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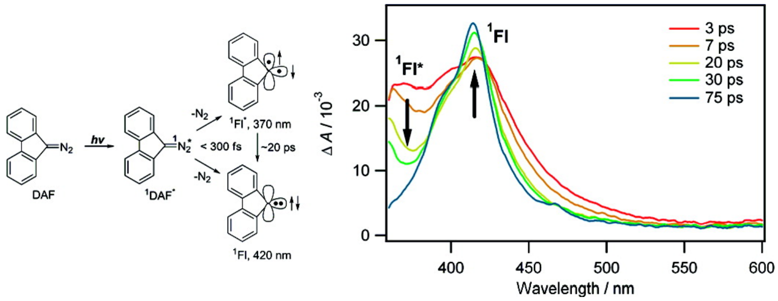

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Ultrafast Study of 9-Diazofluorene: Direct Observation of the First Two Singlet States of Fluorenylidene

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Abstract: Ultrafast photolysis of 9-diazofluorene (DAF) produces a broadly absorbing transient within the instrument time resolution (300 fs), which is assigned to an excited state of the diazo compound. The diazo excited state fragments to form fluorenylidene (Fl) in both its lowest energy singlet state (^{1}Fl, 405−430 nm, depending on the solvent) and a higher energy singlet state (370 nm, ^{1}Fl*). The excited singlet carbene has a lifetime of 20.9 ps in acetonitrile and decays to the lower energy singlet state (^{1}Fl), which relaxes to the triplet ground state (^{3}Fl) in acetonitrile, cyclohexane, benzene, and hexafluorobenzene. The equilibrium mixture of singlet and triplet fluorenylidene reacts with these solvents. Singlet fluorenylidene reacts with methanol and cyclohexene in competition with relaxation to ^{3}Fl. One of the reaction products in methanol is the 9-fluorenyl cation. The rate of intersystem crossing (ISC) in hexafluorobenzene and other halogenated solvents is remarkably slow given that carbene ISC rates are generally fastest in nonpolar solvents. An explanation of this effect is advanced.

1. Introduction

Fluorenylidene has played a large role in the development of mechanistic carbene chemistry. Jones and Rettig discovered that the addition of hexafluorobenzene (HFB) to solutions of alkenes led to changes in the nature of the cyclopropane products formed from fluorenylidene.[1] In neat alkene solvent the cyclopropanes were formed with a high degree of stereospecificity and the same orientation present in the original alkene. As the alkene was diluted with HFB the stereospecificity was lost. Jones and Rettig concluded that the presence of HFB lengthened the lifetime of the initially formed singlet fluorenylidene (^{1}Fl) by decreasing the rate of bimolecular reaction of carbene with the alkene. As ^{1}Fl forms stereospecific products, dilution with HFB increased the likelihood of its intersystem crossing (ISC) to the lower energy triplet state (^{3}Fl) which forms a stereorandom mixture of cyclopropanes in its reactions with alkenes.[1]

Physical organic chemists began to study carbenes with the then new technique of nanosecond (ns) time-resolved laser flash photolysis (LFP) about 30 years ago. Fluorenylidene was one of the first carbenes to be studied by ns time-resolved LFP methods.[2−4] Although singlet fluorenylidene was not observed in these experiments two products derived from it, triplet fluorenylidene[4] and an acetonitrile-carbene ylide,[2] were detected. The 9-fluorenyl radical (FlH•), derived from reaction of triplet fluorenylidene, was also observed by ns spectroscopy.[2]

The Schuster group reported an early application of picosecond time-resolved spectroscopy and used this technique to measure the rate of formation of triplet fluorenylidene, and by extension the lifetime of singlet fluorenylidene.[3,4] The latter species was not detected in this study.

Herein we report the use of femtosecond time-resolved spectroscopy to study the photochemistry of 9-diazofluorene (DAF) and the chemistry of fluorenylidene. We will report the first direct observation of relaxed singlet fluorenylidene (^{1}Fl) and the first excited singlet state of this carbene (^{1}Fl*) as well. This will allow us to draw conclusions as to the timing of intersystem crossing relative to chemical reactions of the singlet carbene.

2. Ultrafast Spectroscopic Results

2.1. Acetonitrile. Ultrafast photolysis of 9-diazofluorene (DAF) in acetonitrile (ACN) solution with a 300 fs pulse of 308 nm light results in the spectral changes shown in Figure 1. A broad transient absorption is detected between 360 and 600 nm at the earliest times observable (Figure 1a). The broad transient absorption decays within our instrument response function (300 fs), and it is possible to observe a simultaneous growth in transient absorption between 360 and 440 nm. Subsequently, the decay ($\tau = 20.9$ ps) of the 370 nm absorption is accompanied by additional growth of transient absorption

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(1) Jones, M., Jr.; Rettig, K. R. *J. Am. Chem. Soc.* **1965**, *87*, 4013−4015.
(2) Griller, D.; Montgomery, C. R.; Scaiano, J. C.; Platz, M. S.; Hadel, L. *J. Am. Chem. Soc.* **1982**, *104*, 6813−6814.
(3) Brauer, B. E.; Grasse, P. B.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 6814−6816.
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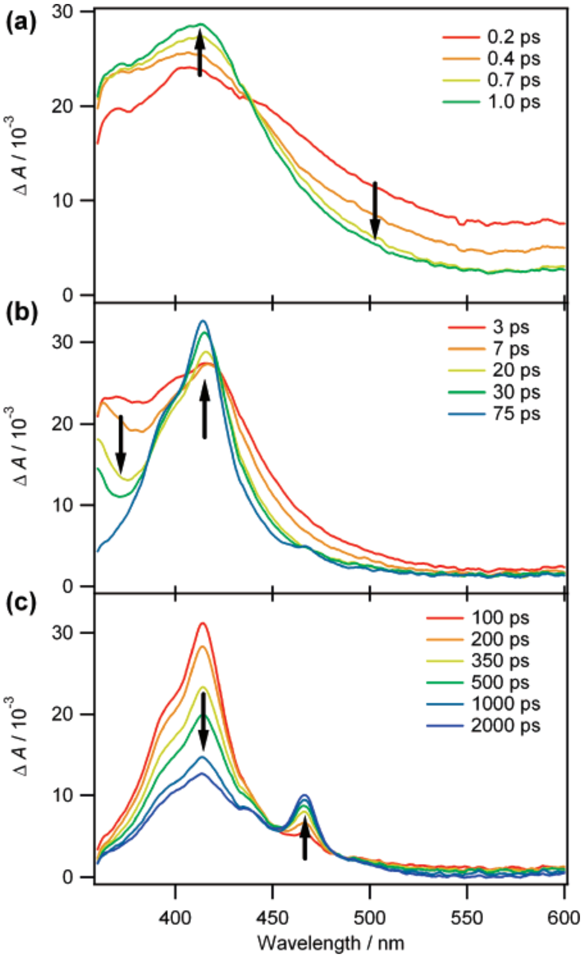

