Picosecond Spectroscopic Detection of Diphenylcarbenium Ion in the Photolysis of Diphenyldiazomethane in Aliphatic Alcohols

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Laser flash photolysis studies support a protonation mechanism in the O–H insertion reaction of diphenylcarbene with alcohols.

Recently, Kirmse, Kilian and Steenken[1] presented convincing evidence that diarylcarbenium ions could be generated by protonation of diarylcarbenes with water or 2,2,2-trifluoroethanol (TFE). The electronic absorption spectra of several *p*-substituted diphenylcarbocations were detected following nanosecond laser flash photolysis (LFP) of the respective diazo compounds in either solutions of MeCN–H_2O or MeCN–TFE. There was, however, no detection of the parent diphenylcarbenium ion ($Ph_2\overset{+}{C}H$) in MeCN–H_2O due to rapid nucleophilic attack by H_2O.† Herein, we report the picosecond detection of $Ph_2\overset{+}{C}H$ observed following LFP of diphenyldiazomethane (Ph_2CN_2) in MeCN–H_2O, as well as, in neat methanol, ethanol and propan-2-ol.

The picosecond LFP apparatus has previously been described.[2] A mode-locked Quantel YG-501 DP Nd:YAG laser, pulse width ~18 ps full width at half maximum (fwhm), supplied both the 266 or 355 nm excitation pulses and a 1064 nm pumped white light continuum (1 : 1, H_2O : D_2O solution) was used as the probe. All LFP experiments were performed using a flow cell system at 21 °C.

For a spectral comparison, nanosecond LFP (266 nm, ~8 mJ) of diphenylchloromethane (Ph_2CHCl) in MeCN resulted in both photohomolytic and photoheterolytic carbon–chlorine bond cleavage to generate diphenylmethyl radical, λ_{max} 330 nm, and $Ph_2\overset{+}{C}H$, λ_{max} 435 nm (Fig. 1, top right). The absorption maximum and reactivity of $Ph_2\overset{+}{C}H$ were identical to those previously reported.[3] For direct comparison, picosecond LFP (266 nm, ~1.1 mJ) of Ph_2CHCl in MeCN also resulted in the absorption spectrum of $Ph_2\overset{+}{C}H$ [(*a*) in Fig. 1]. Under the same conditions in pure MeCN LFP of Ph_2CN_2 resulted in no observable absorption between 400 and 600 nm.

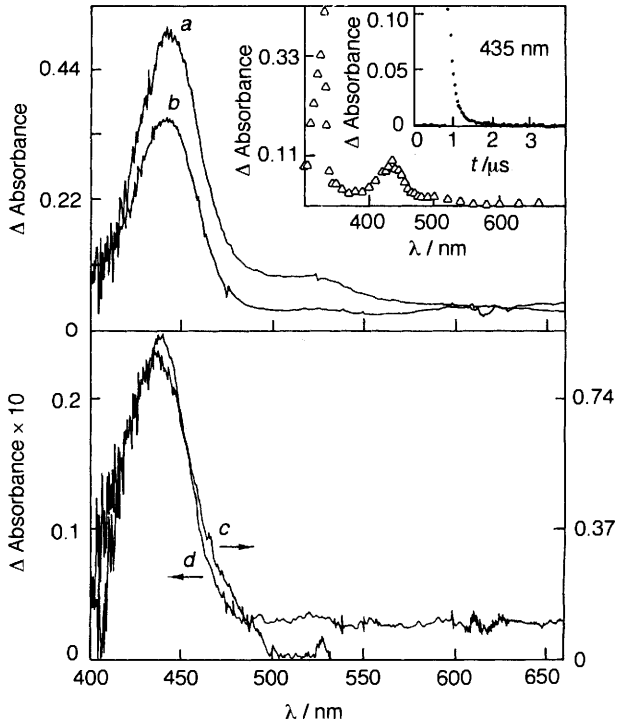

Fig. 1 UV–VIS absorption spectrum (top, right) observed 80 ns after 266 nm nanosecond LFP of Ph_2CHCl in MeCN (insert represents decay trace observed at 435 nm). Visible absorption spectra (*a*)–(*d*) were observed upon full completion of the 18 ps (fwhm) excitation pulse following: (*a*) 266 nm LFP of Ph_2CHCl in MeCN; (*b*) 266 nm LFP of Ph_2CN_2 in 2 : 1 MeCN : H_2O; (*c*) 355 nm LFP of Ph_2CN_2 in 1 : 1 MeCN : H_2O; and (*d*) 355 nm LFP of Ph_2CN_2 in neat propan-2-ol.

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† $Ph_2\overset{+}{C}H$ was observed in (1 : 1.6) MeCN–TFE.

In dramatic contrast, LFP of Ph_2CN_2 in 2:1 MeCN:H_2O resulted in an absorption spectrum [(*b*) in Fig. 1] identical to that of $Ph_2\overset{+}{C}H$ generated from Ph_2CHCl photolysis. Picosecond 355 nm LFP of Ph_2CN_2 in 1:1 MeCN:H_2O resulted in an absorption spectrum [(*c*) in Fig. 1] nearly identical to (*a*) and (*b*) in Fig. 1. The slight band shape distortion is attributed to higher concentration and absorption of the diazo precursor. Monitoring at 440 nm, the signal is formed within the laser pulse and a linear plot of Δ optical density *vs.* laser intensity indicates $Ph_2\overset{+}{C}H$ is generated monophotolytically. An exponential fit to the signal decay yielded a pseudo-first-order decay rate constant of $1.33 \times 10^9\ s^{-1}$, *i.e.* $\tau = 750$ ps.

Picosecond 355 nm LFP of Ph_2CN_2 in neat, anhydrous propan-2-ol yielded a spectrum [(*d*) in Fig. 1] identical to that observed in aqueous MeCN, as did LFP of Ph_2CN_2 in ethanol and methanol. In each case, $Ph_2\overset{+}{C}H$ was formed within the laser pulse and decayed with first-order kinetics resulting in lifetimes ($1/k$) of 85, 70 and 40 ps in Pr^iOH, EtOH and MeOH, respectively. The rates of decay observed represent the nucleophilicity of each solvent towards $Ph_2\overset{+}{C}H$.[1,3] These results support the protonation mechanism first suggested by Kirmse[4] in the 'insertion' reaction of Ph_2C: with alcohols to form diphenylmethyl ethers.

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