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Photodecomposition Mechanism of 2-Methoxy-1,2-diphenyl Diazoethane

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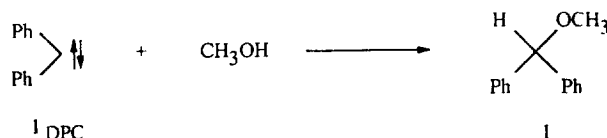
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The mechanism of the photodecomposition of 2-methoxy-1,2-diphenyl diazoethane has been investigated in methanol and isoprene using time-resolved laser flash photolysis techniques. The reaction of triplet carbene which is generated from 2-methoxy-1,2-diphenyl diazoethane with methanol is believed to proceed *via* thermal excitation to the singlet state. The activation energy and enthalpy are consistent with a mechanism involving thermal equilibrium between the triplet and singlet state followed by the reaction of the singlet with methanol to give ether.

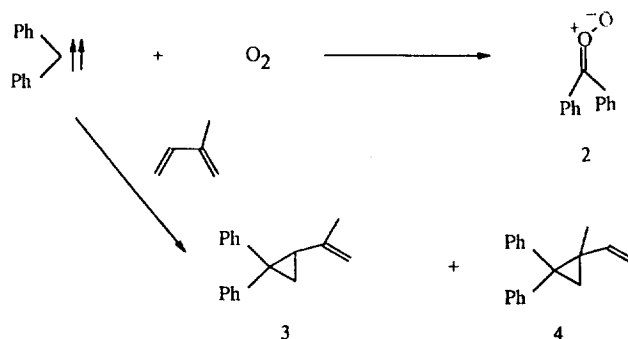
Introduction

The reactivity of carbene is determined by their spin multiplicity.¹ Carbenes have singlet and triplet electronic states. Generally triplet carbenes react by two-step radical processes, whereas singlet carbenes can undergo singlet-step bond insertion. Methylene is well known as a simple carbene.² It is well appreciated that there are two chemically important states of methylene.³ Their two states can each be detected spectroscopically as ¹A₁ and ³B₂.⁴ Organic chemistry have also been eager to measure the singlet-triplet energy gap in large systems such as phenyl carbene, diphenyl carbene and naphthyl carbene.⁵ However, in these systems, it has only proven possible to detect the triplet ground state by spectroscopic methods. It is also questionable whether gas phase spectroscopy and high-level calculation can be applied to molecules of such size and complexity to give accurate values of enthalpy between the singlet and triplet states. Many results are focused on the points of combination of product analyses and kinetics as a tool which can be interpreted the reactivity for the molecules of aromatic carbenes. For example, the quenching of a triplet aromatic carbene is used for the standard reaction of probing the singlet-triplet energy gap.⁶ It is pointed out that this treatment would make an error for application to some aromatic carbene.⁷ Recently carbenes have been detected by electron paramagnetic resonance (EPR) spectroscopy. It is known that diphenylcarbene has a triplet at the ground state⁸⁻¹¹ and the coincidence of recent opinion supports the results that the triplet and singlet states are in thermal equilibrium at room temperature.^{5,12} 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 reacts with alcohols to give ethers.^{5,12} It is widely believed that it is possible to obtain spin-specific products from diphenylcarbene.

The diagnostic reaction of diphenylcarbene of singlet state (¹DPC) with methanol gives ether 1:



and that of the triplet state (³DPC) with oxygen or isoprene gives 2 or 3 and 4.



The reaction mechanism on which these conclusions are described above can be augmented with measurements made by flash photolysis. In the standard approach,^{5,12} 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 alcohol. It is assumed that only the singlet state of carbene will react with alcohol, and thus information about the relationship between the singlet and triplet states can be discernible from the experimental results.

Closs and Rabinow¹³ were the first to measure an absolute rate constant for a carbene reaction in solution. Flash photolysis of diphenyldiazomethane in an inert solvent such as

benzene generates triplet diphenylcarbene, whose transient absorption is readily monitored between 300 and 320 nm.

