from 2,4-hexadienes. In these cases, we have found that the product composition is virtually unaffected by dilution or O_2. This behavior contrasts with that of trimethylenemethane cyclo-additions, where capture of *two* sequentially formed intermediates, a singlet and a triplet, permits the product composition to be manipulated by such perturbations.[15]

The cycloadditions to *cis,cis-* and *trans,trans-*2,4-hexadiene preserve the stereochemistry about the propenyl side chain in the indan product, but the relative configuration (assigned by NMR) of the new pair of asymmetric centers of the indan ring is predominantly trans, regardless of the starting diene. Thus, the indan products from *cis,cis-* and *trans,trans-*2,4-hexadiene, respectively, are 5.4:1 and 6.9:1 trans/cis mixtures. The major components differ only in the stereochemistry of the propenyl side chain, and upon diimide reduction to propyl derivatives, they each give the *same* product.

These results are consistent with capture of only one type of intermediate, which reacts in a two-step cycloaddition mechanism through a long-lived adduct biradical. That the true reactive intermediate has static or time-averaged bilateral symmetry is shown by the equal amounts of deuterium at positions a and b in product **13** from butadiene and **10**-9,9-d_2 (^2H NMR). Although direct evidence on the spin state of the intermediate is not available, the observed symmetry properties and cycloaddition stereochemistry are those expected of the triplet state of biradical **1**.

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Table I. Intersystem Crossing Rate of Diphenylcarbene in Various Solvents

solvent[a]	$10^{-9}k_{ST}$, s^{-1}	$E_T(30)$,[b] kcal/mol
isooctane	10.52 ± 0.95	30.9
3-methylpentane	10.52 ± 0.93	30.9
diethyl ether	7.69 ± 0.65	34.6
tetrahydrofuran	5.5 ± 0.45	37.4
butyronitrile	3.57 ± 0.26	43.1
acetonitrile	3.23 ± 0.19	46.0
acetonitrile, 274 K	2.90 ± 0.25	46.9[c]
acetonitrile, 253 K	2.60 ± 0.26	47.9[c]

[a] Temperature at 300 K unless specified otherwise. [b] Reference 7a; $E_T(30)$ values of isooctane and 3-methylpentane were assumed equal to those of *n*-hexane. [c] This work.
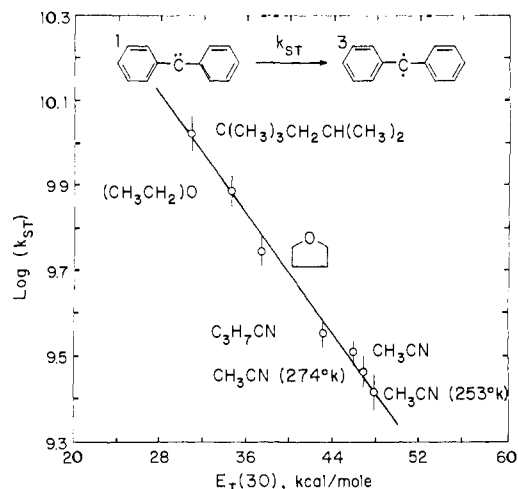

Figure 1. Plot of log (k_{ST}) as a function of the solvent polarity parameter $E_T(30)$ for various solvents.

Intermolecular Effects on Intersystem Crossing Studied on the Picosecond Time Scale: The Solvent Polarity Effect on the Rate of Singlet to Triplet Intersystem Crossing of Diphenylcarbene

E. V. Sitzmann, J. Langan, and K. B. Eisenthal*

*Department of Chemistry, Columbia University
New York, New York 10027*

Received December 27, 1983

Intersystem crossing plays a critical role in defining the intramolecular dynamics of diphenylcarbene (DPC) and thereby directly affects its spin state dependent chemistry.[1,2] For example, the chemistry of DPC depends on the rapid thermal equilibration that takes place between its ground triplet state and its low-lying singlet state.[3,4] In fluid solution, at room temperature, the singlet to triplet conversion step has been found[4,5] to proceed at a rate on the order of 10^{10} s^{-1}, while the reverse triplet to singlet con-

version step is roughly 3 orders of magnitude slower. Beyond this information little is actually known about the intersystem crossing rates associated with the carbene system. The problem of characterizing the factors, which include both intermolecular and intramolecular effects on the intersystem crossing dynamics of the carbene, remains an outstanding issue. In particular, an extremely important question is the extent to which the environment can affect the intramolecular spin conversion dynamics of the carbene. In this communication we wish to report the observation of a novel solvent polarity effect on the singlet to triplet intersystem crossing rate of DPC. A similar observation on the ground triplet formation rate of another carbene, fluorenylidene, in two solvents has been reported recently.[6]