Figure 1. Transient spectra were generated by ultrafast LFP ($\lambda_{ex} = 308$ nm) of 9-diazofluorene in acetonitrile with time windows of (a) 0.2−1.0 ps, (b) 3−75 ps, and (c) 100−2000 ps.

centered at 415 nm (Figures 1b and 2a). Two isosbestic points can be observed at 405 and 420 nm. Within experimental error, the time constant of the decay recorded at 370 nm is the same as that of the growth of transient absorption monitored at 415 nm. At longer times, a new band centered at 470 nm is formed with the consumption of the 415 nm band ($\tau = 440$ ps), and there is an isosbestic point at 450 nm (Figures 1c and 2b). It is interesting to note that the 415 nm band does not decay to the baseline and maintains the same intensity 2 ns after the laser pulse in acetonitrile.

Based on previous studies,[2−4] the 470 nm band can be readily assigned to the triplet state of fluorenylidene (^{3}Fl). TD-DFT calculations[5] predict ^{3}Fl has a vertical transition at 424 nm ($f = 0.0371$) in fair agreement with the assignment of the carrier of the 470 nm band (Supporting Information (SI), Table S1). In an inert solvent, the disappearance of a singlet carbene is controlled by intersystem crossing (ISC) to form the ground state triplet. Thus, the carrier of the 415 nm band, the precursor of ^{3}Fl, can be confidently assigned to singlet fluorenylidene. The lifetime of ^{1}Fl is 440 ± 40 ps in acetonitrile at ambient temperature (Table 1). By monitoring the growth of ^{3}Fl, Schuster and co-workers[4] deduced the lifetime[6] of ^{1}Fl to be 400 ± 130 ps in ACN, which is in excellent agreement with our results given the experimental error. TD-DFT calculations predict ^{1}Fl has a vertical transition at 375 nm ($f = 0.1234$) in fair agreement with the 415 nm assignment (SI, Table S2).

The initially formed broadly absorbing transient is assigned to an excited singlet state of the precursor (^{1}DAF*), following Kohler's studies of diphenyldiazomethane[7] and our recent ultrafast studies on *p*-biphenyldiazomethane[8] and ethane.[9] The carrier of transient absorption in the 370 nm region is a precursor to ^{1}Fl and produces this species with a time constant of 20.9 ps. This intermediate could, in principle, be a lower excited singlet state of DAF or an excited state of the singlet carbene, ^{1}Fl*. The former assignment could hold true only if the initially formed broadly absorbing transient was at least the second excited singlet state (S_2) of the precursor. We prefer to assign the carrier of the 370 nm transient absorption to the excited open shell singlet carbene, ^{1}Fl*, for reasons that will be later detailed. As the excited state of DAF and ^{1}Fl* both absorb at 415 nm, we cannot clearly monitor the growth of ^{1}Fl. It is therefore possible that ^{1}Fl is formed from both DAF* and ^{1}Fl* as shown in Scheme 1. Furthermore, ^{1}Fl* has some absorption in the range from 400 to 450 nm, overlapping with the absorption of ^{1}Fl. This can account for the two isosbestic points observed at 405 and 420 nm. Global analysis on the acetonitrile data 2 ps after the laser pulse can provide the Species Associated Spectra (SAS) for ^{1}Fl*, ^{1}Fl, and ^{3}Fl (SI, Figure S1). It is clear in the SAS that ^{1}Fl* absorbs broadly in the region between 360 and 550 nm, although the shape of the ^{1}Fl* spectrum depends on the initial concentrations of ^{1}Fl* and ^{1}Fl formed from the diazo excited state. This analysis further supports the proposal that ^{1}Fl* has a very broad absorption.

In acetonitrile-d_3, the lifetimes of both ^{1}Fl and ^{1}Fl* are the same as those in acetonitrile, within experimental error. The lack of a kinetic isotope effect (KIE) indicates that neither hydrogen abstraction nor C−H insertion is an important process for both ^{1}Fl and ^{1}Fl* in acetonitrile. Intersystem crossing is the main deactivation pathway for ^{1}Fl. In addition, it is interesting to note that, after 2 ns, the decay of ^{1}Fl and the growth of ^{3}Fl cease and the absorption of ^{1}Fl does not decay to the baseline. This indicates that fluorenylidene reaches its singlet−triplet equilibrium after 2 ns. The lifetime of the equilibrium mixture in acetonitrile determined by Shuster and co-workers,[4] by monitoring ^{3}Fl, is 25 ± 3 ns. The absorption of ^{1}Fl at 2 ns is ∼40% of its maximum absorption determined 75 ps after the laser pulse (Figure 1c). Thus, it can be deduced that in the equilibrium mixture there is ∼60% of ^{3}Fl and ∼40% of ^{1}Fl, which corresponds to an equilibrium constant $K_{eq} = [^{3}\mathrm{Fl}]_{eq}/[^{1}\mathrm{Fl}]_{eq} = 1.5$, where $[^{1}\mathrm{Fl}]_{eq}$ and $[^{3}\mathrm{Fl}]_{eq}$ are the singlet and triplet fluorenylidene concentrations at equilibrium, and the singlet−triplet energy gap $\Delta G_{ST} = 0.2$ kcal·mol^{-1}. Schuster and co-workers deduced an upper limit of the singlet−triplet (S−T) energy gap of 1.1 kcal·mol^{-1}, which is consistent with our result. Since K_{eq} is small, the reverse intersystem crossing from ^{3}Fl to ^{1}Fl should be considered when deriving the ISC rate constant from ^{1}Fl to ^{3}Fl k_{ST}. The time constant of 440 ps observed in acetonitrile is an apparent time constant of the decay of ^{1}Fl.

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(5) Frisch, M. J. et al. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(6) In ref 4, half-life $t_{1/2}$ was used instead of lifetime τ as in this paper, $\tau = t_{1/2}/\ln 2$.

(7) Peon, J.; Polshakov, D.; Kohler, B. *J. Am. Chem. Soc.* **2002**, *124*, 6428−6438.

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(9) Wang, J.; Burdzinski, G.; Gustafson, T. L.; Platz, M. S. *J. Am. Chem. Soc.* **2007**, *129*, 2597−2606.

