

Ultrafast Spectroscopic Study of the Photochemistry and Photophysics of Arylhalodiazirines: Direct Observation of Carbene and Zwitterion Formation

Jin Wang,[†] Gotard Burdzinski,^{†,‡} Jacek Kubicki,^{†,‡} Matthew S. Platz,^{*,†} Robert A. Moss,^{*,§} Xiaolin Fu,[§] Piotr Piotrowiak,^{*,¶} and Mykhaylo Myahkostupov[¶]

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, Quantum Electronics Laboratory, Faculty of Physics, Adam Mickiewicz University, 85 Umultowska, Poznan 61-614, Poland, Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903, and Department of Chemistry, Rutgers, The State University of New Jersey, Newark, New Jersey 07102

Received October 8, 2006; E-mail: platz.1@osu.edu; moss@rutchem.rutgers.edu; piotr@andromeda.rutgers.edu

Arylbromo and chlorodiazirines are conveniently prepared by Graham's reaction,¹ and their fluoro analogues are obtained by fluoride exchange reactions.² Nanosecond time-resolved spectroscopic studies of arylhalocarbenes led to an understanding of the factors that control their bimolecular reactivity.³ Now we report the first femto- and picosecond time-resolved studies of the photophysics and photochemistry of their arylhalodiazirine precursors, which provide important insight into the photochemical formation of arylhalocarbenes.

Ultrafast photolysis ($\lambda_{\text{ex}} = 350$ or 360 nm)^{4,5} of fluorophenyldiazirine in acetonitrile at ambient temperature produces the transient spectra shown in Figure 1. A broadly absorbing transient ($\lambda_{\text{max}} = 620$ nm) is formed within the laser pulse (300 fs). The transient decay is monoexponential (Table 1). Similar transient spectra are obtained in alkane solvents, although the decay in cyclohexane is biexponential and the lifetime of the visible absorbing transient shortens from 352 ps (acetonitrile) to 117 ps (cyclohexane, long component).

It is possible to monitor the absorbance changes at 350 nm (Figure 2) when fluorophenyldiazirine is excited at short wavelength ($\lambda_{\text{ex}} = 270$ nm) in acetonitrile. The instantaneous formation of transient absorption at 350 nm is followed by biexponential decays of 0.9 and 16.3 ps (Figure S1). As 350 nm is at the extreme red-edge of the absorption of thermalized fluorophenylcarbene,⁶ the long decay component measured at 350 nm can be readily assigned to vibrational cooling of the carbene.^{7,8} There is a difference in the transient spectra produced with 350 and 270 nm excitation in the 450 nm region at short times (e.g., after 0.5 ps). With a 270 nm pump, this is likely due to the presence of excited zwitterion (see below), which then relaxes, while with 350 nm excitation, we observed mostly relaxed zwitterion at 620 nm. The lifetime of the excited zwitterion form (270 nm) is likely ~ 0.9 ps (see Figure S1).

Ultrafast photolysis ($\lambda_{\text{ex}} = 360$ nm) of chloro- and bromophenyldiazirine in acetonitrile and cyclohexane largely produces transient spectra similar to those observed with the fluoro analogue (Figures S2 and S3), but the transient decays are clearly biexponential (Figure 3 and Figures S4 and S5).⁹ Changes in transient absorptions of chloro- and bromophenylcarbene also can be followed at 350 nm^{3,6} when the corresponding diazirines are excited at 270 nm (Figures S6 and S7). In the case of chlorophenylcarbene, the growth in transient absorption at 350 nm (Figure S6) is entirely within the instrument response (300 fs) exactly as observed with the fluoro analogue (Figure S1). The long decay component measured at 350 nm (11 ps for X = Cl) is again assigned to vibrational cooling of

