EFFECTS OF SOLVENT POLARITY AND STRUCTURE ON INTERSYSTEM CROSSING IN DIPHENYLCARBENES.
A PICOSECOND LASER STUDY ON DIMESITYLCARBENE

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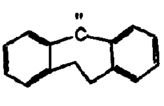
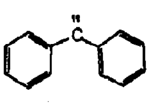
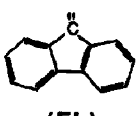
The singlet to triplet intersystem crossing rate (k_{ST}) for a series of diphenylcarbene derivatives is found to be a sensitive function of the energy splitting (ΔE_{ST}), which in turn depends on the solvent polarity and on the structure of the carbene. A turn-over in the dependence of k_{ST} on ΔE_{ST} is found for the case of dimesitylcarbene (DMC), where k_{ST} is a decreasing function of ΔE_{ST}. The results for DMC provide the first example of intersystem crossing in the large gap limit for a carbene.

1. Introduction

A fundamental problem concerning carbenes is the elucidation of the intramolecular and intermolecular factors which determine the singlet–triplet energy splitting and the intersystem crossing dynamics between the lowest singlet and triplet states of these important chemical intermediates [1–7]. The investigation of diarylcarbenes has yielded much information regarding this issue. For example, dibenzocycloheptadienylidene (DCHD), diphenylcarbene (DPC) and fluorenylidene (FL) have been shown to undergo rapid thermal equilibration between their ground triplet and their low-lying singlet states [8–22].

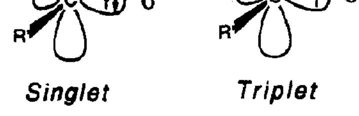

(DCHD)


(DPC)


(FL)

In comparing the three arylcarbenes it is found that both k_{ST} and ΔE_{ST} decrease in magnitude in the order given by DCHD>DPC>FL [23–25]. Furthermore, an unusual solvent polarity effect on k_{ST} and ΔE_{ST} is manifested. It has been found, for each of these carbenes, that ΔE_{ST} decreases with increasing solvent polarity [12–14,23–25]. The intermolecular solvent parity effect is attributed to the selective stabilization of the low-lying polar singlet state (σ^2) relative to the nonpolar ground triplet state ($\sigma^1\pi^1$) by polar solvents [12–14,23–26] (scheme 1).

An important consequence of the dependence of ΔE_{ST} on solvent polarity is that it provides one with an opportunity to probe for corresponding changes in k_{ST} as a function of ΔE_{ST} for a given carbene. Again, for each of these three carbenes it is found that k_{ST} decreases with decreasing ΔE_{ST}. In other words, these carbenes exhibit an "inverse" gap effect, i.e. the time for intersystem crossing increases as the energy gap decreases, and is in sharp contrast to the usual behavior exhibited by large molecules [27–30]. The inverse gap effect on intersystem crossing can be explained by an off resonance cou-



Scheme 1. Electronic configuration of lowest singlet (σ^2) and triplet ($\sigma^1\pi^1$) states in carbene.

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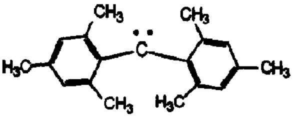
pling model in which singlet-to-triplet intersystem crossing occurs from the singlet into a sparse triplet vibronic manifold characteristic of a small energy gap [27–36].

A particularly intriguing question is to consider at what value of the singlet–triplet splitting will be a carbene start to exhibit the relaxation dynamics typically seen for large molecules? In other words, it is desirable to determine the intersystem crossing rate and its dependence on its energy gap for a carbene that falls into the large gap limit. An attractive candidate to consider in this regard is dimesitylcarbene (DMC).