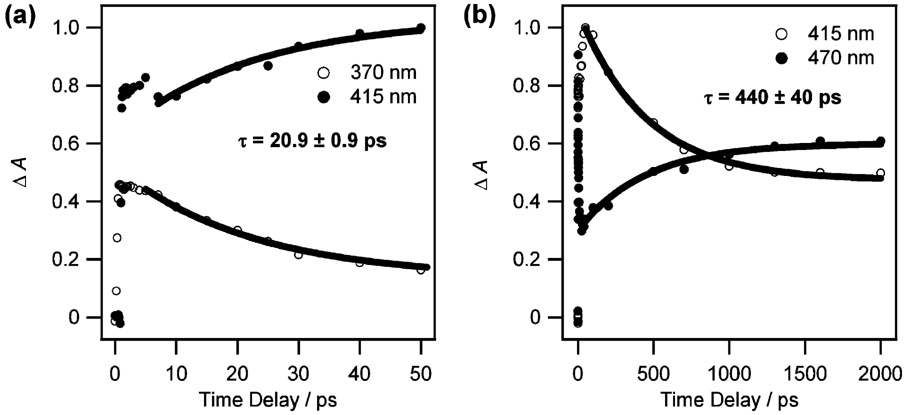

Figure 2. Normalized kinetic traces were produced by ultrafast LFP (λ_{ex} = 308 nm) of 9-diazofluorene in acetonitrile. The kinetic traces were probed at (a) 370 nm (○) and 415 nm (●) and (b) 415 nm (○) and 470 nm (●) and globally fitted in monoexponential equations.

Table 1. Lifetimes (ps) of Singlet Fluorenylidene (^{1}Fl) and Singlet Excited Fluorenylidene (^{1}Fl*) and Intersystem Crossing Rates (s^{-1}) and Singlet−Triplet Energy Gap (kcal·mol^{-1}) in Different Solvents

	^{1}Fl	^{1}Fl*	ISC rate		S–T gap
	τ	τ^d	$10^{-9}k_{ST}$	$10^{-9}k_{TS}$	ΔG_{ST}
acetonitrile	440 ± 40[a]	20.9 ± 0.9	1.4	0.9	0.2[e]
acetonitrile-d_3	470 ± 30[a]	20.9 ± 0.6			
cyclohexane	88 ± 11[b]	20.1 ± 1.6	9.5	1.9	1.0[f]
cyclohexane-d_{12}	90 ± 9[b]	20.5 ± 1.1			
cyclohexene	49 ± 7[b]	16.2 ± 1.4			
methanol	22 ± 2[c]	10.6 ± 0.7			
methanol-O-*d*	33 ± 3[c]	10.0 ± 0.3			
benzene	100 ± 12[a]	19.0 ± 1.0			
hexafluorobenzene	490 ± 90[a]	27 ± 8	1.4	0.7	0.4[e]

[a] Probing wavelength is 415 nm. [b] Probing wavelength is 405 nm. [c] Probing wavelength is 430 nm. [d] Probing wavelength is 370 nm. [e] Measured by spectroscopy. [f] Derived from Stern−Volmer analysis.

Scheme 1

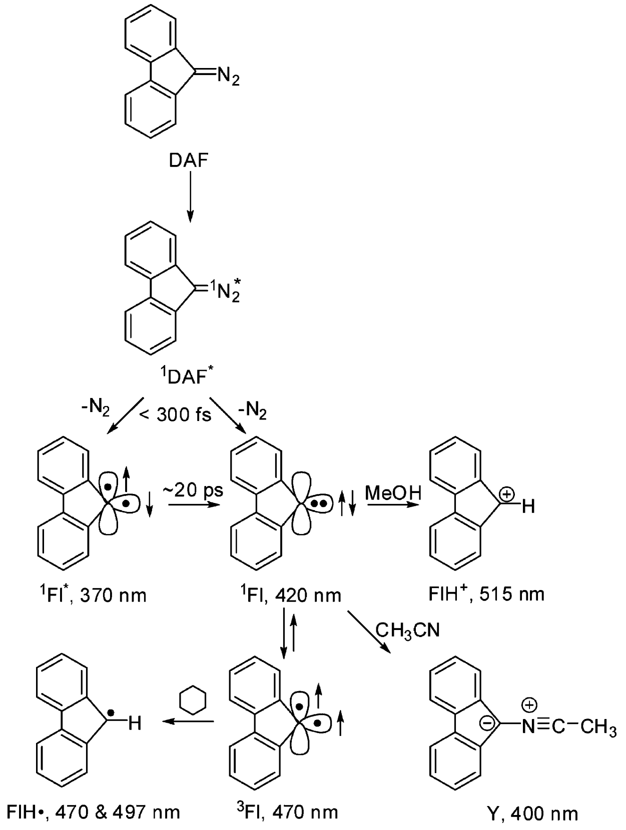

Table 2. Calculated Singlet−Triplet Energy Gaps (kcal·mol^{-1}) for Fluorenylidene in the Gas Phase, Cyclohexane, and Acetonitrile

	B3LYP/6-311+G(d,p)//B3LYP/6-31G(d)[a]			CBS-QB3
	gas phase	cyclohexane[b]	acetonitrile[b]	gas phase
ΔE_{ST}(0 K)	4.11	2.13	−1.33	1.91
ΔH_{ST}(298 K)	4.13	2.19	−1.25	2.10
ΔG_{ST}(298 K)	4.24	2.36	−1.05	2.21

[a] The energy is calculated at the B3LYP/6-311+G(d,p) level of theory using the B3LYP/6-31G(d) geometry and scaled zero-point vibrational energy (scaling factor 0.9806) and thermal and entropic corrections as appropriate. A positive value of the singlet−triplet energy gap indicates that the triplet state is more stable. [b] Using the PCM implicit solvation model.

One can derive from the kinetic model[10] that $k_{obs} = k_{ST}(1 + 1/K_{eq})$, from which we deduce that the ISC rate constant from ^{1}Fl to ^{3}Fl $k_{ST} = 1.4 \times 10^9$ s^{-1} and from ^{3}Fl to ^{1}Fl $k_{TS} = 9.1 \times 10^8$ s^{-1} in acetonitrile.

Recently, Woodcock et al.[11] used an empirical correction factor of 2.84 kcal·mol^{-1} to predict the gas-phase S−T gaps of aromatic carbenes using B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) calculations. Among the carbenes they studied, there are only three experimental benchmarks. Unfortunately, the S−T gap for diphenylcarbene (ΔE_{ST} = 2.6 kcal·mol^{-1}), one of the three selected experimental benchmarks, is measured in acetonitrile.[12] The diphenylcarbene S−T gap (ΔE_{ST} = 4.1 kcal·mol^{-1}) measured in the nonpolar solvent isooctane will be a better benchmark for the gas-phase calculations.[12] It remains to be seen if DFT calculations of different carbenes have the same error.

