Laser Flash Photolysis Studies of the Reaction of Arylhalocarbenes with Tetramethylethylene as a Function of Solvent

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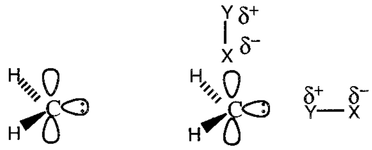
Absolute rate constants of reaction of chlorophenylcarbene, bromophenylcarbene, and chloro-*p*-nitrophenylcarbene with tetramethylethylene (TME; k_{TME}) are similar in alkane solvent, Freon-113, benzene, tetrahydrofuran, and acetonitrile. Solvation of the carbenes has little influence on k_{TME}. Strong specific solvation which impedes cycloaddition reactions of the arylhalocarbenes with TME is not found with these carbenes, but the existence of weakly bound complexes with spectra and kinetics similar to those of free carbenes cannot be ruled out.

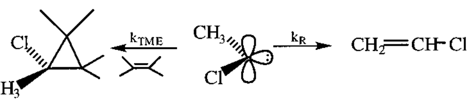
I. Introduction

Singlet carbenes contain a filled, in plane, orbital and an empty, out of plane, pure p orbital.[1] Because of their zwitterionic character, chemists have long wondered whether singlet carbenes might be specifically solvated by a dipolar solvent (X−Y) or by a polarizable substrate such as benzene. Using photoacoustic calorimetry, Khan and Goodman deduced that singlet methylene reacts with benzene to form a charge-transfer complex which has a dissociation energy of 8.7 kcal/mol. RHF/6-31G* calculations and electron correlation provided support for the existence of the methylene−benzene complex.[2]

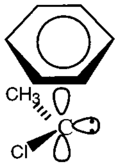


Two recent reports add urgency to these considerations. Ruck and Jones have reported dramatic solvent effects on the distribution of rearrangement products formed from *tert*-butylcarbene. It is not certain whether these are due to solvent effects on carbene reactions or whether the products derive from carbene−solvent ylides.[3]

Moss, Yan, and Krogh-Jespersen discovered that the ratio of rearrangement products to bimolecular cycloaddition products of alkylchlorocarbenes is sensitive to solvent.[4]



In aromatic solvents the ratio of k_R/k_{TME} increases relative to that in isooctane solvent because complexation to benzene, as pictured for **1,** shields the carbene center from the alkene nucleophile and further lowers its reactivity by donating electrons to the empty p-orbital of the carbene.



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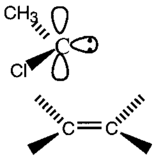
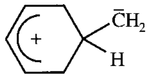
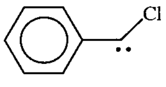


2

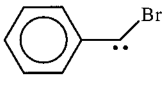
Carbene−alkene complexes (e.g., **2**) have been invoked[5] to explain certain kinetic anomalies, but other explanations of these phenomena have also been advanced.[6,7] Calculations on carbene−alkene π complexes[6] (e.g., **2**) consistently predict that these species are not minima and that they collapse immediately to form cyclopropanes. On the other hand, recent calculations find that chlorocarbene−benzene and dibenzene π complexes are minima[4] which should have finite lifetimes and thus can, in principle, be directly observable. Calculations do not find support for the intermediacy of a σ-type complex.[8]



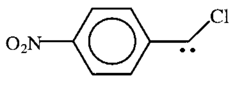
These reports provided motivation for this study of the kinetics of reaction of chlorophenylcarbene (CPC), bromophenylcarbene (BPC), and chloro-*p*-nitrophenylcarbene (CNP) with tetramethylethylene (TME) in aromatic solvents and strongly coordinating solvents. The effect of solvent on the absolute rate constant of cycloaddition with TME has been found to be minimal with these carbenes.



CPC



BPC



CNP

II. Experimental Section

Diazirine precursors to CPC, BPC, and CNP were prepared as described.[9] The laser flash photolysis spectrometer utilizes a pulse from a Lumonics excimer laser (351 nm, 35 mJ, 17 ns) and has been described in detail elsewhere.[10]

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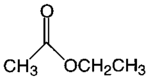
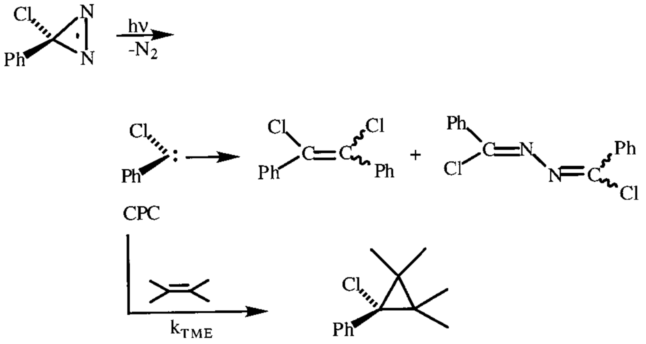
TABLE 1: Values of k_{TME} of CPC Measured at Ambient Temperature as a Function of Solvent

