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Laser flash photolysis of 2-adamantane-2,3^1-[3H]-diazirine: a reinvestigation

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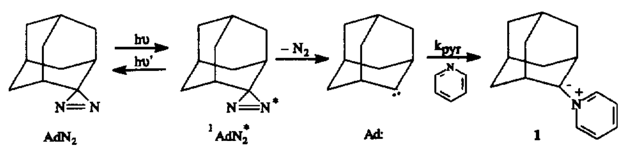
Abstract

Two of us (MSP and SM) previously reported [S. Morgan, J.E. Jackson, M.S. Platz, J. Am. Chem. Soc. 113 (1991) 2782] that adamantylidene (Ad:) reacts with thiophene to form an ylide which absorbs at 320 nm. It was concluded that Ad: has a lifetime of 2.2 μs in benzene and rather low absolute rate constants of reaction with thiophene and pyridine (1.75×10^6 M^{-1} s^{-1} and 1.54×10^6 M^{-1} s^{-1} respectively). The present study shows that the previously reported data, while reproducible, were misinterpreted. Ad: is shown to be a more short-lived carbene in benzene and alkane solvents and to react with pyridine with $k_{pyr} = 2.0 \times 10^9$ M^{-1} s^{-1} (benzene) or 2.6×10^9 M^{-1} s^{-1} (cyclohexane) as per other simple carbenes. This interpretation is consistent with that of Bonneau, Liu, Hellrung and Wirz (accompanying paper) whose work, as well as a personal communication from the Canadian co-authors of this paper, stimulated this study. Ad: reacts rapidly with spiro[adamantane-2,3^1-[3H]-diazirine] in argon purged benzene at ambient temperature with $k = 1.1 \times 10^9$ M^{-1} s^{-1} to form a species with $\lambda_{max} = 290$–300 nm. The lifetime of Ad: in argon purged benzene at ambient temperature, extrapolated to infinite diazirine dilution, is 69 ns, under these conditions. However, the lifetime of Ad: is extremely sensitive to trace amounts of water and oxygen. In rigorously purified benzene, the lifetime of Ad: is at least 553 ns at ambient temperature.

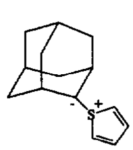
Keywords: Adamantylidene; Alkyl carbene; Pyridine ylide; Thiophene ylide

1. Introduction

In 1991, Morgan, Jackson and Platz (MJP) reported a laser flash photolysis (LFP) study of spiro[adamantane-2,3^1-[3H]-diazirine] (AdN_2). [1] LFP (351 nm, KrF excimer laser) of the diazirine produces adamantylidene (Ad:) which reacts with pyridine to form pyridine ylide **1** with $\lambda_{max} = 390$ nm in benzene [1]. However, in that study, it was not possible to resolve the growth of **1** because the spectrometer in use at that time could not time resolve the ylide absorption from the fluorescence of the diazirine [2,3].



MJP discovered that LFP of AdN_2 in the presence of thiophene produced a transient with $\lambda_{max} = 320$ nm, well to the blue of the diazirine fluorescence. The rate of formation of this species was resolved and found to be first order in the concentration of thiophene. For this reason MJP associated the transient with ylide **2**.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Using probe methodology [4] absolute rate constants of Ad: ($k_{pyr} = 1.54 \times 10^6$ M^{-1} s^{-1}) and its lifetime (2.2 μs) in benzene were deduced [1]. Since 1991 many carbenes have been studied by the pyridine ylide technique and the reported values of MJP of τ and k_{pyr} now look suspiciously low [5,6].

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Recent work by Bonneau, Liu, Hellrung and Wirz (BLHW—accompanying paper [7]), as well as a personal communication from the Canadian co-authors, reignited our (MSP, SM) interest in this system and prompted this reinvestigation. Our new results agree with those of BLHW, where they overlap, and demonstrate that while the previous work is reproducible, it was misinterpreted. The new results demonstrate that the lifetime and reactivity of Ad: are comparable to those of other simple carbenes [5,6].

2. Materials and methods

AdN_2 was synthesized according to literature procedures [8–10]. Benzene and thiophene were distilled over Na prior to use and stored over molecular sieves. Pyridine was distilled from and kept over NaOH. Cyclohexane was dried with $MgSO_4$, distilled from P_2O_5 and stored over molecular sieves.