We performed B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) calculations for fluorenylidene in the gas phase and in acetonitrile and cyclohexane, simulated by PCM models. The calculated S−T gaps ΔG_{ST}(298 K) for fluorenylidene are 4.24, 2.36, and −1.05 kcal·mol^{-1} in the gas phase, cyclohexane, and acetonitrile, respectively, where a negative sign indicates that a singlet ground state is more stable (Table 2). Although the DFT calculations[5] obviously overestimate the singlet carbene stability in acetonitrile, the trend for the energy gaps is consistent with the experimental data. The high level calculation CBS-QB3[5]

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(10) Connors, K. A. *Chemical Kinetics. The Study of Reaction Rates in Solution*; VCH Publisher, Inc.: New York, 1990; pp 60−61.
(11) Woodcock, H. L.; Moran, D.; Brooks, B. R.; Schleyer, P. v. R.; Schaefer, H. F., III *J. Am. Chem. Soc.* **2007**, *129*, 3763−3770.
(12) Eisenthal, K. B.; Moss, R. A.; Turro, N. J. *Science* **1984**, *225*, 1439−1445.

predicts a smaller S−T gap (2.21 kcal•mol^{-1}) for fluorenylidene in the gas phase (Table 2).

Another feature of note is that 3 ns after the laser pulse we can observe the ^{1}Fl band at 415 nm but the carbene-acetonitrile ylide[2] (λ_{max} = 400 nm) is only barely observed at 400 nm. This indicates that the Fl-acetonitrile ylide is produced by the reaction between acetonitrile and the singlet−triplet carbene equilibrium mixture on a 3−20 ns time scale. In contrast, the monoarylcarbene *p*-biphenylylcarbene reacts with acetonitrile prior to complete spin equilibration.[8] This difference can be easily accounted for by steric effects. In this regard, fluorenylidene resembles singlet *p*-biphenylylmethylcarbene,[9] which is more sterically hindered than *p*-biphenylylcarbene, and forms little acetonitrile ylide and undergoes 1,2 migration of hydrogen instead.

2.2. Cyclohexane. Ultrafast photolysis (308 nm) of DAF in cyclohexane gave results similar to those obtained in acetonitrile with a few notable exceptions. After the laser pulse, the broad absorption of the DAF excited state is formed. In contrast to the data in acetonitrile, the decay of transient absorption at 370 nm (^{1}Fl*) is not clearly accompanied by the growth of ^{1}Fl monitored at 415 nm. In this solvent, the conversion of excited singlet carbene (^{1}Fl*) to the lower energy singlet carbene is not as obvious as in acetonitrile (SI, Figure S2). This is likely due to the fact that the lifetimes of ^{1}Fl and ^{1}Fl* are somewhat comparable in cyclohexane but are quite different in acetonitrile. An alternative explanation could be that ^{1}Fl* has a broad absorption in the region between 380 and 450 nm in cyclohexane. Thus, due to the overlap between ^{1}Fl* and ^{1}Fl, the growth of relaxed ^{1}Fl is obscured. As ^{1}Fl decays, the absorption of ^{3}Fl, centered at 470 nm, is formed. After 500 ps, a sharp band centered at 497 nm is formed. Griller et al.[2] showed that the 9-fluorenyl radical (FlH•) absorbs at both 470 and 497 nm. Therefore, the newly formed 497 nm band can be readily assigned to FlH•. TD-DFT calculations predict FlH• has a vertical transition at 454 nm (f = 0.0494) in fair agreement with the 497 nm assignment (SI, Table S3). The lifetime of ^{1}Fl in cyclohexane is 88 ± 11 ps (Table 1), in fair agreement with the data of Grasse et al.[4] (140 ps) within experimental error.[5]

Previously, Schuster and co-workers[4] reported a Stern−Volmer analysis of the yield of radical FlH• (497 nm) in spiropentane as a function of ethanol concentration. The lifetime of the equilibrium mixture of ^{1}Fl and ^{3}Fl in spiropentane is 29 ns, and upon analysis of the published data[4] we deduce that the absolute bimolecular reaction rate constant between the singlet−triplet equilibrium mixture of fluorenylidene and ethanol $k_{EtOH(ST)}$ is 1.9×10^8 M^{-1} s^{-1}. The concentration of neat ethanol is 17.1 M. The lifetime of nonequilibrated ^{1}Fl in ethanol is 62 ± 9 ps,[13] measured by ultrafast photolysis (λ_{ex} = 308 nm) of DAF in ethanol. Thus, the bimolecular reaction rate constant between ^{1}Fl and ethanol is $k_{EtOH(S)} = 9.4 \times 10^8$ M^{-1} s^{-1}. If one assumes that $k_{EtOH(S)}$ in spiropentane is no faster than that in neat ethanol, then based on the relationship that $k_{EtOH(ST)} = k_{EtOH(S)}/K_{eq}$, one can conclude that $K_{eq} \leq 5.0$ and that $\Delta G_{ST} \leq$ 1.0 kcal•mol^{-1} in spiropentane.

The time constant of 88 ps observed in cyclohexane is the apparent time constant of the decay of ^{1}Fl by intersystem crossing. Following the kinetic model[10] $k_{obs} = k_{ST}(1 + 1/K_{eq})$ in section 2.1 and assuming K_{eq} is the same in spiropentane and cyclohexane, one can conclude that $k_{ST} = 9.5 \times 10^9$ s^{-1} and $k_{TS} = 1.9 \times 10^9$ s^{-1} in nonpolar alkane solvents.

The lifetime of ^{1}Fl in cyclohexane is shorter than that recorded in acetonitrile. This solvent effect is consistent with all previously reported studies of aryl carbenes[14,4,7−9] which report that ISC rates are faster in alkanes than in polar solvents. In cyclohexane-d_{12}, the lifetime of ^{1}Fl remains unchanged compared with that recorded in cyclohexane. Thus, we can safely conclude that ^{1}Fl does not react with cyclohexane before undergoing intersystem crossing to ^{3}Fl. Grasse et al.[4] observed that the optical yields[15] of FlH• and FlD• are the same in cyclohexane and cyclohexane-d_{12}, and that group concluded that hydrogen abstraction by ^{3}Fl in the spin equilibrated mixture of carbenes is the main reaction pathway in cyclohexane rather than C−H insertion reactions of ^{1}Fl. This observation also requires that the yields of ^{3}Fl formation are the same in cyclohexane and cyclohexane-d_{12}, consistent with our own and previous observations.

