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A probe method for studying dibromocarbene by time resolved infrared spectroscopy

George Holinga and Matthew S. Platz*

Department of Chemistry, The Ohio State University, Columbus, OH 43210, USA

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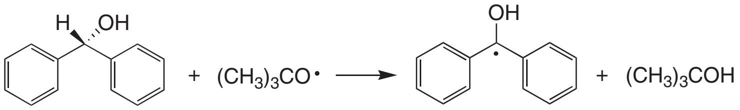
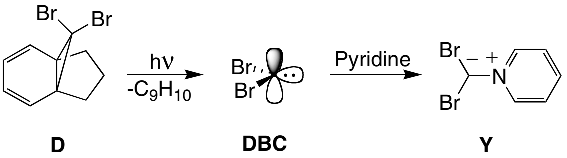
Abstract—Dibromocarbene reacts with *tertiary*-butylisocyanide to form a ketenimine. The absolute rate constant of the reaction ($k_{TBI} = 2.3 \times 10^9\ M^{-1}\ s^{-1}$) was determined by laser flash photolysis techniques with UV–vis detection of the dibromocarbene–pyridine ylide. The ketenimine was detected by TRIR spectroscopy at 2040 cm^{-1}. Isocyanide trapping of carbenes to form ketenimines is proposed as a general method of studying IR silent carbenes by TRIR spectroscopy.

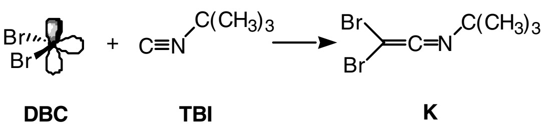
Scaiano and co-workers have developed probe methods for studying radicals which lack chromophores for ready observation using laser flash photolysis (LFP) methods with UV–vis detection. In this experiment, a UV–vis inactive radical such as *tertiary*-butoxyl reacts with a trap, in this case benzhydrol, to form *tertiary*-butanol and a ketyl radical. The latter species is a probe molecule because it absorbs strongly at 525 nm and allows facile study of the dynamics of *tertiary*-butoxyl radical, a species which lacks a useful UV–vis absorption. This technology has led to thorough studies of the kinetics of free radicals.[1]



The dynamics of carbenes have been studied by probe methods using pyridine. As shown below, dibromocarbene (**DBC**) can be produced by pulsed laser photolysis of a diene (**D**). Reaction of **DBC** with pyridine forms a UV–vis ylide (**Y**).[2,3]



Carbenes which contain strong vibrational bands can be studied by nanosecond (ns) time resolved infrared (TRIR) spectroscopy.[4] A probe method for studying carbenes which lack strong vibrational bands by TRIR spectroscopy, analogous to pyridine ylides, is certainly desirable. We reasoned that carbenes will react with isocyanides with large rate constants to form ketenimines which possess an intense, characteristic vibrational band. As expected, density functional theoretical[5,6] (DFT) calculations (BSLYP/6-31G*) predict that the ketenimine (**K**) formed by reaction of dibromocarbene with *tertiary*-butyl isocyanide (**TBI**) will absorb strongly at 2050 cm^{-1} after scaling by a factor of 0.9614.[7]



First, we set out to confirm that dibromocarbene will react rapidly with **TBI** using the pyridine ylide probe method. LFP (308 nm) of diene **D** in dichloromethane containing pyridine at ambient temperature produced

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Keywords: Carbene; Ketenimine; FTIR spectroscopy.

* Corresponding author. Tel.: +1 614 292 0401; fax: +1 614 292 5151; e-mail: platz.1@osu.edu

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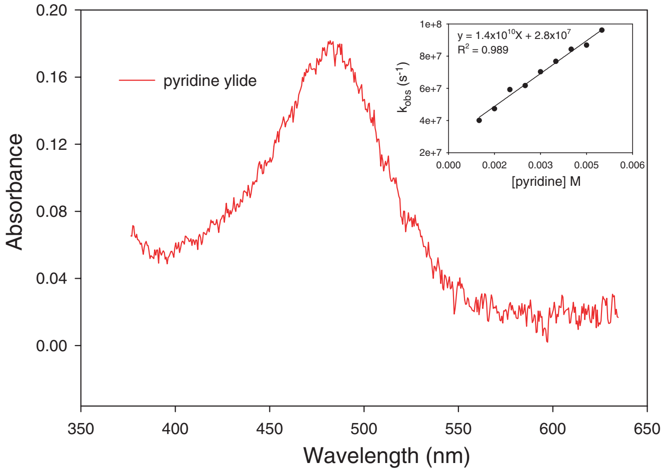

Figure 1. The transient spectrum of pyridine ylide **Y** produced by LFP of 1.05 mM diene **D** in dichloromethane containing 5 mM pyridine. Inset: a plot of k_{obs} versus [pyridine] measured at 482 nm and ambient temperature in CH_2Cl_2.

the transient spectrum of Figure 1. The peak observed at 482 nm is not observed in the absence of pyridine.

