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A search for dichlorocarbene ether solvent interactions

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Abstract—The absolute rate constant of reaction of dichlorocarbene with pyridine and with tetramethylethylene was determined in Freon-113 ($CF_2ClCFCl_2$), dioxane, and tetrahydrofuran. No evidence of specific solvation was obtained.
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Singlet carbenes have closed shell electron configurations with both a filled and empty orbital.[1] This has led chemists to wonder if singlet carbenes may form weak complexes with coordinating solvents. Tomioka et al.,[2] Ruck and Jones,[3] and Moss et al.[4] have probed for evidence of complexation using product based studies. Khan and Goodman[5] have used photoacoustic spectroscopy to gather evidence of an interaction between singlet methylene and benzene.

We have reasoned that solvent complexation will reduce the absolute bimolecular reaction rate constants of carbenes. In previous work we found that the absolute rate constant of reaction of arylhalocarbenes with tetramethyethlylene (TME) is essentially the same in coordinating and noncoordinating solvents.[6,7] We speculated that the stabilizing influence of the aryl group weakened any carbene solvent interaction past the point of kinetic significance. This led us to study a simpler carbene—dichlorocarbene.

Dichlorocarbene was generated by laser flash photolysis[8] of diene **1**[9] using 308 nm radiation. The carbene was visualized by trapping with pyridine to form ylide **2**, which is easily detected at 400 nm.[10]

The intensity of absorption of ylide **2** increases exponentially after the laser pulse (Fig. 1). The exponential growth can be analyzed to yield an observed rate constant, k_{obs}, which can be equated to the elementary rate constants of Scheme 1 in Eq. 1.

$$k_{obs} = k_0 + k_{pyr}[\text{pyridine}] \qquad (1)$$

A plot of k_{obs} versus [pyridine] is linear (Fig. 2) with slope k_{pyr}.

The presence of TME, at constant pyridine concentration increases k_{obs} as shown in Eq. 2. We also carried out independent product studies in all three solvents to confirm that :CCl_2 does indeed form the cycloadduct with the trap, as expected, when TME is present in the reaction mixture. In the absence of TME, the carbene adds to the precursor itself and no products from insertion of :CCl_2 into the solvent were found.
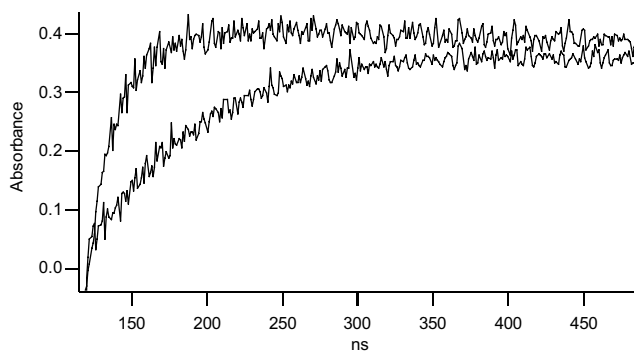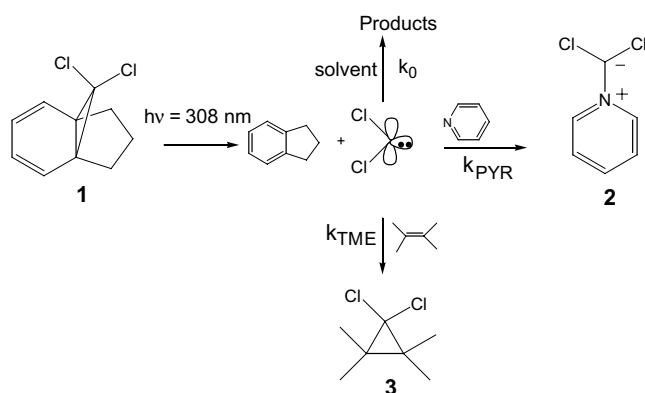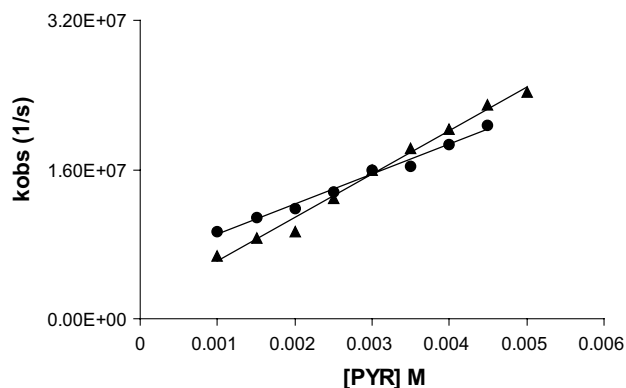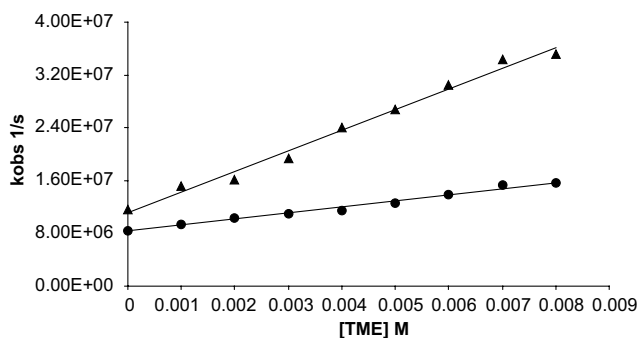

Figure 1. Transient absorbance of ylide **2** at 400 nm in Freon-113. Top: 0.005 M pyridine, bottom: 0.001 M pyridine.

Table 1. Values of k_{TME} and k_{PYR} for **1** at ambient temperature as a function of solvent

Solvent	k_{pyr} (M^{-1} s^{-1})	τ (ns)	k_{TME} (M^{-1} s^{-1})	k_{TME}(Freon)/k_{TME}(solvent)
Freon-113[a]	4.63×10^9	684	3.13×10^9	1
Tetrahydrofuran[a]	3.22×10^9	125	1.20×10^9	2.6
Dioxane[a]	6.16×10^9	172	9.28×10^8	3.4
Cyclohexane[b]	7.9×10^9		3.81×10^9	

[a] This work.
[b] Ref. 10.

Scheme 1.

$$k_{obs} = k_0 + k_{pyr}[\text{pyridine}] + k_{TME}[\text{TME}] \quad (2)$$

Plots of k_{TME} versus [TME] are linear with slopes of k_{TME} (Fig. 3).

Values of k_{pyr}, k_0 ($= 1/\tau$), and k_{TME} are collected in Table 1.

Table 1 reveals that the lifetime of dichlorocarbene is shorter in ether solvents than in Freon-113 ($CF_2ClCFCl_2$). Our values of k_{pyr} and k_{TME} in Freon-113 are very similar to that found previously in cyclohexane.[10] Tetrahydrofuran and dioxane have very little influence on these values. Thus, we find no kinetic evidence of specific solvation for this particular carbene, :CCl_2, by ethereal solvents.

Acknowledgements

Figure 2. A plot of k_{obs} versus [pyridine] in Freon-113 (▲) and dioxane (●) at ambient temperature.

Figure 3. A plot of k_{obs} of formation of ylide **3** versus tetramethylethylene at constant [pyridine] (0.002 M) in Freon-113 (▲) and dioxane (●) at ambient temperature.

References and Notes

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