In cyclohexane, 500 ps after the laser pulse, FlH• (497 nm) begins to appear in the spectra (SI, Figure S2c). Therefore, shortly after the singlet−triplet equilibrium mixture of fluorenylidene is fully established, ^{3}Fl begins to react with the solvent to form FlH•.

The excited carbene ^{1}Fl*, absorbing in the 370 nm region, has a lifetime of ∼20 ps in both cyclohexane and cyclohexane-d_{12}. The excited carbene relaxes to its ground state more rapidly than it reacts with solvent.

2.3. Cyclohexene and Benzene. Ultrafast photolysis (308 nm) of DAF in cyclohexene produces spectra similar to those in cyclohexane. ^{1}Fl*, ^{1}Fl, ^{3}Fl, and FlH• are all observed in this alkene solvent. In cyclohexene, the lifetime of ^{1}Fl is 49 ± 7 ps, which is shorter than that recorded in cyclohexane (88 ps, Table 1). Due to the similar polarities of cyclohexane and cyclohexene, we believe that the ISC rates should be similar in both solvents. Assuming that the ISC rate is the same in cyclohexane and in cyclohexene, it can be concluded that ^{1}Fl reacts with cyclohexene before complete relaxation to its singlet−triplet equilibrium mixture. This explains why Jones and Rettig observed an alkene dilution effect in the presence of an additive, hexafluorobenzene.[1] Based on the previous assumption regarding ISC rates and that the concentration of neat cyclohexene is 9.9 M, we can deduce that approximately one-third of the nascent ^{1}Fl reacts with cyclohexene and approximately two-thirds of the singlet carbene undergoes ISC and that the bimolecular rate constant of ^{1}Fl and cyclohexene is 7.0×10^8 M^{-1}•s^{-1}.

In benzene, the spectra produced by ultrafast photolysis (308 nm) of DAF also resembles those observed in cyclohexane with the only exception being that FlH• cannot be detected 3 ns after the laser pulse. This is not surprising since the C−H bonds in benzene are all attached to sp^2 hybridized carbons and are stronger than the sp^3 C−H bonds in cyclohexane and cyclohexene. Thus there is less efficient formation of FlH• by hydrogen abstraction of ^{3}Fl. In benzene, the lifetime of ^{1}Fl is 100 ± 12 ps, the same as that in cyclohexane, within experimental error, indicating that ^{1}Fl does not react with

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(13) Because carbene ISC rates are slow in polar solvents, we assume that the ISC rate constants in ethanol and acetonitrile ($k_{ST} = 1.4 \times 10^9$) are the same. Thus, we propose that ^{1}Fl is not in equilibrium with ^{3}Fl in neat ethanol and the dynamics measured are those of ^{1}Fl and not the equilibrium mixture.

(14) 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.

(15) Optical yield is defined as the maximum value of transient absorption.

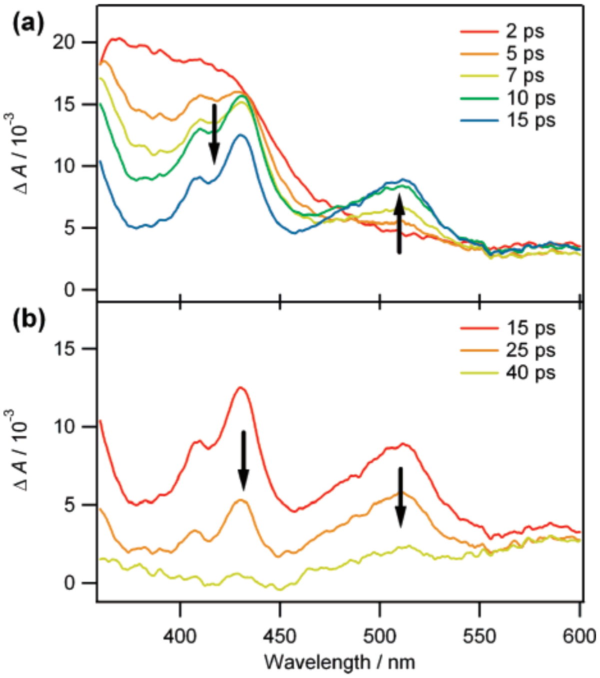

Figure 3. Transient spectra were generated by ultrafast LFP (λ_{ex} = 308 nm) of 9-diazofluorene in methanol with time windows of (a) 2−15 ps and (b) 15−40 ps.

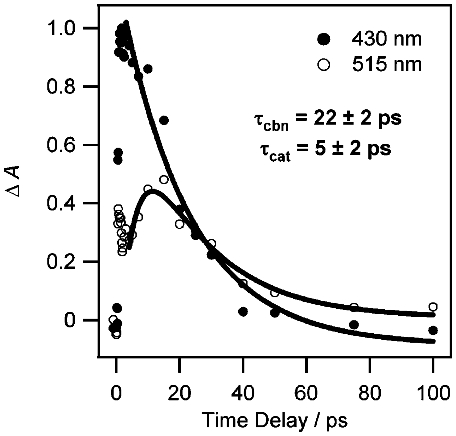

Figure 4. Normalized kinetic traces were produced by ultrafast LFP (λ_{ex} = 308 nm) of 9-diazofluorene in methanol. The decay of singlet fluorenylidene (●) and the growth and decay of transient absorption of 9-fluorenyl cation (○) were probed at 430 and 515 nm, respectively. The time constants τ_{cbn} (the lifetime of singlet fluorenylidene) and τ_{cat} (the lifetime of the 9-fluorenyl cation) were obtained by globally fitting the decay at 430 nm in the function $\Delta OD = A_1 \exp(-t/\tau_{\mathrm{cbn}}) + A_2$ and the growth and decay at 515 nm in the function $\Delta OD = A_3[\tau_{\mathrm{cat}}/(\tau_{\mathrm{cat}} - \tau_{\mathrm{cbn}})][\exp(-t/\tau_{\mathrm{cat}}) - \exp(-t/\tau_{\mathrm{cbn}})] + A_4$.

benzene before its relaxation to the lower energy triplet state. It is the singlet−triplet equilibrium mixture of Fl which reacts with benzene solvent.

The excited fluorenylidene ^{1}Fl*, probed at 370 nm, has a lifetime of 16 ps in cyclohexene. The lifetime is shorter than those observed in cyclohexane and may be an indication that the excited carbene reacts with cyclohexene. Reactions of an excited, open shell singlet carbene with alkenes need not be stereospecific as is the case with the lower energy closed shell singlet carbenes. This could be responsible for some of the nonstereospecific product formed in neat alkene.[1] The lifetime of ^{1}Fl* is 19 ps in benzene, similar to the values obtained in acetonitrile and cyclohexane. This indicates that ^{1}Fl* does not react with benzene.

