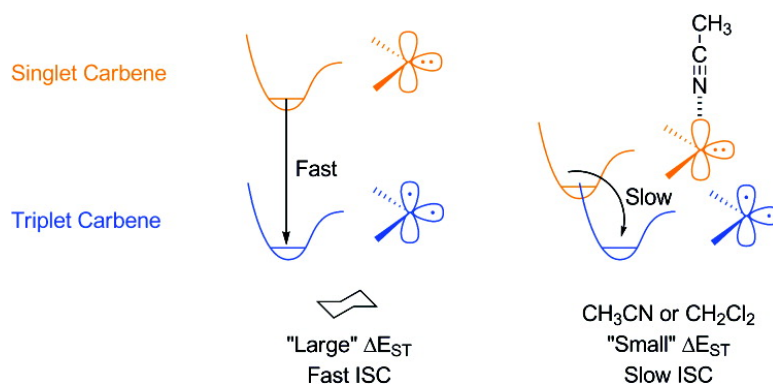


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Influence of Solvent on Carbene Intersystem Crossing Rates

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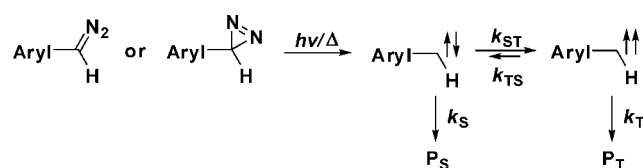
Abstract: The influence of coordinating solvents on singlet-to-triplet carbene intersystem crossing (ISC) rates has been studied with diphenylcarbene (DPC) and *para*-biphenyltrifluoromethylcarbene (BpCCF₃) by using ultrafast time-resolved spectroscopy. DPC has a triplet ground state in all of the solvents considered, and the concentration of singlet carbene at equilibrium is too small to be measured. It is found that the lifetime of ¹DPC is extended in acetonitrile, benzene, tetrahydrofuran, dichloromethane, and halobenzene solvents relative to cyclohexane. The solvent effect does not well correlate with bulk measures of solvent polarity. The singlet–triplet energy separation of BpCCF₃ is close to zero. The data demonstrates that BpCCF₃ has a triplet ground state in benzene, fluorobenzene, and hexafluorobenzene. Halogenated solvents are found to dramatically retard the rate of ISC in ¹BpCCF₃. We postulate that the empty p orbital of a singlet carbene coordinates with a nonbonding pair of electrons of a halogen atom of the solvent to form a pseudoylide solvent complex, stabilize the singlet carbene, and decrease the singlet–triplet (S–T) energy gap. The “golden rule” of radiationless transitions posits that the smaller the energy gap between the two states, the faster their rate of interconversion. To explain the apparent violation of the golden rule of radiationless transitions for the carbene ISC processes monitored in this study, we propose that the significantly different specific solvation of the singlet and triplet carbenes imposes a Franck–Condon-like factor on the ISC process. Those solvents that most solvate the singlet carbene will also have the greatest structural difference between singlet carbene–solvent complex and their triplet spin isomer–solvent complex, the smallest S–T gap, and the slowest ISC rate. Alternatively, one can propose that a highly solvated singlet carbene must desolvate prior to ISC, and that this requirement decelerates the radiationless transition.

1. Introduction

It is well-known that carbenes can exist in either of two spin states, singlet or triplet.¹ The prototypical arylcarbenes phenyl- (PC) and diphenylcarbene (DPC) have triplet ground states.² Singlet carbenes are released by activation of a precursor (typically a diazirine or diazo compound, Scheme 1).² The nascent singlet carbene can then undergo either intramolecular or intermolecular reactions to form products P_S (Scheme 1) or in the case of arylcarbenes, relax to the lower energy triplet carbene which undergoes distinctly different reactions than the singlet carbene to form products P_T (Scheme 1). It is important, therefore, to understand the relationship between carbene intersystem crossing (ISC) rates k_{ST} and k_{TS} and singlet–triplet (S–T) energy gaps in order to understand carbene chemistry in a quantitative manner.

There are only a few scattered studies of ISC rates of carbenes. In pioneering work, Eisenthal and co-workers^{3–6}

Scheme 1. Generation of Singlet and Triplet Carbenes Where P_S and P_T Are Stable Products Derived from the Singlet and Triplet Carbene, Respectively



studied the rates of ISC of DPC as a function of solvent. The lifetime of singlet DPC in acetonitrile is 310 ps at ambient temperature, which shortens to 95 ps in isooctane. A plot of the log of the first-order rate constant of ISC of ¹DPC versus the Dimroth $E_T(30)$ ⁷ parameter was linear over the solvents used in this study. These solvents include isooctane, 3-methylpentane, diethyl ether, tetrahydrofuran, butyronitrile, and acetonitrile at different temperatures (253, 274, and 300 K). Halogenated solvents were not studied in this seminal work.

