PICOSECOND LASER STUDIES OF THE EFFECTS OF REACTANTS ON INTRAMOLECULAR ENERGY RELAXATION OF DIPHENYLCARBENE: REACTION OF DIPHENYLCARBENE WITH ALCOHOLS

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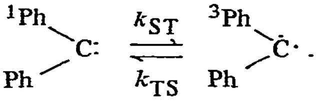
Picosecond laser induced fluorescence measurements provide for the first time the direct measurement of the intramolecular and intermolecular energy decay dynamics of singlet diphenylcarbene (^{1}DPC) in the presence of reactive molecules. As exemplified by the reaction of ^{1}DPC with alcohols it is found that reactive molecules provide ^{1}DPC with not only a chemical decay channel but also an intramolecular decay channel which is due to a solvent polarity effect. These chemical and physical effects can act in opposite directions leading to novel results such as a significant increase in the singlet state lifetime upon addition of reacting molecules. The absolute reaction rate constants of ^{1}DPC with alcohols, in different solvents, obtained by direct measurements are also reported.

1. Introduction

Unravelling the dynamics of carbenes has been a key to the elucidation of the chemical and physical properties of these important chemical intermediates [1–4]. An important feature of the carbene system is that its intramolecular dynamics, dominated mainly by intersystem crossing between the singlet and triplet states, can have a profound effect on its spin state dependent chemical reactions that comprise the intermolecular decay channels for the carbene [5–19]. This is especially true for cases when thermal equilibrium between the singlet and triplet can be achieved during the carbene lifetime. Certain arylcarbenes fit into this category. For example, diphenylcarbenes (DPC) has been shown to undergo rapid thermal equilibration [17–21] between its ground triplet and its lowest singlet, which lies approximately 2.5–4 kcal/mole above the triplet [20,21]



$$\mathrm{^1Ph(Ph)C{:}}\ \underset{k_{\mathrm{TS}}}{\overset{k_{\mathrm{ST}}}{\rightleftharpoons}}\ \mathrm{^3Ph(Ph)\dot{C}\cdot}\,. \qquad (1)$$

Recently, the ultrafast singlet to triplet intersystem crossing rate (k_{ST}) of DPC was found to be strongly dependent on the polarity of the solvent [22,23]. The phenomenon of the solvent polarity effect on the intersystem crossing rate was shown to be related to corresponding changes in the energy splitting of the singlet and triplet states. It was found that both k_{ST} and the energy gap decrease with increasing polarity of the medium [20–23]. For example, the time for intersystem crossing in DPC increases from 95 ps in non-polar alkane solvents to 310 ps in the polar solvent acetonitrile. Furthermore it was found that the singlet–triplet energy splitting changes from 1400 to 950 cm^{-1} in going from isooctane to acetonitrile. The polarity effect on ΔE_{ST} was accounted for by a preferential stabilization of the polar singlet state relative to the non-polar triplet state of the carbene by polar solvents. The observed solvent effects demonstrated an important physical property of the carbene system which is the "inverse" gap effect, i.e. k_{ST} increases as ΔE_{ST} increases, which contrasts with the usual behavior observed in large molecules. The "inverse" gap effect on intersystem crossing can be explained by an off-resonance intersystem crossing from the singlet to a sparse vibronic triplet manifold characteristic of a small energy gap. These results, besides providing insight into the mechanism of carbene intersystem crossing, show that an environmental effect can sharply perturb intramolecular dynamics (e.g. rate of singlet–triplet equilibration) of the carbene. Because the chemistry

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of the carbene depends on the nature of spin equilibration, an important ramification of the polarity effect will therefore be its effect on the spin state dependent reactions of the carbene.