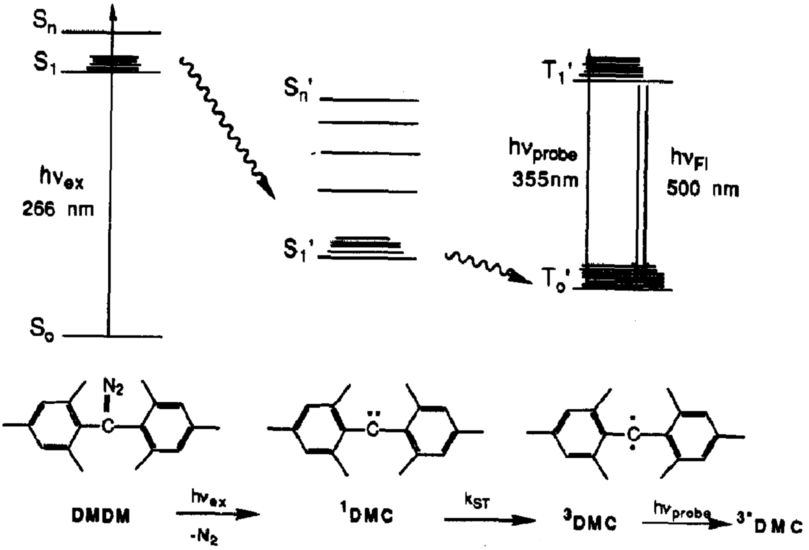


(DMC)

DMC is similar to DCHD, DPC and FL insofar as it is a simple divalent aromatic hydrocarbon which possesses a triplet ground state [37–40]. Evidence based on its chemical reactivity strongly suggests, however, that thermal population of the lowest singlet state is insignificant during the lifetime of DMC in fluid solution [37–40], unlike that for other carbenes discussed. Based on these results it is concluded that ΔE_{ST} for DMC is substantially larger than what is found for the other carbenes where spin equilibration is easily achieved. In this paper we wish to report on the solvent dependence of the dynamics of singlet-to-triplet spin conversion in DMC and its relation to molecular structure and the singlet–triplet energy gap. The results we obtain demonstrate that the rate of intersystem crossing increases with increasing solvent polarity, unlike DCHD, DPC and FL. We attribute this solvent dependence to the large singlet–triplet energy splitting in DMC, which yields the characteristic radiationless decay to a dense manifold of final states, i.e. an increase in the transition rate with decreasing energy gap.

2. Experimental

The picosecond laser induced fluorescence experiments consisted of the irradiation of a vacuum degassed solution of dimesityldiazomethane (5×10^{-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) [41]. The formation rate of ^{3}DMC was monitored by its laser induced fluorescence using a weak probe pulse at 355 nm at variable time delays. Preparation and purification of



Scheme 2. Laser induced fluorescence of ^{3}DMC following photodecomposition of dimesityldiazomethane.

dimesityldiazomethane, the carbene precursor, has been described before [37,40]. All solvents were purified before use, as described previously [23].

3. Results and discussion

Picosecond laser irradiation at 266 nm of dimesityldiazomethane (DMDM) leads to the extrusion of nitrogen resulting in the formation of ^{1}DMC. Once formed, ^{1}DMC undergoes efficient energy relaxation to populate the ground state triplet, ^{3}DMC. Using a 355 nm laser pulse a strong laser induced fluorescence of ^{3}DMC can be detected at 293 K, which has $\lambda_{max} = 500$ nm. A time resolved laser induced fluorescence experiment of ^{3}DMC can provide a quantitative means to obtain the formation kinetics of ^{3}DMC and hence the intersystem crossing rate (k_{ST}), as given by scheme 2. Typical results for DMC using this method are shown in fig. 1. As given in table 1, there is a significant solvent effect on intersystem crossing for DMC, where the rate of spin conversion is faster in the more polar solvent. As shown in fig. 2, the logarithm of k_{ST} may be expressed as a linearly increasing function of the solvent polarity parameter $E_T(30)$. The solvent effect on the intersystem crossing dynamics in DMC is opposite to the behavior of other arylcarbenes, e.g. FL, DPC, and DCHD, where the singlet-to-triplet intersystem crossing time is slower in more polar solvents (fig. 3).

