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INVERSE DEUTERIUM ISOTOPE EFFECT IN THE INTERSYSTEM CROSSING OF DIPHENYLCARBENE

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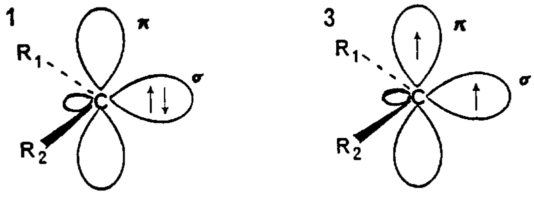
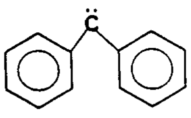
The singlet-to-triplet intersystem crossing rate (k_{ST}) of diphenylcarbene (DPC) is found to exhibit an inverse isotope effect in various solvents. An off-resonance coupling model between the initial singlet state and a sparse triplet vibronic manifold accounts for k_{ST} showing both an inverse isotope effect in a given solvent as well as an inverse energy gap effect in a solvent series.

1. Introduction

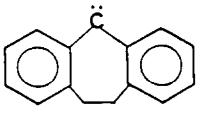
Carbenes are interesting short-lived intermediates that contain two non-bonding electrons, which are either paired or unpaired, leading to singlet and triplet states respectively. They are important chemical intermediates whose spin state dependent chemistry is implicated in a large number of organic reactions [1–4]. An important feature relevant to an understanding of many of their physical and chemical properties is the small energy gap separating the lowest singlet and triplet states. In fact for a number of carbenes these two states are in equilibrium at room temperature [5]. The ground state of these molecules can be either singlet or triplet depending on substituents and possibly geometry [6]. For the molecules we have studied, diphenylcarbene (DPC) and dibenzocycloheptadienylidene (DCHD), the ground state is a triplet.



Scheme 1.



DPC



DCHD

The small energy separation between the singlet and ground triplet leads to unusual energy relaxation. We have recently shown that the intersystem crossing rate (k_{ST}) exhibits an inverse gap effect [7]. By inverse gap effect it is meant that the rate of intersystem crossing (k_{ST}) decreases as the energy splitting (ΔE_{ST}) decreases. This is contrary to the usual energy gap dependence [8] exhibited in energy relaxation. This inverse effect is attributed to the small singlet–triplet energy gap in these aromatic carbenes. In the so called usual energy relaxation dependence the energy gap is large, there is a dense manifold of final states, and it is the decrease in the Franck–Condon factors with increasing energy which leads to the smaller decay rates for larger energy gaps. For the small gap case, which is applicable to a number of arylcarbenes having gaps roughly in the range of 500–2500 cm^{-1}, the intersystem crossing occurs from the singlet state into a sparse manifold of triplet vibronic levels. As the energy gap increases the triplet level structure becomes more congested in the vicinity of the singlet and the intersystem crossing is enhanced. When the gap is several thousand cm^{-1}, perhaps as low as 3000 cm^{-1}, then the statistical, "large" gap case is approached and the "usual" decrease in energy decay rate with further increase in energy is expected.

One way to gain further insight into radiationless transitions for the small energy gap case and to further test the explanation of the variation of k_{ST} with ΔE_{ST} in carbenes is to determine the effects of deuteration on intersystem crossing. Isotope effects on radiationless transitions are well known for a number of molecules which undergo intersystem crossing [8]. In the large gap, statistical limit, the main effect of deuteration on intersystem crossing from the lowest excited singlet to the excited triplet manifold is a reduction of the Franck–Condon overlap factor thereby decreasing the rate. However there are several cases in which isotopic substitution increases the rate of S → T intersystem crossing [9,10]. In these cases there is believed to be a moderate to small energy separation between the states coupled. Most recently, Amirav, Sonnenschein and Jortner [10] have reported a large inverse deuterium isotope effect on the $S_1 \rightarrow T_1$ intersystem crossing of anthracene. In order to explain this effect it was assumed that intersystem crossing was intermediated by higher-lying triplet states. The interaction between S_1 and the triplet states T_x was described by an off-resonance coupling scheme with a sparse manifold of final states [10]. In this case it was shown that the isotope effect eroded at higher vibrational excess energy within the S_1 manifold. If the radiationless $S_1 \rightarrow T_0$ transition of arylcarbenes is dominated by the small energy gap as we propose, then we should find an inverse gap effect as in the $S_1 \rightarrow T_1$ transition of anthracene.