Solvent	k_{TME}($M^{-1}s^{-1}$)	k_{TME}(pentane) / k_{TME} (solvent)
C_5H_{12}	2.0×10^8	1.0
$CF_2ClCFCl_2$	1.8×10^8	1.1
C_6H_6	9.9×10^7	2.0
C_6H_5–OCH_3	1.3×10^8	1.6
	8.9×10^7	2.3
	7.1×10^7	2.9

Protocols for Laser Flash Photolysis (LFP) Measurements. Stock solutions of the diazirine precursors to chlorophenylcarbene, bromophenylcarbene, and chloro-*p*-nitrophenylcarbenewere prepared in dry spectroscopic grade solvents to an optical density (OD) of about 0.4 at 351 nm. LFP studies were performed with a 351 nm XeF laser. Transient absorption spectra were recorded using an EG & G Princeton Applied Research model 1460 optical multichannel analyzer (OMA). In all OMA and kinetic measurement studies, 2 mL of the stock solutions was placed in quartz cells, degassed with oxygen-free argon for approximately 2 min, and irradiated at ambient temperature. The rates of decay of the carbenes were monitored at either 318 or 322 nm.

III. Results

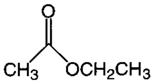
Chlorophenylcarbene, generated by photolysis of chlorophenyldiazirine, has been studied extensively.[11,12] LFP of the diazirine precursor efficiently produces the carbene with λ_{max} = 318 nm. The absorption maximum shows little variation with solvent, which is not surprising considering it is basically a $\pi\pi^*$ transition.[13] The carbene has a lifetime (τ) of many microseconds in hydrocarbon solvents, which is controlled by dimerization and reaction with precursor to form azine.[11,12]



The lifetime (τ) of CPC is decreased in the presence of tetramethylethylene (TME). Plots of 1/τ versus [TME] are linear with slope equal to k_{TME}.[11,12]

Using standard methodology, we have measured values of k_{TME} of CPC at ambient temperature. The data, presented in Table 1, are very similar to those first reported by Moss and Turro[11] and Scaiano et al.[12] Solvent effects are small. There are no data which compel us to invoke complexes such as **1** to explain the data. If specific solvation exists, one expects by the reactivity selectivity principle that k_{TME} in anisole would be much smaller than that measured in benzene. The opposite trend is observed, however! The carbene lifetime in benzene is long (μs) and comparable to that in alkane solvent. Thus, there is neither kinetic nor spectroscopic evidence which compels us to invoke a reaction of CPC with benzene to form a charge-transfer complex at ambient temperature. Of course, we cannot rule out the possibility that such a complex is formed and has properties similar to those of the free carbene.

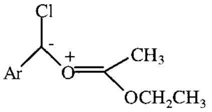
TABLE 2: Values of k_{TME} of BPC Measured at Ambient Temperature as a Function of Solvent

Solvent	k_{TME}($M^{-1}s^{-1}$)	k_{TME}(pentane) / k_{TME} (solvent)
C_5H_{12}	2.9×10^8	1
C_6H_6	1.3×10^8	2.2
C_6H_5–OCH_3	1.8×10^8	1.6
	1.4×10^8	2.1
	1.5×10^8	1.9

The effect of solvent is also modest in solvents such as tetrahydrofuran (THF) and ethyl acetate, which should be highly coordinating. Furthermore, there was no spectroscopic evidence for ylide formation in these solvents.

The conclusion is that CPC receives so much stabilization from the chlorine and aromatic substituents that π donation from the aromatic solvent is not urgently sought by the carbene. Thus, we studied BPC, expecting that bromine will afford less stabilization to the carbene than chlorine. The results, presented in Table 2, follow the same pattern as those of CPC and again provide no urgency to invoke specific solvation which will retard cycloaddition of the carbene to TME.

Chloro-*p*-nitrophenylcarbene. CNP is much more reactive than CPC or BPC.[9,14] This carbene reacts with acetone and ethyl acetate to form ylides **3** and **4** in contrast with the sluggish reactivity of CPC and BPC.[11,12] Thus, we reasoned that CNP would be more highly solvated in coordinating solvents than either CPC or BPC.



