radicals. The results of the preceeding article[4] establish that both the competition between N–H vs. α-C–H transfer and the behavior of the resultant aminyl and α-aminoalkyl radicals are also dependent upon the structure of the excited arene reactant.

In reflecting upon the numerous investigations of aminyl vs. α-aminoalkyl radical formation from aliphatic amines (eq 1), we are reminded of the ancient Indian parable of the elephant and the blind men who attempted to describe the elephant after touching one of its parts. The use of singlet arenes[7] to probe the behavior of aliphatic amines led to the conclusion that aminyl radical formation was their characteristic reaction, whereas the use of triplet benzophenone[2] or alkoxyl radicals led to the conclusion that α-aminoalkyl radical formation was their characteristic reaction. While both observations are correct, the behavior of aliphatic amines, like the appearance of the elephant, cannot be fully characterized on the basis of a single observation.

Experimental Section

General procedures are the same as described in the preceeding article.[4] Primary amine fluorescence-quenching and quantum yields were determined on samples that were degassed by three freeze–pump–thaw cycles. Primary amine fluorescence-quenching constants ($k_{qs}\tau_s$) are determined from the initial portion of the Stern–Volmer plots since upwards curvature occurs at high amine concentrations.

Amines. Diethylamine (Aldrich), diisopropylamine (Aldrich), 2,2,6,6-tetramethylpiperidine (Aldrich), *n*-propylamine (Aldrich), isopropylamine (Aldrich), *tert*-butylamine (Aldrich), and triethylamine (Aldrich) were distilled from NaOH prior to use. Dimethylamine (Eastman) was used without further purification.

Deuterated Amines. Diethylamine, diisopropylamine, isopropylamine, and *n*-propylamine were all N deuterated by exchanging twice with a 5-fold excess of D_2O (Aldrich, 99.8 atom % D), the amine being distilled from the D_2O each time. The amines were dried over barium oxide and distilled. This resulted in >97% deuteration in all cases (by NMR). 2,2,6,6-Tetramethylpiperidine was N deuterated by treatment with *n*-butyllithium in hexane followed by quenching with D_2O.

***N,N*-Dimethyl-9-phenanthrenamine (IIIa).** Irradiation of 9-PCN with dimethylamine by the standard procedure affords IIIa [^{1}H NMR ($CDCl_3$) δ 7.24–8.73 (m, 9 H), 2.94 (s, 6 H); mass spectrum (EI, 70 eV), *m/e* 221 (100), 178 (27)] and I.

***N,N*-Diisopropyl-9-phenanthrenamine (IIIc).** Irradiation of 9-PCN with diisopropylamine by the standard procedure affords IIIc [^{1}H NMR ($CDCl_3$) δ 7.25–8.71 (m, 9 H), 3.73 septet, *J* = 6.4 Hz, 2 H), 1.05 (d, *J* = 6.4 Hz, 12 H); mass spectrum (EI, 70 eV), *m/e* 277 (28), 262 (100), 220 (50), 207 (30)] and I.

***N,N*-Dibenzyl-9-phenanthrenamine (IIId).** Irradiation of 9-PCN with dibenzylamine by the standard procedure affords IIId [^{1}H NMR ($CDCl_3$) δ 7.12–8.70 (m, 19 H), 4.34 (s, 4 H); mass spectrum (EI, 70 eV), *m/e* 91 (100)] and I.

***N*-Allyl-1-(9-phenanthryl)allylamine) (IV).** Irradiation of 9-PCN with diallylamine by the standard procedure affords IV [^{1}H NMR ($CDCl_3$) δ 7.20–8.82 (m, 9 H), 5.69–6.12 (m, 2 H), 5.07–5.32 (m, 4 H), 3.81 (d, *J* = 5.9 Hz, 4 H); mass spectrum (EI, 70 eV), *m/e* 273 (48), 230 (100), 215 (100)] and I. Also detected by GC–MS was IIIe [mass spectrum (EI, 70 eV, *m/e* 273 (100), 258 (49), 204 (85)].

***N*-*n*-Propyl-9-phenanthrenamine (IIIf).** Irradiation of 9-PCN with *n*-propylamine by the standard procedure affords IIIf [^{1}H NMR ($CDCl_3$) δ 7.24–8.76 (m, 8 H), 6.77 (s, 1 H), 3.34 (t, *J* = 7.0 Hz, 2 H), 1.85 (sextet, *J* = 7.2 Hz, 2 H), 1.12 (t, *J* = 7.0 Hz, 3 H); mass spectrum (EI, 70 eV), *m/e* 236 (38), 235 (50), 207 (56), 206 (100), 178 (40)] and I.

