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Evidence of Hydrogen Migration in an Alkylphenyldiazirine Excited State

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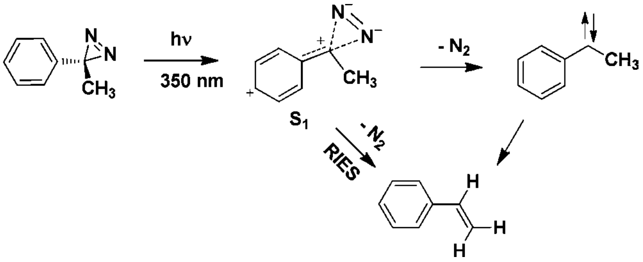
ABSTRACT



Ultrafast photolysis (350 nm) of alkylphenyldiazirines promotes the diazirine to the S_1 excited state. Solvent and substituent effects on the excited state lifetimes indicate that the S_1 state is highly polarized and undergoes a [1,2]-H shift in concert with nitrogen extrusion in cyclohexane.

Alkylphenyldiazirines are convenient thermal and photochemical precursors of carbenes.[1] We have previously proposed that carbene mimetic 1,2 hydrogen migrations can proceed in diazirine excited states,[2] and this process has been named "rearrangement in the excited states" (RIES).[3] Herein, we report femtosecond (fs) time-resolved UV−vis data on alkylaryldiazirines that support this mechanistic proposal.

Photolysis (350 nm) of 3-methyl-3-phenyl diazirine ($PhCN_2CH_3$) produces a transient species with $\lambda_{max} = 580$ nm in acetonitrile (Figure 1). The carrier of the transient spectrum is assigned to the S_1 state of the diazirine as 350 nm light is absorbed by the longest wavelength absorption band of the ground state.

The transient decay is biexponential (Figure 2). The long component is assigned to the lifetime of the S_1 state, and the short component is assigned to intramolecular vibrational relaxation of the Franck−Condon state.[4]

There is a pronounced solvent effect on the lifetime of the S_1 state of 3-methyl-3-phenyl diazirine, which is lengthened in the polar solvent. These trends are also evident upon excitation of parent phenyldiazirine and other alkylphenyldiazirines (Table 1). The data is consistent with a previous report of Wang et al. regarding arylhalodiazirines.[5]

The lifetime of 3-methyl-3-phenyl diazirine (long component) is about 5 times longer than that of the S_1 state of parent phenyldiazirine ($PhCN_2H$, Table 1). This indicates that positive charge has developed on the diazirine carbon and is better stabilized, as expected, by a methyl group as compared to a hydrogen atom.[6]

Following Wang et al.[5] we conclude that this state is highly polarized, although theory predicts that the diazirine ring

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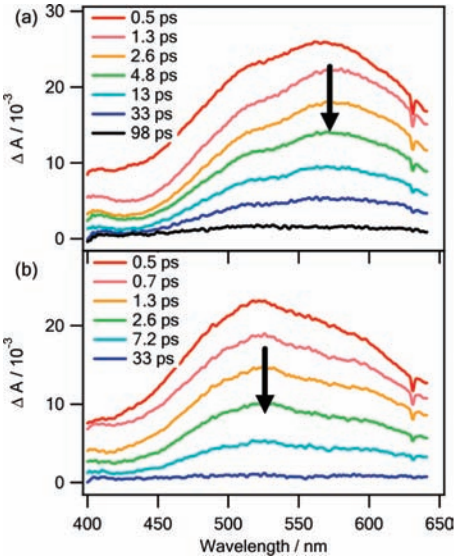


Figure 1. Transient spectra produced by photolysis of 3-phenyl-3-methyldiazirine ($\lambda_{ex} = 350$ nm) in (a) acetonitrile and (b) cyclohexane at selected time delays.

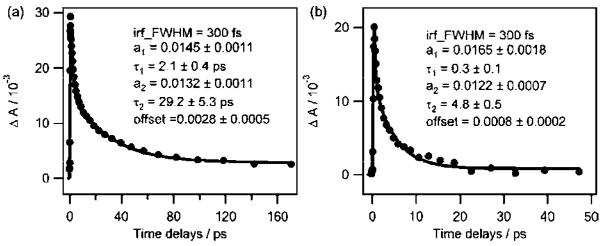


Figure 2. Decay of transient absorption produced by ultrafast LFP (350 nm) of 3-methyl-3-phenyl diazirine. The kinetic traces were recorded in (a) acetonitrile and (b) cyclohexane and fitted to biexponential functions.