2.4. Methanol. The results obtained in methanol (Figure 3), an excellent trap of singlet carbenes, differ substantially from those obtained in acetonitrile and cyclohexane. The broad absorption of the DAF excited state is still formed within the laser pulse. The subsequent decay of transient absorbance in the 370 nm region, with a time constant of 11 ps, is not accompanied by the growth of the 415 nm band of ^{1}Fl. But ^{1}Fl is readily visible 7 ps after the laser pulse. As the ^{1}Fl signal decays, a broad new band, centered at 515 nm, forms. The decay of ^{1}Fl and the growth of the 515 nm band share the same time constant (22 ps). The lifetime of the carrier of the 515 nm band is 5 ps (Figure 4).

The carrier of the 515 nm band is assigned to the 9-fluorenyl cation (FlH$^+$), in excellent agreement with the spectra reported by Mecklenburg and Hilinski.[16] TD-DFT calculations predict that FlH$^+$ has a vertical transition at 443 nm (f = 0.2382) in fair agreement with the 515 nm assignment (SI, Table S4). The cation is formed by abstraction of a proton of methanol by the singlet carbene, following the precedents established by Kirmse and Steenken,[17] Chateauneuf,[18] Dix and Goodman,[19] Peon and Kohler,[7] and Wang et al.[8,9] In methanol, the protonation time constants for diphenylcarbene[7] and *p*-biphenylylcarbene[8] are 9 and 8 ps, respectively. The protonation time constant for ^{1}Fl is substantially larger than those of the other carbenes. This can be explained by the fact that FlH$^+$ is an antiaromatic cation and the formation of such species is less exothermic and has a higher activation barrier and a slower rate than the analogous cations.

Carbenes react with alcohols by a variety of mechanisms. Peon and Kohler[7] demonstrated that methanol protonation of diphenylcarbene is a relatively minor reaction path even though it is the only mechanism that generates a UV−vis active species, benzhydryl cation. Methanol protonation of ^{1}Fl is probably once again a minor component of the reaction of the carbene with the alcohol.

Previously, Schuster and co-workers[4] reported that the bimolecular reaction rate constant between the singlet−triplet equilibrium mixture of fluorenylidene and methanol $k_{\mathrm{MeOH(ST)}}$ is 8.6×10^8 M^{-1} s^{-1} in acetonitrile. Following the same calculations described in section 2.2, one can derive that the absolute bimolecular reaction rate constant between nonequilibrated ^{1}Fl and methanol $k_{\mathrm{MeOH(S)}} = 1.8 \times 10^9$ M^{-1} s^{-1}, based on the fact that the concentration of neat methanol is 24.7 M and that the lifetime of ^{1}Fl in methanol is 22 ps. If one assumes that $k_{\mathrm{MeOH(S)}}$ in acetonitrile is no faster than that in neat methanol, then based on the relationship that $k_{\mathrm{MeOH(ST)}} = k_{\mathrm{MeOH(S)}}/K_{\mathrm{eq}}$, one can conclude that $K_{\mathrm{eq}} \leq 2.1$ and that $\Delta G_{\mathrm{ST}} \leq 0.4$ kcal·mol^{-1} in acetonitrile. This is in excellent agreement with our earlier estimate that $K_{\mathrm{eq}} = 1.5$ and $\Delta G_{\mathrm{ST}} = 0.2$ kcal·mol^{-1}, a value which was obtained by spectroscopy with no kinetic assumptions.

The lifetime of ^{1}Fl in methanol-OD does not show a large isotope effect (KIE = 1.5), as previously observed for other

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(18) Chateauneuf, J. E. *Res. Chem. Intermed.* **1994**, *20*, 249−263.

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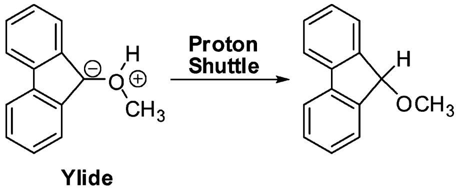
carbenes.[7−9] The small KIE value indicates that ^{1}Fl may react with methanol primarily by direct O−H insertion and/or ylide formation followed by a proton shuttle. The decay rate in methanol-OD for the excited ^{1}Fl, in the 370 nm region, is the same as that in methanol within experimental error.



2.5. Hexafluorobenzene. The data obtained in hexafluorobenzene (HFB) are very similar to those obtained in acetonitrile. The broad diazo excited state is formed within the laser pulse. The subsequent decay in the 370 nm region, with a time constant of 27 ps, results in the growth of ^{1}Fl, monitored at 415 nm, with an isosbestic point at 400 nm (SI, Figure S3). The lifetime of ^{1}Fl in HFB is 490 ± 90 ps, which is consistent with the result (450 ± 70 ps) obtained by Schuster and coworkers.[4] The decay of ^{1}Fl produces ^{3}Fl, which absorbs at 470 nm. Similar to the data in acetonitrile, the decay of ^{1}Fl and the growth of ^{3}Fl cease 2 ns after the laser pulse and the absorption of ^{1}Fl does not decay to the baseline. This indicates that fluorenylidene reaches its singlet−triplet equilibrium after 2 ns. The lifetime of the equilibrium mixture determined by Schuster and co-workers,[4] by monitoring ^{3}Fl, is 100 ± 6 ns in hexafluorobenzene. The absorption of ^{1}Fl at 2 ns is ~33% of its maximum absorption at 100 ps (SI, Figure S3b). Following the same calculations described in section 2.1, one can deduce that the equilibrium constant $K_{eq} = 2.0$, $\Delta G_{ST} = 0.4$ kcal·mol^{-1}, $k_{ST} = 1.4 \times 10^9$ s^{-1}, and $k_{TS} = 6.8 \times 10^8$ s^{-1} in hexafluorobenzene.

Schuster and co-workers reported that the bimolecular reaction rate constant between the singlet−triplet equilibrium mixture of fluorenylidene and methanol $k_{MeOH(ST)}$ is 1.2×10^8 M^{-1} s^{-1}. Following the same calculations described in section 2.4, one can deduce that $K_{eq} = 15$ and $\Delta G_{ST} = 1.6$ kcal·mol^{-1} in hexafluorobenzene. These values are not in good agreement with those obtained by the more reliable spectroscopic method, where $K_{eq} = 2.0$ and $\Delta G_{ST} = 0.4$ kcal·mol^{-1}. The error in the kinetics based calculation is mainly introduced by the assumption that $k_{MeOH(S)}$ is the same in neat methanol and in hexafluorobenzene. Based on the relationship that $k_{MeOH(ST)} = k_{MeOH(S)}/K_{eq}$ and applying $K_{eq} = 2.0$, one can deduce that $k_{MeOH(S)} = 2.4 \times 10^8$ M^{-1} s^{-1} in hexafluorobenzene, which is much smaller than the assumed value of $k_{MeOH(S)} = 1.8 \times 10^9$ M^{-1} s^{-1}. This type of calculation reasonably deduced the S−T gap in acetonitrile but fails in hexafluorobenzene, which may be due to the fact that hexafluorobenzene is a nonpolar solvent and retards the reaction rate between ^{1}Fl and methanol.