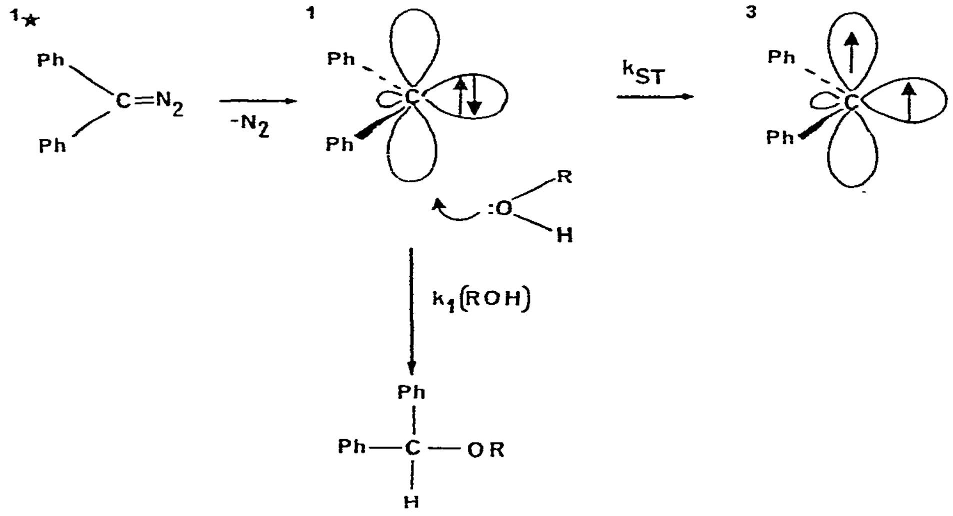
A particularly important carbene reaction is the quenching of the singlet state of DPC with alcohols to form ethers [24–26]. Although it is a classic carbene reaction, no direct kinetic information is known about it. In this paper we wish to report on the picosecond measurements of the alcohol reaction with the singlet state of DPC. The results are explained in terms of alcohols exerting a two-fold effect on the dynamics of the singlet carbene. It is argued that the reactant molecules not only provide a chemical channel for reducing the lifetime of ^{1}DPC but also can affect the lifetime of ^{1}DPC by a physical channel, namely the change in k_{ST} due to the polarity of the reactant molecules. These chemical and physical effects can act in opposite directions leading to novel results such as the increase in the lifetime of the ^{1}DPC state on addition of reacting molecules.

2. Experimental

The picosecond experiments consisted of the irradiation of a vacuum degassed solution of diphenyldiazomethane (8×10^{-4} M), at 293 K, with a picosecond laser pulse at 266 nm using a passively mode-locked Nd : YAG laser (fwhm 20–30 ps, <0.02 mJ). The formation rate of ^{3}DPC was monitored by its laser-induced fluorescence using a weak probe pulse at 266 nm at variable time delays [27]. Preparation and purification of diphenyldiazomethane, the carbene precursor, has been described before [20,28]. Acetonitrile was spectrograde OmniSolv, obtained from MCB, and was used as received. 3-pentanol was distilled over CaO, under nitrogen before use. Methanol, Fisher Reagent, was used as received. Anhydrous diethylether was distilled over $LiAlH_4$, under nitrogen, before use. The value of $E_T(30)$ for solvent mixtures containing alcohol was measured using pyridinium N-phenoxide betaine dye, which was obtained as a gift from Chr. Reichardt and K. Dimroth.

3. Results and discussion

Photoexcitation of diphenyldiazomethane in the ultraviolet yields singlet diphenylcarbene (^{1}DPC) upon loss of nitrogen from the excited singlet state of the diazo compound. Once formed, ^{1}DPC can either react with alcohol to form ether or can decay via intersystem crossing into the ground triplet manifold (scheme I). The rate of triplet formation (^3k_f) in this case should then be equal to the sum of the rate



Scheme I. Alcohol quenching of singlet diphenylcarbene.

of singlet–triplet conversion (k_{ST}) and the pseudo-first-order rate of singlet quenching (k_1 [ROH]),

$$1/\tau_{1\ \mathrm{DPC}} = {}^3k_f = k_{ST} + k_1[\mathrm{ROH}] \ . \qquad (2)$$

The value of ^3k_f was measured by means of the laser induced fluorescence experiment, and can be used to evaluate the effects of alcohol on the singlet state dynamics.

The results given by table 1 show that ^3k_f depends on the choice of alcohol and solvent. Using methanol as the quencher, it is found that ^3k_f exhibits a dependence on alcohol concentration which deviates from the linear dependence expected from eq. (2). Fig. 1 shows that with increasing concentration of methanol the value of ^3k_f initially decreases and then, after reaching a minimum, increases linearly. An even more dramatic effect is produced when diethylether is used as solvent, where a sharp minimum in ^3k_f is clearly seen as the concentration of methanol is increased.

Table 1
Formation rate of ^{3}DPC in the presence of alcohols at 20°C

Alcohol concentration (M)	$10^{-9}\ ^3k_f(\mathrm{s}^{-1})$	Solvent
methanol		diethylether
0.000	7.69 ± 0.65	
0.009	6.90 ± 0.41	
0.025	6.67 ± 0.52	
0.050	7.14 ± 0.65	
0.075	8.33 ± 0.67	
0.10	9.09 ± 0.89	
0.15	9.52 ± 0.88	
methanol		acetonitrile
0.000	3.23 ± 0.19	
0.015	3.13 ± 0.29	
0.045	3.13 ± 0.29	
0.10	3.23 ± 0.16	
0.20	3.77 ± 0.35	
0.30	3.92 ± 0.36	
3-pentanol		acetonitrile
0.176	3.64 ± 0.25	
0.40	4.17 ± 0.21	
0.78	5.00 ± 0.29	
1.48	6.25 ± 0.59	