***N*-Isopropyl-9-phenanthrenamine (IIIg).** Irradiation of 9-PCN with isopropylamine by the standard procedure affords IIIg [^{1}H NMR ($CDCl_3$) δ 6.94–8.73 (m, 9 H), 3.92 (septet *J* = 6.2 Hz, 1 H), 1.41 (d, *J* = 6.2 Hz, 6 H); mass spectrum (EI, 70 eV), *m/e* 236 (28), 235 (66), 221 (40), 220 (100) 178 (19)] and I.

Acknowledgment. Support of this work by the National Science Foundation (CHE-8026020) is gratefully acknowledged.

Registry No. I, 56666-55-8; IIIa, 87884-68-2; IIIc, 25943-37-7; IIId, 87884-69-3; IIIf, 87884-71-7; IIIg, 87884-72-8; IV, 87884-70-6; 9-PCN, 2510-55-6; dimethylamine, 124-40-3; diethylamine, 109-89-7; diisopropylamine, 108-18-9; diisopropylamine-*N-d*, 25837-82-5; dibenzylamine, 103-49-1; diallylamine, 124-02-7; isopropylamine, 75-31-0; triethylamine, 121-44-8; piperidine, 110-89-4; 2,2,6,6-tetramethylpiperidine, 768-66-1; propylamine, 107-10-8; *tert*-butylamine, 75-64-9; diethylamine-*N-d*, 997-11-5; dibenzylamine-*N-d*, 87884-66-0; diallylamine-*N-d*, 87884-67-1.

Reaction of Diphenylcarbene with Methanol[1]

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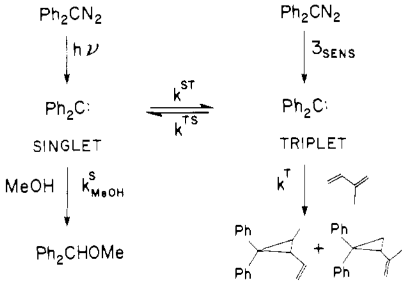
Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6. *Received March 22, 1983*

Abstract: The reaction of triplet diphenylcarbene with methanol is believed to proceed via thermal excitation to the singlet state followed by reaction of that state with the alcohol. Analysis of the related reaction kinetics led to a reported enthalpy difference of 3–5 kcal mol^{-1} between the singlet and its triplet ground state. We report measurements of the activation energy, E_{obsd}, for reaction of triplet diphenylcarbene with methanol in various solvents and find, for example, $E_{obsd} = 1.66 \pm 0.20$ kcal mol^{-1} in acetonitrile. These and other results are inconsistent with published interpretations of the data and dictate a reevaluation of earlier experiments and the mechanistic conclusions drawn from them.

The nature of the energy gap between singlet and triplet diphenylcarbene has been a subject of interest for some years.[2-8] Electron paramagnetic resonance studies have shown that the carbene has a triplet ground state,[9-12] and the consensus of current opinion supports the idea that the triplet and singlet states are

Scheme I



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[1] Issued as NRCC Publication No. 22862.

[2] Bethell, D.; Stevens, G.; Tickle, P. *Chem. Commun.* **1970**, 792.

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[4] Bethell, D.; Hayes, J.; Newell, A. R. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1307.

[5] Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190.

[6] Gaspar, P. P.; Whitsel, B. L.; Jones, M., Jr.; Lambert, J. B. *J. Am. Chem. Soc.* **1980**, *102*, 6108.

[7] (a) Eisenthal, K. B.; Turro, N. J.; Aikawa, M.; Butcher, J. A., Jr.; DuPuy, C.; Hefferon, G.; Hetherington, W.; Korenowski, G. M.; McAuliffe, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 6563. (b) Turro, N. J. *Tetrahedron* **1982**, *38*, 809.

[8] Wang, Y.; Sitzmann, E. V.; Novak, F.; DuPuy, C.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 3238.

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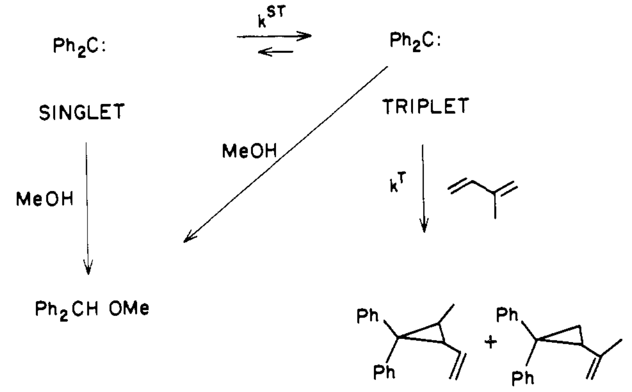
Scheme II



in thermal equilibrium at room temperature.[2,3,5-8] However, evidence supporting this conclusion is based on the assumption that singlet and triplet states of the carbene carry out certain stereotypical reactions. In particular it has been assumed that only the singlet state of the carbene will react with alcohols to form ethers.[2,3,5-8]

The reaction scheme on which these conclusions are based was first advanced by Bethell, Stevens, and Tickle[2] and has subsequently been used by other authors.[5-8] Scheme I shows its most recent adaptation.[7]

The mechanistic scheme described above can be augmented with measurements made by flash photolysis. In the standard approach,[5,7,8] an absolute rate constant for the reaction of a triplet carbene with a diene is determined by laser flash photolysis. Competition studies are then carried out in which the carbene is generated in mixtures of the diene and an alcohol. It is assumed that only the singlet state of the carbene will react with an alcohol, and thus information about the relationship between the singlet and triplet states can be discernible from the experimental results.