2. Experimental

The laser-induced fluorescence technique has been described previously [11]. Briefly, the output of a passively mode-locked Nd:YAG laser is frequency quadrupled to generate the 266 nm fourth harmonic. The output is then split into two pulses, one of which travels a fixed optical path (excitation) while the second (probe) is optically delayed. The excitation pulse photolyzes the diphenyldiazomethane precursor, generating the carbene in its singlet state which then undergoes intersystem crossing. At some time later the probe pulse excites the ground triplet diphenylcarbene to its first excited triplet state from which it subsequently fluoresces. We monitor the total $(T_1 \rightarrow T_0)$ fluorescence as a function of delay between pump and probe. By this technique we can monitor the population growth of the ground triplet state.

The perdeuterated diphenyldiazomethane was synthesized [12] by base-catalyzed oxidation of the corresponding hydrazone. Perdeuterated benzophenone, used to make the hydrazone, was obtained from Merck, Sharp and Dohme and was sublimed before use. All solvents were freshly distilled under nitrogen and over the appropriate drying agent where applicable.

3. Results and discussion

The intersystem crossing time k_{ST}^{-1} of perdeuterated diphenylcarbene in a number of solvents is listed in table 1. This rate is found to depend on the choice of solvent as demonstrated in fig. 1. The logarithm of k_{ST} is found to be a linear function of the solvent parameter $E_{\mathrm{T}}(30)$. This parameter is an empirical measure of the solvent polarity, increasing as the solvent polarity increases. For diphenylcarbene-h_{10}, k_{ST} was found to vary exponentially with the solvent polarity parameter $E_{\mathrm{T}}(30)$, being smallest in the most polar solvent. This behavior was explained by a model which related [7] the effect of solvent polarity on the singlet–triplet energy splitting ΔE_{ST} [7] upon which intersystem

Table 1
Times for intersystem crossing k_{ST}^{-1} for diphenylcarbene-d_{10} and diphenylcarbene-h_{10} in various solvents at 298 K. $E_{\mathrm{T}}(30)$ is a solvent polarity parameter

Solvent	$10^{12}\ k_{\mathrm{ST}}^{-1}$ (ps)		$E_{\mathrm{T}}(30)$ [b]
	DPC-d_{10}	DPC-h_{10} [a]	
acetonitrile	260 ± 20	310 ± 18	46.0
butyronitrile	220 ± 14	280 ± 20	43.1
pivalonitrile	170 ± 11	190 ± 16	39.7
tetrahydrofuran	140 ± 9	180 ± 14	37.9
diethylether	120 ± 5	130 ± 11	34.6
isooctane	95 ± 7	95 ± 9	30.9

[a] See ref. [7]. [b] See ref. [13].

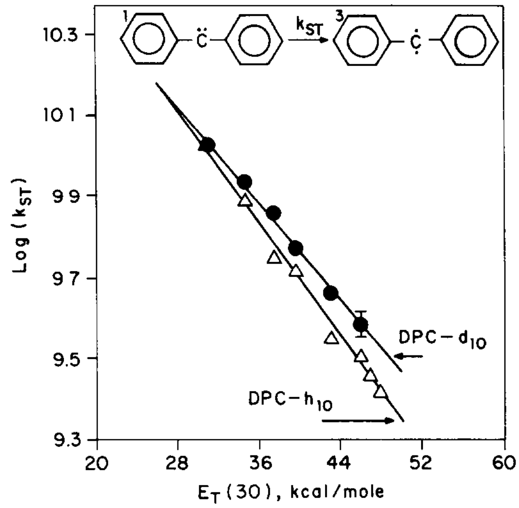


Fig. 1. Plot of the logarithm of k_{ST} versus the solvent polarity parameter $E_T(30)$ for diphenylcarbene-h_{10} (△) and diphenylcarbene-d_{10} (●).