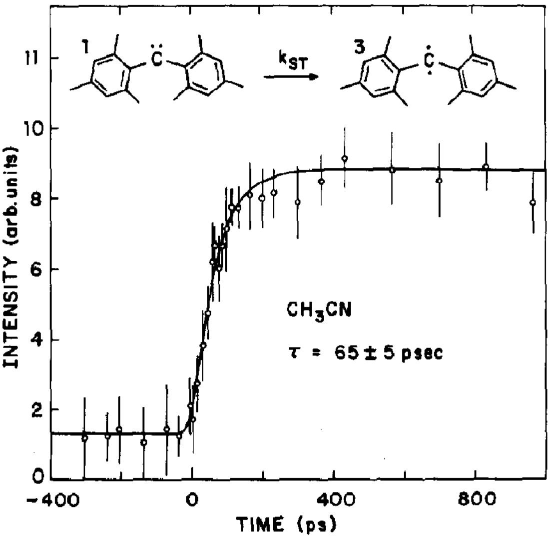


Fig. 1. Laser induced fluorescence of dimesitylcarbene as a function of time, using acetonitrile as solvent at 293 K. The solid curve is a calculated fit.

Table 1
Intersystem crossing rate for dimesitylcarbene in various solvents, at 20°C

Solvent	$10^{-9} k_{ST}$ (s^{-1})	$E_T(30)$ (kcal/mol) [a]
isooctane	10.53±0.72	30.9
3-methylpentane	10.53±0.53	30.9
diethylether	11.77±0.78	34.6
tetrahydrofuran	12.50±0.87	37.4
butyronitrile	13.33±0.67	43.1
acetonitrile	15.39±1.09	46.0

[a] Ref. [42].

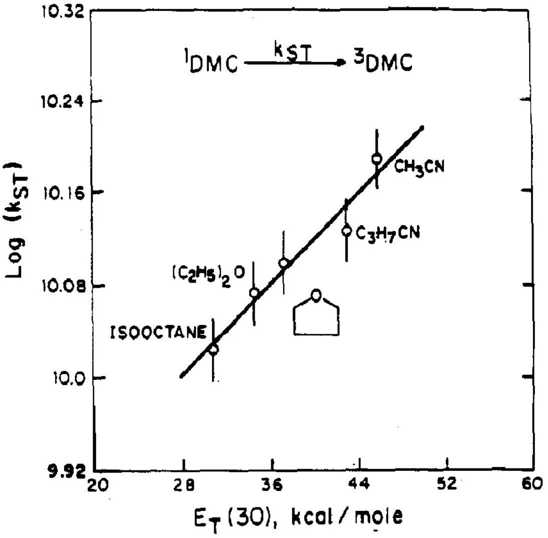


Fig. 2. Intersystem crossing rate of dimesitylcarbene as a function of the solvent polarity parameter $E_T(30)$.

3.1. Polarity-dependent singlet–triplet energy gap

We previously interpreted the dependence of k_{ST} on solvent as arising from a change in ΔE_{ST}, which thus alters the effective coupling between the lowest singlet and ground triplet states of the carbene. As shown for the case of DPC, an increase in solvent polarity can decrease ΔE_{ST} by as much as 1.4 kcal/mol [23]. For example, the energy splitting in DPC

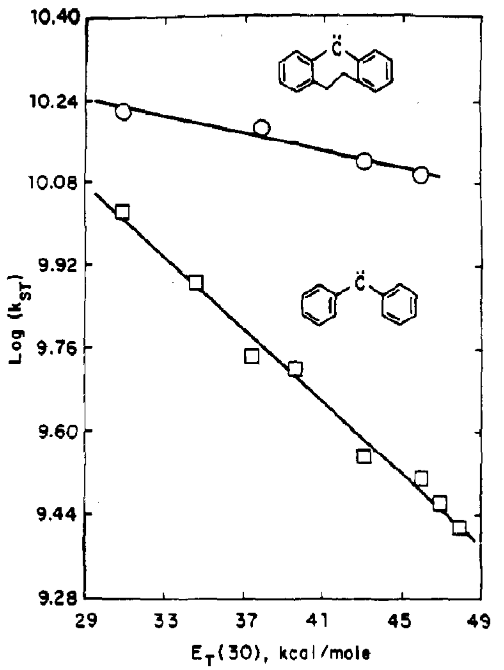


Fig. 3. Intersystem crossing rates of diphenylcarbene (□) and dibenzocycloheptadienylidene (○) as a function of the solvent polarity parameter $E_T(30)$.