Normally, one expects that the rate of ISC will increase as the energy gap between the singlet and triplet state decreases,

[†] The Ohio State University.[‡] Adam Mickiewicz University.(1) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1971.(2) Jones, M. Jr.; Moss, R. A. In *Reactive Intermediate Chemistry*; Moss, R. A., Platz, M. S. Jones, M., Jr., Eds.; Wiley-Interscience: Hoboken, NJ, 2004, pp 273–328.(3) Langan, J. G.; Sitzmann, E. V.; Eisenthal, K. B. *Chem. Phys. Lett.* **1984**, *110*, 521–527.(4) Langan, J. G.; Sitzmann, E. V.; Eisenthal, K. B. *Chem. Phys. Lett.* **1986**, *124*, 59–62.(5) Sitzmann, E. V.; Langan, J. G.; Griller, D.; Eisenthal, K. B. *Chem. Phys. Lett.* **1989**, *161*, 353–360.(6) Sitzmann, E. V.; Langan, J.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1984**, *106*, 1868–1869.(7) Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlmann, F. *Liebigs Ann. Chem.* **1963**, *661*, 1–37.

which is known as the golden rule of radiationless transitions.^{8–10} Eisenthal and co-workers proposed that polar solvents preferentially stabilize singlet relative to triplet arylcarbenes and advanced an argument to explain why the ISC rates of ¹DPC are fastest in nonpolar solvents where the S–T energy gap is larger in solution.⁶ It was proposed that when the S–T gap is small, the singlet carbene overlaps the triplet carbene in a region where its vibrational levels are sparse; thus, there will be less vibronic coupling and a slower ISC rate. It was proposed further that when the S–T energy gap is larger, the singlet carbene will overlap with denser vibrational levels of the triplet carbene. Thus, there will be greater vibronic coupling and a faster ISC rate. When the energy gap becomes too large, this density of states argument fails, and the golden rule is then followed.

The first part of Eisenthal and co-workers' interpretation, the postulation of a smaller S–T gap in polar solvents and a larger S–T gap in nonpolar solvents, was confirmed by the experimental and computational work of Toscano and Hadad that demonstrated that polar solvents do preferentially stabilize singlet relative to triplet carbenes.^{11,12} This is also consistent with our recent studies of a series of arylcarbenes.^{13–15}

Kohler and co-workers¹⁶ used ultrafast time-resolved absorption spectroscopy to demonstrate that singlet DPC has lifetimes of 340 and 110 ps in acetonitrile and in cyclohexane, respectively, which is in good agreement with the findings of the Eisenthal group.⁶ Our group recently reported¹⁵ that the lifetime of singlet fluorenylidene ¹Fl is 440 and 88 ps in acetonitrile and cyclohexane, respectively, which is consistent with the values reported by Schuster and co-workers¹⁷ in a prior study. In the study of Fl, we discovered that the ISC rate of ¹Fl in hexafluorobenzene (HFB), a nonpolar solvent, is very similar to that recorded in acetonitrile.¹⁵ This is a remarkable exception to Eisenthal's finding that in nonpolar solvents, ISC rates are faster. This exception also held true in studies of Fl ISC in halogenated solvents, such as fluorobenzene, chlorobenzene, and dichloromethane. The exceptionally slow ISC rate was not due to a change of the ground state from triplet to singlet carbene, because triplet Fl was observed on the nanosecond time scale in all of the solvents employed in this study. The slow ISC rate was thought instead to be the result of a specific interaction between solvent molecules and the carbene. This can be thought of as a Franck–Condon-like effect on ISC (Figure 1). Therefore, carbene ISC rates are not solely dependent on bulk solvent polarities; other solvent coordinating properties should be considered as well.