Eisenthal, Turro and co-workers expanded the Closs-Rabinow's experiment.¹⁴ First, they were able to measure the rate constant for singlet to triplet interconversion, k_{ST} by picosecond spectroscopy. The activation energy for the reaction of triplet diphenylcarbene with methanol is observed to be 3-4 kcal/mol as shown as the classical mechanism and the activation energy of singlet diphenylcarbene is found to be 2-3 kcal/mol as shown as the essentially diffusion-controlled reaction mechanism. The latter value is only an apparent activation energy which results from the decrease in the rate constants of diffusion-controlled reaction at low temperature due to increased solvent viscosity.¹⁵

These observations are equally consistent with the simple idea that all of the reaction products are derived from the aromatic triplet carbene. As a matter of fact, they can not find a direct evidence for rapid triplet-to-singlet intersystem crossing, as the factor for controlling the kinetics of alcohol quenching. In order to obtain better insight into the mechanistic detail of carbene reactions we have designed experiment to test the feasibility of obtaining quantitative kinetic data of photolysis of 2-methoxy-1,2-diphenyl diazoethane (MDE) in solution and report here.

Experimental

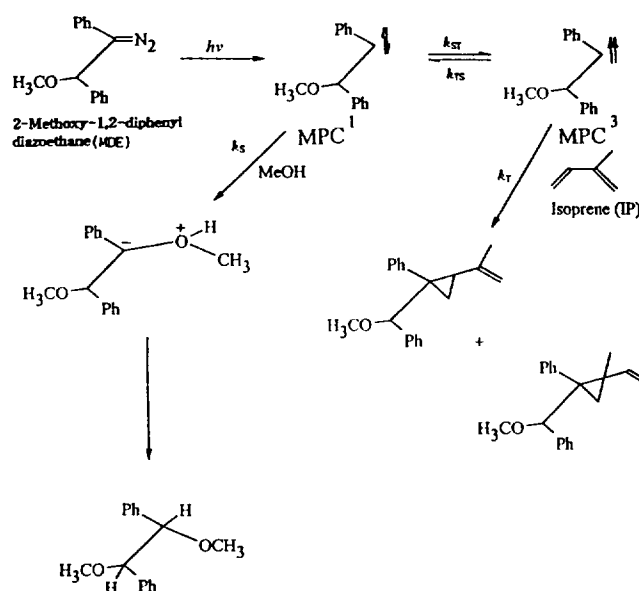
Material. 2-methoxy-1,2-diphenyl diazoethane (MDE) was prepared by base catalyzed HgO oxidation of 2-methoxy-1,2-diphenylethane hydrate in ether as described in the literature.¹⁶

2-Methoxy-1,2-diphenyl diazoethane (MDE) was obtained as a dark red oil; IR (NaCl, neat); 2060 cm^{-1} ; ^1H NMR (CCl_4); δ 7.6-7.1 (m, 8H, ArH), 7.1-6.8 (m, 2H, ArH), 5.3 (s, 1H, -CH), 3.5 (s, 3H, -OCH₃). Methanol (MeOH), isooctane (IO) and acetonitrile (MeCN) used in these experiments were spectroscopic grade and were purified by distillation from calcium hydride. Benzene (Bz) was washed with concentrated sulfuric acid then by water. It was then dried over magnesium sulfate and was finally distilled from calcium hydride. Isoprene (IP) was purified by distillation.

Apparatus and Sample Preparation

(Methoxyphenylmethyl)phenyl carbene (MPC) was generated by its diazo precursor (MDE) dispersed in solvent with 315 nm radiation collected from a 300W ILC Technology, Model LX300 UV high pressure Xenon lamp through a silica prism Jobin-Yvon monochromator. The excitation source was built the cavity-dumped dye laser (Coherent 700 Dye laser) pumped with a mode-locked Ar ion laser. The laser system is used for the generation of the carbene intermediate from the corresponding diazo compound at the synthesis pulse of 309 nm. The cavity-dumped pulse is generated from the dye laser *ca.* 1ps pulse width the average power of 100 MW at 3.8 MHz dumping rate, and 560 nm-607 nm tunability when Rhodamine 6G is used for gain dye.

The fluorescence spectra of MPC was analyzed with a THR 1500 Jobin-Yvon (1.5 m, f/12) scanning spectrometers and a microchannel plates PMT (Hamamatsu R2809V). Photolysis was accomplished by irradiating 5×10^{-5} M of MDE



Scheme 1.

in 500 ml of MeOH while N₂ bubbling.

The reaction vessel was connected to a vacuum line and several freeze-pump-thaw degassing cycles were performed. The optical absorption spectrum of the carbene (MPC) was detected immediately at 320 nm in all the solutions under investigation.