is found to be 1400 cm^{-1} in the nonpolar solvent isooctane but is reduced to the value of 950 cm^{-1} in the polar acetonitrile solvent [12,13,23–25]. Combining this result with the observation that k_{ST} in DPC decreases with increasing solvent polarity reveals that an "inverse" gap effect is operative for DPC. A similar inverse gap effect also appears for DCHD and FL as well [14,24,25]. Such behavior is expected for small ΔE_{ST} where singlet-to-triplet spin conversion would be described as an off resonance intersystem crossing from the singlet into a sparse triplet vibronic manifold. In this small gap limit the decrease in the energy splitting will reduce the number of triplet vibronic states in the vicinity of the singlet and thus cause a reduction in the intersystem crossing rate. Further support of this interpretation of the solvent dependence of the intersystem crossing is obtained from the isotope effect on intersystem crossing in DPC [43]. In that work deuteration of DPC increased the intersystem crossing rate as would be predicted for a sparse gap case since the effect of deuteration is to increase the number of available final states.

3.2. Transition to large gap limit

The inverse gap effect is expected to be most pronounced for carbenes possessing small ΔE_{ST} but will diminish at higher ΔE_{ST}. It is important to consider that for sufficiently large ΔE_{ST} the vibronic level structure in the triplet will be sufficiently dense so that an increase in ΔE_{ST} results mainly in decrease in the Franck–Condon factors, which will consequently cause the inverse gap effect to erode. In this limit of a large energy gap the intersystem crossing rate will be a decreasing function of ΔE_{ST}, i.e. a normal gap dependence, which is what is typically found for large molecules [27–35]. This situation appears applicable to DMC, which is recognized to have a large ΔE_{ST} and where k_{ST} is found to increase with increasing solvent polarity.

3.3. Singlet–triplet gap for DMC

At issue now is the determination of the energy splitting for the lowest singlet and ground triplet states of DMC. We can evaluate this from an estimation of the equilibrium constant, obtained from the combination of k_{ST} with the kinetic results obtained from alcohol quenching of DMC. Nanosecond laser flash photolysis experiments have shown that in the presence of alcohol the yield of triplet DMC is reduced by the reaction of ^{1}DMC with alcohol [38]. Kinetic analysis gives a value of $^1k/k_{ST}$ equal to 0.144 for methanol in nonpolar alkane solvents, where ^1k is the rate constant of ^{1}DMC reacting with alcohol. By using the value of k_{ST} obtained from direct measurements, gives $^1k = 1.52\times10^9$ M^{-1} s^{-1}. Since it is found that the ground triplet state lifetime (200 μs) is unaffected by methanol up to 1.2 M [38], it then requires that $^1k[CH_3OH]/K_{eq} < 5\times10^3$ s^{-1}. By substitution, one arrives at $K_{eq} > 4\times10^5$, and thus $\Delta G_{ST} > 7.6$ kcal/mol. By employing kinetic data obtained by picosecond and nanosecond time resolved experiments it is thus found that the energy splitting of DMC is > 7 kcal/mol (2500 cm^{-1}) and confirms earlier chemical evidence [15–17], which suggested that DMC has a large singlet–triplet energy gap.