Closs and Rabinow were the first to use this approach.[5] They assumed a value for $k^S \leqslant 5 \times 10^9$ M^{-1} s^{-1}. This was combined with data obtained in flash photolysis and product studies to yield $k^{ST}/k^{TS} \geqslant 5 \times 10^2$. With the further assumption that the entropy difference between the singlet and triplet states arises only from the triple degeneracy of the latter, they concluded[5] that $-\Delta H$, the singlet–triplet energy gap, was $\leqslant$3 kcal mol^{-1}.

Eisenthal, Turro, and their colleagues[7a] used the same approach but additionally measured k^{ST} by a picosecond laser flash photolysis technique. With this extra piece of data and similar assumptions about the equilibrium these authors were able to measure the free energy gap of $-\Delta G = 5.1 \pm 1$ kcal mol^{-1} (5.4 ± 1 kcal mol^{-1}, in a more recent publication).[7b]

The complexity of these more recent experiments tends to obscure what Bethell et al. were careful to point out in their original work,[2] which is that all the experimental observations are equally consistent with the simple idea that all of the reaction products are derived from the triplet carbene (Scheme II). In essence, there is no direct evidence for rapid triplet-to-singlet intersystem crossing,[13] as the factor controlling the kinetics of alcohol quenching.

In this work we have designed experiments to test the validity of Scheme I and find that it cannot be used to explain all the available experimental data, implying that part of these data may be in error or that Scheme I requires major revision.

Experimental Section

Materials. Diphenyldiazomethane was synthesized by the standard method[14] and was purified by sublimation at room temperature. Diphenyldiazomethane-^{13}C was synthesized from appropriately labeled benzophenone (isotopic purity = 90%, Merck Sharp and Dohme).

The methanol, isooctane, and acetonitrile used in these experiments were spectroscopic grade and were purified by distillation from calcium hydride. Benzene was washed with concentrated sulfuric acid and then by water. It was then dried over magnesium sulfate and was finally distilled from calcium hydride. Chlorobenzene was purified by distillation.

Product Studies. Product studies on the photodecomposition of diphenyldiazomethane in the presence of methanol were carried out in each of the solvents investigated in this work. Thus, diphenyldiazomethane (0.038 M) and methanol (0.49 M) were dissolved in a given solvent. The mixture was purged with nitrogen and was then photolyzed with a visible-light source until the characteristic red color due to the diazo compound could not be detected. The solutions were then concentrated to a quarter of their original volume by distillation of the solvent. The products were analyzed by gas chromatography with a mass spectrometer as a detector.

Apparatus. The laser flash photolysis system used in this work has been described in detail elsewhere.[15] Samples were photolyzed at 308 nm with an excimer laser operated with Xe/HCl mixtures (pulse width ~5 ns, up to 80 mJ/pulse). In a typical experiment nitrogen-purged solutions of diphenyldiazomethane (6.5×10^{-5} M) containing varying concentrations of methanol were allowed to flow through the sample chamber (flow rate 0.3 mL/pulse). The optical absorption spectrum of diphenylcarbene was detected immediately after the laser pulse. Its decay was monitored at 320 nm in all the solutions under investigation.

An early series of preliminary experiments was carried out with a nitrogen laser (337 nm) for excitation; these experiments required higher precursor concentrations (>1 mM) and involved a substantially smaller laser dose (approximately a factor of 8). The Arrhenius parameters obtained in benzene (the only solvent examined with this laser) were in full agreement with those obtained by using the excimer laser, as described above.

Results and Discussion

Two flash-photolysis studies have focused upon the measurement of absolute rate constants for the reactions of diphenylcarbene in solution. In their pioneering work, Closs and Rabinow[5] found that the reaction of triplet diphenylcarbene with 1,3-butadiene in benzene proceeds with a rate constant of 6.4×10^5 M^{-1} s^{-1} at 25 °C. Eisenthal, Turro, and their colleagues[7] showed that the analogous reaction with isoprene in acetonitrile had a rate constant of $(3.5 \pm 0.5) \times 10^5$ M^{-1} s^{-1} at 25 °C. Moreover these authors showed that the ratio of cis and trans cyclopropanes formed in this reaction was independent of the isoprene concentration and remained unchanged when diphenylcarbene was generated by triplet-sensitized decomposition of diphenyldiazomethane. They therefore concluded that, under their conditions, singlet diphenylcarbene, which was presumably formed in the direct photodecomposition of the diazo compound, underwent intersystem crossing to the triplet ground state without being scavenged by isoprene. That is, isoprene was a selective trap for the triplet carbene.