Table 1. Lifetimes of Transient Absorptions, Measured at Maximum Absorption, Produced by 350 nm Ultrafast LFP of Alkylphenyldiazirines

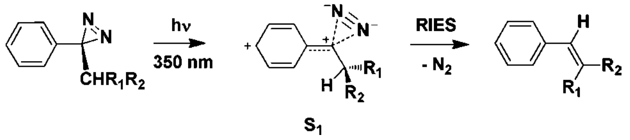
	acetonitrile		cyclohexane	
diazirines	τ_1 (ps)[a]	τ_2 (ps)[b]	τ_1 (ps)[a]	τ_2 (ps)[b]
$PhCN_2H$	0.8 ± 0.2	5.9 ± 1.2	0.05 ± 0.03	1.2 ± 0.1
$PhCN_2CH_3$	2.1 ± 0.4	29.2 ± 5.3	0.3 ± 0.1	4.8 ± 0.5
$PhCN_2Et$	0.9 ± 0.2	20.9 ± 2.1	1.2 ± 0.2	7.8 ± 1.6
$PhCN_2$-*i*Pr	0.7 ± 0.1	13.0 ± 0.8	1.3 ± 0.2	5.3 ± 1.6
$PhCN_2$-*t*Bu	3.0 ± 0.4	21.4 ± 2.1	1.6 ± 0.6	14.6 ± 3.1
$PhCN_2CD_3$	1.7 ± 0.3	24.9 ± 4.0	1.0 ± 0.2	7.5 ± 1.6

[a] τ_1 is the time constant of intramolecular vibrational relaxation. [b] τ_2 is the lifetime of the S_1 state.

remains intact with equivalent C−N bonds in the S_1 states of aryldiazirines.[6]

Diazirine excited states decay by a variety of processes (internal conversion to S_0, isomerization to diazo, carbene formation).[1] Two points persuade us that the S_1 lifetimes (τ_2) recorded for different alkyl substitution (CH_3, CD_3, Et, *i*-Pr, and *t*-Bu) in cyclohexane are consistent with the presence of an additional, competitive decay pathway from the S_1 state: the previously proposed 1,2 migration of hydrogen that proceeds in concert with alkene formation and nitrogen extrusion (RIES, Scheme 1).

Scheme 1. Rearrangement in the Excited State of Alkylphenyldiazirines



First there is a kinetic isotope effect (KIE) on the lifetimes of 3-trideuteromethyl-3-phenyl diazirine ($PhCN_2CD_3$,Table 1) versus 3-methyl-3-phenyl diazirine ($PhCN_2CH_3$) in cyclohexane, but there is no normal KIE, within experimental error, in acetonitrile. The data reported in Table 1 were based on fits perfomed at a few selected wavelengths over the entire spectral range recorded (e.g., at the maximum of the transient absorption band). To gain greater confidence in our conclusion a global fit (simultaneous fitting in the 400−650 nm spectral range) of the $PhCN_2CH_3$ and $PhCN_2CD_3$ data was also employed, to deduce the decay rate constants using all of the recorded data. The S_1 lifetimes obtained using global fitting (5.2 ± 0.3 ps for $PhCN_2CH_3$ and 6.7 ± 0.5 ps for $PhCN_2CD_3$; see Figure S6 in Supporting Information) has lower error limits than single wavelength analysis. These results are entirely consistent with the data given in Table 1, but the lower error limits resulting from global analysis convince us that the $PhCN_2CD_3$ lifetime is definitely longer than that of $PhCN_2CH_3$. We believe that this is strong evidence for the presence of a KIE on the excited state decay. The DAS (decay associated spectra) show that the spectra for the S_1 states of both compounds are very similar (Figure S6 in Supporting Information), consistent with the fact that the same species, the S_1 state, was observed for both compounds.

Finally, the lifetime of the 3-*tert*-butyl-3-phenyl diazirine ($PhCN_2$−*t*-Bu) in cyclohexane (Table 1), where RIES of hydrogen is not possible, is quite long relative to the other alkylphenyldiazirines (the lifetimes of methyl∼ethyl∼isopropyl, where RIES is possible), but this trend is not observed in acetonitrile. Thus, we conclude that the polarity of the solvent determines the partitioning of the excited state decay mechanisms (carbene formation versus 1,2 hydrogen migration to form alkene in concert with nitrogen extrusion) which control the decay of the S_1 excited states of alkylphenyldiazirines. The lack of RIES in acetonitrile is attributed to

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the enhanced solvent stabilization of the highly polarized S_1 states in this solvent.

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Supporting Information Available: Short description of the spectrometer, kinetic traces, and global analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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