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Solvent Dependence of the 2-Naphthyl(carbomethoxy)carbene Singlet−Triplet Energy Gap

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Received September 6, 2001

Abstract: The solvent dependence of the 2-naphthyl(carbomethoxy)carbene (**2**) singlet−triplet energy gap has been examined by time-resolved infrared (TRIR) and computational methods. The ground state of **2** changes from the triplet state in hexane to the singlet state in acetonitrile. Preferential stabilization of the singlet carbene is the result of its increased dipole moment in polar solvents. Variable-temperature TRIR experiments provide measurements of the enthalpic and entropic differences between ^{1}**2** and ^{3}**2** and suggest that solvent and geometry effects on the entropy of singlet and triplet carbenes can offset differences arising from spin multiplicity. B3LYP calculations using the polarizable continuum solvation model (PCM) reproduce the general trends in enthalpic differences seen experimentally.

Introduction

One of the most fundamental properties that determines a carbene's reactivity is its spin state. However, even in those cases where the triplet state is of lower energy, chemistry often arises from the higher lying, but more reactive singlet carbene. Two mechanistic schemes have emerged to explain such observations. The classical mechanism, first advanced by Bethell and co-workers,[1] predicts that the observed barrier (E_a(obsd), eq 1) for the reaction of a singlet carbene in rapid equilibrium with its triplet ground state is given by the actual activation barrier of the reaction (E_a(rxn)) plus the energy required to populate the singlet from the lower energy triplet carbene (ΔH_{ST}).

$$E_a(\mathrm{obsd}) = E_a(\mathrm{rxn}) + \Delta H_{ST} \tag{1}$$

The alternative, proposed by Griller, Nazran, and Scaiano,[2] is an avoided surface-crossing mechanism in which the triplet carbene surface crosses the singlet carbene to product surface at a point below the energy of the singlet carbene leading to an E_a(obsd) that is lower than the sum of E_a(rxn) and ΔH_{ST}. In this case, if the activation energy for the singlet carbene reaction is very small, one might experimentally observe an activation barrier less than the singlet−triplet energy gap. Indeed, the avoided surface-crossing mechanism was originally formulated to explain such an observation for the reaction of diphenylcarbene with methanol, discussed below.[2]

Thus, accurate measurements of carbene singlet−triplet energy gaps are both fundamentally and mechanistically very important. The singlet−triplet splittings of several carbenes have been directly measured in the gas phase by photoelectron spectroscopy.[3] Direct measurements of carbene singlet−triplet splittings in solution, however, have proven much more elusive. Previous experimental estimates usually employ a combination of product studies and kinetic measurements and have been forced to rely on assumptions concerning the spin selectivity of carbene-trapping reagents.[4] For example, alcohols are thought to be selective traps of singlet carbenes; molecular oxygen and isoprene are believed to be selective triplet carbene traps. Any inaccuracy in these suppositions could lead to critical errors in the estimated energy difference between the two carbene spin states.

Following the pioneering work of Closs and Rabinow,[5] Eisenthal, Turro, and co-workers[6] examined the singlet−triplet

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10.1021/ja012139v CCC: $22.00 © 2002 American Chemical Society

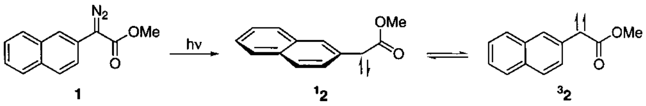
energy gap of diphenylcarbene in both nonpolar (isooctane) and polar (acetonitrile) solvents. Since only the triplet ground state of diphenylcarbene could be observed spectroscopically, estimations of the singlet−triplet energy gap were obtained with a combination of pico- and nanosecond time-resolved UV−vis measurements, chemical quenching, and triplet sensitization experiments. This analysis relied on kinetic equations derived for the diphenylcarbene system assuming the validity of eq 1 and on the use of spin-selective carbene traps such as methanol and isoprene. The estimated free energy difference between the two carbene spin states (ΔG_{ST}) was found to be 4.6 kcal/mol in isooctane and 3.2 kcal/mol in acetonitrile (the latter value in good agreement with Closs's original experiments). The assumption that the only entropic difference between singlet and triplet diphenylcarbene arises from their different spin multiplicity (R ln 3) led to derived ΔH_{ST} values of 4.0 and 2.5 kcal/mol in isooctane and acetonitrile, respectively. Due to the zwitterionic nature of singlet carbenes,[7] singlet diphenylcarbene is stabilized relative to triplet diphenylcarbene in polar solvents. Such solvent stabilization effects on the reactivity of singlet carbenes in equilibrium with their triplet ground states has also been observed experimentally in other arylcarbene derivatives.[8]