Closs and Rabinow also investigated the quenching of triplet diphenylcarbene by methanol. The observed rate constant, k_{obsd}, was found to be $(6.8 \pm 2.1) \times 10^6$ M^{-1} s^{-1},[5] but it was interpreted as being due to reaction by the thermally populated singlet carbene; i.e.

$$k_{obsd} = k^S/K_{eq} \qquad (1)$$

where k^S is the rate constant for the reaction of singlet carbene with methanol and K_{eq} is the singlet $\leftrightarrow$ triplet equilibrium constant (Scheme I). More recently, the rate constant for singlet-to-triplet intersystem crossing was measured by following the growth of triplet diphenylcarbene in the picosecond time domain and was found to be $(9.1 \pm 1) \times 10^9$ s^{-1} in acetonitrile.[7]

Out of experimental necessity, all of the kinetic measurements described above were made by monitoring the triplet carbene. No optical absorption or fluorescence due to the singlet carbene has yet been detected. Thus, any interpretation of the data in terms of the singlet carbene must be based on an assumption, and the

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[9] Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763.

[10] Trozzolo, A. M. *Acc. Chem. Res.* **1968**, *1*, 329.

[11] Trozzolo, A. M.; Wasserman, E. In "Carbenes"; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1973; Vol. II, p 185.

[12] Hutchison, C. A., Jr.; Kohler, B. E. *J. Chem. Phys.* **1969**, *51*, 3327.

[13] A different approach[6] has been used to adduce such evidence but was based on arguments which were circular.

[14] Smith, L. I.; Howard, K. L. "Organic Syntheses"; Wiley: New York, 1955; Collect Vol. III, p 351.

[15] Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

most favored assumption has been that methanol is a selective trap for singlet diphenylcarbene. It is further assumed that the singlet carbene in equilibrium with the triplet is identical with that generated via nitrogen loss from the excited diazo compound.

The notion that methanol is a selective trap for singlet carbenes is based on the concept that since the methanol and the ether derived from it (Scheme I) have singlet ground states, then the reaction that leads from one to the other must involve another singlet species, namely the singlet carbene.

In this work we do not dispute the observation that singlet diphenylcarbene shows a high reactivity toward methanol. However, if all of the available experimental data are correct we are forced to question the concept that quenching of the triplet carbene by methanol necessarily proceeds through the thermally populated singlet.

The kinetic results outlined above are insufficient in themselves to allow a calculation of the singlet–triplet energy gap. The information missing is a value for k^{TS}. This was obtained by combining product studies with the flash-photolysis data.

Eisenthal, Turro, and their co-workers[7] measured the quantum yield of triplet-derived cyclopropanes ($^3\Phi$) vs. that of singlet-derived ether ($^1\Phi$) using a fixed concentration of methanol (0.05 M) and varying amounts of isoprene[7] in acetonitrile solvent. The kinetic expression[16] used in the experiment is given in eq 2, where the

$$^3\Phi/^1\Phi = \frac{k^{ST}k^{T}[IP]}{(k^{TS} + k^{T}[IP])k^{S}[MeOH]} \qquad (2)$$

rate constants are defined in Scheme I and IP represents isoprene. At low isoprene concentrations $k^{TS} \gg k^{T}[IP]$; and hence (2) reduces to (3), whereas at high isoprene concentrations $^3\Phi/^1\Phi$

$$^3\Phi/^1\Phi = \frac{k^{ST}k^{T}[IP]}{k^{TS}k^{S}[MeOH]} \qquad (3)$$

became independent of [IP], implying that $k^{TS} \ll k^{T}[IP]$ when (2) reduces to (4).

$$^3\Phi/^1\Phi = k^{ST}/(k^{S}[MeOH]) \qquad (4)$$

The data obtained from studies of the relative quantum yields were combined with rate constants obtained by flash photolysis to yield $k^S = (3.5 \pm 0.5) \times 10^{10}$ M^{-1} s^{-1} and $k^{TS} = (1.7 \pm 0.3) \times 10^6$ s^{-1}. Since k^{ST} and k^{TS} were then known, K_{eq} was calculated to be $(5.4 \pm 1) \times 10^3$, from which $-\Delta G$ was found to be 5.1 ± 1 kcal mol^{-1}.[7,17]