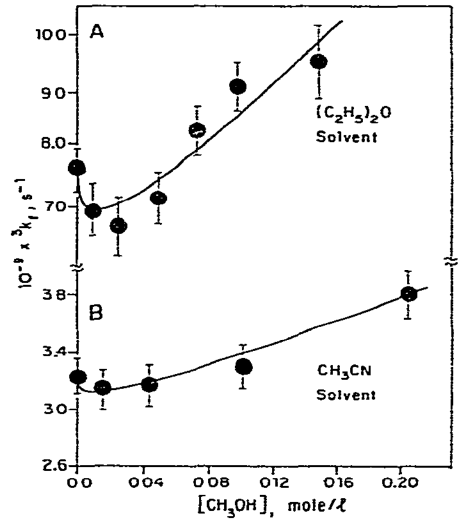


Fig. 1. ^3k_f as a function of methanol concentration, using diethylether (A) and acetonitrile (B) as solvent. The solid curves are calculated fits.

These observations can be explained by recognizing the effect of solvent polarity on the singlet to triplet spin conversion rate. It was previously shown that the intersystem crossing rate is strongly dependent on solvent polarity and can be expressed as an exponentially decreasing function of the solvent polarity parameter, $E_T(30)$ [22,23]. A consequence of this dependence for bimolecular reactions of the carbene will be that a significant change in the carbene spin equilibration rate may result by the addition of reactant molecules. In other words k_{ST} may no longer remain a constant, but may change as the concentration of the quencher changes. In this case the quencher will change the lifetime of the carbene not only by the chemical decay channel (i.e. bimolecular reaction) but also by the physical channel (i.e. intersystem crossing). Hence if solvent polarity is a rapidly varying function of alcohol concentration k_{ST} must then become a function of alcohol concentration as well. Since methanol is much more polar than acetonitrile and diethylether [29], it is expected that k_{ST} will decrease upon addition of methanol to the solvent, due to the increase in polarity of the mixture. At a low methanol concentration the rate of chemical quenching is small compared to k_{ST} and in this domain polarity effects will dominate the singlet state dynamics resulting in an increase in the singlet state lifetime. At high methanol concentration, the chemical decay channal dominates the singlet state dynamics, dwarfing the effects of alcohol on k_{ST}, and ^3k_f

increases with quencher concentration in a linear fashion.

In order to evaluate k_1 from the methanol quenching experiments, therefore, the explicit dependence of k_{ST} on the polarity of the solvent mixture must be taken into account. This dependence is expressed by

$$k_{ST} = A \exp[-BE_T(30)] , \qquad (3)$$

where $E_T(30)$ is the measured value of the solvent mixture containing alcohol and the coefficients determined experimentally are given by $A = 1.194 \times 10^{11}$ s^{-1} and $B = 7.985 \times 10^{-2}$ mole/kcal. Substituting eq. (3) for k_{ST} into eq. (2) yields the relation

$$^3k_r = A \exp[-BE_T(30)] + k_1[\mathrm{ROH}] \qquad (4)$$

which is fitted to the data using k_1 as the adjustable parameter [30] *. As shown by the solid curves in fig. 1, good agreement is found between the observed and the expected behavior using $k_1 = (5.0 \pm 0.8) \times 10^9$ M^{-1} s^{-1} for methanol in acetonitrile and $k_1 = (3 \pm 1) \times 10^{10}$ M^{-1} s^{-1} for methanol in diethylether. The diffusion controlled bimolecular rate constant in acetonitrile is $\approx 2 \times 10^{10}$ M^{-1} s^{-1} [31] and in diethylether it is $\approx 3 \times 10^{10}$ M^{-1} s^{-1} [31]. Hence in acetonitrile, the reaction of ^{1}DPC with methanol is less than diffusion controlled, whereas the reaction in diethylether appears to be diffusion controlled. The origin of the difference in the rate of reaction in acetonitrile versus that in diethylether we believe is due to the stabilization of an intermediate reaction complex [25,26,32] formed between the alcohol and ^{1}DPC, to be discussed in a future paper [33].

It is pointed out that if one were to use an alcohol and a solvent which have the same polarities, then no change in k_{ST} is expected on adding alcohol; for this case a simple linear dependence of ^3k_r is expected. Verification of this idea is obtained (fig. 2) by choosing 3-pentanol ($E_T(30) = 45.7$ kcal/mole) as the reactant molecule and acetonitrile ($E_T(30) = 46.0$ kcal/mole) as the solvent. It is found that ^3k_r is a linearly increasing function of the 3-pentanol concentration. The slope of the fitted line yields the rate constant of $k_1 = (2.04 \pm 0.08) \times 10^9$ M^{-1} s^{-1}. The intercept, which according to eq. (2) must equal k_{ST}, is found to be equal to $(3.29 \pm 0.04) \times 10^9$ s^{-1}, the same as the experimentally determined value of k_{ST} in the neat solvent, $(3.23 \pm 0.19) \times 10^9$ s^{-1}. After correcting for the polarity effects due to the addition of the alcohol quencher one can obtain the intrinsic reactivity of ^{1}DPC with different alcohols in a given solvent. In this way it is found that methanol is 2.5 times more reactive than 3-pentanol with ^{1}DPC, in acetonitrile. This result is consistent with the model which relates reactivity with the O–H bond lability of the alcohol [20,34,35].