The above analysis has been questioned by Griller, Nazran, and Scaiano,[2] who measured the activation energy for the reaction of triplet diphenylcarbene with methanol (E_a(obsd) = 3.61 and 1.66 kcal/mol in isooctane and acetonitrile, respectively). According to eq 1, E_a(obsd) should be equal to the sum of ΔH_{ST} and the presumably diffusion-controlled reaction of singlet diphenylcarbene with methanol (1−3 kcal/mol). This latter value is an apparent activation energy that reflects the temperature dependence of the solvent viscosity. Thus, the measured E_a(obsd) values are less than expected and subsequently led to the formulation of the avoided surface-crossing mechanism. Griller, Nazran, and Scaiano also considered a model where the added methanol affects the singlet−triplet gap by changing the polarity of the medium or by associating to a different extent with each of the two carbene spin states.[2]

As previously noted,[2,4] one resolution to this dilemma would be if the entropic difference between singlet and triplet diphenylcarbene is larger than R ln 3. Reasonably, the polar nature of singlet carbenes could result in a more ordered solvent medium. Any increase in ΔS_{ST} would reduce ΔH_{ST}, potentially enough to bring the expected activation energy close to that measured.

We became interested in solvent effects on carbene singlet−triplet energy gaps during our time-resolved infrared (TRIR) study of 2-naphthyl(carbomethoxy)carbene (**2**) produced upon photolysis of diazoester **1** (Scheme 1).[9] Detection of IR bands from *both* the singlet (^{1}**2**) and triplet (^{3}**2**) states of spin-equilibrated carbene **2** allowed a direct experimental estimate of the free energy difference between ^{1}**2** and ^{3}**2** in Freon-113 (1,1,2-trichlorotrifluoroethane) solution.[9b] Reported herein is an extension of this previous work to different solvents. In addition, variable-temperature TRIR experiments have allowed investigation of solvent effects on ΔH_{ST} and ΔS_{ST} for carbene **2**. Our experimental analysis is supported by B3LYP calculations[10] using the polarizable continuum model (PCM) for solvation.[11]

Scheme 1



Results and Discussion

Our analysis of the singlet−triplet energy gap of **2** relies on comparing the intensities of IR bands due to ^{1}**2** relative to those of ^{3}**2** as a function of solvent. Since the ratio of these signals is directly related to the ratio of singlet to triplet carbene, a corresponding equilibrium constant and, hence, a standard free energy difference (ΔG_{ST}) can be easily derived. Such an analysis requires the following: (1) the two spin states must be equilibrated, (2) IR signals from each spin state must be clearly distinguishable, (3) the ratios of extinction coefficients for these signals must be known, and (4) ΔG_{ST} must be small enough to allow experimental observation of the solvent perturbation of the equilibrium constant. As discussed below, carbene **2** fulfills all of these requirements.

In our original TRIR study in Freon-113, we found that IR signals due to ^{1}**2** and ^{3}**2** decay at equal rates and that quenching rate constants derived for a singlet band and a triplet band with reagents that could potentially react in a multiplicity-dependent fashion (e.g., methanol and oxygen) are equivalent, consistent with rapid spin equilibration of carbene **2**. More recently, Kohler, Platz, and co-workers used femtosecond absorption spectroscopy to demonstrate that singlet−triplet spin equilibration is complete within 50 ps.[12]

Distinct IR bands for singlet and triplet carbonyl carbenes (RCC(=O)R′) are expected since theoretical calculations indicate that their geometries are significantly different.[13] A very recent high-level computational analysis of carbonyl carbenes has been provided by Radom and co-workers.[14] While triplet carbonyl carbenes are planar (RCCO dihedral angles of 0°), their singlet counterparts are nonplanar with nearly orthogonal RCCO dihedral angles. This orthogonal orientation allows donation of the in-plane oxygen lone pair of the carbonyl group to the empty p orbital of the singlet carbene. In addition, this arrangement also allows the filled σ^2 orbital of the carbene to conjugate with the π system of the carbonyl group.

Estimations of singlet−triplet extinction coefficient ratios of **2** are available from the recent low-temperature study of Bally, McMahon, and co-workers, who were able to characterize independently both ^{1}**2** and ^{3}**2** by matrix IR spectroscopy.[9a] Interestingly, they observed that the two carbene spin states can

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Table 1. Measured Extinction Coefficients for Methyl 2-Naphthyl Acetate ($NpCH_2CO_2Me$) IR Bands

mode	hexane[a]	Freon-113[a]	CH_2Cl_2[a]	CH_3CN[a]
C═O str	1751 (467)	1748 (439)	1737 (418)	1739 (437)
C═C Ar str	1637 (17)	1637 (19)	1636 (21)	1636 (19)
C═C Ar str	1603 (24)	1605 (22)	1602 (30)	1603 (27)
CH_2 bend	1330 (63)	*b*	1335 (84)	1335 (67)
CH_2 bend	1300 (55)	*b*	1301 (65)	1302 (43)
CH_2 bend	1271 (110)	*b*	*b*	1271 (110)
C−O str	1258 (134)	*b*	*b*	1266 (109)
C−O−C str	1200 (134)	*b*	1202 (117)	1200 (113)
C−O str	1158 (164)	*b*	1165 (170)	1167 (160)

[a] Frequencies are reported in cm^{-1}; extinction coefficients (in parentheses) are reported in M^{-1} cm^{-1}. [b] Unavailable spectral window due to solvent absorbance.