These results suffer from two weaknesses. First, since $k^T = (3.5 \pm 0.5) \times 10^5$ M^{-1} s^{-1} the boundary condition $k^{TS} \ll k^{T}[IP]$ is not satisfied by the rate constants derived by assuming that condition, even at the highest concentration of isoprene used (10 M).[7] Second, progressive substitution of acetonitrile solvent by isoprene (up to 10 M isoprene) may well have changed the reactivity of the OH bond in methanol, which was the competitive reagent.[17,18]

We have applied two simple tests to check the validity of current interpretations of the reported data and the applicability of Scheme I. The first involves the measurement of the activation energy for methanol quenching of the triplet carbene. According to the above mechanism this should require 3–5 kcal mol^{-1} for triplet-to-singlet conversion and 1–3 kcal mol^{-1} for the essentially diffusion-controlled reaction of the singlet carbene with methanol.[20]

Table I. Temperature Dependence for the Quenching of Diphenylcarbene by Methanol

T/K	solvent	E_a/ (kcal mol^{-1})^a	log (A/ (M^{-1} s^{-1}))^a	k_{obsd}/ (M^{-1} s^{-1})^b
248–342	isooctane	3.61 ± 0.36	9.51 ± 0.27	6.43×10^6
255–320	chlorobenzene	2.48 ± 0.44	9.30 ± 0.34	2.75×10^7
242–336	acetonitrile	1.66 ± 0.20	8.62 ± 0.16	2.39×10^7
282–328	benzene	1.17 ± 0.36	8.17 ± 0.26	1.97×10^7

^{a} Corrected to take into account the temperature coefficient of the solvent density. ^{b} At 293 K.

Table II. Percentage Yields of Products Formed in the Reaction of Diphenylcarbene with Methanol at 300 K

	solvent		
product	benzene	isooctane	acetonitrile
Ph_2CHOMe	93	94	90
Ph_2CH_2	3	2	3
Ph_2CO	1	1	3
unidentified	3	3	4

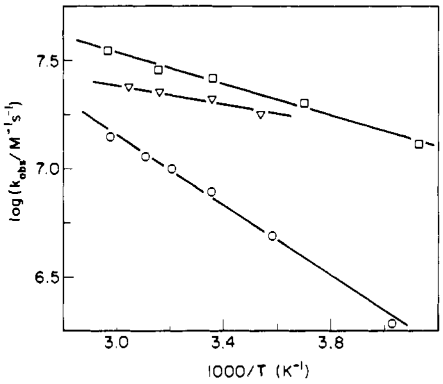

Figure 1. Arrhenius plots for the quenching of triplet diphenylcarbene by methanol in acetonitrile (□), benzene (▽), and isooctane (○).

Activation Energies. The observed rate constant for this reaction, k_{obsd}, was measured at a given temperature by monitoring the lifetime of triplet diphenylcarbene at different methanol concentrations. The pseudo-first-order rate constant for carbene decay, k_{decay}, is related to the first-order constant for its decay in the absence of methanol, k_0, and to k_{obsd}, according to eq 5, where $k_{obsd} = k^S/K_{eq}$ *if Scheme I is valid.*

$$k_{decay} = k_0 + k_{obsd}[CH_3OH] \qquad (5)$$

Data of this kind were collected at a variety of temperatures in acetonitrile, benzene, chlorobenzene, and isooctane solvents and plotted according to eq 5. The individual values of k_{obsd} obtained in these experiments are available as supplementary material. Arrhenius A factors and activation energies were calculated from these results and are shown in Table I, where the error limits shown represent two standard deviations. Figure 1 shows the corresponding Arrhenius plots. Special care was taken to work at low concentrations of methanol, <0.2 M, so as to avoid the possibility of disrupting the efficient singlet–triplet equilibration that was proposed in earlier work.[5,7]

The products of the reaction between diphenylcarbene and methanol were investigated in benzene, isooctane, and acetonitrile as solvents (see Experimental Section). In all cases the expected ether was formed in ≥90% yield as well as trace amounts of benzophenone and diphenylmethane. The latter were presumably produced respectively by reaction of the carbene with residual oxygen and with solvent or ether product. The yields are given in Table II.

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(16) The reciprocal form of eq 2 represents a far more convenient expression for treatment of the data. However, for simplicity we have adhered to the formulas used by the original authors.[7]

(17) The most recent estimate gives $-\Delta H \simeq 4$ kcal mol^{-1}: Turro, N. J.; Eisenthal, K. B., private communication.

(18) Joesten, M. D.; Schaad, L. J. "Hydrogen Bonding"; Marcel Dekker: New York, 1974; Chapter 5.

(19) Griller, D.; Liu, M. T. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5549.

(20) The temperature dependence of other close to diffusion-controlled processes is known to reflect the temperature dependence of the solvent viscosity.[21,22]

(21) For free radicals see: Fischer, H.; Schuh, H.-H. *Helv. Chim. Acta* **1978**, *61*, 2130.