In a recent study of *p*-biphenyltrifluoromethylcarbene (BpCCF₃), the lifetimes of ¹BpCCF₃ in halogenated solvents were found to exceed 800 ps, values much longer than those observed

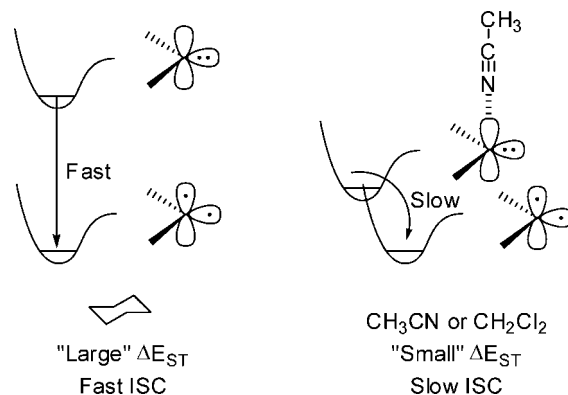


Figure 1. Illustration of a Franck–Condon-like factor on the ISC process.

in cyclohexane and in acetonitrile.¹⁸ However, ¹BpCCF₃ reacts with cyclohexane and acetonitrile in competition with ISC, which confounds a simple comparison of the lifetimes of ¹BpCCF₃ determined in halogenated solvents with those in cyclohexane and in acetonitrile. This stimulated the additional experiments of this study. Herein, we report a study of the influence of solvent on the ISC rates of DPC and BpCCF₃ and compare the data with the results previously obtained for Fl.

2. Results

2.1. DPC. Time-resolved studies of DPC have been reported by the groups of Closs,¹⁹ Eisenthal,²⁰ and Kohler.¹⁶ Singlet and triplet DPC have bands centered at 370¹⁶ and 300 nm,¹⁹ respectively. In this study, diphenyldiazomethane in cyclohexane solution was excited with a 308 nm ultrafast laser pulse to produce ¹DPC. The lifetime of ¹DPC is 120 ± 10 ps in cyclohexane (Table 1), in excellent agreement with the values measured by Kohler and co-workers in the same solvent.¹⁶ In cyclohexane-*d*₁₂, the lifetime of ¹DPC is unchanged (Table 1), indicating that ¹DPC relaxes to its triplet state prior to any chemical reactions, consistent with previous chemical trapping studies of this carbene.²¹

The lifetime of ¹DPC was also measured in HFB, a nonpolar solvent with an *E*_T(30) value of 34.2 kcal/mol, similar to that of cyclohexane (30.9 kcal/mol). The lifetime of ¹DPC is 260 ps in HFB (Table 1). This is more than twice the value recorded in cyclohexane. To further study the influence of HFB, a series of cyclohexane–HFB binary solvent mixtures with different volume ratios were considered. The lifetimes of ¹DPC in the cyclohexane–HFB mixtures are listed in Table 2. The plot of the observed first-ordered rate constants versus the concentration of HFB is curved (Figure 2), indicating that the lengthening of the ¹DPC lifetime by the addition of HFB to cyclohexane is not a simple linear effect.

It should be noted that cyclohexane is a chemically inert solvent in the sense that it does not scavenge ¹DPC prior to relaxation to ³DPC as evidenced by the lack of a kinetic isotope effect (KIE) on the carbene lifetime in cyclohexane. HFB does

- (8) Jortner, J.; Rice, S. A.; Hochstrasser, R. M. *Adv. Photochem.* **1969**, *7*, 149–309.
 (9) Robinson, G. W.; Frosch, R. P. *J. Chem. Phys.* **1962**, *37*, 1962–1973.
 (10) Robinson, G. W.; Frosch, R. P. *J. Chem. Phys.* **1963**, *38*, 1187–1203.
 (11) Geise, C. M.; Wang, Y.; Mykhaylova, O.; Frink, B. T.; Toscano, J. P.; Hadad, C. M. *J. Org. Chem.* **2002**, *67*, 3079–3088.
 (12) Wang, Y.; Hadad, C. M.; Toscano, J. P. *J. Am. Chem. Soc.* **2002**, *124*, 1761–1767.
 (13) Wang, J.; Burdzinski, G.; Gustafson, T. L.; Platz, M. S. *J. Org. Chem.* **2006**, *71*, 6221–6228.
 (14) Wang, J.; Burdzinski, G.; Gustafson, T. L.; Platz, M. S. *J. Am. Chem. Soc.* **2007**, *129*, 2597–2606.
 (15) Wang, J.; Kubicki, J.; Hilinski, E. F.; Mecklenburg, S. L.; Gustafson, T. L.; Platz, M. S. *J. Am. Chem. Soc.* **2007**, *129*, 13683–13690.
 (16) Peon, J.; Polshakov, D.; Kohler, B. *J. Am. Chem. Soc.* **2002**, *124*, 6428–6438.
 (17) Grasse, P. B.; Brauer, B. E.; Zupancic, J. J.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 6833–6845.