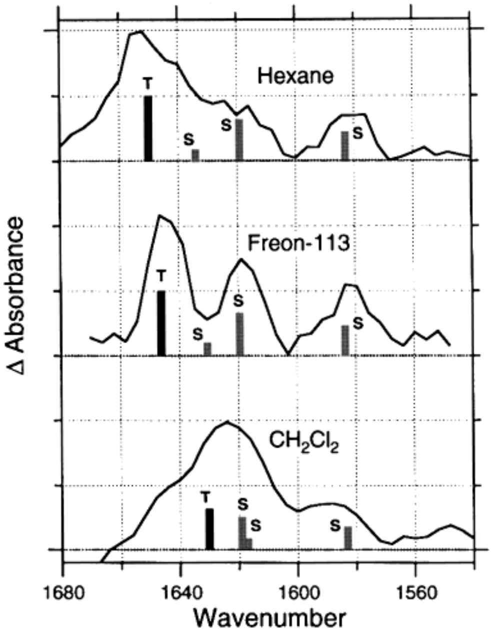

Figure 1. TRIR difference spectra observed in the 1680−1540 cm^{-1} spectral region. Data are averaged over 0−0.5 μs following 266 nm laser photolysis (5 ns, 1 mJ) of diazoester **1** (1.1 mM) in argon-saturated solvent. The bars represent our interpretation of the singlet (S) and triplet (T) carbene contribution to the observed spectrum as discussed in the text.

be interconverted photochemically and also that ^{1}**2** thermally relaxes only to ^{3}**2** over several hours at 12 K in an argon matrix. Thus, the intensity ratio of a final ^{3}**2** IR band to an initial ^{1}**2** IR band, following thermal relaxation, reflects the ratio of their extinction coefficients. Of course, for our analysis to be valid in solution, we have to assume that the relevant extinction coefficients of ^{1}**2** and ^{3}**2** do not vary with solvent. To address this concern, we have examined the FTIR spectrum of the parent methyl 2-naphthyl acetate ($NpCH_2CO_2Me$) as a function of solvent. As shown in Table 1, extinction coefficients for all major IR bands in the region 1100−1800 cm^{-1} are reasonably constant with most deviating from the average by less than 10%. This potential variation has been considered in estimating errors for our experimentally measured equilibrium constants, discussed below.

We have examined carbene **2** by TRIR spectroscopy in hexane, Freon-113, dichloromethane, and acetonitrile solutions. Data observed following 266 nm laser excitation of **1** in argon-saturated solutions are shown in Figure 1 for the 1680−1540 cm^{-1} spectral region. (TRIR data in acetonitrile are not displayed for this spectral region since analysis is complicated by a broad, overlapping carbene−acetonitrile ylide band at 1656 cm^{-1}.) The Freon-113 data are best resolved and are most easily compared with the low-temperature matrix data of Bally and McMahon,[9a] who observed a triplet carbene band at 1660 cm^{-1} (C═O stretch) and singlet carbene bands at 1640 (C═O stretch), 1625 (aromatic C═C stretch), and 1590 cm^{-1} (aromatic C═C stretch). The matrix-derived extinction coefficient ratios of the singlet bands are 0.5:1.4:1.0 (ϵ_{1640}:ϵ_{1625}:ϵ_{1590}). On the basis of these observations, we have previously assigned the TRIR band detected at 1650 cm^{-1} to the carbonyl stretch of ^{3}**2** and those detected at 1620 and 1584 cm^{-1} to aromatic C═C stretches of ^{1}**2**. The 1640 cm^{-1} matrix band is not resolved in our TRIR experiments as a result of its low intensity and the relative broadness of solution IR bands. We assume that this singlet carbonyl band appears near 1630 cm^{-1} in Freon-113 with an intensity approximated from the matrix-derived intensity ratios of the singlet carbene bands as indicated in Figure 1.

The 1650 cm^{-1} band of ^{3}**2** and the 1584 cm^{-1} band of ^{1}**2** were used to evaluate ΔG_{ST} in Freon-113 solution (Table 2). The low-temperature, matrix-determined ratio (^{3}**2**/^{1}**2**) for these signals is approximately 1.5; the Freon-113 solution, TRIR-determined ratio at 294 K is 2.1. These values lead to an equilibrium constant of 1.4 ± 0.2 at 294 K and $\Delta G_{ST} = 0.2 \pm 0.1$ kcal/mol. (A positive value indicates that the triplet carbene is lower in energy.) An analogous treatment in hexane leads to a ΔG_{ST} value of 0.3 ± 0.09 kcal/mol.