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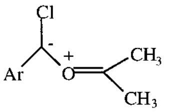

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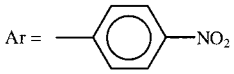


Pulsed photolysis of chloro-*p*-nitrophenyldiazirine (**D**) in $CF_2ClCFCl_2$ produces the carbene which absorbs as reported at 322 nm.[9,14] The nitrophenylcarbene, produced by LFP of **D**, reacts with TME with $k_{TME} = 1.3 \times 10^9$ M^{-1} s^{-1} in Freon-113. Values of k_{TME} (ambient temperature) were measured in hydrocarbon, benzene, and Freon-113 solution. Once again, the effect of solvent on k_{TME} is trivial (Table 3). It is true that k_{TME} in benzene is only 41% of that reported in isooctane, but it is virtually identical to the value measured in Freon-113. Again, there is no urgency to conclude that solvation of CNP is more specific in benzene than in Freon-113.

TABLE 3: Absolute Rate Constants of Reaction of Chloro-*p*-nitrophenylcarbene as a Function of Solvent, Monitored at 322 nm, at Ambient Temperature

solvent	k_{TME} ($M^{-1} s^{-1}$)	solvent	k_{TME} ($M^{-1} s^{-1}$)	solvent	k_{TME} ($M^{-1} s^{-1}$)
isooctane	$2.7 \times 10^{9\,a}$	$CHCl_3$	$8.7 \times 10^{8\,a}$	CH_3CN	1.1×10^9
CCl_4	$1.1 \times 10^{9\,a}$	$CF_2ClCFCl_2$	1.2×10^9	THF	7.4×10^8
CH_2Cl_2	$9.9 \times 10^{8\,a}$	C_6H_6	1.2×10^9		

[a] Reference 9b.

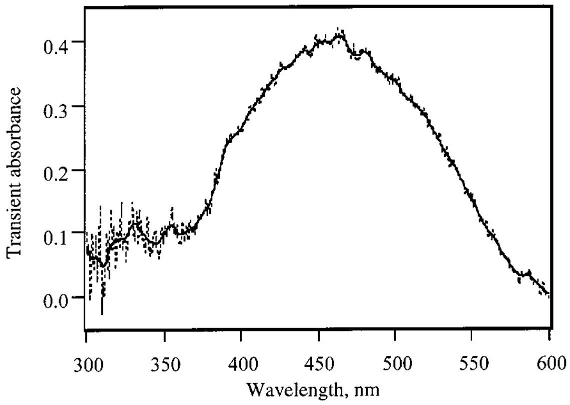
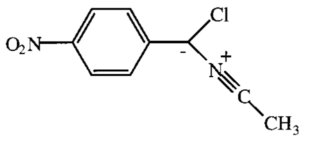


Figure 1. Transient spectrum of nitrile ylide **5** produced by LFP (351 nm) of diazirine **D** in acetonitrile at ambient temperature.

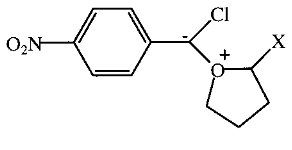
Upon LFP of diazirine **D** in acetonitrile an ylide is formed (Figure 1), attributed to **5**. The ylide is formed in an exponential



5

process with a time constant of 120 ns. It was possible to obtain k_{TME} of the carbene in acetonitrile by studying the effect of increasing TME concentration on the rate of formation of ylide **5**. As seen in Table 3, even though CNP reacts with acetonitrile to form an ylide, solvation of CNP by acetonitrile has little influence on k_{TME}.

Photolysis (350 nm) of **D** in glassy 2-methyltetrahydrofuran (2-MTHF) produces the persistent spectrum of ether ylide **6** (Figure 2). LFP of **D** in tetrahydrofuran produces the transient spectrum of Figure 3, attributed to ylide **7**.



6 X = CH_3, **7**, X = H

The observed rate constant of formation (k_{OBS}) of ylide **7** was measured in Freon-113 as a function of THF concentration. A plot of k_{OBS} versus [THF] is linear (Figure 4) with a slope of $k_{THF} = 7.7 \times 10^7\ M^{-1}\ s^{-1}$. One can extrapolate this result to neat THF (12.3 M) and conclude that the lifetime of CNP in neat THF is 1.1 ns.