Results

To find out various relationships between the rate constants for reactions of MPC with MeOH or IP, we have used a method of selective spin traps in competitive experiments similar to those of the literatures.^{13,14}

The carbene (MPC) has been generated at various temperatures from its diazo precursor (MDE) in N₂-saturated solvents in the presence of selective spin traps. There is a possibility to interpret the kinetic data in terms of the singlet carbene based on an assumption⁵ that direct irradiation leads initially to formation of singlet state of carbene (¹MPC). Out of experimental necessity, all of the kinetic measurements described above have been monitored by the triplet carbene (³MPC). No optical absorption or fluorescence due to the singlet carbene has yet been detected. In this work we have designed experiments and conditions which allow us to assume that only four processes are available to the carbene reaction as follows as; (a) singlet to triplet interconversion (k_{ST}) (b) triplet to singlet interconversion (k_{TS}) (c) singlet reaction with a singlet trap (k_S) or (d) triplet reaction with a triplet trap (k_T) as shown in Scheme 1.

It is further assumed as well as shown as the literatures that the singlet carbene (MPC¹) in equilibrium with the triplet is identical with that generated through nitrogen loss from the excited diazo compound (MDE).¹⁷ The fact that methanol is well known as a selective trap for singlet carbene.¹⁷ However, if all of the experimental data¹⁸ and calculated data¹⁹ are correct a question arises the concept that quenching of the triplet carbene by methanol necessarily proceeds through the thermally populated singlet. Kinetic analysis of outlined

Table 1. The Ratio of the Quantum Yields (${}^3\Phi/{}^1\Phi$) from the Reaction of MPC Carbene* at Fixed Concentration of Methanol (0.05 M) and Various Concentrations of Isoprene in Acetonitrile at 273 K

[IP], M	${}^3\Phi/{}^1\Phi$
0.10	0.1-0.2
0.50	0.6
1.0	1.1-1.2
1.5	1.6
2.0	2.3
3.0	3.5
4.0	4.2
5.0	4.7-4.8
6.0	6.3
7.0	6.7
8.0	7.1
9.0	7.3
10.0	7.4

*MPC is generated from direct irradiation of 2-methoxy-1,2-diphenyl diazoethane (MDE).

above mentioned system provides relationships between the rate constants k_{ST} , k_{TS} , k_S and k_T , respectively. Of the four rate constants that characterize this system, k_S and k_T 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_S . The rate constants, k_S and k_{TS} were obtained from competitive quenching experiments analyzed according to Scheme 1. Kinetic analysis of Scheme 1, assuming that there is an equilibrium between the spin state predicts the ratio of quantum yield of triplet products (${}^3\Phi$) vs. that of singlet products (${}^1\Phi$) and will obey Eq. (1).

$${}^3\Phi/{}^1\Phi = \frac{k_T k_{ST} [\text{IP}]}{k_S [\text{MeOH}] (k_{TS} + k_T [\text{IP}])} \quad (1)$$

Eisenthal, Turro and their co-workers²⁰ derived Eq. (1) and measured the ratio of the quantum yield for diphenyl carbene. Under conditions where $k_{TS} \gg k_T [\text{IP}]$, Eq. (1) reduces to Eq. (2).

$${}^3\Phi/{}^1\Phi = \frac{k_T k_{ST} [\text{IP}]}{k_S k_{TS} [\text{MeOH}]} \quad (2)$$

In this domain, ${}^3\Phi/{}^1\Phi$ should exhibit a linear dependence on isoprene concentration, at a fixed MeOH concentration, with slope $k_T k_{ST} / k_S k_{TS} [\text{MeOH}]$. In a region of isoprene such that $k_{TS} \ll k_T [\text{IP}]$, the ${}^3\Phi/{}^1\Phi$ should be independent of [IP] as give by Eq. (3).

$${}^3\Phi/{}^1\Phi = k_{ST} / k_S [\text{MeOH}] \quad (3)$$

Direct irradiation of MDE (2.3×10^{-3} M) in nitrogen bubbled isooctane solutions at 273 K in the presence of a fixed amount of MeOH (0.05 M) and varying amounts of IP (0.1-10 M) allowed an experimental test of Scheme 1. In all cases, steady state photolysis of MDE leads to produce 1,2-dimethoxy-1,2-diphenyl ethane (DDE, $\geq 95\%$ yield) which could be product and relatively small amounts of isomeric cyclo-

