90% of the excited state triplets are quenched.[24] Thus addition of more isoprene leads to no further detectible quenching. That no further quenching of the ground triplet carbene yield occurs confirms the previous proposal that the singlet state of DPM does not react with isoprene. Furthermore these results provide unambiguous evidence that the quenching of ^{3}DPM* by isoprene is due to a chemical reaction of the excited triplet state, and not merely physical quenching. These experiments demonstrate the problems which can arise when using high intensity light sources for excitation,[25a] however it is not expected that reactions due to the excited triplet are important under low light level steady-state photolysis conditions.

Recent time resolved flash photolysis measurements have demonstrated other complications that must be considered for carbene reactions which are studied in acetonitrile or in the presence of high concentrations of hydrogen bonding reagents such as alcohols: (1) acetonitrile has been shown to form an ylide with arylcarbenes such as 1-naphthylmethylene and fluorenlidene,[5b,25b] but not with DPM, and (2) the reactivity of carbenes toward hydrogen bonded dimers (and higher aggregates)[25c] differ from that toward the monomer. Additionally close scrutiny of the data given in Table 7 reveals a small solvent effect on the evaluated k_1 values. One finds that there is an increase in k_1 for isooctane relative to acetonitrile. A solvent influence on the reactivity of the O—H bond may be responsible for this interesting effect. However, the good general overall consistency of our data and its agreement with that of Closs and Rabinow[6] who worked in hydrocarbon solvents and with that of the general theory of carbene reactions leads us to conclude that any quantitative corrections are likely to be small.

Finally, the results of a recent study by Griller *et al.*[25d] on the kinetics of the apparent quenching of ^{3}DPM by methanol have been taken, by these authors, as evidence that Scheme 1 is incorrect. Firstly it was found that the apparent activation energy for the quenching reaction lies between 1.2 and 3.6 kcal/mol depending on the solvent, and secondly it was found that the maximum rate of ^{3}DPM disappearance at high methanol concentrations is $2\times10^7\ \mathrm{s^{-1}}$. The observed activation energy should equal the energy gap between ^{1}DPM and ^{3}DPM, plus the activation energy for the reaction between ^{1}DPM and methanol. Also, the rate of ^{3}DPM disappearance should become independent of methanol concentration when the intersystem crossing rate of ^{1}DPM to ^{3}DPM becomes the rate determining step for ether product formation. Since the observed activation energies were less than the expected values, and the maximum observed rate for ^{3}DPM decay was greater than the previously reported value for k_{TS},[9] it was concluded that methanol reacts with ^{3}DPM directly, and not with the equilibrated ^{1}DPM. We do not believe, however, that these criticisms of Scheme 1 are valid, since the observed maximum rate of $2\times10^7\ \mathrm{s^{-1}}$ is close to that evaluated from the sensitized decomposition experiment with fixed isoprene concentration (Table 7) and this value for k_{TS} requires only a small revision of the calculated value of ΔG_{ST}, within the experimental error associated with this number reported herein. Additionally several complications concerning the measurement of activation energies for singlet carbene reactions may arise. For example, the aggregation of methanol monomers, especially in nonpolar solvents has been shown to lead to an observed negative activation energy.[5c] A case in point is the reaction of singlet phenylchlorocarbene with methanol having an apparent activation energy equal to −4.5 kcal/mol.[25e] Even with nonaggregating substrates, zero or negative activation energies for reaction of singlet carbene quenchers have been observed,[5c] and has been explained in terms of reversible intermediate formation in the reaction sequence. Indeed evidence for this same phenomenon has recently been found, on the basis of kinetic isotope studies, for the reaction of singlet fluorenylidine with alcohols.[25f] In view of the consistent manner in which Scheme 1 predicts the quantum yield behavior for conditions of direct and photosensitized decomposition of diphenyldiazomethane, and for two different solvent systems, we conclude that Scheme 1 is a valid description of the chemical system and also provides a working model for the evaluation of the free energy gap between ^{1}DPM and ^{3}DPM in homogeneous solution.

SUMMARY AND CONCLUSIONS

We have combined the use of competitive quenching experiments and nanosecond and picosecond spectroscopy to obtain important information about the reactions of DPM in solution. The experimental behavior of the reaction of DPM conforms to the derived kinetics of Scheme 1, which supports the proposal that an equilibrium between carbene spin states is established in a time that is short compared to most reactions. Triplet sensitized experiments have confirmed that under the proper conditions the ratio $^3\phi/^1\phi$ is independent of the initially formed spin state because of the presence of this rapid equilibrium. Additionally, the results in isooctane confirm that establishment of the equilibrium is independent of the solvent mixture.