Analysis in the 1680−1540 cm^{-1} spectral region becomes more complicated in polar solvent. As expected (e.g., Table 1), carbonyl bands shift to lower frequency with increasing solvent polarity, while aromatic bands are unaffected. In dichloromethane (and acetonitrile), the triplet carbonyl band (at 1650 cm^{-1} in Freon-113) shifts down to overlap with the singlet aromatic stretch at 1620 cm^{-1}. As indicated in Figure 1, we have assumed that both the triplet and singlet carbonyl bands shift in dichloromethane from their Freon-113 values by an amount equal to that observed for the carbonyl band of methyl 2-naphthyl acetate (11 cm^{-1}, Table 1). (Similarly, these bands were assumed to shift to higher frequency by 3 cm^{-1} when solvent was changed from Freon-113 to hexane.) These shifts are fairly consistent with B3LYP/6-31G* calculations using the PCM solvation model (Table 3). Thus, the broad peak observed at 1624 cm^{-1} in dichloromethane is believed to be made up of three peaks—the singlet and triplet carbonyl bands and a singlet aromatic C═C stretch. We have estimated the portion of this peak that is due to singlet carbene signals using the intensity of the observed 1584 cm^{-1} band and the matrix-derived intensity ratios for the singlet peaks. The remaining portion of the 1624 cm^{-1} band is assumed to be due to the triplet carbonyl, which is then compared with the intensity of the singlet 1584 cm^{-1} band to give the estimated ΔG_{ST} shown in Table 2.

Complications of shifting bands are avoided in the 1260−1140 cm^{-1} spectral range, where several distinguishable singlet and triplet carbene IR bands are also observed in Bally and McMahon's matrix experiments.[9a] Due to solvent broadening and the spectral resolution at which our TRIR data are collected (16 cm^{-1}), we observe only two major IR bands (1216 and 1170 cm^{-1}) in this spectral region (Figure 2). (TRIR data in Freon-113 are not displayed for this spectral region due to interference from strong solvent IR bands.) On the basis of the matrix IR data, we have assigned the 1216 cm^{-1} band to mainly ^{3}**2** (81%

Table 2. Experimental Thermochemical Parameters for 2-Naphthyl(carbomethoxy)carbene (**2**) Derived in Two Spectral Regions

		1680–1540 cm^{-1}				1260–1140 cm^{-1}		
solvent	T (K)	ΔG_{ST} (kcal/mol)	ΔH_{ST} (kcal/mol)	ΔS_{ST} (cal/mol·K)	T (K)	ΔG_{ST} (kcal/mol)	ΔH_{ST} (kcal/mol)	ΔS_{ST} (cal/mol·K)
hexane	294	0.3 ± 0.09	0.8 ± 0.3	1.5 ± 1.3	294	0.4 ± 0.1	*a*	*a*
	233	0.4 ± 0.1				*a*		
Freon-113	294	0.2 ± 0.1	0.7 ± 0.8	1.7 ± 3.0		*b*	*b*	*b*
	262	0.3 ± 0.1						
CH_2Cl_2	294	0.1 ± 0.1	0.2 ± 0.6	−0.3 ± 2.4	294	−0.06 ± 0.1	−0.2 ± 0.7	−0.5 ± 2.7
	243	0.1 ± 0.1			238	−0.09 ± 0.07		
CH_3CN		*c*	*c*	*c*	294	−0.2 ± 0.08	−0.4 ± 0.6	−1.5 ± 2.5
					253	−0.3 ± 0.07		

[a] Lower temperature data complicated by low signal intensity. [b] Unavailable spectral window due to solvent absorbance. [c] Analysis complicated by overlap with IR bands due to a carbene−acetonitrile ylide.

Table 3. Selected Low-Temperature Matrix and Calculated IR Bands (cm^{-1}) of 2-Naphthyl(carbomethoxy)carbene

mode	matrix	gas phase[a]	heptane[a]	Freon-113[a]	CH_2Cl_2[a]	CH_3CN[a]
			Singlet Carbene			
C═O str	1642	1626	1624	1623	1619	1620
C═C Ar str	1625	1607	1609	1609	1607	1606
C═C Ar str	1590	1580	1581	1587	1581	1580
C−O str	1250	1230	1230	1229	1229	1228
C−O str	1218	1202	1204	1204	1203	1202
O−CH_3 wag	1184	1168	1167	1166	1165	1164
C−O str	1179	1160	1160	1159	1157	1155
Ar CH bend	1174	1144	1146	1146	1146	1146
			Triplet Carbene			
C═O str	1660	1633	1630	1630	1625	1623
C−O str	1238	1229	1230	1229	1229	1228
C−O str	1214	1197	1197	1196	1205	1196
O−CH_3 wag	1208	1180	1180	1180		1185
O−C−O str	1194	1166	1167	1166	1167	1167

[a] B3LYP/6-31G* using the PCM solvation model, scaled by 0.96.