Table 2. The Ratio of the Quantum Yields (${}^1\Phi/{}^3\Phi$) from the Irradiation of an Acetonitrile solution of the Reaction of MPC Carbene* at Fixed Concentration of Isoprene (1.0 M) and Varying Concentrations of Methanol at 273 K

[IP], M	${}^1\Phi/{}^3\Phi$
0.7	9.3
0.6	9.2
0.5	9.1
0.4	6.9
0.3	5.5
0.2	4.7
0.1	2.4
0.05	0.74
0.01	0.18

*MPC is generated from direct irradiation of 2-methoxy-1,2-diphenyl diazoethane (MDE).

ropenes at low concentration (0.1 M) of IP. These results justify a kinetic analysis incorporating only the four processes shown in Scheme 1. Therefore under the conditions of above experiments, the ${}^3\Phi/{}^1\Phi$ ratio can be accurately estimated by the relative yields of cyclopropanes to DDE. The values of this ratio as a function of IP concentration at a fixed MeOH concentration are given in Table 1.

The kinetic behavior for the system which has achieved a singlet-triplet equilibrium is confirmed by the correlation between the ${}^3\Phi/{}^1\Phi$ ratio and the function of the IP concentration. The validity of the kinetic model can also be tested by determining the relative yields of products for varying concentrations of MeOH in the presence of a fixed concentration of IP. 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:

$${}^1\Phi/{}^3\Phi = \frac{k_S [\text{MeOH}] (k_{TS} + k_T [\text{IP}])}{k_{ST} k_T [\text{IP}]} \quad (4)$$

The test was performed by the irradiation of MDE at a constant IP concentration of 1 M, while varying the concentration of MeOH from 0.01 to 0.7 M at 273 K. The data for ${}^1\Phi/{}^3\Phi$ under these conditions are given in Table 2. According to Eq. (4) the ratio of ${}^1\Phi/{}^3\Phi$ should follow a linear dependence on MeOH concentration as is observed experimentally.

The k_S and k_{TS} values are in quite good agreement with those values obtained from the competition experiment in which IP concentration has been varied at fixed MeOH concentration.

The observed first-order rate constants are not readily attributed to any specific reaction in the absence of any scavengers as oxygen and water. The laser flash photolysis kinetic data obtained from the decomposition of MDE in solvent containing varying concentrations of IP have been evaluated in terms of a composite second- and first-order reaction. In this case the first-order behavior is attributed in part to the pseudo-first-order scavenging of MPC carbene by IP.

By running at variable IP concentrations, it is possible to extract the second-order rate constant for the cyclopropane

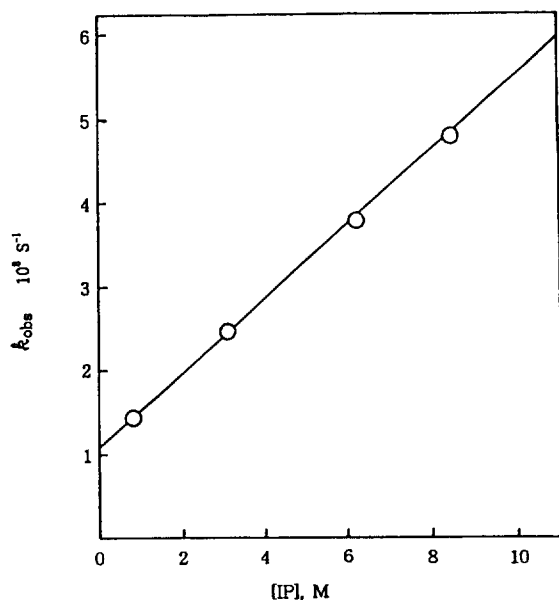


Figure 1. Plot of k_{obs} measured at 273 K for the quenching of triplet [1-methoxy-1-(phenylmethyl)]phenyl carbene vs. isoprene concentration in isooctane solvent.

nation step. The results are shown in Figure 1, where the nonzero intercept shows the presence of the side reactions.

It should be pointed out that IP is not completely inert to the photolysis flash and that the absorbance of the solution is changed due to these side reactions. Corrections had to be made and this accounts in part for the relatively large uncertainty of the determinations of the second-order rate constants.