- (18) Wang, J.; Kubicki, J.; Gustafson, T. L.; Platz, M. S. *J. Am. Chem. Soc.* **2008**, *130*, 2304–2313.
 (19) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190–8198.
 (20) Eisenthal, K. B.; Turro, N. J.; Aikawa, M.; Butcher, J. A., Jr.; DuPuy, C.; Hefferon, G.; Hetherington, W.; Korenowski, G. M.; McAuliffe, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 6563–6565.
 (21) Closs, G. L. In *Carbenes Vol. II*; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1973, p 159.

Table 1. Lifetimes of ¹DPC, ¹BpCCF₃, ¹FI in Various Solvents and Solvent Parameters

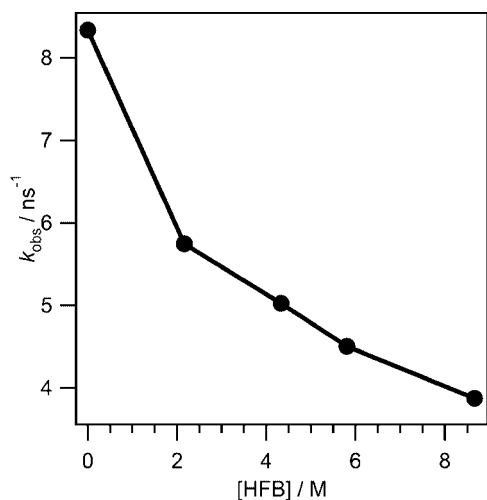
solvent	τ_{DPC} (ps)	τ_{DPC}^a (ps)	τ_{BpCCF_3} (ps)	τ_{FI}^c (ps)	η^d	$E_{\text{T}}(30)^e$ (kcal/mol)
acetonitrile	340 ± 20	310 ± 18	580 ± 60	440 ± 40	0.369	45.6
acetonitrile, 274 K		345 ± 30			0.400	46.9 ^f
acetonitrile, 253 K		385 ± 38				47.9 ^f
butyronitrile		280 ± 20				43.1
cyclohexane	120 ± 10	95 ± 9	200 ± 10	88 ± 11	0.894	30.9
cyclohexane- <i>d</i> ₁₂	110 ± 10		300 ± 20	90 ± 9		
HFB	260 ± 20		NR ^b	490 ± 90	2.79	34.2
fluorobenzene	250 ± 13		860 ± 60		0.550	37.0
chlorobenzene	230 ± 30		NR ^b		0.753	36.8
dichloromethane	295 ± 31		NR ^b		0.413	40.7
benzene	200 ± 7		800 ± 40	100 ± 12	0.604	34.3
tetrahydrofuran	150 ± 16	180 ± 14	90 ± 10		0.456	37.4
diethyl ether		130 ± 11			0.224	34.6
1,4-dioxane	230 ± 8		79 ± 5	84 ± 8	1.177	36.0
dimethyl sulfoxide	240 ± 35		19 ± 2		1.987	45.1

^a The data were taken from Eisenthal and co-workers.⁶ ^b Not resolved. The lifetime is too long to be resolved on the spectrometer. ^c The data are obtained from ref 15. ^d The viscosity data (25 °C) are in mPa·s and obtained from *CRC Handbook of Chemistry and Physics, 87th ed.* ^e The $E_{\text{T}}(30)$ data are in kcal·mol⁻¹ and obtained from Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319, unless otherwise specified. ^f The $E_{\text{T}}(30)$ data were measured by Eisenthal and co-workers.⁶

Table 2. Lifetimes of ¹DPC as a Function of HFB Concentration in HFB–Cyclohexane Mixtures

HFB volume (%)	[HFB] (M)	τ_{DPC} (ps)	k_{obs}^a (ns ⁻¹)
0	0	120 ± 10	8.3
25	2.2	175 ± 15	5.7
50	4.3	200 ± 12	5.0
67	5.8	220 ± 15	4.5
100	8.7	260 ± 20	3.9

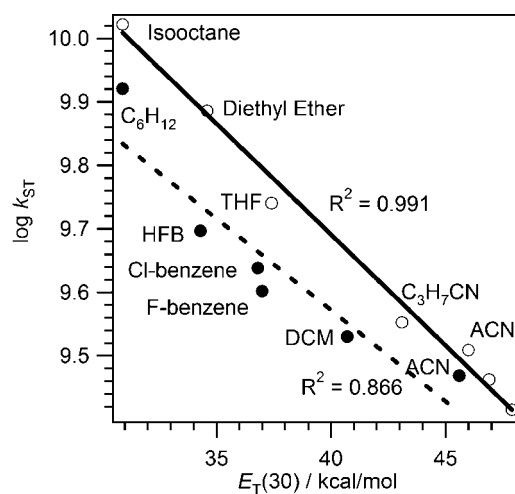
^a $k_{\text{obs}} = 1/\tau_{\text{DPC}}$.

