PICOSECOND LASER STUDIES OF THE CHARGE-TRANSFER REACTION OF EXCITED TRIPLET DIPHENYLCARBENE WITH ELECTRON DONORS

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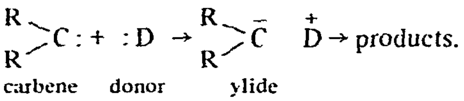
Evidence of a one-electron transfer process in a carbene reaction has been observed for the first time. The example is the quenching of the photoexcited triplet state of diphenylcarbene (^{3*}DPC) by electron donors. Measurement of the fluorescence lifetime as a function of donor concentration yielded the bimolecular rate constant, $^{3*}k$. An explanation is offered as to why ^{3*}DPC and ^{1}DPC react efficiently with amines as well as alcohols, whereas the ground triplet, ^{3}DPC, does not.

1. Introduction

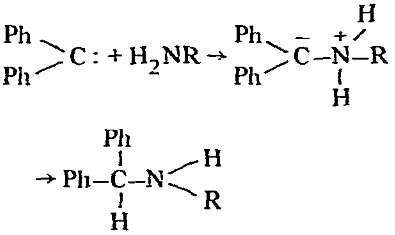
Carbenes have evoked considerable interest because of their spectroscopy, structures and the unusual ways they react with other molecules in a spin selective mode [1–6]. As an example of the novelty of carbene chemistry one can cite the recent evidence of ylide formation in the reactions of arylcarbenes, R_2C:, with nitriles, carbonyls, and amines [7–11],



$$R_2C: + :D \rightarrow R_2\bar{C}\ \overset{+}{D} \rightarrow \text{products}. \qquad (1)$$

carbene donor ylide

Ylide formation in this case simply means bond formation between a carbene and a molecule that donates a pair of electrons to produce a zwitterionic species. The ylide, however, should be differentiated from species produced by single electron transfer processes, such as a charge-transfer complex or an ion pair. The nature of the ylide formation is interesting because (a) it appears to occur mainly for the singlet state of the carbene which is at an energy slightly higher than the ground state triplet carbene [4–6], and (b) the involvement of ylides may be central to the mechanism of other important reactions of carbenes [12–14]. In the specific case of diphenylcarbene (DPC) it is known that although its ylides are not as easily formed as is true of other arylcarbenes [10], they are nevertheless, implicated in certain of its reaction schemes [12–14]. As postulated by Bethell [12–14], ^{1}DPC will insert into the N–H bond of amines and the O–H bond of alcohols via an ylide intermediate, as given by



$$Ph_2C: + H_2NR \rightarrow Ph_2\bar{C}\text{–}\overset{+}{N}H_2R \rightarrow Ph_2CH\text{–}NHR \qquad (2)$$

In a recent study the reactivity of the excited triplet state of diphenylcarbene (^{3*}DPC) with alcohols was examined [15,16]. It was shown that like ^{1}DPC the excited triplet attacks the labile O–H bond of the alcohol. In fact it was found that the pattern of the relative rates of reaction of ^{1}DPC and ^{3*}DPC were essentially identical and followed the relative acidity of the alcohols ($CH_3OH > i\text{-}PrOH > t\text{-}BuOH$). A simple model which accounts for the similar reactivity of both ^{1}DPC and ^{3*}DPC is given by the orbital filling scheme involving the highest occupied non-bonding molecular orbitals (σ,p) and the antibonding (π^*) orbital of the carbene (scheme I).

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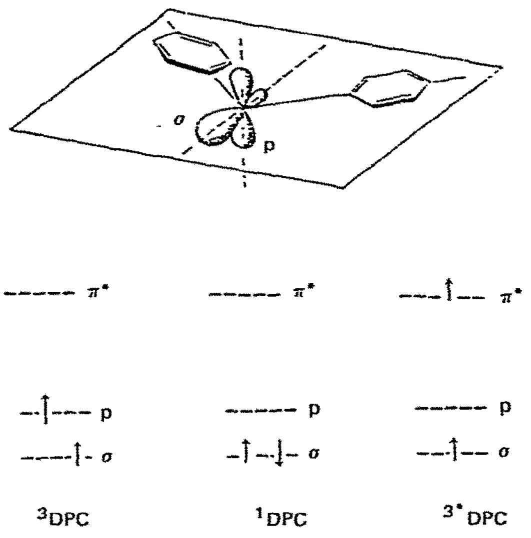