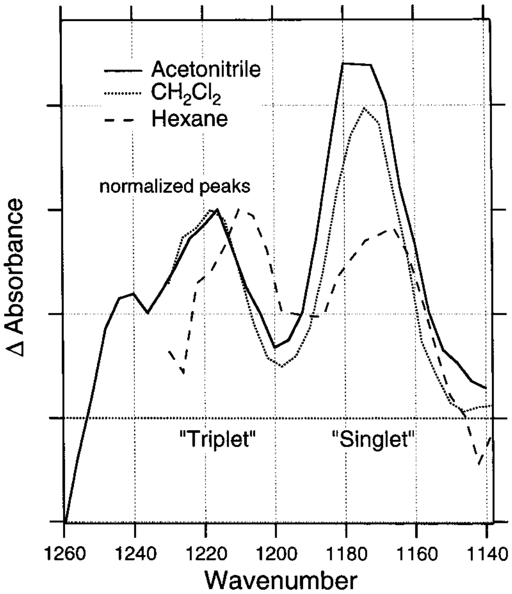

Figure 2. TRIR difference spectra observed in the 1260−1140 cm^{-1} spectral region. Data are averaged over 0−0.5 μs following 266 nm laser photolysis (5 ns, 1 mJ) of diazoester **1** (1.1 mM) in argon-saturated solvent.

triplet, 19% singlet) and the 1170 cm^{-1} band to mainly ^{1}**2** (20% triplet, 80% singlet). Calculations indicate that these bands correspond to vibrational modes involving stretching of the C−O single bond.

Figure 2 clearly shows that the population of ^{1}**2** increases in more polar solvent. To derive ΔG_{ST} values in each solvent, we again rely on the matrix IR data[9a] to estimate extinction coefficient ratios for the singlet and triplet contribution to the 1216 and 1170 cm^{-1} TRIR signals. These ratios (ϵ_{1216-S}:ϵ_{1216-T}:ϵ_{1170-S}:ϵ_{1170-T} = 1.0:4.3:5.9:1.5) lead to the derived ΔG_{ST} values in hexane, dichloromethane, and acetonitrile that are shown in Table 2. The values for hexane and dichloromethane compare reasonably well with those derived from the 1680−1540 cm^{-1} TRIR data of Figure 1. As was the case for diphenylcarbene,[6] our derived values of ΔG_{ST} for **2** correlate very well with the solvent polarity parameter $E_T(30)$ (Figure 3).[15] That there is such a good correlation of ΔG_{ST} with solvent polarity suggests specific carbene−solvent complexes, as have been postulated for other systems,[16] do not play a significant role in determining carbene stability for the solvents examined in the present investigation.[17]

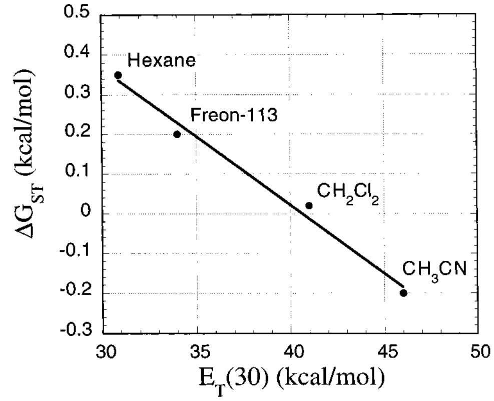

Figure 3. Plot of experimentally derived ΔG_{ST} at 294 K as a function of solvent polarity parameter $E_T(30)$. When possible, the average of the ΔG_{ST} values derived in the 1680−1540 and 1260−1140 cm^{-1} spectral regions is used.

Variable-temperature TRIR experiments allow investigation of the enthalpy (ΔH_{ST}) and entropy (ΔS_{ST}) differences between ^{1}**2** and ^{3}**2**. Solvent freezing point and flow cell limitations restrict the available temperature range (ca. 60 °C) for these experiments. Thus, the values for ΔH_{ST} and ΔS_{ST} derived for **2** in hexane, Freon-113, dichloromethane, and acetonitrile are reported (Table 2) with a fair amount of error.[18] Despite these

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(17) We intend to extend our investigations to benzene and related solvents to determine if carbene−aromatic solvent complexes[16] influence the singlet−triplet energy gap for **2**.

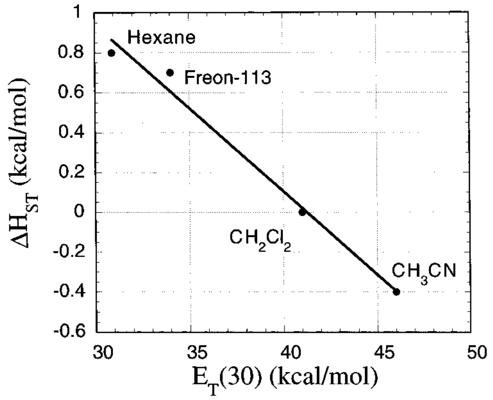

Figure 4. Plot of experimentally derived ΔH_{ST} as a function of solvent polarity parameter $E_T(30)$. When possible, the average of the ΔH_{ST} values derived in the 1680−1540 and 1260−1140 cm^{-1} spectral regions is used.