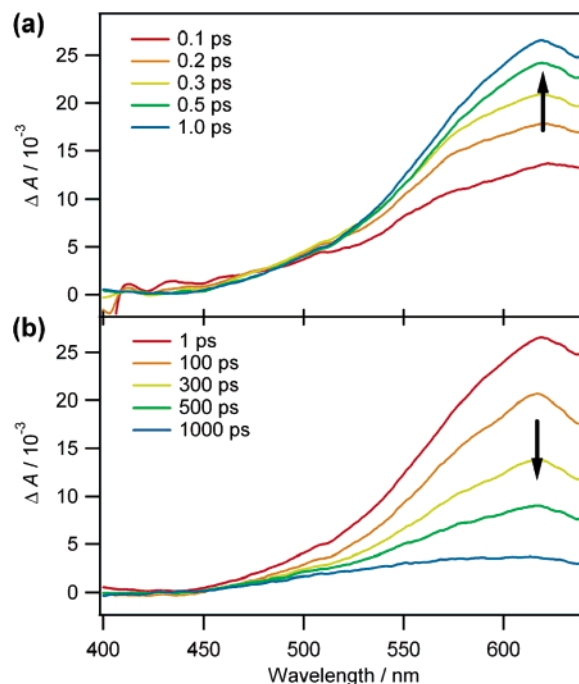


Figure 1. Transient spectra of fluorophenyldiazirine in acetonitrile.⁴ Spectra were generated by ultrafast LFP (360 nm) with time windows of (a) 0.1–1 ps and (b) 1–1000 ps.

the carbene. However, in the case of bromophenylcarbene, transient absorption growth at 350 nm and decay at 600 nm are both biexponential (time constants of 100–600 fs and 4–10 ps, Figures S7 and S8). This demonstrates a correlation between the slow growth of bromophenylcarbene (270 nm excitation) and the slow decay component of the 620 nm absorbing transient (360 nm excitation) and is not attributed to vibrational cooling as we are monitoring the center rather than the red-edge of the absorption band. The different behavior observed with bromophenyl relative to the other two carbenes is explained by their different absorption spectra (Figure S9).¹⁰

Modern theory predicts that the characteristic absorption of ground state diazirine and of dimethyldiazirine above 300 nm is due to an n to π^* transition. In the gas phase, the n π^* excited state deactivates by passage through a conical intersection to form a diradical-like structure.¹¹ Theory has not yet considered the photophysics of asymmetrically substituted diazirines, as studied here, in either the gas phase, polar, or nonpolar solvents.

The data presented in Table 1 indicate that the 620 nm absorbing species detected in this work have dipolar or even zwitterionic character. In support of the latter, note the responses of τ_2 to solvent

[†] The Ohio State University.

[‡] Adam Mickiewicz University.

[§] Rutgers, The State University of New Jersey at New Brunswick.

[¶] Rutgers, The State University of New Jersey at Newark.

Table 1. Normalized Amplitudes and Lifetimes of Transient Absorptions, Measured at 600 nm, Produced by 350^a or 360^b nm Ultrafast LFP of Halophenyldiazirines^c

diazirine	λ_{ex}	solvent	A_1	τ_1/ps	A_2	τ_2/ps	A_∞	A_1/A_2
Ph-C(N ₂)F	360	acetonitrile			0.89	352 ± 27	0.11	
Ph-C(N ₂)Cl	360	acetonitrile	0.41	0.92 ± 0.1	0.52	50 ± 4	0.07	0.8
Ph-C(N ₂)Br	360	acetonitrile	0.53	0.88 ± 0.1	0.42	28 ± 2	0.05	1.3
Ph-C(N ₂)F	360	cyclohexane	0.34	2.4 ± 0.4	0.57	117 ± 13	0.10	0.6
Ph-C(N ₂)Cl	360	cyclohexane	0.58	0.45 ± 0.1	0.37	22 ± 3	0.06	1.6
Ph-C(N ₂)Br	360	cyclohexane	0.79	0.32 ± 0.2	0.16	10 ± 3	0.04	4.9
<i>p</i> -CF ₃ -Ph-C(N ₂)F	350	acetonitrile	0.19	9.9 ± 1.4	0.81	149 ± 33	-0.05 ^d	0.2

^a At Rutgers University. ^b At Ohio State University. ^c See the Supporting Information for an explanation of data selection. ^d The error bar is ±0.12, so that this small (5%) negative A_∞ can be treated as zero.