In the studies reported here the diphenylcarbene is generated by photoexcitation of diphenyldiazomethane in the ultraviolet, which yields ^{1}DPC upon loss of nitrogen from the excited singlet state of the diazo compound. Once formed, ^{1}DPC will undergo energy relaxation via intersystem crossing to produce the ground triplet, ^{3}DPC (eq 1). The rate of ^{3}DPC formation (k_{ST}) was

$$^{1*}Ph_2C{=}N_2 \xrightarrow[-N_2]{} {}^1Ph_2C \xrightarrow{k_{ST}} {}^3Ph_2C \qquad (I)$$
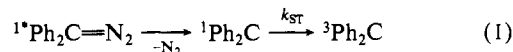
measured by means of a laser-induced fluorescence experiment.[5] The experiment consisted of the irradiation of a vacuum degassed solution of diphenyldiazomethane (8 × 10^{-4} M) with a picosecond laser pulse at 266 nm using a passively mode-locked Nd/YAG laser (25-30-ps fwhm, < 0.02 mJ). The formation rate of ^{3}DPC was monitored by its laser-induced fluorescence using a weak probe pulse at 266 nm at variable time delays.

The results given in Table I show that the intersystem crossing rate constant depends strongly on the choice of solvent. A key

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difference between the various solvents used is polarity. Inspection of Table I shows that a clear ordering exists between the rate of singlet to triplet conversion and the polarity of the solvent, the rate being larger in the less polar solvents. As given in Figure 1, a linear correlation exists between the logarithm of the rate and the empirical solvent polarity parameter, $E_T(30)$.[7,8] We have also found that there is a modest decrease in k_{ST} as the temperature decreases. The observed temperature dependence of k_{ST} is, however, quantitatively accounted for by the change in polarity with temperature. This indicates that there is either no barrier, or a very small one, separating the singlet and triplet states. The absence of a significant activation energy argues against carbene–solvent complexes as a factor in the intersystem crossing process. It is also to be noted that no correlation of k_{ST} with solvent viscosity was found.

To understand the effects of solvent polarity it is helpful to consider the electronic nature of the singlet and triplet states. The singlet state being highly polar (in fact it is often described as zwitterionic[2]) will be strongly stabilized in polar solvents whereas the less polar triplet will only experience a weak stabilization. Thus, it is expected that the singlet–triplet energy gap, ΔE_{ST}, will decrease as the solvent polarity increases. This is confirmed experimentally, where it is found that there is a 1.5 kcal/mol decrease in ΔE_{ST} for DPC in acetonitrile compared to isooctane.[4b] Since intersystem crossing is dependent on the energy gap we note that the solvent polarity affecting ΔE_{ST} will lead to a solvent dependence in k_{ST}. The issue then is to understand the direction of the observed change.

In the domain of small energy gaps there are two potentially opposing factors. One is the density of accepting modes, which increases as the energy increases from 870 to 1400 cm⁻¹;[4b] i.e., there are an increasing number of ways to make up the energy gap as well as the availability of new vibrational modes >870 cm⁻¹. Opposing this at some energy are the Franck–Condon factors, which will decrease as the energy increases.[9] The observed increase in k_{ST} as ΔE_{ST} increases argues in favor of the density of accepting modes as winning for this small energy gap case. For larger energy gaps one would anticipate that the Franck–Condon factors would dominate, and thus k_{ST} would decrease as ΔE_{ST} increases in line with what is commonly observed in large molecules.[9]

There is one other factor to be considered in the solvent dependence of k_{ST}, that being the effect of solvent on the expected difference[10] between the singlet and triplet geometries. If the difference between the geometries of the singlet and triplet, e.g., the phenyl–carbonyl–phenyl angle, changes with solvent then the Franck–Condon factors would also change, thus affecting the intersystem crossing rate. That this is probably not a dominant factor in the solvent dependence of k_{ST} is supported by the observed solvent effect (which appears to be similar to the one reported here for DPC) in the case of fluorenylidene,[6] which has a rigid structure.