(22) For triplet energy-transfer processes see: Scaiano, J. C.; Leigh, W. J., manuscript in preparation.

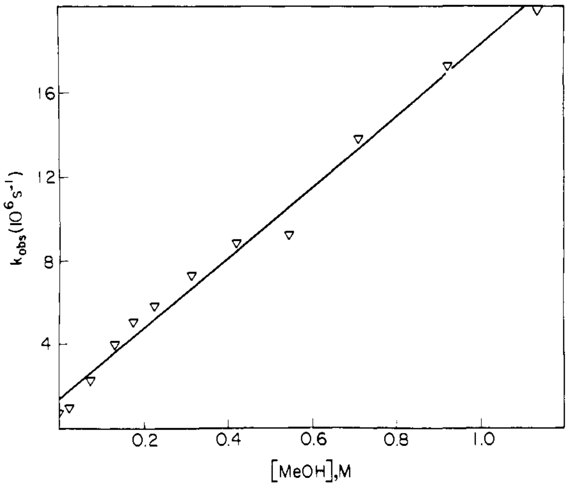

Figure 2. Plot of k_{obsd} measured at 293 K for the quenching of triplet diphenylcarbene vs. methanol concentration in acetonitrile solvent.

The observation of an activation energy of 1.66 ± 0.20 kcal mol^{-1} in acetonitrile and of low activation energies in the other solvents is clearly inconsistent with the expected activation energy of ~6 kcal mol^{-1}, which was based on the interpretation of all of the other available experimental data in terms of Scheme I. Moreover, it should be carefully noted that any model which is advanced to explain the acetonitrile result must be equally applied to the results of the earlier competition studies since these represent a study of the same reaction in the same solvent.

It is important at this point to gain some insight into the kinetic analysis corresponding to Scheme I. Application of the steady-state assumption to the singlet carbene under conditions where k_0 is unimportant yields eq 6, where T represents the triplet

$$\frac{-\partial[\mathrm{T}]}{\partial t} = \frac{k^{\mathrm{TS}}k^{\mathrm{S}}[\mathrm{MeOH}]}{k^{\mathrm{S}}[\mathrm{MeOH}] + k^{\mathrm{ST}}}[\mathrm{T}] \qquad (6)$$

carbene and t the time. Two limiting situations can be recognized. At the singlet–triplet equilibration limit we have $k^{\mathrm{ST}} \gg k^{\mathrm{S}}[\mathrm{CH_3OH}]$ and the expression reduces to eq 7, which following

$$\frac{-\partial[\mathrm{T}]}{\partial t} = \frac{k^{\mathrm{TS}}}{k^{\mathrm{ST}}}k^{\mathrm{S}}[\mathrm{MeOH}][\mathrm{T}] \qquad (7)$$

integration corresponds to eq 1. The data in Table I and Figure 1 would satisfy this condition if Scheme I were valid. The other limiting situation brings us to our second test of Scheme I and to what we will refer as "kinetic saturation".

Kinetic Saturation. Under the condition of kinetic saturation $k^{\mathrm{ST}} \ll k^{\mathrm{S}}[\mathrm{CH_3OH}]$, which leads to eq 8, and corresponds to k_{decay}

$$\frac{-\partial[\mathrm{T}]}{\partial t} = k^{\mathrm{TS}}[\mathrm{T}] \qquad (8)$$

$= k^{\mathrm{TS}}$. Thus, at sufficiently high methanol concentration the rate of triplet carbene decay would be expected to become independent of the methanol concentration. The limiting value of k_{decay} would be k^{TS}, which on the basis of Scheme I has been evaluated[7] as ~2×10^6 s^{-1}.

The experiments are difficult because the triplet yields decrease with methanol concentration (vide infra); however, we were able to make measurements at least 1 order of magnitude faster than the expected saturation value for k_{decay}. Thus, for [MeOH] = 1.13 M in acetonitrile we measured $k_{\mathrm{decay}} = 2.0 \times 10^7$ s^{-1}. Even at this high methanol concentration the plots of k_{decay} vs. [MeOH] remain linear (Figure 2). The situation is similar in benzene, where for [MeOH] = 0.65 M we obtained $k_{\mathrm{decay}} = 1.9 \times 10^7$ s^{-1}.