3.4. Molecular structure and singlet–triplet gap

A possible explanation for the large singlet–triplet splitting in DMC is to consider the effect of the substituents on the bond angle, θ_{RCR}, about the central methylene carbon atom. Theoretical calculations indicate that the energy splitting varies with the change in the angle defined by the two bonds to the central carbon atom and its interplanar twist [44–47]. As the molecule goes from a bent towards a linear geometry, i.e. the angle increases, the percent 2s character in the nonbonding σ orbital decreases thereby increasing the orbital energy. This equates out to a more destabilized singlet (σ^2) compared to the triplet ($\sigma^1\pi^1$) and thus an increase in the energy gap as the bond angle increases. It can be argued that due to the steric repulsion between the mesityl groups bonded to the central methylene carbon that DMC will achieve a more linear geometry, and hence a larger ΔE_{ST} compared to either DPC or DCHD [24,25]. Additional evidence that supports the idea that there is an increase in the central angle in the series DMC>DCHD>DPC>FL is obtained from EPR data [39,48–50]. The value of the zero-field splitting parameter $|E|/hc$, which is a measure of the deviation of the spin–spin interaction from cylindrical symmetry in the spin dipole–dipole Hamiltonian, is an indication of the 2s character in the orbital. As previously noted [39] $|E|/hc$ decreases as the bond angle increases and is therefore a measure of the percent 2s character in the non-bonding σ orbital [51]. As shown in fig. 4, ΔE_{ST} increases as $|E|/hc$ decreases, showing that an increase in the central methylene bond angle could be the structural change responsible for the change in ΔE_{ST}.

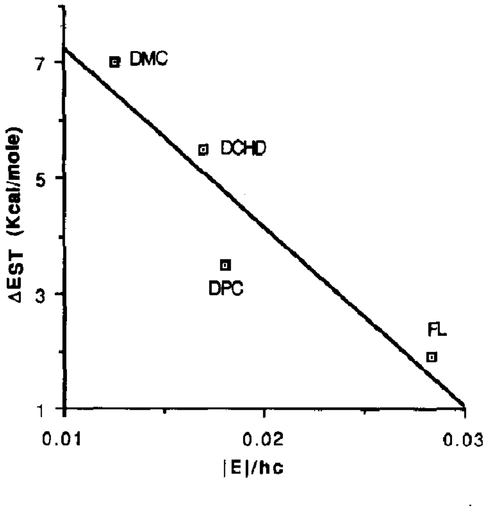


Fig. 4. Plot of ΔE_{ST} versus the zero-field splitting parameter $|E|/hc$ for various carbenes.

3.5. Electronic versus steric effects on ΔE_{ST}

As shown in the elegant studies carried out by Schuster and coworkers [3,14,52–60] on fluorenylidene and its derivatives the singlet–triplet splitting can be significantly modified by a change in the electronic nature of the substituents. It was found, for instance, that shifts in ΔE_{ST} within a series of fluorenylidene derivatives could be explained by the effect of the electronic mixing of the substituent orbital with the methylene orbital. Such electronic effects are distinctly different from steric effects (which can induce a change in θ_{RCR} and thus also change ΔE_{ST}). Although we recognize the importance of electronic effects, particularly for the planar arylcarbenes such as fluorenylidene, we can, however, rationalize our data on the diphenylcarbenes simply in terms of steric induced changes in θ_{RCR}, which cause a change in ΔE_{ST}. In other words, in terms of the ability to affect a change in ΔE_{ST} the steric effects (due to simple alkyl substitution) apparently win out over the perturbations due to electronic orbital mixing of the ligand for the diphenylcarbenes examined.

3.6. Linear free-energy relationship of intersystem crossing rates in diphenylcarbenes

Comparing the three carbenes DMC, DCHD and DPC reveals a clear ordering of the solvent dependence of intersystem crossing rates with respect to the energy splitting of the carbene. Taking the slope (β) of the line obtained from $\log(k_{ST})$ versus $E_T(30)$ as a measure of the solvent polarity dependence on intersystem crossing rates it is seen that the slope increases in value in the order of DMC>DCHD>DPC, which is identical to the ordering the energy gaps (table 2). We thus find that DPC, which has the smallest energy gap, has a large negative β. For the carbenes with larger energy gaps, e.g. DCHD and