**Figure 2.** Plot of the first-order rate constants for the decay of singlet DPC versus the concentration of HFB in cyclohexane.

not extend the lifetime of ¹DPC in cyclohexane by replacing a more chemically reactive solvent with a less reactive solvent. The presence of HFB must be retarding the rate of ISC.

In all the solvents of this study, ¹DPC deactivates by ISC and decays to baseline within 3 ns. This demonstrates that ¹DPC has a negligibly small concentration relative to ³DPC in the S–T equilibrium mixture.

We have reproduced Eisenthal's $\log k_{\text{ST}}$ versus $E_{\text{T}}(30)$ plot and superimposed upon the data of this study (Figure 3). Where the solvents overlap, we find that the ISC rate constants of this study are slightly smaller than those reported previously. After correcting for this systematic deviation, it is clear that the ISC rate constants of ¹DPC are still unusually small in HFB and

**Figure 3.** Plot of $\log k_{\text{obs}} = k_{\text{ST}}$ with this carbene for DPC as a function of the solvent empirical polarity parameter $E_{\text{T}}(30)$ for various solvents. Open circles are data reproduced from Eisenthal's paper. Solid circles are data obtained in this study. C₆H₁₂, cyclohexane; THF, tetrahydrofuran; HFB, hexafluorobenzene; Cl-benzene, chlorobenzene; F-benzene, fluorobenzene; DCM, dichloromethane; C₃H₇CN, butyronitrile; ACN, acetonitrile. The three open-circle data points in the right corner were all obtained in acetonitrile but with different temperatures, 300, 274, and 253 K. The linear correlation (solid line) of Eisenthal's data (open circles) has a R^2 value of 0.991. The linear correlation (dashed line) of our data (solid circles) is poor and has a R^2 value of 0.866.

other halogenated solvents, such as fluorobenzene, chlorobenzene, and dichloromethane (Table 1). Eisenthal's data (solid line in Figure 3) has an R^2 value of 0.991. The linear correlation between the data of this study and solvent $E_{\text{T}}(30)$ values (dashed line in Figure 3) is poor and has an R^2 value of 0.866.

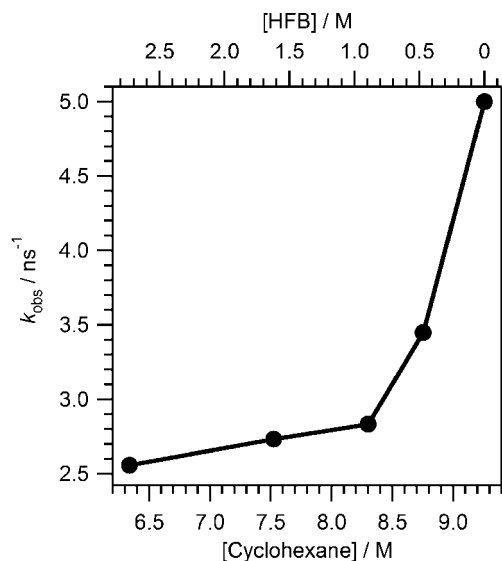
The lifetime of ¹DPC in benzene ($\tau = 200$ ps) is also long relative to the value recorded in cyclohexane (Table 1) and is reminiscent of the data observed in halogenated solvents. We believe that this is evidence for a specific interaction between the carbene and the aromatic solvent.

2.2. BpCCF₃. Previously, we have reported a detailed ultrafast study of carbene BpCCF₃.¹⁸ Transient absorptions of singlet and triplet BpCCF₃ are centered at 385 and 325 nm in cyclohexane, respectively. We have found that the lifetimes of ¹BpCCF₃ are 200 and 300 ps in cyclohexane and in cyclohexane-*d*₁₂, respectively (Table 1). The KIE indicates that ¹BpCCF₃

Table 3. Lifetimes of $^1\text{BpCCF}_3$ as a Function of HFB Concentration in HFB–Cyclohexane Mixtures

HFB volume (%)	[HFB] (M)	[C ₆ H ₁₂] (M)	τ_{BpCCF_3} (ps)	k_{obs}^a (ns ⁻¹)
0	0	9.3	200	5.0
5	0.47	8.8	290	3.4
10	0.89	8.3	350	2.8
19	1.6	7.5	370	2.7
32	2.7	6.3	390	2.6