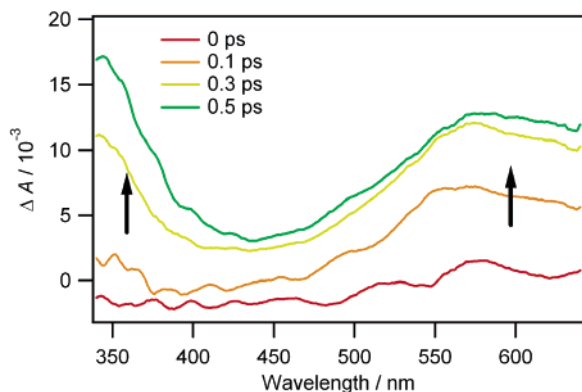


Figure 2. Transient spectra of fluorophenyldiazirine in acetonitrile.⁴ Spectra were generated by ultrafast LFP (270 nm) with a time window of 0–0.5 ps.

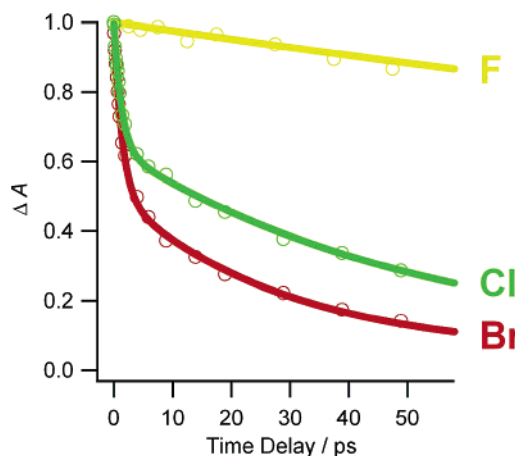
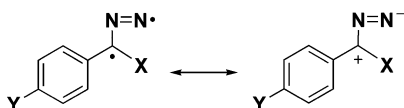


Figure 3. Normalized kinetic traces of fluorophenyldiazirine (yellow), chlorophenyldiazirine (green), and bromophenyldiazirine (red) in acetonitrile; excited by ultrafast LFP at 360 nm and probed at 600 nm.⁴

polarity ($\tau_{2,\text{Acetonitrile}} > \tau_{2,\text{Cyclohexane}}$), the para aryl substituent [$\tau_{2-}(\text{H}) > \tau_{2-}(\text{CF}_3)$], and the identity of X (F > Cl > Br; see Figure 3), consistent with σ^+ or σ^+_{R} values of the halogens.¹²



We propose that UV excitation of arylhalodiazirines leads rapidly (femtoseconds) to the formation of a diradical/zwitterion¹¹ (see above) with excess vibrational energy which decays in hundreds of femtoseconds by two mechanisms: (a) loss of nitrogen to form carbene, and (b) relaxation to the thermalized species. The relaxed

diradical/zwitterion decays in picoseconds by cyclization to re-form the initial diazirine, (possibly) by isomerization to form a diazo compound, and by fragmentation to form the arylhalocarbene. The lifetime of the zwitterions is extended by polar solvent and by electron donation from the halogen substituent at the diazirine carbon, with fluorine the most effective halogen,¹² and is decreased by a para substituent which destabilizes cationic centers.

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Supporting Information Available: Discussion of data selection in Table 1, descriptions of the spectrometers, Figures S1–S9. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) The absorption maximum of relaxed fluorophenylcarbene is at 270 nm.⁶ Vibrationally excited molecules are commonly produced upon photolysis and typically exhibit broad and red-shifted spectra.⁸
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- (9) In acetonitrile, the ratio of fast/slow transient decay increases from fluoro- to chloro- to bromophenyldiazirine, hence the decay of the fluoro compound alone appears to be substantially monoexponential. The shape of the transient spectra obtained by excitation of the arylhalodiazirines does not change with time, consistent with the presence of a single absorbing intermediate in each system. Control experiments with all three halophenyldiazirines reveal that ultrafast photolysis (270 nm) of acetonitrile solutions of arylhalodiazirines, previously bleached by exposure to 266 nm radiation, does not produce the same transients observed by photolysis of fresh solutions of the diazirines. This demonstrates that the initially observed transients for the studied diazirines are not formed by re-excitation of stable reaction products.
- (10) The picosecond growth of transient absorption is only observed with bromophenylcarbene because it has the longest wavelength absorption (Figure S9),⁶ and we are now monitoring the center of the band.
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