Scheme I

It can be seen by this representation that ¹DPC and ³*DPC will be similar to each other insofar as they both possess an empty low-lying orbital. The ground triplet, ³DPC, on the other hand, has no empty low-lying orbitals available to it. Therefore this scheme offers a convenient explanation for the fact that the excited triplet would undergo certain reactions that the ground triplet would not and furthermore, ³*DPC would appear to resemble ¹DPC in certain of its reactions. The similar ordering of alcohol reactivities for both ¹DPC and ³*DPC implies that they share a common reaction mechanism. However, the excited triplet does not appear to react with alcohols by initial attack on the hetero-atom (to produce an ylide type species). If the primary step were interaction with the oxygen atom, then one would expect ethers as well as alcohols to quench ³*DPC. The two ethers, diethylether and tetrahydrofuran, are found not to quench ³*DPC [16]. From this result it was inferred that the hydrogen attached to the oxygen plays a key role in the reaction process; a conclusion supported by an observed kinetic isotope effect [16]. Since ³*DPC appears to mimic qualitatively the behavior of ¹DPC with alcohols in attacking the O–H bond, the question is whether this similarity will also be present in the reactions of ³*DPC with amines. The issue addressed here is important, not only in establishing the chemistry of ³*DPC with amines, but also to determine whether a triplet state of a carbene can undergo a reaction with electron donors, and if so, establish if it follows the singlet mechanism (ylide mechanism) or some other mechanism. In this paper, we report on the behavior of ³*DPC with a series of amines which shows that the excited triplet carbene undergoes a charge-transfer process with electron donors, a heretofore unknown pathway in carbene chemistry.

2. Experimental

Diphenylcarbene was generated upon laser photolysis of diphenyldiazomethane by a TEM$_{00}$, fourth harmonic UV pulse from either a passively mode-locked Nd : YAG laser (fwhm 25–30 ps, λ = 266 nm) or a Nd^{3+} phosphate glass laser (fwhm 8–10 ps, λ = 264 nm). A second UV laser pulse also at the same wavelength was time delayed by 8 ns after the first laser pulse and was used to excite the carbene fragment, thereby producing the excited triplet diphenylcarbene. The fluorescence of diphenylcarbene was monitored with an Imacon streak camera coupled to a PAR optical multichannel analyzer. Streak speed was calibrated with an etalon. Linearity of the intensity response is checked in every experiment and each shot is corrected for the streak camera–OMA response function. All data were eventually digitized, stored and analyzed using a MINC-11 minicomputer. Preparation and purification of diphenyldiazomethane was done according to literature procedure [17]. Acetonitrile was spectrograde OmniSolv, obtained from MCR, and was used as received. 1,4-diaza(2,2,2)bicyclooctane (DABCO) and 1-aza(2,2,2)bicyclooctane (ABCO) were freshly sublimed before use. Triethylamine and diethylamine were reagent grade and were distilled from P_2O_5, under nitrogen before use. *n*-butylamine, *t*-butylamine and di-*n*-butylsulfide were reagent grade and were distilled under nitrogen before use. Dimethylamine was obtained from Matheson and was used as received. The sample solutions were deoxygenated by repetitive freeze-pump-thaw cycles. In all experiments the diphenyldiazomethane concentration was constant at 1.5×10^{-3} M and the temperature was 20°C.

3. Results and discussion

Table 1 gives the quenching rate constants of ^{3*}DPC as determined from a Stern–Volmer analysis of the changes in fluorescence lifetime induced by the addition of the amines at several different concentrations. Inspection of the data reveals a significant variation in the rate of quenching in the series of amines studied. For example, tertiary amines such as DABCO and triethylamine quench ^{3*}DPC at or near the diffusion controlled limit while the primary amines quench the excited triplet state at a rate which is three orders of magnitude slower. To determine whether a charge-transfer interaction is responsible for the ordering of reactivity a plot was made of $\log(^{3*}k)$ versus the ionization potential of the quenchers given in table 1. As shown in fig. 1, the logarithm of the quenching rate constants is a linear function of the quencher ionization potential with a slope = –(0.079 ± 0.006) mole/kcal. Such behavior can be accounted for by a charge-transfer mechanism which predicts that $\log(^{3*}k)$ will be proportional to the ionization potential of an electron donor quencher with negative slope [19–22]. Indeed, a result similar to the one observed here is also found for the quenching of triplet benzophenone with amines [23–32], which is known to proceed by full electron transfer [30–32].