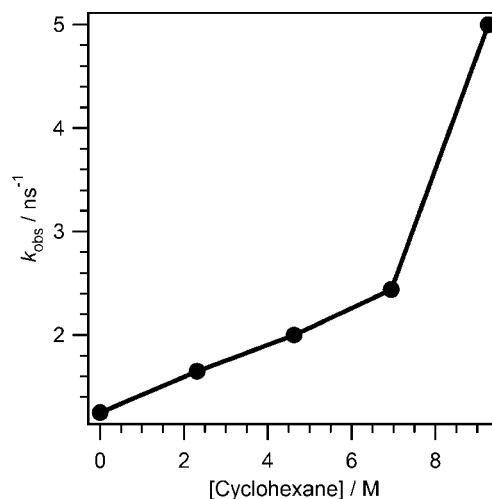
$$^a k_{\text{obs}} = 1/\tau_{\text{BpCCF}_3}$$

**Figure 4.** Plot of the first-order rate constants for the decay of singlet BpCCF_3 versus the concentration of cyclohexane (bottom axis) and HFB (top axis) in HFB–cyclohexane mixtures.

reacts with cyclohexane by C–H insertion in competition with ISC. In this solvent, $^3\text{BpCCF}_3$ is the ground state, as it can be observed by nanosecond time-resolved spectroscopy, long after the singlet carbene signal has decayed to the baseline.¹⁸

The lifetime of $^1\text{BpCCF}_3$ in HFB is particularly long (estimated to be 1–5 ns) and for this reason cannot be measured accurately on the ultrafast spectrometer. One may legitimately argue in this case that the long lifetime in HFB may be due to a dilution effect because there is a chemical reaction in cyclohexane that competes with ISC. The shorter lifetime in cyclohexane relative to HFB must be due in part to the C–H insertion reaction in cyclohexane, which is not possible in HFB. If this were the only effect, however, one would expect a linear plot for the apparent first-order rate constant k_{obs} of singlet carbene decay versus the concentration of cyclohexane in cyclohexane–HFB mixtures. The lifetimes of $^1\text{BpCCF}_3$ in the cyclohexane–HFB mixtures are listed in Table 3. As shown in Figure 4, such a plot is actually substantially curved. This indicates that in cyclohexane–HFB mixtures, $^1\text{BpCCF}_3$ interacts with HFB above a critical concentration, ~ 1 M, and this interaction dramatically retards the ISC rate. The unusual long lifetime (estimated to be 1–5 ns) for $^1\text{BpCCF}_3$ in HFB is not unique to this solvent but must be a general property of halogenated solvents because it is also observed in fluorobenzene, chlorobenzene, dichloromethane, and chloroform.

The lifetime of $^1\text{BpCCF}_3$ was also measured in benzene and found to be 800 ps (Table 1). Once again, this is substantially longer than the value recorded in cyclohexane. The plot of the

**Figure 5.** Plot of the first-order rate constants for the decay of singlet BpCCF_3 versus the concentration of cyclohexane in benzene–cyclohexane mixtures.

apparent first-order rate constant k_{obs} versus the concentration of cyclohexane in cyclohexane–benzene mixtures (Figure 5) is also curved. It is interesting to note that the curvature of the cyclohexane–benzene plot (Figure 5) is smaller than that of the cyclohexane–HFB plot (Figure 4). This suggests that $^1\text{BpCCF}_3$ has a stronger interaction with HFB than with benzene.

Nanosecond time-resolved laser flash photolysis (LFP, $\lambda_{\text{ex}} = 308$ nm) of BpCN_2CF_3 in HFB produces two transient absorption bands at 320 and 390 nm. As before, the longer wavelength band is assigned to $^1\text{BpCCF}_3$ (Supporting Information, Figure S1). The 320 nm band cannot be due to a radical formed by hydrogen abstraction from the solvent because it is observed in both benzene and HFB. The two transient absorption bands have the same first-order decay rate constant within experimental error. The rate of disappearance of both bands accelerates in the presence of oxygen (Supporting Information, Table S1). On the basis of these results and time-dependent density functional theory (TD-DFT) calculations (Supporting Information, Table S2), the 320 nm band is attributed to $^3\text{BpCCF}_3$. In benzene and HFB, the S–T gap must be close to zero because both spin isomers are observable at equilibrium. The nanosecond LFP results for BpCN_2CF_3 in benzene, the halogenated benzenes, and methanes are similar to those of HFB (Supporting Information, Table S1) because both singlet and triplet BpCCF_3 spectra are observed, again indicating that the S–T energy gaps for BpCCF_3 are close to zero in these solvents. It is possible to estimate the lower limits of the S–T gaps of BpCCF_3 in certain solvents on the basis of the percentage of decay of $^1\text{BpCCF}_3$ from its initial value to the magnitude recorded 2–3 ns after the laser pulse (Supporting Information, Table S1. For spectra, see Figures S3–S8 in ref 18). On this basis (percent decay of the original singlet carbene absorbance to its smaller value at equilibrium), we are certain that BpCCF_3 has a triplet ground state in benzene, fluorobenzene, and HFB. The ground-state multiplicity for BpCCF_3 in chlorobenzene, dichloromethane, and chloroform is not certain because there is substantial singlet carbene absorption at equilibrium, as demonstrated by nanosecond spectroscopy, but the S–T gaps must be close to zero. It is possible that BpCCF_3 has a singlet ground state in these chlorinated solvents. There is a recent precedent for these conclusions as an aryl- CF_3 carbene with a

