Spectroscopy and Dynamics of *p*-Nitrophenylchlorocarbene

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The absolute rate constants for the reaction of *p*-nitrophenylchlorocarbene with pyridine and tetramethylethylene were found to be respectively 7.5×10^9 and 2.9×10^9 l mol^{-1} s^{-1}.

There have been many laser flash photolysis (LFP) studies on singlet arylhalogenocarbenes.[1] Preliminary experiments using LFP on *p*-nitrophenylchlorocarbene (NPCC) in acetonitrile/iso-octane solvent have been described[2] but the absorption spectrum ($\lambda_{max.}$ 450 nm) which was ascribed to NPCC has never been verified. We herein report the detection of NPCC and its reaction with pyridine to form an ylide. The kinetics of the reactions of carbene enable us to confirm unambiguously the spectral assignment for NPCC.

3-Chloro-3-*p*-nitrophenyldiazirine (**1**) was prepared by Graham's method.[3] Thermolysis and photolysis of (**1**) in cyclohexene produce the corresponding norcarane and the presence of a carbene intermediate is indicated. The absence of an e.s.r. signal on irradiation of (**1**) at 4 K suggests that the NPCC has a singlet ground state. LFP† of (**1**) in iso-octane

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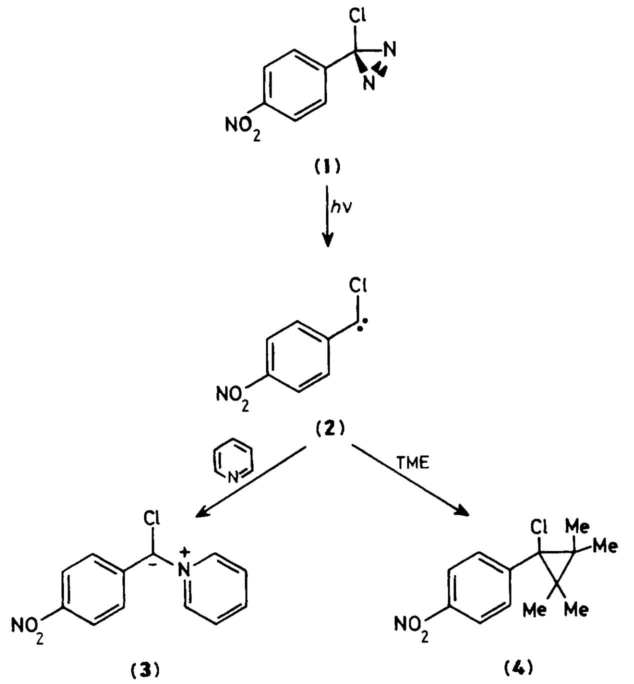
† The LFP set-up uses a crossed-beams arrangement. The sample in a 10 × 10 mm cell is excited at 355 nm by single light pulses (200 ps duration, 5—30 mJ energy) provided by a frequency tripled mode-locked Nd-YAG (Quantel) laser. The detection system includes a pulsed Xe arc, a monochromator, a red-sensitive photomultiplier (Hamamatsu R446), and a fast transient recorder (Tektronix 7912) and has a response time around 5 ns.



Scheme 1

produces a transient at 320 nm which decays within a few μs in the absence of quenchers. This transient is attributed to NPCC (**2**) (Scheme 1). Phenylchlorocarbene and t-butylchlorocarbene have been shown to react with pyridine to form ylides.[4] LFP of (**1**) in the presence of pyridine at 25 °C produces the transient spectrum of ylide (**3**) shown in Figure 1. This transient is not present in the absence of pyridine. In comparison with the phenylchlorocarbene pyridinium ylide, the absorption spectrum of this transient is red shifted by *ca.* 100 nm. The rate of formation of the ylide (**3**) can be used to monitor the reactions of NPCC. Theoretically, the rate of disappearance of NPCC in the presence of pyridine must be equal to the rate of formation of (**3**). Thus, the kinetics of the growth of the absorption at 605 nm as a function of pyridine concentration were measured. A plot of the observed pseudo-first-order rate constants *vs.* [pyridine] is linear and the slope yields an absolute rate constant for the reaction of NPCC with pyridine of 7.5×10^9 l mol^{-1} s^{-1}. Concurrently, the rate of decay of NPCC monitored at 320 nm increases linearly with the pyridine concentration and the slope yields a value of 7.2×10^9 l mol^{-1} s^{-1} for the rate constant. The rate of formation of ylide from NPCC and pyridine is close to diffusion-controlled and represents one of the fastest reactions known in carbene chemistry. The rate of reaction of phenylchlorocarbene with pyridine[4] is 3.4×10^8 l mol^{-1} s^{-1}.

