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A Search for Carbene–Solvent Interactions Using Time-Resolved Infrared Spectroscopy

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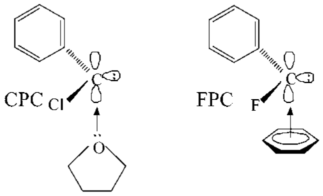
ABSTRACT

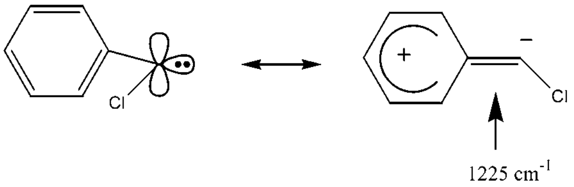


The time-resolved infrared (TRIR) spectra of chlorophenylcarbene (CPC) and fluorophenylcarbene (FPC) were recorded in heptane at ambient temperature. The C–C and C–F vibrational frequencies involving the carbene carbon were obtained in heptane, benzene, and acetonitrile and in heptane containing 0. 1M tetrahydrofuran or benzene. It is concluded that carbene–solvent interactions of CPC and FPC are quite weak.

Singlet carbenes have a zwitterionic character,[1] which has led chemists to consider the possibility of their specific solvation as shown in the abstract for chlorophenylcarbene (CPC) and tetrahydrofuran and flurophenylcarbene (FPC) and benzene. Tomioka and co-workers reported the effect of dioxane on carbene selectivity.[2] In recent years, Khan and Goodman concluded that singlet methylene forms a charge-transfer complex with benzene.[3] Ruck and Jones[4] discovered dramatic solvent effects on the distribution of rearrangement products formed from *tert*-butylcarbene and Moss, Yan, and Krogh-Jesperson[5] discovered experimental and computational evidence in favor of halocarbene−benzene complexes.

The matrix IR spectrum of CPC is known and has been analyzed by Sheridan and co-workers.[6] In argon, CPC has prominent vibrational bands at 1590, 1225, 1170, and 848 cm^{-1}. The vibrational frequencies of CPC are well-simulated using density functional theory (DFT) calculations, which indicate that the 1225 cm^{-1} band largely involves stretching of the partial double bond between the carbene carbon and aromatic ring[6,7] (Scheme 1). The band at 1170 cm^{-1} is assigned to bending of aromatic ring hydrogens on the basis of the DFT calculations. Intuition suggests that electron pair

Scheme 1. Carbene Electron Delocalization



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donation from a coordinating solvent, such as THF, acetonitrile, or benzene into the empty p orbital of CPC will reduce the partial double bond character to the carbene center. This argument predicts that solvation will shift the vibrational frequency to a lower value.

Thus, chlorophenyl diazirine[8] was pulsed with 355 nm radiation[9] and the time-resolved infrared (TRIR) spectrum[10] of the carbene was recorded at ambient temperature as a function of solvent. TRIR spectra were recorded in neat heptane, acetonitrile, and benzene and in heptane containing 0.1 M benzene or 0.1 M THF. Figure 1 shows that at a modest ligand concentration (0.l M) there is little effect on the carbene bands. Dramatic changes in the TRIR spectra were not observed in neat solvent either.

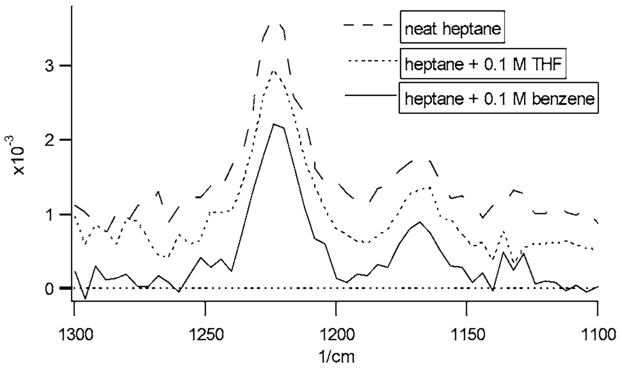

Figure 1. Time-resolved IR spectra for chlorophenylcarbene. The spectra were recorded over a window of 1000 ns, 50 ns after the laser pulse. (Dashed line spectra are offset on the *y*-axis.)

The effect of a fluorine substituent was also examined. Fluorophenylcarbene was produced by flash photolysis of fluorophenyl diazirine.[11] FPC has the analogous C−C vibration in heptane at 1220 cm^{-1}, but additionally, a C−F vibration at 1108 cm^{-1} (Figure 2). DFT calculations[12,13] (Table 1) predict that the C−F bands of the carbene and precursor will be observed at 1102 and 1163 cm^{-1}, respectively. Benzene and acetonitrile slightly shift and broaden the carbene bands (Figure 2). However, the C−F vibration of the diazirine precursor also shifts slightly in these solvents, suggesting that a bulk solvent effect rather than complexation is responsible.

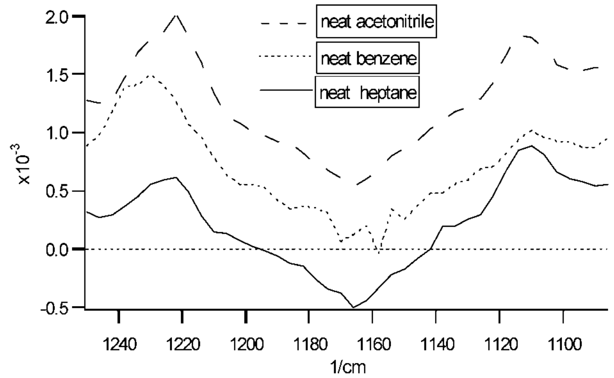

Figure 2. Time-resolved IR spectra for fluorophenylcarbene. The spectra were recorded over a window of 1000 ns, 50 ns after the laser pulse. (Dashed line spectra are offset on the *y*-axis.)

Table 1. Experimental and DFT Calculations for FCP and Its Precursor (B3LYP/6-31G*; scaled)

compound	expt (cm^{-1})	calcd (cm^{-1})	vibration
$FC(N_2)Ph$	1165	1163	[C−F]
FCP	1220−1230	1199	[Ph−C]
FCP	1110	1102	[C−F]

Thus, there is no compelling evidence by TRIR spectroscopy of specific solute−solvent interactions of CPC and FPC using either low or high concentrations of potential ligands. Specific solvation of nucleophiles by hydrogen bonding is evident in the reduction of rate of S_N2 reactions in aprotic solvents upon addition of water.[14] Previously, Celebi, Tsao, and Platz[15] demonstrated that chelating solvents have little influence on the reactivity of CPC and chloro-*p*-nitrophenylcarbene (CNP) with tetramethylethene (TME). Inspection of Table 2 reveals that chelating solvents have little influence on the absolute reactivity of FPC with TME. Together with the TRIR data, these observations argue against strong

Table 2. Absolute Rate Constants of Selected Arylhalocarbenes with Tetramethylethene (k_{TME}) as a Function of Solvent

	k_{TME} ($\times$ 10^8 M^{-1} s^{-1})		
solvent	FPC	CPC[15]	CNP[15]
acetonitrile	1.0		11
tetrahydrofuran	0.8	0.71	7.4
ethyl acetate		0.89	
anisole		1.3	
benzene	1.3	0.99	12
isooctane	1.6	2.8	
pentane	2.2	2	
Freon-113		1.8	12

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carbene−solvent interactions of CPC and FPC. It is possible that the aryl halo carbenes are so well-stabilized that these carbenes have particularly weak interactions with solvent. Thus, we are extending the TRIR method to more electron-demanding carbenes.

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