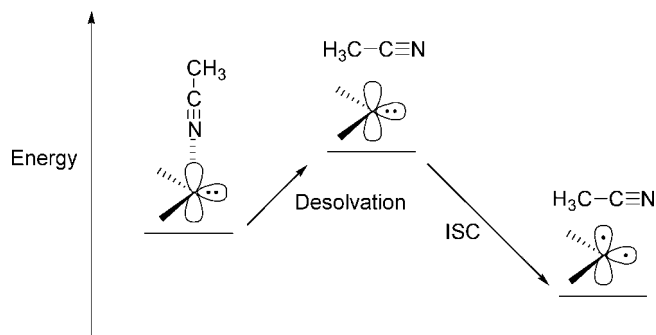


Figure 6. Illustration of singlet carbene desolvation effect on the ISC process.

singlet ground state was discovered by Wang and Sheridan.²² They found that 2-benzothienyl(trifluoromethyl)-carbene has a singlet ground state in a nitrogen matrix at 10 K.

3. Discussion

3.1. Halogenated Solvents. It is remarkable that the ISC rates for ¹DPC and ¹BpCCF₃ decelerate in halogenated solvents. To explain the data, we speculate that the singlet carbene coordinates with the halogenated solvent. We propose that the empty p orbital of the singlet carbene coordinates with a nonbonding pair of electrons of the halogen to form a pseudoylide solvent complex. This interaction will selectively stabilize a singlet carbene relative to its triplet state, depress the S–T gap, and following Eisenthal's analysis, slow the rate of ISC.^{3–6} In our previous study of FI, it was found that the S–T splitting of FI in HFB (0.4 kcal·mol⁻¹) is more similar to that of acetonitrile (0.2 kcal·mol⁻¹) than that of cyclohexane (1.0 kcal·mol⁻¹), which persuades us that there is indeed a specific carbene–solvent interaction that differentially stabilizes a singlet carbene, reduces the S–T gap, and decelerates ISC.

We again¹⁵ propose that the significantly different specific solvation of the singlet and triplet carbenes may impose a Franck–Condon-like factor on the ISC process (Figure 1). Those solvents that most solvate the singlet carbene will also have the greatest structural difference between singlet carbene–solvent complex and their triplet spin isomer–solvent complex, the smallest S–T gap, and the slowest ISC rate; hence, there is only an apparent violation of the golden rule of radiationless transitions.^{8–10}

Another explanation is possible, however. One can also propose that the singlet carbene must desolvate prior to ISC (Figure 6). The process of desolvation will retard the rate of ISC.

Comparing the plots (the apparent first-order rate constant k_{obs} versus the concentration of cyclohexane in cyclohexane–HFB mixtures) for ¹DPC and ¹BpCCF₃, we find that the curvature of the ¹BpCCF₃ plot is steeper than that of the ¹DPC plot. Also, much less HFB was required in the case of ¹BpCCF₃ to achieve retardation of the ISC rate. This is also consistent with our coordination model. ¹BpCCF₃ has a more positively charged carbene center than ¹DPC because of the electronic withdrawing effect of the trifluoromethyl group. Thus, ¹BpCCF₃ is more electron deficient at the carbene center and will have a stronger interaction with the lone pairs of halogenated solvents.

3.2. Aromatic Solvents. Khan and Goodman²³ reported the formation of weak complexes between singlet methylene and benzene by using picosecond optical grating calorimetry. Moss, Yan, and Krogh-Jespersen²⁴ also observed a modulation of carbene reactivities by aromatic solvents by analyzing the stable reaction products and an extension of singlet carbene lifetimes in aromatic solvents by using the indirect pyridine probe method. Buttressed by ab initio calculations, they proposed π -complexation between singlet carbenes and aromatic solvents. Ruck and Jones²⁵ also observed a similar aromatic solvent effect in the study of intramolecular reactivity for *t*-butylcarbene.