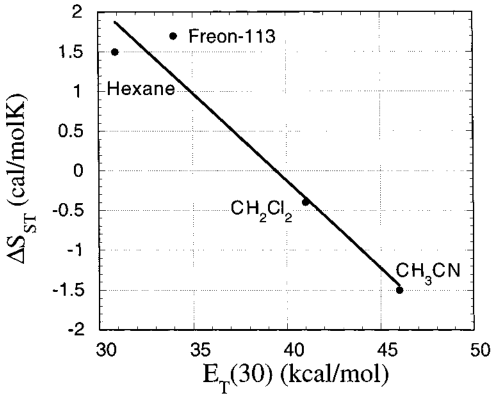

Figure 5. Plot of experimentally derived ΔS_{ST} as a function of solvent polarity parameter $E_T(30)$. When possible, the average of the ΔS_{ST} values derived in the 1680−1540 and 1260−1140 cm^{-1} spectral regions is used.

errors, however, the experimental trends for the enthalpy and entropy differences between the singlet and triplet carbenes are clear and also correlate quite well with $E_T(30)$ values (Figures 4 and 5).[15,19]

Our experiments suggest that ^{3}**2** is favored enthalpically in hexane, but that ^{1}**2** is favored in acetonitrile. These results are in good agreement with calculations using the PCM solvation model at the B3LYP/6-311+G**//B3LYP/6-31G* level (Tables 4 and 5). There is a large basis set effect on the relative energies, but Table 5 demonstrates that single-point energy evaluations at the B3LYP/6-311+G**//B3LYP/6-31G* level provide results similar to full geometry optimizations at the B3LYP/6-311+G** level. The calculations indicate that $\Delta H_{ST} = 1.4$ kcal/mol in heptane (triplet state being lower in energy), but $\Delta H_{ST} = -0.6$ kcal/mol in acetonitrile (singlet state being lower in energy). Relative to our experimental values, the B3LYP calculations seem to overestimate the stability of the triplet carbene by approximately 0.6 kcal/mol, although there is still a good correlation with $E_T(30)$ values (Supporting Information).[20] Such overestimations of triplet carbene stability by density functional theory methods have been noted previously.[14,21] As shown in Table 4, the difference in calculated dipole moment between ^{1}**2** and ^{3}**2** ($\Delta\mu_{ST}$) increases with solvent polarity. This increase is mainly due to solvent effects on the singlet carbene's dipole moment and results in preferential stabilization of the singlet carbene in polar solvents.

The experimental ΔS_{ST} values (Table 2 and Figure 4) suggest that ^{1}**2** is favored entropically in hexane, but that ^{3}**2** is favored in acetonitrile, opposite to the enthalpic trend noted above. (The enthalpic contribution to the total free energy, however, is greater and ΔG_{ST} is negative (singlet state being more stable) in a polar solvent.) Entropic differences between ^{1}**2** and ^{3}**2** in general can originate from (1) differences in the molecular contribution (S_{mol}) and (2) differences in solvent organization contribution (S_{solv}) to the total entropy. The molecular contribution to the total entropy for the singlet or triplet carbene can be derived from statistical mechanics and is given by

$$S_{mol} = S_{trans} + S_{rot} + S_{vib} + S_{elec} - nR[\ln(nN_0) - 1] \quad (2)$$

where S_{trans}, S_{rot}, S_{vib}, and S_{elec} are the translational, rotational, vibrational, and electronic contributions, respectively, n = number of moles, R = gas constant, and N_0 = Avogadro's number.[22] Differences in S_{mol} between ^{1}**2** and ^{3}**2** are expected to arise mainly from differences in S_{vib} and S_{elec}. The difference in electronic contribution (R ln 3, 2.2 cal/mol·K) is, of course, due to the difference in spin multiplicity as previously discussed. Differences in S_{vib}, which is defined in eq 3

$$S_{vib} = nR\sum_i [\mu_i(e^{\mu_i} - 1)^{-1} - \ln(1 - e^{-\mu_i})] \quad (3)$$

(where ν_i = vibrational frequencies, k = Boltzmann's constant, and T = temperature; $\mu_i = h\nu_i/kT$), arise from bonding differences between ^{1}**2** and ^{3}**2**. Note that low-frequency vibrations have the largest effect on S_{vib}. Differences in solvent organization (S_{solv}) for ^{1}**2** and ^{3}**2** are expected due to their dissimilar dipole moments. Solvation of the more polar singlet carbene will be more ordered in polar solvents, resulting in an unfavorable solvent contribution to the total entropy of ^{1}**2** relative to ^{3}**2**.

Based on the above discussion, we expect that the contribution to experimentally observed ΔS_{ST} values will be negative from the S_{solv} and S_{elec} differences (triplet carbene being entropically favored). The ΔS_{ST} value being greater than zero in nonpolar solvents indicates that the contribution from the S_{vib} difference is positive and greater than the sum of the S_{solv} and S_{elec} differences in nonpolar solvent. Since the S_{elec} difference is constant, the negative ΔS_{ST} value observed in polar solvents indicates that the contribution from the S_{solv} difference now outweighs that from S_{vib}. This observation is consistent with the increased difference in dipole moment between ^{1}**2** and ^{3}**2** in polar solvent. Thus, our results suggest that both solvent and geometrical effects on the entropic difference between singlet and triplet carbenes should be considered when assessing energetic differences between carbene spin states.