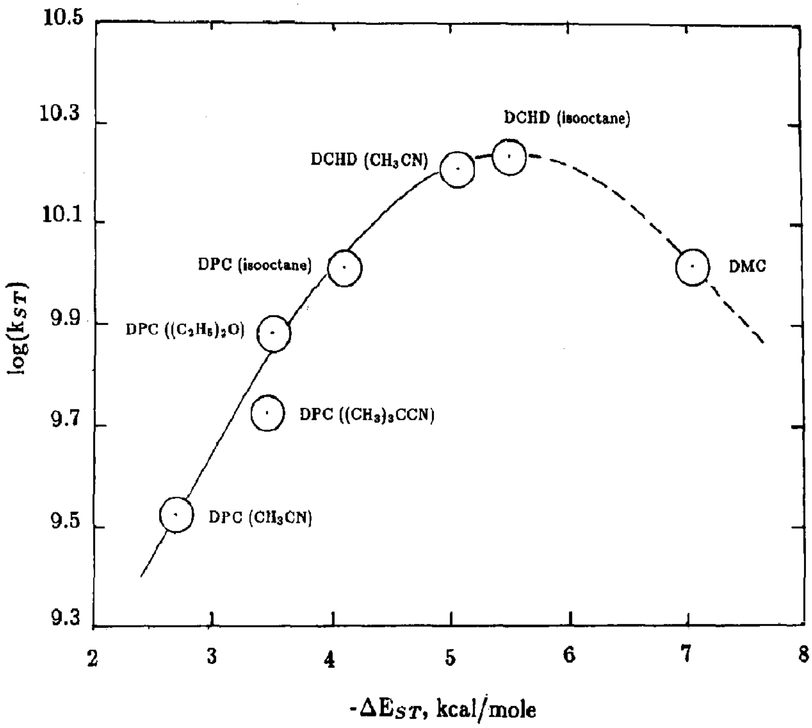


Fig. 5. Plot of the intersystem crossing rate (k_{ST}) as a function of ΔE_{ST}, for various arylcarbenes.

Table 2
Dependence of the intersystem crossing rate on solvent polarity as a function of the singlet–triplet splitting for arylcarbenes

Carbene	$10^3\beta$ [a]	ΔE_{ST} (kcal/mol)
dimesitylcarbene	$+9.70 \pm 1.34$	>7 [b]
dibenzocycloheptadienylidene	-8.36 ± 1.13	5.5–6.3 [c]
diphenylcarbene	-34.6 ± 1.48	2.5–4.0 [d]

[a] Obtained from linear least squares fitting of $\log k_{ST} = \alpha + \beta [E_T(30)]$.

[b] This work.

[c] Refs. [24,25]. [d] Refs. [12,13,23].

DMC, the dependence on solvent polarity is weaker. Of particular significance is the fact that we see a turn over in the solvent polarity dependence in going from DCHD to DMC. Namely, β is negative for DCHD but positive for DMC. Such a result is reasonable if the triplet vibronic level structure in the vicinity of the singlet switches from the limit of a sparse manifold to the statistical limit of a dense manifold when the ΔE_{ST} is made large, as shown in fig. 5.

4. Conclusions

A consistent picture of the relaxation dynamics in aromatic carbenes, obtained from picosecond laser studies, is presented in terms of the dependence of the intersystem crossing rate on the singlet–triplet energy gap, which in turn depends on the structure of the carbene and the polarity of its solvent environment. The carbenes examined could be grouped into two main categories. Those that possess small ΔE_{ST} (<2000 cm^{-1}) such as DPC, DCHD and FL, fall into the small gap limit, and will exhibit an "inverse" gap effect, i.e. the intersystem crossing rate decreases as ΔE_{ST} decreases. The second group, as exemplified by DMC, is characterized by having a large ΔE_{ST} (>2500 cm^{-1}) and a consequent dense manifold of states, which results in the rate of intersystem crossing being a decreasing function of the energy splitting. The key molecular parameter in determining the energy splitting in diphenylcarbenes is the angle and twist of the moieties attached to the central carbon. In DMC the large energy splitting is accounted for by the large angle caused by the repulsive interactions between the two mesityl ligands. The other carbenes have a smaller central angle with the result that their gaps are in the small gap limit of radiationless transitions. The observed solvent polarity effect on the dynamics for the carbenes is a consequence of the greater solvent stabilization of the more polar singlet state, which results in a decrease in ΔE_{ST} with solvent polarity.

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