As pointed out above, the triplet yield, approximately 5–10 ns after the laser pulse, decreases with increasing methanol concentration. This is entirely expected if the nascent singlet carbene partitions between intersystem crossing and methanol quenching. A Stern–Volmer analysis of the data, based on the transient optical density at 320 nm, can yield $k^{\mathrm{S}}/k^{\mathrm{ST}}$; i.e.

$$\frac{(\mathrm{OD})^0}{(\mathrm{OD})} = 1 + \frac{k^{\mathrm{S}}}{k^{\mathrm{ST}}}[\mathrm{MeOH}] \qquad (9)$$

The values of $k^{\mathrm{S}}/k^{\mathrm{ST}}$ obtained in this way are 5 ± 2 M^{-1} and 12 ± 5 M^{-1} in acetonitrile and benzene, respectively. If the result for acetonitrile is combined with the picosecond flash-photolysis measurement[7] of k^{ST}, then $k^{\mathrm{S}} = 5 \times 10^{10}$ M^{-1} s^{-1}. It should be noted that this result does not involve any assumptions regarding singlet–triplet equilibration (Scheme I).

Experiments in isooctane and in benzene, generating the diphenylcarbene-^{13}C, led to the same rate constants (±10%) as those with the unlabeled precursor.

The Reaction Mechanism. The simplest explanation of all of the available experimental data is to assume that all of the reaction products are derived from a single precursor, triplet diphenylcarbene, and that triplet-to-singlet intersystem crossing does not control the kinetics of the process. The experimental results obtained in other studies, which were summarized at the start of this section, would be quite consistent with such a scheme, as is the observation that diphenylcarbene adds to alcohols even at 77 K.[23] Indeed, this possibility was first discussed in 1974 to explain results obtained in a study of the reaction between diphenylcarbene and amines.[4] Clearly if triplet diphenylcarbene is to react with methanol, intersystem crossing must occur at some point in order for a ground-state product to be formed.

A note of caution should, however, be added to mechanistic interpretations when methanol is a substrate. This is because methanol partitions between monomer, dimer, and higher hydrogen-bonded oligomers. The distribution of these forms is strongly dependent upon the temperature, methanol concentration, and solvent. We have shown that singlet phenylchlorocarbene shows different reactivity toward methanol monomer and oligomers.[18] The difference is not expected to be that large for systems that approach diffusion control.

The results reported herein negate the conclusions of earlier work.[5,7] In this section we explore some of the mechanistic implications of these additional data.

A central feature of the earlier experiments[7] was the measurement of quantum yields for singlet and triplet pathways as a function of isoprene concentration (Scheme I, eq 2). We have already discussed some of the possible deficiencies of this experiment, namely the change of solvent from acetonitrile to isoprene and the inconsistency of the rate constants derived. In addition, we note that conclusions were drawn from the observation that the ratio of quantum yields was invariant at isoprene concentrations >6 M. This is not an entirely satisfactory condition since at these high concentrations the solvent cage surrounding the carbene must contain several molecules of isoprene. It is therefore argueable that any variation of the formal concentration of this substrate may not have a proportional effect on the rate of reaction.

Setting aside conclusions based on the quantum yields experiment, we are still left with the measurement of k^{ST} in the picosecond time domain[7] as an independent viable result. Combining this result with our own measurement of $k^{\mathrm{S}}/k^{\mathrm{ST}}$ in acetonitrile gave $k^{\mathrm{S}} = 5 \times 10^{10}$ M^{-1} s^{-1} at 293 K. These conclusions do not rely on Scheme I but reflect a simple competition between singlet-to-triplet intersystem crossing vs. the reaction of the initially formed singlet with methanol.

Let us now assume that Scheme I is applicable but that the only correct data at our disposal are the measurements k^{ST}, k^{S}, and k_{obsd}; what are the implications? First, eq 1 leads to a value of $K_{\mathrm{eq}} = 2.1 \times 10^3$ at 293 K and hence $-\Delta G = 4.5$ kcal mol^{-1}. However, it follows from eq 1 that

$$E_{\mathrm{obsd}} = -\Delta H_{\mathrm{eq}} + E_{\mathrm{s}} \qquad (10)$$

where E_{obsd} and E_{s} are the activation energies relating to k_{obsd} and k^{S}. Since the extremely high value of k^{S} indicates that this reaction

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(23) Tomioka, H.; Miwa, T.; Suzuki, S.; Izawa, Y., *Bull. Chem. Soc. Jpn.* **1980**, *53*, 753.

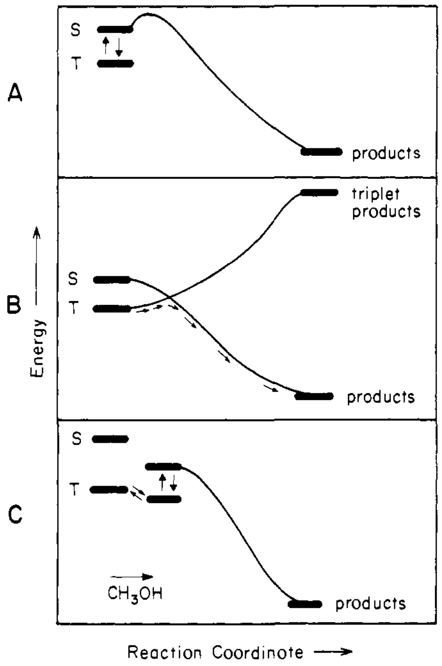

Figure 3. Possible mechanisms describing the reaction of diphenylcarbene with methanol.

is diffusion controlled, it shows that $E_s \simeq$ 1–2 kcal mol^{-1} [21,24] and is therefore approximately equal to E_{obsd}. This means that $\Delta H \simeq 0$ kcal mol^{-1} and hence $\Delta G/T \simeq \Delta S \simeq 15$ cal deg^{-1} mol^{-1}.