The corresponding second-order rate constants, k_{IP} , measuring the carbene addition rate to IP are given in Table 3.

Within large error limit there is no noticeable solvent effect. All of the activation energies show very low comparing with the other aromatic carbenes.²⁰ According to the classical mechanism, the activation energy for the reactions of aromatic carbene with alkenes should be $-6 \text{ Kcal}\cdot\text{mol}^{-1}$, which was based on the interpretation of all of the other available experimental data in terms of Scheme 1. This is perhaps to be expected that the rate-limiting attack on IP molecule occurs *via* the σ -orbital on the carbene, which is largely orthogonal to the π system. An activation energy of 1.72-3.73 $\text{Kcal}\cdot\text{mol}^{-1}$ is required to deform the carbene bonds by a smaller angular displacement than is involved in the three-bond deformation of a trivalent radical at the transition state of addition. The corresponding second-order rate constants, k_{MeOH} , measuring the carbene addition rate to MeOH are given in Table 4.

The reaction kinetics could be fitted to a rate law of simultaneous first- and second-order decomposition. The second-order rate is attributed to the dimerization of the carbene, while the first-order parts are the pseudo-first-order reactions with methanol and a small amount of impurities. Variation of the MeOH concentration obeys a second-order rate constant for the reaction of MPC carbene with MeOH as shown in Figure 2.

Table 3. Rate Constants for Reaction of (1-Methoxy-1-phenylmethyl)Phenyl Carbene with Isoprene

Solvent	Temperature (K)	$k_{IP}/$ ($\text{M}^{-1} \text{s}^{-1}$)	E_a ($\text{kcal}\cdot\text{mol}^{-1}$)	ΔH ($\text{kcal}\cdot\text{mol}^{-1}$)
isooctane	303	8.68×10^7	3.73 ± 0.17	3.14 ± 0.26
	298	7.84×10^7		
	273	4.41×10^7		
acetonitrile	303	4.14×10^8	1.99 ± 0.45	1.40 ± 0.24
	298	3.92×10^8		
	273	2.88×10^8		
	77	2.53×10^4		
benzene	303	2.99×10^8	1.72 ± 0.27	1.13 ± 0.19
	298	2.85×10^8		
	273	2.19×10^8		
	77	6.82×10^4		
cyclohexane	303	6.29×10^8	2.06 ± 0.36	1.47 ± 0.39
	298	5.94×10^8		
	273	4.32×10^8		
	77	2.73×10^4		

Table 4. Rate Constants for Reaction of (1-Methoxy-1-phenylmethyl)Phenyl Carbene with Methanol

Solvent	Temperature (K)	$k_{MeOH}/$ ($\text{M}^{-1} \text{s}^{-1}$)	E_a ($\text{kcal}\cdot\text{mol}^{-1}$)	ΔH ($\text{kcal}\cdot\text{mol}^{-1}$)
isooctane	303	9.72×10^6	4.13 ± 0.24	3.54 ± 0.31
	298	8.65×10^6		
	273	4.58×10^6		
acetonitrile	303	4.89×10^7	2.07 ± 0.19	1.48 ± 0.42
	298	4.61×10^7		
	273	3.35×10^7		
	77	2.23×10^3		
benzene	303	4.89×10^7	1.94 ± 0.28	1.35 ± 0.37
	298	4.61×10^7		
	273	3.35×10^7		
	77	2.23×10^3		
cyclohexane	303	7.36×10^7	2.28 ± 0.39	1.69 ± 0.29
	298	6.90×10^7		
	273	4.85×10^7		
	77	1.21×10^3		

Since the carbene is assumed to react from the singlet state, these rate constant correspond to k_{MeOH}/K_{eq} , where $K_{eq} = k_{ST}/k_{TS}$ in terms of Scheme 1 and k_{MeOH} is the second-order rate constant for reaction of MPC carbene with MeOH. The intercept of the plot of the first-order rate constant against MeOH concentrations, while still larger than zero, is smaller than in the reaction MPC carbene with IP. This is presumably due to the more efficient degassing that is possible in the MeOH trapping experiments. Using the appropriate values of k_{ST} and k_{TS} the equilibrium constant, K_{eq} can be cal-