Extension of the steady state competitive quenching experiments carried out by Closs and Rabinow[6] and Bethell *et al.*[8] permitted evaluation of all four rate constants given in Scheme 1. Analysis of the data allows the determination of the free energy difference ($-\Delta G_{ST} = 3.2 \pm 0.3$ kcal/mol) between the singlet and triplet state of DPM in acetonitrile. Similarly, a value of $-\Delta G_{ST} = 4.6 \pm 0.3$ kcal/mol is determined in isooctane.

Absolute rate constants for the reaction of ^{1}DPM with several alcohols have been determined. These rate constants were obtained by steady-state competitive quenching experiments and were independently confirmed by time-resolved laser flash photolysis measurements. It is found that the alcohol reaction with ^{1}DPM is very efficient, and proceeds near the diffusion controlled limit. Furthermore, the relative rates of alcohol quenching of ^{1}DPM can be correlated to the relative lability and/or acidity of the O—H bond of the alcohol.

EXPERIMENTAL

Apparatus. ^{1}H-NMR spectra were taken on Perkin–Elmer R-32 (90 MHz) and Varian T-60 (60 MHz) spectrometers. Chemical shifts are reported in ppm downfield from an internal Tms standard [$(CH_3)_4Si$, δ 0.0]. IR spectra were recorded on a JASCO IRA-1 diffraction grating spectrometer. UV-visible absorption spectra were obtained using a Cary 17 spectrophotometer with solutions in 1 cm^2 cells of optical grade quartz. Reported m.ps are uncorrected.

GLC analyses were performed on a Varian Series 1200 gas chromatograph with a flame ionization detector. All GLC analyses were done on an 8 ft × 1/8 in. 10% SE-30 on Chromosorb W column, column temp 105°, injector and detector temps 180°, unless specified otherwise. The area of the chromatogram's peaks was measured by triangulation. The error inherent in this method was assumed to be ±10%.

Materials. Diphenyldiazomethane was prepared by a base catalyzed HgO oxidation of benzophenone hydrazone in anhyd ether as described in the lit.[26] It was found that the production of benzophenone as an impurity could be eliminated by carrying out the reaction under N_2 and in the dark. Diphenyldiazomethane was obtained as a violet solid: m.p. 30–31° (lit. m.p. = 29–30°); UV (CH_3CN): 255 nm (ε 80), 288 nm (ε 1.9×10^4); IR (CCl_4): ν 2020 cm^{-1}. The IR showed the absence of benzophenone, ν 1665 cm^{-1}.

Tetraphenyloxirane,[28] tetraphenylethane[29] and benzophenone azine[30] were prepared via lit. procedures. All other compounds were obtained commercially and used without further purification.

Procedure for direct irradiations. Irradiations were carried out in acetonitrile solns contained in tubes cooled to 0° in a Dewar, with one unsilvered face. Pyrex glassware was used for both direct and photosensitized irradiations of diphenyldiazomethane and quartz glassware was used for studies involving tetraphenyloxirane. All solns were N_2 bubbled through a thin capillary for 10 min before irradiation and during photolysis. The samples were kept at 0° to minimize changes in concentrations due to evaporation caused by the bubbling. Irradiations were done using a Conrad–Havovia 150 W high pressure Xe lamp.

Identification of products from the photolysis of diphenyldiazomethane in methanol or isoprene

Photolysis was accomplished by irradiating 20 mg of diphenyldiazomethane in 5 ml of MeOH while N_2 bubbling. After the color of the soln had bleached (~30 min), the MeOH was removed on the rotary evaporator. The residue showed one peak by GLC and was identified by NMR to be benzhydryl methyl ether. NMR ($CDCl_3$): δ 3.4 (2, 3H), 5.25 (s, 1H), 7.15–7.50 (m, 10H). Control experiments showed no decomposition of diphenyldiazomethane over a period of 1 hr in the absence of light.

In the same manner, diphenyldiazomethane (20 mg) was irradiated in isoprene (5 ml). After removal of the isoprene, GLC showed a mixture of two products of very similar retention times.