We expect that the effect of solvent polarity on singlet–triplet energy relaxation will be general for other arylcarbenes in addition to fluorenylidene and diphenylcarbene. It is of interest that this

is to our knowledge the only case where the rate of intersystem crossing increases as the energy gap increases, what we might call an inverse gap effect.

Unusual Metal–Metal Bonding in Transition-Metal Carbonyl Cluster Compounds. The Synthesis, Reactivity, and Crystal and Molecular Structure of [Os₃(CO)₈(μ₃-S)₂]₂

Richard D. Adams* and István T. Horváth

*Department of Chemistry, Yale University
New Haven, Connecticut 06511*

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The 18-electron rule is widely recognized as one of the most fundamental precepts for understanding electronic structure and bonding in organometallic compounds.[1,2] In metal carbonyl cluster compounds the metal atoms usually achieve 18-electron configurations through the formation of metal–metal bonds in which a pair of electrons is shared between two nuclei.[3,4] However, recent studies of higher nuclearity clusters have revealed a growing number of compounds in which the bonding cannot be explained by these basic principles. The polyhedral skeletal electron pair theory has been developed[3–5] and can explain the bonding of most of these anomalies, yet all new examples of this unusual bonding are a source of curiosity, in general, and a challenge to both the theorist and the practicing chemist.

We now wish to report the synthesis, structure, and some reactions of the new compound [Os₃(CO)₈(μ₃-S)₂]₂ (I) which exhibits this anomalous bonding in a most surprising and dramatic fashion. Compound I is formed in 34% yield when solutions of Os₃(CO)₉(μ₃-S)₂,[6] (II) are exposed to UV irradiation under a rapid purge with nitrogen. The molecular structure of I was determined by single-crystal X-ray diffraction techniques,[8,9] and an ORTEP diagram of it is shown in Figure 1.[10] The molecule consists of an extended array of six osmium atoms with four triply bridging sulfido ligands. A central group of four metal atoms, Os(1)–Os(4),

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(7) Compound 1 is dark green and was isolated in 34% yield by TLC on silica gel with hexane/CH₂Cl₂ (90/10) solvent. IR ν(CO) cm⁻¹ in CH₂CL₂: 2093 vs, 2078 vs, 2030 vs, 2021 sh, 2013 m, 2009 m, 1923 w.

(8) Intensity data were collected on an Enraf-Nonius CAD-4 automatic diffractometer by using MO Kᾱ radiation and the ω-scan technique. All calculations were performed on a Digital Equipment Corp. PDP 11/45 computer by using the Enraf-Nonius SDP program library, version 18.

(9) Space group *P*2₁/*n*, *a* = 13.880 (4) Å, *b* = 12.061 (4) Å, *c* = 18.168 (5) Å, *β* = 106.43 (2)°, *V* = 2917 (3) Å³, *Z* = 4, ρ_{calc} = 3.91 g/cm³. The structure was solved by direct methods (MULTAN, 220 reflections, *E* ≥ 2.05). After correction for absorption, full-matrix least-squares refinement (2942 reflections, $F^2 \geq 3.0\sigma(F^2)$) yielded the residuals *R* = 0.067, R_w = 0.079.

(10) Selected interatomic distances (Å) and angles (deg) for I are as follows: Os(1)–Os(2) = 2.834 (1), Os(1)–Os(3) = 2.973 (1), Os(1)–Os(4) = 2.941 (1), Os(2)–Os(3) = 2.957 (1), Os(2)–Os(4) = 2.971 (1), Os(1)–Os(5) = 2.789 (1), Os(2)–Os(6) = 2.792 (1); Os(3)–Os(1)–Os(4) = 109.60 (4), Os(3)–Os(2)–Os(4) = 109.23 (4), Os(3)–Os(1)–Os(5) = 132.00 (4), Os-(4)–Os(2)–Os(6) = 132.09 (4).

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(8) An equally good correlation is found by using a different solvent polarity index parameter, namely the Z solvent parameter that is based on the pyridinium iodide solvatochromic dye, as developed by Kosower.[7d]

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