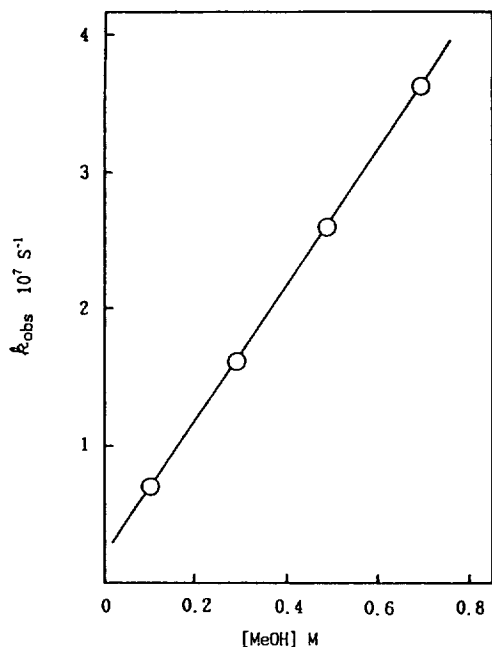


Figure 2. Plot of k_{obs} measured at 273 K for the quenching of singlet [1-methoxy-1-(phenylmethyl)]phenyl carbene vs. methanol concentration in isoctane solvent.

culated between the singlet and triplet states of MPC carbene.

The average values of K_{eq} and $-\Delta G_{ST}$ determined in all solvents are 0.296-0.473 and 3.23-4.10 Kcal/mol, respectively. The free energy difference (ΔG_{ST}) between singlet and triplet states follows directly from K_{eq} by use of Eq. (5).

$$\Delta G_{ST} = -RT \ln K_{eq} \quad (5)$$

These results mean that triplet MPC carbene is more stable than singlet MPC carbene. It appears that the reaction of singlet MPC carbene with MeOH is very fast and is at or near the diffusion controlled rate expected for a bimolecular reaction under the conditions employed.

Discussion

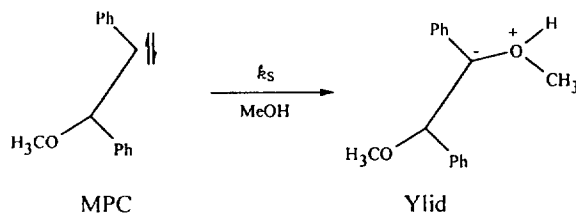
Two series of steady-state photolyses of MDE have been carried by use of quenching experiments to obtain important information about the reaction of different carbene states. The experimental behavior of the reaction of MDE conforms to the derived kinetics of Scheme 1, which supports the proposal that an equilibrium between MPC carbene spin states is established in a time that is short compared to other reactions.

Extension of the steady state competitive quenching experiments for diphenyl diazomethane carried out by Closs and Rabinow¹³ and Bethell *et al.*⁵ permitted determination of all four rate constants given in Scheme 1. Analysis of the kinetic data allows the determination of the free energy difference ($-\Delta G_{ST} = 3.2 \pm 0.3 \text{ Kcal} \cdot \text{mol}^{-1}$) between the singlet and triplet state of diphenyl carbene produced from diphenyl diazomethane in acetonitrile. The time resolved flash photolysis measurements have demonstrated other complications that must be considered for a different carbene reactions which

are studied in acetonitrile or in the presence of high concentrations of hydrogen bonding alcohols. A kind of 1-naphthyl carbene and fluorenylidene has been shown to form an ylide in acetonitrile but not with diphenyl carbene.²¹ The reactivity of carbenes toward hydrogen bonded dimers differ from that toward the monomer. The kinetic data given in Table 3 and 4 have not shown a regular solvent effect to applicate their solvent properties such as vapor pressure, refractive index, viscosity, electrical properties including specific conductance and dielectric constant.