It seems extremely improbable that the difference in entropy between the singlet and triplet states can be this large; indeed it is normally thought that the only entropic difference arises from the triple degeneracy of the triplet state. We therefore rule out the mechanism involving unperturbed singlet–triplet equilibration as being an adequate description of the reaction mechanism (Scheme I and Figure 3A).

Figure 3B shows a possible reaction mechanism involving an avoided crossing of the singlet and triplet surfaces. In this case, one can expect the experimental activation energy to be less than the T–S energy gap, provided the activation energy for the singlet reaction is very small or zero. Thus, our data would require the energy surfaces to show considerable solvent dependence, perhaps a reflection of the marked dependence of the properties of methanol itself.

Another possible reaction sequence is shown in Figure 3C. Here the triplet carbene is assumed to associate weakly with methanol. One can expect the relatively polar singlet state to be lowered substantially more than the triplet, leading to a reduction of the T–S energy gap. The effect of methanol on the T–S energy gap may be the result of a stoichiometric and/or medium (solvent) effect. The ultimate behavior in a mechanism of this type will depend on a delicate balance of rate constants and their solvent dependence.

We come now to the question as to whether a simple, uncomplicated reaction of the triplet carbene with methanol could be the explanation for our data. From a kinetic point of view the answer is clearly yes. While it is hard to envision a "simple" mechanism that starting from triplet would yield the ether in the ground state, it is possible to rationalize such a process in terms of an "avoided crossing" of the triplet and singlet energy surfaces (Figure 3B). Other possible mechanisms, such as complexation with the solvent leading to a different energy gap or reactivity toward methanol for the carbene (Figure 3C), are also possible. It is hard, however, to see what delicate balance of kinetic parameters could make a mechanism of the type of Scheme I basically correct and useful for the estimation of T–S gaps and yet incorrectly predict the overall temperature dependence of the reaction.

It should be noted that the above conclusions depend entirely upon the assumption that the measured value[7] of k^{ST} is correct and that it applies to the reaction of the singlet carbene in equilibrium with its triplet ground state. If this assumption is incorrect, then it still remains possible to rationalize the data in terms of Scheme I, by proposing that the reported value[7] of k^{ST} is too high by around 1 order of magnitude.

With this in mind, two distinct possibilities arise. First, photolysis of diphenyldiazomethane may lead to an excited singlet state of the carbene which may undergo intersystem crossing to the triplet more rapidly than its ground-state counterpart. The second possibility is that the measurement of k^{ST} is simply in error. While it is difficult to see how such a carefully executed experiment[7] could lead to an incorrect result, we can nevertheless accept the possibility and explore the consequences.

The data reported herein which were based on the quantum yield for triplet formation as a function of the methanol concentration gave $k^S/k^{ST} = 5 \pm 2$ M^{-1} in acetonitrile solvent (eq 9). Since we were unable to detect the growth of the triplet carbene with 8-ns time resolution it further follows that $k^{ST} > 10^8$ s^{-1}. Finally, measurements on the observed rate of triplet quenching by methanol in acetonitrile gave $k_{obsd} = 2 \times 10^7$ M^{-1} s^{-1}. When these results are combined in eq 1, it follows that the present data only require that $K_{eq} > 30$ and admits the possibility of a very small value for ΔH, which would be consistent with the observed activation energies for triplet quenching by methanol.

Conclusion

If the available data on the reaction of diphenylcarbene with methanol are correct, it follows that the triplet state reacts with methanol to give the corresponding ether as product, in a process that must access (Figure 3B) or modify (Figure 3C) the singlet surface at some point along the reaction path. However, if the reported value for singlet-to-triplet intersystem crossing is in error, being too high, then the data may be consistent with a mechanism involving thermal equilibrium between the triplet and singlet states followed by the reaction of the singlet with methanol to give ether. In this case, the value of ΔH would be ca. 1–2 kcal mol^{-1}. Clearly, more detailed investigation of this and related systems is required.

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Registry No. Diphenylcarbene, 3129-17-7; methanol, 67-56-1.

Supplementary Material Available: Tables III–VIII giving full kinetic details (12 pages). Ordering information is given on any current masthead page.