The lifetimes of ¹BpCCF₃ and ¹DPC are also longer in benzene than in cyclohexane. After our studies in halogenated solvents, we postulate that ¹BpCCF₃ and ¹DPC can form a π -complex with benzene to stabilize singlet carbenes. Again, significantly different specific solvation of the singlet and triplet carbenes imposes a Franck–Condon-like factor on the ISC process (Figure 1), or the carbene–solvent complex must desolvate prior to ISC (Figure 6). If the former explanation is operative, there must be a structural difference between singlet carbene–benzene complex and the triplet spin isomer–solvent complex, a small S–T gap, and a slow ISC rate, hence another apparent violation of the golden rule of radiationless transitions.^{8–10} The complexes we propose in benzene have the same character as those recently described by Moss and co-workers with chloromethylcarbene.²⁶ In these studies, the evidence for complexation was spectroscopic and computational and was not revealed by ISC rates because chloromethylcarbene has a singlet ground state.

4. Experimental Section

4.1. Ultrafast Spectroscopy. Ultrafast UV–vis broadband absorption measurements were performed by using the home-built spectrometer described previously.²⁷ Samples were prepared in 50 mL of solvent with an absorption of 1.0 at the excitation wavelength with a 1.0 mm optical length.

4.2. Materials. All materials and solvents were purchased from Aldrich. The solvents for ultrafast studies were spectrophotometric grade from Burdick & Jackson and used as received. Diphenyldiazomethane was prepared by the oxidation of the corresponding hydrazone by known procedures.^{17,28–30} The preparation of BpCN₂CF₃ has been described previously.¹⁸

5. Conclusions

The ISC rates of singlet carbenes are retarded by halogenated compounds and in benzene. We postulate that the empty p orbital of a singlet carbene coordinates with a nonbonding pair of electrons of the halogen to form a pseudoylide solvent complex, stabilize the singlet carbene, decrease the S–T energy gap, and following Eisenthal's analysis, slow the ISC rate. A similar effect of solvent coordination can also be observed for

(22) Wang, J.; Sheridan, R. S. *Org. Lett.* **2007**, *9*, 3177–3180.

(23) Khan, M. I.; Goodman, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 6635–6636.

(24) Moss, R. A.; Yan, S.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1998**, *120*, 1088–1089.

(25) Ruck, R. T.; Jones, M., Jr. *Tetrahedron Lett.* **1998**, *39*, 2277–2280.

(26) Moss, R. A.; Tian, J.; Sauer, R. R.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **2007**, *129*, 10019–10028.

(27) Burdzinski, G.; Hackett, J. C.; Wang, J.; Gustafson, T. L.; Hadad, C. M.; Platz, M. S. *J. Am. Chem. Soc.* **2006**, *128*, 13402–13411.

(28) Brauer, B. E.; Grasse, P. B.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 6814–6816.

(29) Griller, D.; Montgomery, C. R.; Scaiano, J. C.; Platz, M. S.; Hadel, L. *J. Am. Chem. Soc.* **1982**, *104*, 6813–6814.

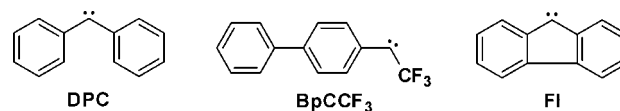
(30) Jones, M., Jr.; Rettig, K. R. *J. Am. Chem. Soc.* **1965**, *87*, 4013–4015.

acetonitrile and in oxygenated solvents when the carbene does not chemically react with the solvent, and ISC is the major deactivation pathway for singlet carbenes. The complexation observed in benzene is weaker and must involve complexation to the aromatic ring as described by Moss and co-workers.²⁴

To explain the apparent violation of the golden rule of radiationless transitions^{8–10} for carbene ISC processes, we propose that the significantly different specific solvation of the singlet and triplet carbenes imposes a Franck–Condon-like factor on the ISC process. Those solvents that most solvate the singlet carbene will also have the greatest structural difference between singlet carbene–solvent complex and their triplet spin isomer–solvent complex, the smallest S–T gap, and the slowest ISC rate. Alternatively, it is possible that the carbene–solvent complex must desolvate prior to ISC, and this results in a retardation of the ISC rate.

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Scheme 2. Structures of the Carbenes in this Study



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Supporting Information Available: Lifetimes, S–T carbene energy gaps, and TD-DFT calculations of triplet BpCCF₃ in Tables S1 and S2. Nanosecond LFP transient spectra of BpCN₂CF₃ in HFB in Figure S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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