The value of k_{TME} in THF was determined by studying the effect of added TME on the optical yield of ylide **7**; increasing concentrations of TME decreased the yield of ylide **7**. Stern−Volmer treatment of the data yields a linear plot (Figure 5) with a slope of $k_{TME}\tau$. The value of k_{TME} in THF is deduced to be $7.4 \times 10^8\ M^{-1}\ s^{-1}$ in neat THF. The value of k_{TME} in THF is

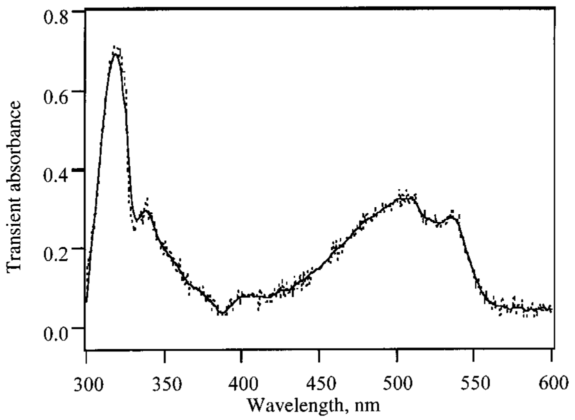


Figure 2. Persistent spectrum of carbene ether ylide **6** in 2-MTHF at 77 K.

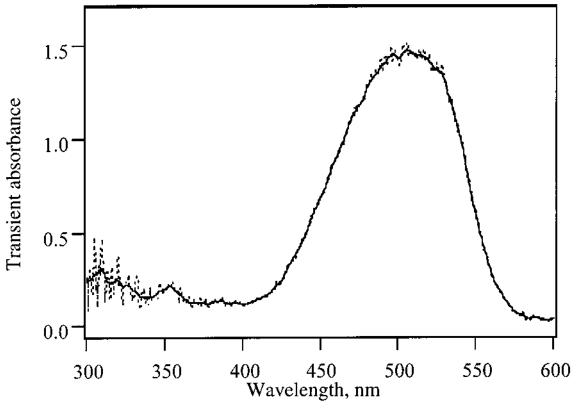


Figure 3. Transient spectrum of carbene ether ylide **7** produced upon LFP of **D** in THF at ambient temperature.

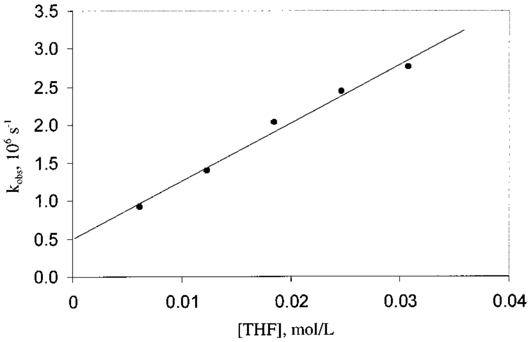


Figure 4. A plot of k_{OBS} versus [THF] in Freon-113.

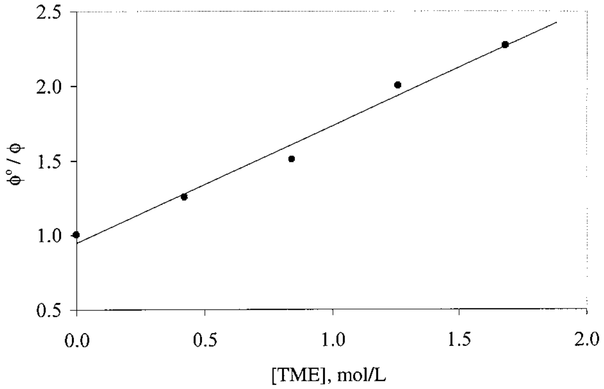
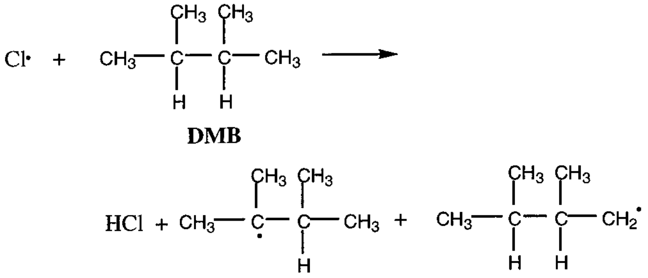


Figure 5. Stern−Volmer quenching of the yield of ylide **7** as a function of [TME].

less reliable than those in other solvents because of its indirect measurement. This value is only 62% of the value of k_{TME} determined in Freon-113. It is tempting to propose that solvation of the carbene is responsible for the reduction of the rate constant, but the effect, if real, is hardly dramatic.