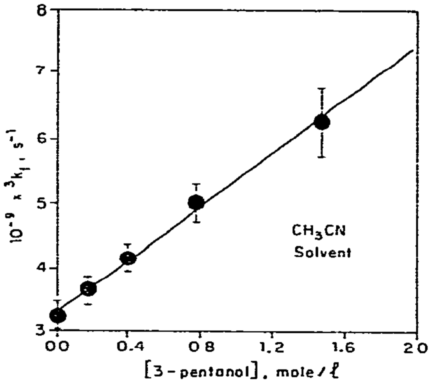


Fig. 2. ^3k_r as a function of 3-pentanol concentration, using acetonitrile as solvent.

Comparison of the reaction rate constants obtained from direct measurements to that obtained from steady state results is informative. As shown in table 2, there is reasonably good agreement. These facts lend further support to the kinetic model used in the steady-state analysis which assumes that singlet–

Table 2
Comparison of rate constants for reaction of singlet diphenylcarbene with alcohol from direct and steady state studies

Alcohol	Solvent	$10^{-9}k_1(M^{-1}s^{-1})$	
		direct [a]	steady state [b]
methanol	diethylether	30 ± 10	
methanol	acetonitrile	5.0 ± 0.8	5.6
3-pentanol	acetonitrile	2.04 ± 0.08	3.2 [c]

[a] This work.
[b] Evaluated from steady-state quenching experiments, see ref. [20].
[c] Rate constant obtained for isopropanol, which is assumed equal to the value of 3-pentanol.

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* The non-linear least-squares subroutine STEPIT written by Chandler [30] was used in the data analysis.

triplet equilibration is fast and that alcohol (e.g. methanol) is singlet state selective. It is emphasized, however, that the picosecond measurements underscore the need to recognize the dual role played by alcohols on carbene dynamics. Hence, an allowance should be made for changes in the spin equilibration rates and the energy gap due to corresponding changes in the solvent polarity which influences the results of competitive quenching experiments that are often used to obtain these values. As the competitive quenching study is usually designed, one employs two state selective quenchers (e.g. alcohol is the singlet quencher and isoprene is the triplet quencher) where the concentration of one quencher is fixed while the other is varied [19,20]. When alcohol is chosen as the quencher in which its concentration is varied, then the complication of change in polarity will occur. Since increased polarity decreases the singlet–triplet energy gap, the requirement of a large range of alcohol concentration will ultimately mean that a lower value for K_{eq} and ΔE_{ST} will be determined. One way to minimize these difficulties is to employ an alcohol that approximates the polarity of the solvent, e.g. 3-pentanol with acetonitrile, or design the experiment such that the alcohol concentration is fixed and the polarity of the secondary quencher (which is usually not polar) is the one whose concentration is varied.

4. Conclusions

It is found that carbene scavengers have a chemical as well as a physical effect on the dynamics of the carbene. As exemplified by the reaction of ^{1}DPC with alcohols, these two distinct effects can act in opposite directions leading to anomalous reaction kinetics. If the addition of the reactant molecules causes a large change in the polarity of the bulk medium, then a significant deviation from normal kinetics as dictated by scheme I will result. This is the apparent situation encountered for the methanol reaction with ^{1}DPC in either acetonitrile or diethylether solvents. In diethylether, for example, the lifetime of the singlet state can be increased by 16% over that found in the absence of quencher in spite of the fact that it is still being consumed by the alcohol. Secondly, the direct measurement of the bimolecular reaction rate constants of ^{1}DPC with alcohols has been made for the first time. The values obtained from steady-state results, where it is assumed that there is spin equilibration, and that ether formation is a singlet state selective reaction, is in agreement with our direct measurement of the singlet carbene reacting with alcohol. We thus conclude that the steady-state assumptions based on the model of spin equilibration and singlet state selectivity are correct. The picosecond measurements do prove, however, that quenchers can inhibit the rate of singlet to triplet spin conversion by the solvent polarity effect mechanism, which points out the need to recognize the nature of the quencher not only in terms of its effect on the chemical channels potentially available but also its effect on the physical channels of relaxation for the carbene.

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