As mentioned previously the ISC rates of carbenes depend on solvent polarity.[20] It is curious that the lifetime of ^{1}Fl in HFB, whose polarity is similar to that of cyclohexane, is so long. In a separate study of *p*-biphenylyltrifluoromethylcarbene,[21] the presence of small amounts of HFB in cyclohexane was found to retard the rate of ISC indicating that there may be a specific interaction between the carbene and HFB. We have found that the hexafluorobenzene effect is also observed with other halogenated solvents, dichloromethane and monofluorobenzene (SI, Figures S4 and S5). The lifetimes of ^{1}Fl in these halogenated solvents are longer than 500 ps. The transient spectra recorded in these solvents on the ps and ns timescales demonstrate that the decay of ^{1}Fl in these halogenated solvents is still accompanied by the growth of ^{3}Fl.[22] Thus, the long lifetimes of the singlet carbenes are due to a depression in the rate constants of intersystem crossing in the halogenated solvents and are not due to the singlet state becoming the ground state of the carbene.

3. Discussion

3.1. Excited Singlet Carbene. Theory predicts that the S_1 state of diazomethane is 67.5−71.5 kcal·mol^{-1} above the ground state.[23] It is also predicted that the S_1 state of diazomethane has sufficient energy to decompose to form methylene in an excited open shell, singlet state. Furthermore, modern theory predicts that the S_1, electronically excited singlet state of diazomethane can both fragment to form methylene in its lowest energy singlet state (major) and, in a minor process, decompose to form methylene in an electronically singlet excited state.[23−26]

Prior to these calculations, Chang and Shechter[27] reported that photolysis of a precursor of *tert*-butyl carbene gives a different, less specific mixture of products than pyrolysis of precursors to the same carbene. They posited that photolysis produced an excited singlet state of *tert*-butyl carbene which rearranged to a unique mixture of products at a rate competitive with relaxation to the closed shell singlet carbene.

The Eisenthal group[20,28,29] demonstrated that photolysis of diphenyldiazomethane with 266 nm light produced diphenylcarbene in an electronically excited triplet state, which was detected by fluorescence spectroscopy. It was posited that the excited triplet carbene was formed by relaxation of singlet excited diphenylcarbene initially produced by monophotonic excitation of the diazo precursor. The electronically excited singlet state of diphenylcarbene was not observed in this study. The lifetime of excited triplet diphenylcarbene is 4 ns in solution.[28]

Given this background we posit that UV photolysis of DAF produces an excited state of DAF (^{1}DAF*) which fragments to form the lowest energy closed shell singlet carbene (^{1}Fl, major, 415 nm) and a small amount of the excited, open shell carbene ^{1}Fl*. The fact that the carrier of 370 nm transient absorption decays to ^{1}Fl in acetonitrile and hexafluorobenzene supports

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[22] The signal of triplet fluorenylidene is very weak in dichloromethane and fluorobenzene. The spectra (Figures S4b and S5b) have been averaged 10 000 times to improve the signal-to-noise ratio.

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its assignment as ^{1}Fl*. We think it unlikely that an excited triplet state of fluorenylidene would relax to the lowest energy singlet carbene at a rate competitive with that for fluorescence or internal conversion to ground state triplet ^{3}Fl. The fact that excited triplet diphenylcarbene has a lifetime of 4 ns in solution further argues against assigning the carrier of 370 nm absorption to ^{3}Fl*.[28]

The carrier of 370 nm absorption reacts with methanol and cyclohexene. That seems to be another reasonable property to attribute to ^{1}Fl* as relaxed singlet fluorenylidene reacts rapidly with both reagents and excited triplet diphenylcarbene reacts rapidly with alcohols as well.[28,29]

Alternatively, one can posit that UV photolysis of DAF produced the S_2 state of diazofluorene and that this was the state detected right after the laser pulse (see Figure 1a). This state would decay rapidly to the S_1 state of DAF which one could assign to the carrier of 370 nm transient absorption, which has a lifetime of 20.9 ps in acetonitrile. Given that theory predicts that the S_1 state of diazomethane will pass through a conical intersection and fragment to methylene in femtoseconds,[24−26] we are reluctant to attribute the carrier of 370 nm transient absorption to the S_1 state of 9-diazofluorene. However, we recognize that this interpretation remains viable. Unfortunately, we cannot pump DAF to S_1 using visible light and probe the UV region of the transient spectrum to test this possibility.

3.2. Influence of Hexafluorobenzene. Eisenthal and co-workers[20,30−32] have studied the rates of intersystem crossing (ISC) of diphenylcarbene (DPC) as a function of solvent. The lifetime of singlet DPC in acetonitrile is 310 ps, and this lifetime shortens to 95 ps in isooctane. A plot of the log of the first-order rate constant of ISC of ^{1}DPC versus the Dimroth $E_T(30)$[33] parameter was linear. Normally, one expects that the rate of ISC will increase as the energy gap between the singlet and triplet states decreases.[34−36] However, Eisenthal and co-workers proposed that polar solvents preferentially stabilize the singlet relative to triplet aryl carbenes, a postulate to later receive experimental[37] and computational support[38] in seeming contradiction to expectations. Eisenthal et al. advanced density of states arguments to explain why ISC rates of ^{1}DPC are fastest in nonpolar solvents where the singlet−triplet energy gap is largest in solution. We have reported that *p*-biphenylylcarbene follows the same pattern: fast ISC in nonpolar cyclohexane and slower ISC in polar acetonitrile. Schuster and co-workers[4] first reported the same pattern with fluorenylidene, a trend we have reproduced in this work as well. Given that HFB and cyclohexane have comparable Dimroth $E_T(30)$[33] values it is indeed remarkable that ISC is so slow in hexafluorobenzene. We speculate that the singlet carbene coordinates with the solvent. Either the empty p-orbital of the singlet carbene coordinates with a nonbonding pair of electrons of the halogen to form a pseudo-ylide solvent complex or the filled orbital of closed shell singlet fluorenylidene forms a weak Meisenheimer type solvent complex[39] with electron-poor hexafluorobenzene as first postulated by Gaspar and Jones.[40] Either of these interactions will selectively stabilize ^{1}Fl relative to ^{3}Fl, depress the singlet−triplet gap, and, following Eisenthal's analysis, slow the rate of ISC.[20,30−32] The fact that the singlet−triplet splitting of fluorenylidene in HFB (0.4 kcal•mol^{-1}) is more similar to that of acetonitrile (0.2 kcal•mol^{-1}) than cyclohexane (1.0 kcal•mol^{-1}) persuades us that there is a specific carbene−solvent interaction that differentially stabilizes ^{1}Fl, reduces the S−T gap, and decelerates intersystem crossing. We have found that dichloromethane and fluorobenzene also depress the rate constants of intersystem crossing. For this reason we conclude that the specific solvation of singlet fluorenylidene involves coordination of the empty p-orbital with nonbonding electrons of fluorine or chlorines of the solvent.