crossing depends. The solvent effect on ΔE_{ST} is due to the fact that the singlet state with both electrons localized in the σ orbital (see scheme 1) is more polar than the ground triplet state. Therefore in polar solvents the singlet would be stabilized to a greater extent than the triplet, resulting in a smaller energy gap. For diphenylcarbene this picture has been confirmed [14]. In isooctane it was found that $\Delta E_{ST} = 1400$ cm^{-1} whereas in the more polar acetonitrile this gap was found to decrease to a value of 950 cm^{-1}. A consequence of the smaller splitting in the polar solvents is that there are fewer triplet vibronic levels in the vicinity of the singlet state, resulting in a slower rate of intersystem crossing. It is seen in fig. 1 that the same model accounts for the solvent dependence of the intersystem crossing rate in perdeuterated diphenylcarbene.

If we compare k_{ST} for DPC-d_{10} with that for DPC-h_{10} in the same polar solvent we see that there is an enhancement of the rate of intersystem crossing upon deuteration. To understand this "inverse" deuterium isotope effect it is helpful to reexamine the physical model invoked for explaining the inverse energy gap effect. As stated previously the model used is an off-resonance coupling between S_1 and a number of ground triplet vibronic levels T_f. The intersystem crossing rate for a transition from an initial state to a sparse manifold of final states has been obtained by Nitzan and Jortner [15] which for the off-resonance case is

$$k_{ST} \propto \sum_{T_f} (H_{SO})^2_{S,T_f}\Gamma^2_{T_f}/[(E_S - E_{T_f})^2 + (\tfrac{1}{2}\Gamma_{T_f})^2], \qquad (1)$$

where $(H_{SO})_{S,T_f}$ is the spin–orbit coupling term between the singlet state S_1 and the particular triplet vibronic state T_f, i.e.

$$(H_{SO})_{S,T_f} = \langle S_1(q,Q)|H_{SO}|T_f(q,Q)\rangle.$$

Γ_{T_f} is the width of T_f due to coupling with other vibrations and the solvent.

As noted, this model was used previously by Amirav, Sonnenschein and Jortner [10] to explain the inverse isotope effect of the $S_1 \rightarrow T_1$ transition of anthracene. It was argued that the isotope effect presents itself in the energy splitting term $(E_S - E_{T_f})^2$. The level structure of the triplet manifold, being sensitive to deuteration, becomes more congested upon isotopic substitution. Therefore, the contribution of some energy defect terms are substantially larger for anthracene-d_{10} than for anthracene-h_{10}, resulting in an enhancement of the rate of decay for the deuterated compound. They also argued that H_{SO} would exhibit a small, normal isotope effect and therefore could not be responsible for the increase in the decay rate of $S_1(0)$.

The same arguments are applicable to the $S_1 \rightarrow T_0$ transition of diphenylcarbene. The small energy separation between S_1 and T_0 results in a sparse manifold of final triplet vibronic levels and is analogous to a small-molecule limit. In DPC-d_{10} the congestion of final states near S_1 increases due to the deuteration. Some triplet vibronic states will be closer in energy to the singlet, thereby decreasing the energy difference in the denominator of eq. (1) and will enhance the intersystem crossing rate. As the polarity of the solvent decreases (i.e. the energy splitting increases) the effect of deuteration on k_{ST} diminishes until finally in isooctane the rate is the same for both compounds. This is explained by the fact that as the energy gap increases the level structure of both compounds becomes more dense and the relative importance of deuteration as a mechanism for increasing the number of triplet vibronic states in the vicinity of the singlet state decreases. This erosion in the effect of deuteration on k_{ST} with increasing energy gap finally leads to equal intersystem crossing rates for both compounds in isooctane where the gap is largest.

4. Conclusion

We have observed an inverse deuterium isotope effect on the $S_1 \rightarrow T_0$ intersystem crossing of diphenylcarbene, namely an increase in the radiationless transition rate on deuteration. The origin of this effect is the small singlet–triplet splitting in diphenylcarbene which results in an intersystem crossing to a sparse manifold of triplet vibronic states. Deuteration increases the number of final triplet vibronic states in the vicinity of the singlet and in that way increase the intersystem crossing rate. The magnitude of the isotope effect is dependent upon the solvent used. This dependence is caused by the variation of the singlet–triplet energy gap with solvent, the isotope effect being largest in the solvent for which diphenylcarbene has the smallest gap. We thus find a description of intersystem crossing in diphenylcarbene as a transition from S_1 to a sparse triplet manifold, due to the small energy gap, accounts for both the dependence of intersystem crossing on solvent polarity (an inverse gap effect), as well as the inverse isotope effect in a given solvent.