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(18) Errors in ΔG_{ST}, ΔH_{ST}, and ΔS_{ST} are directly related to errors in measured equilibrium constants. Contributions to equilibrium constant errors include uncertainty in the measurements themselves (calculated as the standard deviation from three separate measurements, ±2−4%), error in extinction coefficient ratios (±5−10%), and error due to overlapping bands (±0−5%).

(19) Although solvent dielectric constant does increase with increasing temperature, the temperature ranges examined in this study lead to changes that are small enough such that the Onsager function is essentially constant.

(20) Correlation with the Onsager function, however, is not as good−see Supporting Information.

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Table 4. Calculated Geometry, Dipole Moment, and Thermochemical Parameters of 2-Naphthyl(carbomethoxy)carbene (**2**)

		singlet[a]		triplet[a]					
	ϵ	dihedral angle (C–C–C═O)	carbene angle (C–C–C)	dihedral angle (C–C–C═O)	carbene angle (C–C–C)	$\Delta\mu_{ST}$ (D)[b,c]	ΔG_{ST}[b] (kcal/mol)	ΔH_{ST}[b] (kcal/mol)	ΔS_{ST}[b] (cal/mol·K)
gas	1.0	83.3	120.6	0.003	135.0	3.8	2.3	2.2	−0.3
heptane	1.9	83.9	121.1	−0.30	135.3	4.3	0.9	1.4	1.7
benzene	2.2	84.6	121.0	−0.18	135.3	4.4	2.1	1.1	−3.3
Freon-113[d]	2.4	84.2	121.0	−0.03	135.4	4.4	2.2	1.3	−2.9
CH_2Cl_2	8.9	85.4	121.5	−0.22	135.6	5.0	−1.1	0.5	5.2
MeOH	32.6	86.7	122.0	0.36	135.7	5.3	−1.7	−2.0	−1.2
CH_3CN	36.6	87.1	121.6	0.62	135.5	5.3	−0.7	−0.6	0.3

[a] B3LYP/6-31G* geometry with the PCM solvation model. [b] B3LYP/6-311+G**//B3LYP/6-31G* level using the PCM solvation model and corrected to 298 K. [c] Individual dipole moments are given as Supporting Information. [d] The Freon-113 calculations are somewhat suspect as both ^{1}**2** and ^{3}**2** structures had one small ($<60i$ cm^{-1}) imaginary vibrational frequency at the B3LYP/6-31G* level. All attempts to obtain a true minimum with the PCM method in Gaussian98 were unsuccessful, even with analytical (numerical) second derivatives. The thermal and entropic corrections (which depend on the $3N - 6$ vibrational frequencies) are, therefore, suspect.

Table 5. Calculated Singlet/Triplet Energy Gaps (kcal/mol) for 2-Naphthyl(carbomethoxy)carbene (**2**)

	B3LYP/6-31G*//B3LYP/6-31G* [a]			B3LYP/6-311+G**//B3LYP/6-31G* [a]			B3LYP/6-311+G**//B3LYP/6-311+G** [b]
medium	ΔH_{ST} (0 K)	ΔH_{ST} (298 K)	ΔG_{ST} (298 K)	ΔH_{ST} (0 K)	ΔH_{ST} (298 K)	ΔG_{ST} (298 K)	ΔH_{ST} (0 K)
gas ($\epsilon = 1$)	4.6	4.7	4.8	2.1	2.2	2.3	1.9
heptane ($\epsilon = 1.9$)	3.9	4.1	3.6	1.2	1.4	0.9	
benzene ($\epsilon = 2.2$)	3.8	3.9	4.9	1.0	1.1	2.1	
Freon-113 ($\epsilon = 2.2$)[c]	4.1	4.1	5.0	1.4	1.3	2.2	
CH_2Cl_2 ($\epsilon = 8.9$)	2.8	3.5	1.9	−0.2	0.5	−1.1	
methanol ($\epsilon = 32.6$)	1.0	1.0	1.4	−2.1	−2.0	−1.7	
CH_3CN ($\epsilon = 36.6$)	2.3	2.5	2.4	−0.8	−0.6	−0.7	−0.8

[a] Using the scaled B3LYP/6-31G* zero-point vibrational energy (and thermal and entropic corrections as appropriate). A positive ΔE_{ST} indicates that the triplet state is more stable. [b] Fully optimized geometry at the B3LYP/6-311+G** level, but the scaled ZPE correction was taken from the B3LYP/6-31G* vibrational frequency analysis. [c] The Freon-113 solvent was modeled as CCl_4 with the PCM method in Gaussian98.

Unfortunately, the theoretically derived entropies are not very insightful (Table 4) as the PCM method does not have analytical second derivatives and obtaining numerical convergence on the convergence criteria with PCM inclusion was very challenging. Furthermore, the smaller vibrational frequencies contribute the most to the calculated entropy, and these low-energy motions are the most difficult ones to calculate accurately. In addition, the calculated entropies include only effects due to the solute, and do not include any explicit changes in solvent organization. As noted above, however, the trends in calculated ΔH_{ST} are consistent with the experimental results.

