The Kinetics of the Ylid-Forming Reaction Between Triplet Diphenylcarbene and Pyridine

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Abstract: The kinetics of the reaction of triplet diphenylcarbene with pyridine were obtained. The mechanism of the reaction is discussed.

In 1976 Closs and Rabinow reported the kinetics of the reaction of the ground triplet state of diphenylcarbene (DPC) with methanol.¹ Since that time numerous studies have been conducted to determine the mechanism of this reaction.² Although DPC has a triplet ground state,³.³DPC reacts with methanol to produce singlet benzhydryl methyl ether 2 in a formally spin forbidden process. This was rationalized as a consequence of a rapid equilibrium between the singlet and the triplet states of DPC, as shown in Scheme I, and a diffusion controlled reaction of ¹DPC with methanol. This analysis lead to a calculated singlet-triplet gap of 3-4 kcal/mol in DPC.^{1,2}



Subsequently a surface crossing mechanism was proposed by Griller, Nazran, and Scaiano (GNS)⁴ based upon the evidence that the experimentally determined activation energy was much lower than that calculated on the basis of this pre-equilibrium (vide infra).^{1,2,5} We now wish to report the activation parameters for the reaction of ³DPC with pyridine. This data also argues against a simple pre-equilibrium mechanism for a formally spin forbidden reaction.

Laser flash photolysis (351 nm) of diphenyldiazomethane 1 in the presence of pyridine produces a transient species whose growth can be monitored at 500 nm. This transient absorption is attributed to that of the pyridinium ylid 3 (Scheme II). The reaction is first order in pyridine concentration and can be fit to Equation 1,

 $k_{0}b_{sd} = k_{0} + k_{0}v[pyridine].$ (1)

The kinetics and activation parameters for this reaction and for the reaction of DPC with methanol in three different solvents are given in Table 1.



Table 1. Rate constants and activation parameters for the reactions of DPC with pyridine and methanol.

Solvent	k x10 ⁻⁵ (M ⁻¹ s ⁻¹) ^a	E _a (kcal/mol)		log A	
n-Heptane	2.743 <u>+</u> 0.249	1.412 <u>+</u> 0.410	(3.61) ^{b,c}	6.496 <u>+</u> 0.313	(9.51) ^{b,c}
Chlorobenzene	2.794 <u>+</u> 0.896	2.243 <u>+</u> 0.254	(2.48) ^b	7.364 <u>±</u> 0.155	(9.30) ^b
Acetonitrile	4.172 <u>+</u> 1.207	2.667 <u>+</u> 0.751	(1.66) ^b	7.525 <u>+</u> 0.553	(8.62) ^b

^a298K. ^DMethanol reaction, Ref. 4. ^CIsooctane.

A potential energy surface of the singlet-triplet pre-equilibrium model is shown in Figure 1. This mechanism requires that the activation energy of the reaction be equal to the activation energy for conversion of the triplet to the singlet (ΔH_{ST}) plus the activation energy for reaction of the singlet with quencher Q (Equation 2, Q = methanol or pyridine),

$$E_a = \Delta H_{ST} + E_a(S+Q) \approx 5-6 \text{ kcal/mol.}$$





(2)

Figure 2. The non-equilibrium surface crossing model.

The fact that the activation energy for the reaction of ³DPC with methanol is <u>less</u> than the calculated singlet-triplet energy gap (ΔH_{ST}) argues against this mechanism. The lower than expected activation energy reported by GNS can be reconciled with a pre-equilibrium model if the reaction of ¹DPC with methanol involves reversibly formed ylid 4, in which case $k_{obsd} \neq k_{q}K$,



or if the kinetics of the methanol reaction are influenced by oligomerization of the alcohol, or by the large dielectric constant of this quencher ($\epsilon = 32.6$).⁶

However none of these issues should complicate the reaction of ³DPC with pyridine as ylid **3** is formed irreversibly (ylid **3** has a half-life of at least 1 minute in pyridine solution), pyridine does not oligomerize, and the dielectric constant of pyridine is modest ($\varepsilon = 12.3$).⁶ Nevertheless the activation energies for the reaction of ³DPC with pyridine are still significantly smaller than that predicted by the preequilibrium model.

McGimpsey and Scaiano⁷ have reported that ³DPC reacts with adamantanethione to form a singlet ylid with $k_{obsd} = 1.3 \times 10^9 M^{-1}s^{-1}$. This large rate constant may signal a violation of the pre-equilibrium model, or it may be a result of spin conserved addition of the triplet carbene to the thione to form a biradical, which subsequently relaxes to form ylid 5.



It is unlikely that the low activation energies observed in the pyridine reaction are due to a spin conserved reaction as shown in Scheme III,



as the energy gap between yild 3 and putative triplet biradical 6 is probably close to the energy of the electronic transition of the yild (500 nm \approx 57 kcal/mol).⁸ Furthermore ³DPC does not add to benzene in this manner.⁹

The similar activation parameters observed in the reaction of ³DPC with

methanol and pyridine argue in favor of a common reaction mechanism. However, the very low activation energies observed (Table 1) are inconsistent with a simple preequilibrium model and require that the intersystem crossing step occur at a point other than the minimum of ¹DPC (Figure 2). An alternative explanation is that the energy gap in DPC is much smaller than that obtained in previous estimates. Experiments are in progress to refine these possibilities.

Acknowledgements

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