Acknowledgement

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References

[1] W. Kirmse, Carbene chemistry, 2nd Ed. (Academic Press, New York, 1971).
[2] R.A. Moss, R.A. Jones and M. Jones Jr., eds., Carbenes, Vols. 1, 2 (Wiley–Interscience, New York, 1975).
[3] H. Durr, Topics Current Chem. Res. 1 (1968) 329.
[4] D. Bethell, A.R. Newall and D. Whittaker, J. Chem. Soc. (B) (1971) 23;
D. Bethell, A.R. Newall, G. Stevens and D. Whittaker, J. Chem. Soc. (B) (1969) 749;
W. Kirmse, L. Horner and H. Hoffman, Justis Liebigs Ann. Chem. 614 (1958) 19;
D. Bethell, J. Hayes and A.R. Newall, J. Chem. Soc. Perkin II (1974) 1307;
G.L. Closs, in: Topics in stereochemistry, Vol. 3, eds. E.L. Eliel and N.L. Allinger (Interscience, New York, 1968).
[5] G.L. Closs and B.E. Rabinow, J. Am. Chem. Soc. 98 (1976) 8190;
D. Bethell, G. Stevens and P. Tickle, Chem. Commun. (1970) 792;
K.B. Eisenthal, N.J. Turro, M. Aikawa, J.A. Butcher Jr., C. Dupuy, G. Hefferon, W. Hetherington, G.M. Korenowski and M.J. McAuliffe, J. Am. Chem. Soc. 102 (1980) 6563.
[6] J.G. Langan, E.V. Sitzmann and K.B. Eisenthal, Chem. Phys. Letters 110 (1984) 521;
S.C. Lapin, B.E. Brauer and G.B. Schuster, J. Am. Chem. Soc. 106 (1984) 2092;
L.M. Hadel, M.S. Platz, B.B. Wright and J.C. Scaiano, Chem. Phys. Letters 105 (1984) 539;
R. Alt, H.A. Staab, H.P. Reisenauer and G. Maier, Tetrahedron Letters (1984) 633.
[7] E.V. Sitzmann, J. Langan and K.B. Eisenthal, J. Am. Chem. Soc. 106 (1984) 1868.
[8] J. Jortner, S.A. Rice and R.M. Hochstrasser, Advan. Photochem. 7 (1969) 149;
C.A. Hutchison and B.W. Mangum, J. Chem. Phys. 32 (1960) 1261;
M.R. Wright, R.P. Frosch and G.W. Robinson, J. Chem. Phys. 33 (1960) 934.
[9] J.O. Uy and E.C. Lim, Chem. Phys. Letters 7 (1970) 306;
E.C. Lim and H.R. Bhattacharjee, Chem. Phys. Letters 9 (1971) 249.
[10] A. Amirav, M. Sonnenschein and J. Jortner, Chem. Phys. Letters 100 (1983) 488; 102 (1983) 573.
[11] C. Dupuy, G.M. Korenowski, M. McAuliffe, W.M. Hetherington III and K.B. Eisenthal, Chem. Phys. Letters 77 (1981) 272.
[12] J.B. Miller, J. Org. Chem. 24 (1959) 560.
[13] C. Reichardt, in: Molecular interactions, Vol. 3, eds. H. Ratajczak and W.J. Orville-Thomas (Wiley, New York, 1982) pp. 241–282.
[14] K.B. Eisenthal, N.J. Turro, E.V. Sitzmann, I.R. Gould, G. Hefferon, J. Langan and Y. Cha, Tetrahedron 41 (1985) 1543.
[15] A. Nitzan and J. Jortner, Theoret. Chim. Acta 29 (1973) 97;
A. Nitzan, J. Jortner and P.M. Rentzepis, Proc. Roy. Soc. A327 (1972) 367.