We further posit that the significantly different specific solvation of the singlet and triplet carbenes imposes a Franck−Condon like factor on the intersystem crossing process. Those solvents that most solvate the singlet carbene will also have the greatest structural difference between the singlet carbene−solvent complex and their triplet spin isomer solvent complex, on the smallest S−T gap, and on the slowest ISC rate, hence an apparent violation of the "Golden Rule" of radiationless transitions.[34−36]

Our conclusions differ only very slightly from those of the pioneering study of Jones and Rettig.[1] There is no question that seminal singlet fluorenylidene reacts with neat alkene faster than spin equilibrium is achieved with triplet fluorenylidene. Dilution of neat alkene with HFB does depress the rate of singlet fluorenylidene reaction with alkene, but due to a specific carbene−solvent interaction the presence of HFB also reduces the rate of intersystem crossing. Under the conditions of the Jones and Rettig experiment[1] the depression in the rate of carbene plus alkene reaction exceeds the extent of retardation of ISC; hence the dilution effect is observed. Our data predict that the dilution effect on the distribution of products formed in the reaction of singlet fluorenylidene with an alkene will also be observed in acetonitrile and dichloromethane.

4. Experimental Section

4.1. Calculations. DFT, TD-DFT, and CBS-QB3 calculations were performed using the Gaussian 03 suite of programs at The Ohio Supercomputer Center.[5] Geometries were optimized at the B3LYP/6-31G(d) level of theory with single-point energies obtained at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory. Vibrational frequency analyses at the B3LYP/6-31G(d) level were utilized to verify that stationary points obtained corresponded to energy minima. The electronic spectra were computed using the Time-Dependent Density Functional Theory of Gaussian 03 at the B3LYP/6-311+G(d,p) level, and 20 allowed electronic transitions were calculated.

4.2. Ultrafast Spectroscopy. Ultrafast UV−vis broadband absorption measurements were performed using the home-built spectrometer described previously.[41] Samples were prepared in 50 mL of solvent with absorption 1.0 at the excitation wavelength with a 1.0 mm optical length. Ultrafast photolysis of fluorene, fluorenone, and the solution

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obtained by photo bleaching DAF in acetonitrile failed to produce transient spectra similar to those obtained with fresh solutions of DAF.

4.3. Materials. All materials and solvents were purchased from Aldrich. The solvents for ultrafast studies were spectrophotometric grade from Burdick & Jackson and used as received. 9-Diazofluorene was prepared by the oxidation of the corresponding hydrazone according to known procedures.[1−4]

5. Conclusions

Studies of fluorenylidene have been central to the development of mechanistic carbene chemistry. From the study of this carbene, ideas about the specificity of singlet carbene reactions with alkenes and their relaxation to triplet carbenes were solidified.[1] Fluorenylidene was one of the first carbenes whose dynamics on the ns time scale was studied in detail.[2−4]

Femtosecond time-resolved studies of the photochemistry of 9-diazofluorene (DAF) have allowed the first observation of the excited state of this compound (^{1}DAF*). More importantly, we have observed the first two singlet states (closed shell ^{1}Fl and open shell ^{1}Fl*) of fluorenylidene. This is the first observation of an excited singlet carbene in solution.

Relaxed ^{1}Fl undergoes intersystem crossing (ISC) to its lower energy triplet state on the ps time scale. ISC is, as a rule, more rapid in nonpolar solvents. In this regard, ^{1}Fl resembles diphenylcarbene and *p*-biphenylylcarbene. The exceptions to this rule are hexafluorobenzene (HFB) and other halogenated solvents; the ISC rate of ^{1}Fl in HFB is comparable to that in acetonitrile, and the ISC rates in fluorobenzene and dichloromethane are even longer. We speculate that the halogenated solvent effect is due to complexation of ^{1}Fl with halogenated solvents. We propose that the specific solvation of singlet fluorenylidene involves coordination of the empty p-orbital with nonbonding electrons of fluorine or chlorine atoms of the solvent. We further posit that the significantly different specific solvation of the singlet and triplet carbenes imposes a Franck−Condon like factor on the intersystem crossing process. Those solvents that most solvate the singlet carbene will also have the greatest structural difference between the singlet carbene−solvent complex and their triplet spin isomer solvent complex, on the smallest S−T gap, and on the slowest ISC rate, hence an "apparent" violation of the "Golden Rule" of radiationless transitions.[34−36]

^{1}Fl reacts with neat cyclohexene before it completely relaxes to ^{3}Fl. The presence of hexafluorobenzene does reduce the rate of the singlet fluorenylidene reaction with an alkene as first suggested by Jones and Rettig.[1] HFB is an inert diluent as originally proposed[1] in the sense that it does not undergo a chemical reaction with ^{1}Fl at a rate that competes with spin equilibration. Indeed, ^{1}Fl fully relaxes to its singlet−triplet equilibrium mixture in acetonitrile, cyclohexane, and hexafluorobenzene but reacts with neat methanol and cyclohexene prior to complete spin equilibrium. HFB does solvate the singlet carbene, however, and this solvation depresses the rate constant of ISC. The presence of HFB retards the rate of both the singlet carbene reaction with alkene and ISC. At the concentrations of HFB used by Jones and Rettig[1] the effect of HFB on the rate of the bimolecular reaction was greater than its effect on ISC; hence the dilution effect was observed. Our results indicate that such dilution effects on the distribution of products formed in the reaction of fluorenylidene will also be observed in fluorobenzene, acetonitrile, and dichloromethane solvents.

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Supporting Information Available: TD DFT calculations in Table S1−S4, ultrafast LFP spectra in Figure S1−S6, complete ref 5. This material is available free of charge via the Internet at http://pubs.acs.org.

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