The absolute rate constant for the formation of ylide **Y** was determined by varying the concentration of pyridine (1–6 mM) and measuring the observed pseudo first order rate constant of formation (k_{obs}) of ylide **Y**. A plot (Fig. 1, inset) of k_{obs} versus pyridine concentration is linear. The slope of this plot is simply k_{pyr} the absolute rate constant of **DBC** reacting with pyridine; $k_{pyr} = 1.4 \times 10^{10}\ M^{-1}\ s^{-1}$. The lifetime ($\tau$) of dibromocarbene in CH_2Cl_2 in the absence of pyridine is the reciprocal of the intercept of the plot (35 ns) and is controlled by reaction of **DBC** with solvent, diene **D**, and adventitious water. The absolute rate constant and lifetime values determined in this study compare favorably to the reported values of the dibromocarbene-pyridine system in other solvents.[3]

LFP of solutions of diene **D** (1.05 mM in CH_2Cl_2), pyridine (constant 5 mM) were studied with varying concentrations of **TBI** (0–100 mM). The presence of isocyanide reduces the yield of pyridine ylide **Y** and increases the rate of its formation (Fig. 2). In this experiment, the observed rate of formation (k_{obs}) of ylide **Y** was measured as a function of concentration of *tertiary*-butylisocyanide. A plot of k_{obs} versus [**TBI**] at constant [pyridine] was linear (Fig. 2) with slope equal to the absolute rate constant for reaction of **DBC** with **TBI** to form ketenimine **K** ($k_{TBI} = 2.3 \times 10^9\ M^{-1}\ s^{-1}$). This confirms that dibromocarbene reacts with *tertiary*-butyl isocyanide with a near diffusion controlled rate constant.

DFT (B3LYP/6-31G*) calculations predicted a vibrational absorption band of product **K** at $\nu \sim 2050\ cm^{-1}$. LFP (266 nm) of a solution of diene **D** (31 mM) containing 0.53 M **TBI** in CH_2Cl_2 produced the transient IR spectrum of Figure 3. The band at $2040\ cm^{-1}$ was not observed in the absence of **TBI** and is assigned to ketenimine **K**.

It was not possible to resolve the formation of ketenimine **K**. Thus, we determined the optical yield (A_k) of ketenimine **K** at varying concentrations of **TBI.** A plot of $1/(A_k)$ versus 1/[**TBI**] was linear (Fig. 2, inset).[7] Using

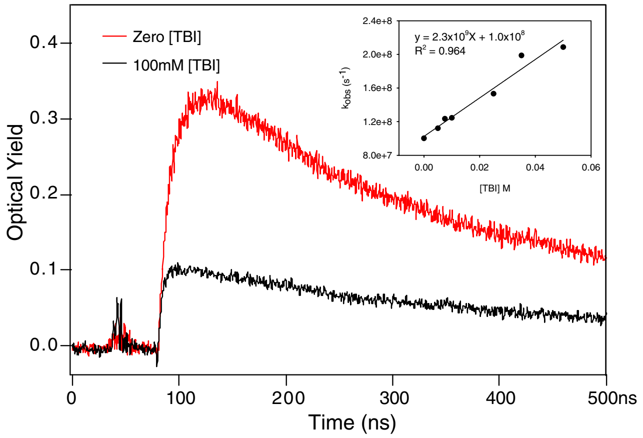

Figure 2. The influence of **TBI** (0–0.1 M) on the formation of pyridine ylide **Y**. Inset: a plot of k_{obs} versus [**TBI**] obtained by LFP of diene **D** (1.05 mM) and pyridine (5 mM) in CH_2Cl_2 at 482 nm.

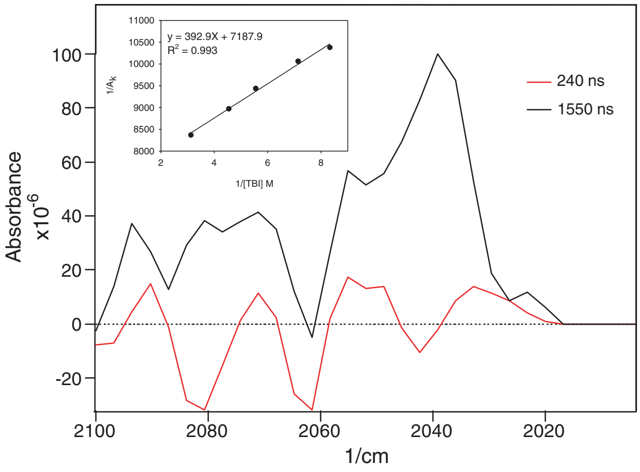

Figure 3. TRIR spectrum produced by LFP of diene **D** (31 mM) and **TBI** (0.53 M) in CH_2Cl_2. Inset: TRIR study of the optical yield of ketenimine **K** produced by LFP of diene D (20 mM) and **TBI** (0.12–0.32 M) in CH_2Cl_2.

the previously determined value of $k_{\mathrm{TBIC}} = 2.3 \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ (LFP experiments, Fig. 3), the lifetime of dibromocarbene was deduced as 8 ns in the absence of pyridine.[8] This is in only fair agreement with the value determined by LFP with UV–vis detection (35 ns, Fig. 2). However, the TRIR experiment used a precursor solution that was 500 times more concentrated than that of the LFP experiments. Since dibromocarbene can react with precursor **D**, it is reasonable to expect that the lifetime of **DBC** (zero [pyridine]) is shorter in TRIR than in LFP experiments.

Our results indicate that *tertiary*-butylisocyanide traps a typical carbene with a near diffusion controlled rate constant to form ketenimines which can be readily detected by nanosecond time resolved infrared spectroscopy. This probe method may be useful when the carbene of interest lacks diagnostic vibrational bands and cannot be directly monitored in TRIR experiments.

Acknowledgements

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