On the basis of the dependence of the observed $^{3*}k$ on ionization potential we therefore favor the mechanism in which ^{3*}DPC undergoes photoreduction by amines, A_m, thereby forming a triplet charge transfer intermediate as the primary step in quenching:

$$^{3*}\mathrm{DPC} + \mathrm{A_m} \rightarrow {}^{3}(\mathrm{DPC}^{-}, \mathrm{A_m^{+}}). \qquad (3)$$

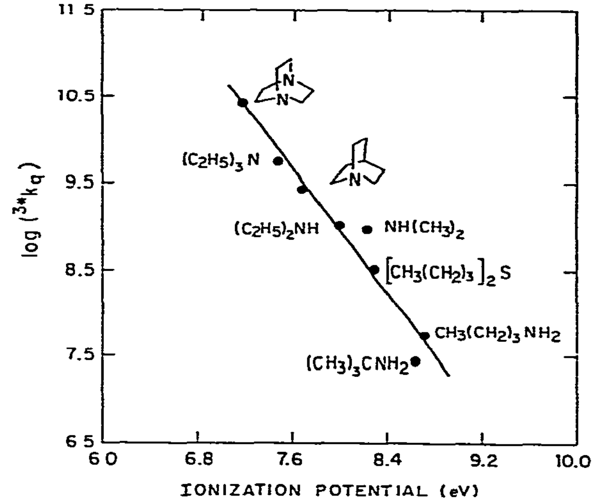
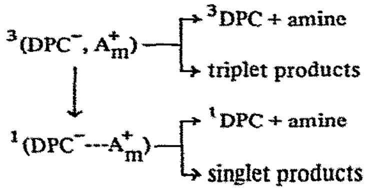


Fig. 1. Quenching of excited triplet diphenylcarbene as a function of donor ionization potential in acetonitrile, at 20°C.

Concerning the fate of the triplet charge-transfer (CT) intermediate, however, it is reasonable to assume that it will decay by one of several pathways, as proposed in scheme II. The triplet CT intermediate can suffer annihilation in the triplet manifold either by back electron transfer to produce ^{3}DPC + amine or by triplet state product production. Alternatively, the triplet CT intermediate can decay by intersystem crossing into the singlet state manifold producing either a singlet charge-transfer complex, an ion pair or ylide. They could then collapse into either ^{1}DPC + amine or singlet reaction products. The production of either triplet or singlet products subsequently arising from the initial event of photoreduction of ^{3*}DPC will of

Table 1
Quenching of ^{3*}DPC by electron donors

Donor	$^{3*}k$ (M^{-1} s^{-1})	IP (eV) [18]
1,4-diaza(2,2,2)bicyclooctane, DABCO	$(2.6 \pm 0.2) \times 10^{10}$	7.20
triethylamine	$(5.4 \pm 0.4) \times 10^{9}$	7.5
1-aza(2,2,2)bicyclooctane, ABCO	$(2.7 \pm 0.3) \times 10^{9}$	7.7
diethylamine	$(9.8 \pm 1.2) \times 10^{8}$	8.01
dimethylamine	$(9.2 \pm 0.6) \times 10^{8}$	8.24
di-*n*-butylsulfide	$(3.2 \pm 0.6) \times 10^{8}$	8.30
n-butylamine	$(5.3 \pm 0.6) \times 10^{7}$	8.71
t-butylamine	$(2.7 \pm 0.4) \times 10^{7}$	8.64



Scheme II. Proposed decay pathways of the triplet charge-transfer intermediate involving carbene and amine.

course depend on the type of amine. It is expected, for example, that N–H insertion type products could be formed for the case of primary and secondary amines. In this way, ^{3*}DPC would appear to follow the mechanism proposed by Bethell for the ^{1}DPC reaction with primary amines. It is emphasized, however, that the ability of an arbitrary electron donor to quench ^{3*}DPC will basically depend on two factors. At a low ionization potential it is expected that a charge-transfer mechanism will dominate. This is the situation for the series of amines studied here as shown by the linearity of the log($^*k$) versus IP plot seen in fig. 1. However, at high ionization potentials, the charge-transfer mechanism will become energetically disfavored and the rate of quenching is expected to be controlled by other mechanisms, such as abstraction and/or one step direct-insertion processes as proposed for the quenching of ^{3*}DPC by alcohols, having IP $>$ 9 eV (e.g. alkyl alcohols). In this later case, it was found that quenching occurred in alcohols since they have a labile O–H bond, thus permitting O–H insertion reactions, but not for ethers which only have strong C–H bonds [16].

4. Conclusions

The excited triplet diphenylcarbene has important new features compared with the ground triplet and lowest singlet state of diphenylcarbene. They include significant excess energy (E_T = 58 kcal/mole) and what is proposed to be central to its chemistry, the presence of an empty low-lying orbital which can accept electrons. The present work is the first example of a charge-transfer interaction of carbenes with simple electron donors. The excited triplet carbene is found to be efficiently quenched by amines, where the ordering of reactivity is given by tertiary $>$ secondary $>$ primary which follows inversely the ionization potential ordering. It is pointed out that the mechanism of reaction with amines is not the same as for its reaction with alcohols. Alcohol reactivities are not ordered by their ionization potentials, but rather by their relative acidities. Finally, the mechanism of the excited triplet carbene reaction is not the same as the proposed mode of reaction followed by the singlet carbene, which involves direct formation of an ylide intermediate.

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