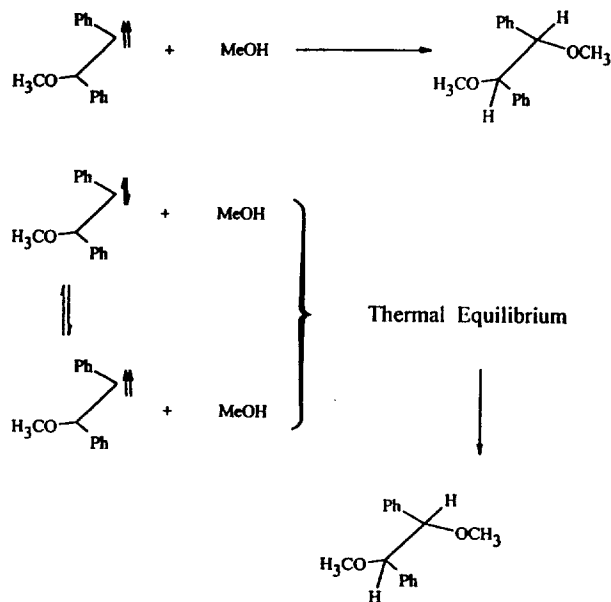
The results of a study by Griller *et al.*¹⁵ on the kinetics of the apparent quenching of triplet diphenyl carbene in MeOH have been taken and they have reported the apparent activation energy for the quenching reaction lies between 1.2 and 3.6 Kcal·mol⁻¹ depending on the solvent.

Their observation of activation energy should equal the energy gap between singlet and triplet diphenyl carbene. Also, the rate of triplet diphenyl carbene disappearance should become independent of MeOH concentration when the intersystem crossing rate of singlet diphenyl carbene to triplet diphenyl carbene becomes the rate determining step for ether formation. The rate constants of the reaction of MPC carbene with IP and MeOH in Tables 3 and 4 are not so sensitive to solvent polarity, with $k_{IP} = 4.14 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in MeCN at 303 K, $k_{IP} = 8.68 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ in IO (isoctane) at 303 K, and also with $k_{MeOH} = 4.89 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ in MeCN at 303 K, $k_{MeOH} = 9.72 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ in IO at 303 K, respectively. This behavior is to be attributed that k_{ST} is not quite sensitive to solvent polarity. But it seems that k_{ST} is much smaller in the mixture of MeCN-MeOH solvent mixture than in pure MeOH. Under the reaction corresponding Scheme 1, singlet MPC carbene will react with MeOH. If triplet MPC is to react with MeOH, intersystem crossing must occur at some point in order for a ground-state product to be formed. A note of caution is needed to understand the mechanism when methanol is a substrate. This is because MeOH distributes between monomer, dimer and higher hydrogen-bonded oligomers. The partition of these forms is strongly depend upon the temperature, MeOH concentration and solvent structure.²² A network of hydrogen bonds in MeOH solvent is possible to react with singlet carbene more than MeOH monomer.²³ Furthermore, because MeOH is highly polar, its sequential addition as a quencher may change the polarity of the medium. It is even possible that singlet carbene of MPC reacts with MeOH to form an ylid.



If the ylid can dissociate to carbene reversely in competition with product formation, then this can explain the unusually low activation energies.

The activation energies of reaction of MPC with MeOH show 2.28-4.13 Kcal·mol⁻¹ in Table 4. According to the classical mechanism, the activation energy for the process of singlet carbene with MeOH should be the activation energy



Scheme 2.

of the essentially diffusion-controlled reaction as 2-3 Kcal·mol⁻¹.^{23a} Our results of activation energies show a little higher than those values of the classical mechanism for the process of singlet carbene with MeOH.

The kinetic data has reported herein which are based on the quantum yield for triplet product formation as a function of IP concentration gives $k_S/k_{ST}=0.48\pm 0.03\text{ M}^{-1}$ in IO solvent. When the rate constants of triplet MPC carbene quenching by IP and the values of k_S/k_{ST} are combined in Eq. ($k_{\text{MeOH}}=k_S/K_{eq}$) data justify that $K_{eq}\cong 0$ and admits the possibility of a very small value for ΔH , which would be consistent with the observed activation energies for triplet MPC carbene quenching by IP. Therefore the rate constants, k_{IP} would be interpreted as being due to reaction by the thermally populated singlet carbenes partially as shown in Scheme 2. This results reported herein are different from the conclusions of the other carbene reactions such as naphthyl carbene and diphenyl carbene.^{13,15} A central problem of the other experiments^{13,15} arises for the measurement of quantum yields for singlet and triplet pathways as a function of diene concentration.

In our experiments we note that conclusions are drawn from the observation that the ratio of quantum yields is almost invariant at IP concentrations above 5 M. This condition is satisfactory since at these high concentrations the solvent cage surrounding the MPC carbene must contain several molecules of IP.

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