IV. Discussion

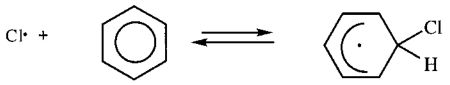
Russell and Brown studied the reaction of chlorine atoms with 2,3-dimethylbutane (DMB). They discovered that the selectivity of chlorine atoms for tertiary relative to primary C−H bonds of DMB increased dramatically in the presence of benzene and other aromatics.[15]



Russell and Brown postulated that chlorine reacts with benzene to form a charge-transfer π-type complex[16] which is less reactive and more selective than a free chlorine atom in its reactions with DMB.

Breslow and Turro and co-workers found even greater enhancement of selectivity by the formation of pyridine−chlorine atom complexes.[17]

Skell and co-workers later proposed that the complexed species is a σ complex, a chlorocyclohexadienyl radical.[18]



Bunce et al. determined that the absolute rate constants of a “free” chlorine atom and the benzene−chlorine atom complex with DMB were 2.6×10^9 and 4.6×10^7 M^{-1} s^{-1}, respectively.[19] Russell and Brown’s intuition was confirmed; the more selective species in benzene is less reactive.[15] In addition, the equilibrium constant to complexation was determined to be 200 M^{-1}.[19] The chlorine atom−benzene complex absorbs broadly in the visible region ($\lambda_{\max} = 490$ nm),[16] and Bunce et al. provide compelling arguments in favor of the complex as a π-type complex, as first postulated by Russell and Brown, and as the structure of the less reactive−more selective hydrogen atom abstracting species.[19]

Bunce et al.[19] found that a chlorine atom reacts rapidly with benzene ($k_{\mathrm{benzene}} = 6.0 \times 10^9$ M^{-1} s^{-1}) to form a charge-transfer complex which absorbs strongly in the visible region. We have not discovered compelling kinetic or spectroscopic evidence that chlorophenylcarbene, bromophenylcarbene, or chloro-*p*-nitrophenylcarbene reacts with benzene to form a charge-transfer complex in a manner reminiscent of the reaction of a chlorine atom and benzene. We cannot rule out the possibility that such complexes are present but have properties similar to those of the free carbene. It is also possible that the carbene exists both free and complexed in benzene solution. The complexes proposed by Moss, Yan, and Krogh-Jespersen[4] should be more tightly bound than those derived from arylhalocarbenes because alkylhalocarbenes do not benefit from conjugation and stabilization of the aromatic substituent. Thus, our data do not argue against their interpretation.

CNP reacts with acetonitrile to form an ylide. This is the absolute rate constant of the solvated carbene with a reagent, acetonitrile, to form a new molecule, ylide **5**. This process is far too slow ($\tau \approx 120$ ns) to reflect the interaction of a solute and a solvent. Surely, the carbene is solvated in acetonitrile, but the reaction of the chloro-*p*-nitrophenylcarbene with TME has very similar rate constants in Freon-113 ($k_{\mathrm{TME}} = 1.3 \times 10^9$ M^{-1} s^{-1}), benzene ($k_{\mathrm{TME}} = 9.3 \times 10^8$ M^{-1} s^{-1}), and acetonitrile ($k = 1.1 \times 10^9$ M^{-1} s^{-1}). The value of k_{TME} of CNP in THF, another reactive ylide-forming solvent, is 7.4×10^8 M^{-1} s^{-1}, which is only slightly smaller than that observed in less reactive solvents. Although the carbene (CNP) reacts with coordinating solvents such as tetrahydrofuran and acetonitrile to form ylides (which are not solvated carbenes), the solvated carbenes interact only very weakly with the solvent. Thus, specific solvation of these carbenes in THF and acetonitrile, if it exists, is ephemeral and too loose to dramatically retard reaction of the solvated carbene with alkene.

V. Conclusions

The absolute rate constants (k_{TME}) of CPC and BPC with TME were measured by laser flash photolysis techniques at ambient temperature. The values of k_{TME} for CPC and BPC in alkane, Freon, benzene, and highly coordinating solvents such as acetonitrile, tetrahydrofuran, and ethyl acetate are very similar, arguing against strong specific solvation of CPC or BPC in these solvents. Similar results were observed with CNP in alkane, Freon, and benzene solvents. CNP reacts with acetonitrile and tetrahydrofuran to form ylides. Nevertheless, the values of k_{TME} of the carbene in these reactive solvents are similar to those observed in unreactive solvents. It is concluded that the interactions of CPC, BPC, and CNP with coordinating solvents such as THF and acetonitrile are weak and ephemereal as they do not dramatically impede cycloaddition reactions. We have not discovered compelling evidence for the existence of arylhalocarbene−benzene complexes, but we cannot rule out the possibility that these complexes are present and have spectroscopic properties and absolute reactivities similar to those of free arylhalocarbenes.

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