The addition of a carbene quencher such as tetramethylethylene (TME) yields a cyclopropane (**4**) and consequently the addition of TME accelerates the carbene decay kinetics. Plotting the reciprocal lifetime of NPCC, monitored at 320 nm, as a function of TME concentration, the absolute rate constant for the reaction of NPCC with TME in iso-octane was found to be 2.9×10^9 l mol^{-1} s^{-1} at 25 °C (Figure 2, line A). This value is in excellent agreement with the results of Hammett correlations established for the reaction of arylchlorocarbenes with TME.[5]

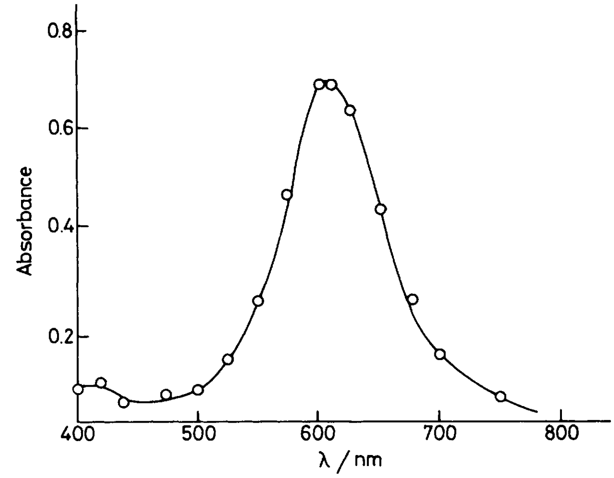


Figure 1. Point by point transient absorption spectrum of ylide (**3**).

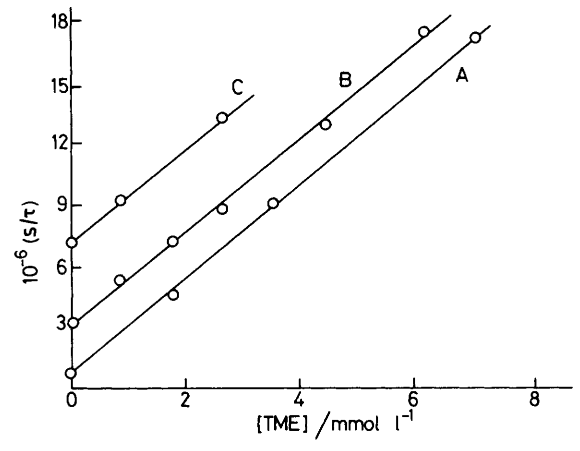


Figure 2. Plots of reciprocal 'lifetime' (1/τ) *vs.* [TME]. A. Decay of NPCC at 320 nm (no pyridine). B. Growth of ylide (**3**) at 605 nm with [pyridine] = 2.8×10^{-4} mol l^{-1}. C. Growth of ylide (**3**) at 440 nm with [pyridine] = 7.8×10^{-4} mol l^{-1}.

With a constant amount of pyridine, the addition of TME increases the rate for ylide growth and decreases the yield of ylide formation. Excellent linearity between ylide growth rate constants and [TME] was observed (Figure 2, line B) with $k = 2.6 \times 10^9$ mol^{-1} s^{-1}. Within experimental error, this is identical to the rate constant obtained by the decay kinetics of NPCC monitored at 320 nm.

A pyridinium ylide such as (**3**) is an ideal probe for monitoring reactions of carbene because it absorbs strongly. The extinction coefficient of ylide (**3**) in iso-octane at 605 nm was found to be 1.64×10^4 l mol^{-1} cm^{-1}. This was determined by comparing the optical density of the ylide adsorption with that of the triplet–triplet absorption of benzophenone[6] in benzene (ε 7.63×10^3 l mol^{-1} cm^{-1}, λ 530 nm). To illustrate this, we followed the kinetics of the growth of the absorption at 440 nm. The amount of pyridine used was constant but 2.8 times greater than in the experiment used to give line B. Line C was obtained, and yielded $k = 2.5 \times 10^9$ l mol^{-1} s^{-1} for the same reaction.

A remaining question is 'what is the species absorbing at 450 nm described in ref. 2?' LFP of (**1**) in pure MeCN produces a transient which gives a strong absorption at 450 nm with a rise time of 130 ns. It is well known that fluorenylidene and the naphthylcarbenes are intercepted by acetonitrile to give ylides.[7] It seems therefore probable that the absorption at 450 nm is due to the nitrile ylide.

In conclusion, the present study clearly establishes that the absorptions at 320 nm and 605 nm are due to NPCC (**2**) and the pyridinium ylide (**3**) respectively. In addition, the electron withdrawing character of the nitro substituent has pronounced effects on carbene reactivity. It enhances the rate of ylide formation and the rate of cyclopropanation with TME by at least a factor of ten when compared with the unsubstituted phenylchlorocarbene. Also, the spectral characteristics of ylide absorption are substantially altered.

We thank Professor R. A. Moss for comments. M.T.H.L. is on leave from the University of Prince Edward Island, Canada.

Received, 12th October 1988; Com. 8/04060E

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