Comparison of the NMR of a purified (preparative GLC; 8 ft × 1/4 in. 19% SE-30 Chromosorb W, column temperature 170°) mixture of these two compounds to the lit. spectrum[13] confirmed the assignment of these peaks to the isomeric cyclopropanes, **2** and **3**.

Direct irradiation of diphenyldiazomethane in solutions containing methanol and isoprene competitive quenching experiments

An N_2 saturated acetonitrile soln of diphenyldiazomethane (2.0–3.0×10^{-3} M) was irradiated in the presence of various concentrations of isoprene and MeOH as described above. After the color had bleached (~5 min), the solvent was removed on the rotary evaporator with slight warming and the residue was analyzed by GLC. Analysis of samples without solvent removal gave identical results except for the diphenylmethane yield. A typical GLC trace showed five peaks identified as diphenylmethane, benzhydryl ether, benzophenone, and the cyclopropanes, **2** and **3** (**2**:**3** = 1.6 ± 0.3). No tetraphenylethane, tetraphenylethylene, or benzophenone azine was detected. In general, only a small amount of benzophenone relative to the other products was observed.

The GLC relative molar response ratio of benzhydryl methyl ether to the cyclopropanes was measured to be 1.0. This was done by comparing the relative GLC peak areas of these compounds in the mixture to the relative NMR integrated areas of the methyl groups in benzhydryl methyl ether to those of the cyclopropanes.

Direct irradiations of tetraphenyloxirane in solutions containing methanol and isoprene

An N_2 saturated acetonitrile soln of tetraphenyloxirane

(2–3×10^{-1} M) was irradiated in the presence of a fixed MeOH concentration (0.05 M) and various amounts of isoprene as described above. Samples were irradiated for 30 min resulting in 20–25% disappearance of the starting material as calculated from the GLC ratio of benzophenone to unreacted tetraphenyloxirane. Except for the enhanced yield of benzophenone resulting from the fragmentation of the oxirane, the GLC trace and analysis for samples with low isoprene concentrations were identical to those for direct irradiation of diphenyldiazomethane. At very high concentrations of isoprene (4–10 M), the formation of unidentified products was observed.

Photosensitized decomposition of diphenyldiazomethane in solutions containing methanol and isoprene

Competitive experiments

An N_2 saturated acetonitrile soln of diphenyldiazomethane (2.0–2.5×10^{-3} M) and 4-phenylbenzophenone ($\sim1\times10^{-2}$ M) in the presence of MeOH and isoprene was irradiated through Corning glass filters 7–51 and 0–52. This allowed excitation between 340 and 420 nm. The absorbance at 370 nm of diphenyldiazomethane under these conditions was 0.03 O.D. and of 4-phenylbenzophenone 1.0–1.5 O.D. Irradiation times were typically 1–1.5 hr depending on the concentration of the scavengers, and resulted in 80–90% destruction of the starting material. Irradiations under the same experimental conditions, but without the sensitizer, gave diphenyldiazomethane decompositions 15–20% that obtained with 4-phenylbenzophenone present.

Biacetyl sensitized irradiations were carried out in a similar manner employing Corning filters 7–51 and 3–75. This allowed selective excitation of the biacetyl at 395 ± 15 nm.

Direct irradiation of diphenyldiazomethane in the presence of competitive singlet diphenylmethylene scavengers

An N_2 saturated acetonitrile soln of diphenyldiazomethane (2.0–2.5×10^{-3} M) was irradiated in the presence of equimolar amounts (0.5 M) of competing alcohols, MeOH and either i-PrOH or t-BuOH. The resulting product mixture showed four compounds by GLC, benzhydryl methyl ether, the other corresponding benzhydryl ether, and smaller amounts of diphenylmethane and benzophenone. The ratio of the peak areas of the ethers was assumed to be equal to the relative rates of the alcohols with singlet diphenylmethylene.

No correction for the relative GLC molar response ratios of these compounds was made in calculating the relative rates of reaction with ^{1}DPM.

Acknowledgements—The authors thank the National Science Foundation, the Air Force Office of Scientific Research, and the Joint Services Electronics Program (DAAG-79-C-0079) for their generous support of this research. The authors thank D. Griller, A. S. Nazran and J. C. Scaiano for sending us a preprint of their recent work on the reaction of diphenylcarbene with methanol. The authors are most grateful to J. J. Zupanic, P. B. Grasse, S. C. Lapin and G. B. Schuster for communicating their results on fluorenylidene to us.

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