Conclusions

The solvent dependence of the singlet−triplet energy gap of **2** has been examined by TRIR and computational methods. The ground state of **2** changes from the triplet state in hexane to the singlet state in acetonitrile. The magnitude of the observed solvent effect (approximately 1 kcal/mol) is comparable to that observed experimentally[6] and computationally[14] for other carbene systems. Preferential stabilization of the singlet carbene is the result of its increased dipole moment in polar solvents. Variable-temperature TRIR experiments provide measurements of ΔH_{ST} and ΔS_{ST} and suggest that solvent and geometrical effects on the entropy of singlet and triplet carbenes can offset entropic differences arising from spin multiplicity.

Calculations at the PCM level reproduce the general trends for ΔH_{ST} seen experimentally; however, the calculated ΔS_{ST} trends are quite scattered due to the poor calculation of low-energy motions which have the greatest contribution to ΔS_{ST}. The calculated (enthalpic) singlet−triplet energy gaps are also overestimated by the B3LYP calculations, but the trends are consistent between experiment and theory. Trends in the solvent dependence of vibrational frequencies and intensities were essential in the practical determination of the singlet−triplet energy gap by TRIR measurements due to overlapping singlet and triplet IR bands.

The synergistic interplay of experiment and theory has provided insight into the role of solvent on the singlet−triplet energy gap of 2-naphthyl(carbomethoxy)carbene. Further application of these techniques to other carbenes will be reported in due course.

Experimental Section

General Methods. Unless otherwise noted, materials were obtained from Aldrich Chemical Co. and used without further purification. Acetonitrile and dichloromethane were distilled from CaH_2 before use. Hexane and Freon-113 were dried by passage through a neutral alumina column and stored under argon. IR spectra were recorded on a Bruker IFS-55 Fourier transform IR spectrometer at 4 cm^{-1} resolution. Methyl 2-diazo-(2-naphthyl)acetate was prepared by the diazo transfer method[23] as described previously.[9b]

Time-Resolved IR Methods. We conducted TRIR experiments following the method of Hamaguchi and co-workers[24] as described previously.[9b] Variable-temperature TRIR experiments were carried out with a flow cell that allowed the solution temperature to be monitored at both the inlet and outlet of the flow cell. The two readings typically varied by 0−3 °C; reported temperatures are the average of the two readings.

Computational Methods. All geometry optimization and vibrational frequency calculations were completed with Gaussian98.[25] In most cases, the B3LYP/6-31G* level was used for geometry optimizations,

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and single-point energy evaluations were conducted at the B3LYP/6-311+G** level utilizing the B3LYP/6-31G* geometries.[10,22b] However, in a few cases, the B3LYP/6-311+G** level was used for the geometry optimization as well in order to compare the single-point energies to the fully relaxed energies with the 6-311+G** basis set. Six Cartesian *d* functions were used with all basis sets.

The triplet states at the B3LYP level had very minimal spin contamination as $<S^2>$ values were typically between 2.0 and 2.05. However, MP2/6-311+G** single-point energy calculations for the triplet states had terrible spin contamination ($<S^2> \sim 3.2$), and led to a very large overestimation of the singlet−triplet energy gap ($\Delta H_{ST} \sim -7$ kcal/mol). Calculations based on unrestricted Hartree−Fock theory were, therefore, considered to be unacceptable for comparison to the non-spin-contaminated B3LYP values, and were not pursued further.

All stationary points, in the gas phase and with the continuum dielectric model, were verified to be minima from the vibrational frequency calculations, by possessing only real vibrational frequencies. For the gas-phase calculations, analytical second derivatives were used, but the PCM vibrational frequency calculations required numerical differentiation of the analytical first derivative. The calculated zero-point vibrational energies were scaled by 0.9806.[26] Thermal and entropic corrections to the bottom-of-the-well energy were performed with Gaussian98 using the unscaled vibrational frequencies.

All of the calculations at the PCM level utilized the default parameters for each solvent as implemented in Gaussian98, but the Freon-113 calculations (reported here) were modeled as CCl_4 solvent. The numerical PCM second derivatives were expensive computationally, and in the Freon-113 case, they were problematic. All four convergence criteria for the vibrational frequency calculations could not be completely achieved for the singlet and triplet states of **2** at the PCM level with Freon-113 due to numerical instabilities in the optimization sequence, despite utilizing numerically derived second derivatives (force constants) for the optimization.

Acknowledgment. We gratefully thank the National Science Foundation (CHE-9733052 to J.P.T. and CHE-9733457 to C.M.H.) for financial support and the Ohio Supercomputer Center for computational resources (C.M.H.). J.P.T. also acknowledges a Camille Dreyfus Teacher−Scholar Award and an Alfred P. Sloan Research Fellowship.

Supporting Information Available: Tables containing the optimized Cartesian coordinates, harmonic frequencies and intensities, and dipole moments discussed in this study. Plots of experimental ΔG_{ST}, ΔH_{ST}, and ΔS_{ST} values vs the Onsager function and calculated ΔG_{ST}, ΔH_{ST}, and ΔS_{ST} values vs both $E_T(30)$ values and the Onsager function. (PDF) This material is available free of charge via the Internet at http://pubs.acs.org.

JA012139V

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