2.1. Carbomethoxy hydrazone of 2-adamantanone

The carbomethoxy hydrazone of 2-adamantanone was prepared by refluxing 2-adamantanone (3.01 g, 0.020 mol) with carbomethoxy hydrazine (1.98 g, 0.022 mol) in benzene for 8 h using a Dean–Stark apparatus. The crude product, isolated as a white solid after removal of the solvent with a rotary evaporator, was recrystallized from ethanol to give 3.65 g (82% yield) of the expected product as a white solid, mp 123.5–124°C, ^1H NMR (200 MHz, $CDCl_3$) δ: 1.66–1.83 (m, 12 H), 2.69–2.93 (m, 2 H), 3.80 (s, 3 H), 7.74 (s, 1 H).

2.2. 5′,5′-Dimethoxyspiro[adamantane-2,2′-[Δ^3-1,3,4]-oxadiazoline] (4)

A solution of the carbomethoxy hydrazone of 2-adamantanone (3.65 g, 0.0164 mol) in 125 ml of methanol was cooled to 0°C in an ice bath and a solution of lead tetraacetate (7.27 g, 0.0164 mol) in 25 ml of methanol was added slowly from a dropping flask, with stirring, over a period of 45 min. When addition was complete, stirring and cooling with ice was continued for one hour before the mixture was allowed to warm to room temperature. Methanol was then removed with a rotary evaporator, the product was dissolved in CH_2Cl_2, and the solution extracted three times with 4% sodium bicarbonate. The organic layer was then dried over magnesium sulfate before the solvent was evaporated. The residue was subjected to centrifugal chromatography on silica gel using a gradient of eluants ranging from hexane to 9:1 hexane:ethyl acetate. Yield, 2.32 g (56%) of a clear viscous oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 1.70–2.53 (m, 14 H), 3.44 (s, 6 H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 26.4 (−) (CH), 27.1 (−) (CH), 34.3 (+) (CH_2), 34.7 (+) (CH_2), 36.9 (+) (CH_2), 51.6 (−) (OCH_3), 124.2 (+) (C5′), 135.3 (+) (C2); MS (e.i.) *m/z*: (molecular ion not observed), 221 $[M–OMe]^+$, 165, 134, 119, 106, 105, 93, 92 (100%), 90, 79, 59; MS (c.i., NH_{33}) *m/z* 270 $[M+NH_4]^+$; UV (pentane) $\lambda_{max} = 328$ nm ($\epsilon = 300$).

2.3. UV-LFP of 5′,5′-dimethoxyspiro[adamantane-2,2′-[Δ^3-1,3,4]oxadiazoline] (4) (Ottawa)

A stock solution of **4** was prepared with freshly distilled cyclohexane so that the OD reading measured by UV–Vis spectroscopy at 308 nm was approximately 1.2 ([oxadiazoline] ca. 5×10^{-3} M). That solution was diluted to half with freshly distilled cyclohexane in a cuvette so that the OD at 308 nm was approximately equal to 0.6 (2 ml solution). After degassing with N_2, the time-resolved UV–Vis spectrum was acquired (300–700 nm) after 308 nm LFP [12a]. No transient absorbing above 310 nm was observed. A stock solution of pyridine (1.0 M) was similarly diluted to half with cyclohexane in a cuvette (total volume of 2 ml) and the UV–Vis time-resolved spectrum acquired (300–700 nm) after 308 nm LFP. Again, no transient intermediate was observed. The stock solution of oxadiazoline was also diluted to half with 1.0 M pyridine in cyclohexane (total volume 2 ml, OD at 308 nm 0.6) and, after degassing with N_2, the time-resolved UV–Vis spectrum was acquired (300–700 nm) after 308 nm LFP. A strong persistent band with λ_{max} at approximately 380 nm was observed and assigned to the π–π^* transition of the pyridine ylide of adamantylidene. A broad absorption in the visible region of the spectrum was also observed and assigned to the n–π^* transition for the pyridine ylide. The lifetime of the transient giving rise to the spectrum assigned to the pyridine ylide of adamantylidene was estimated by measuring the top OD of the pyridine ylide signal as a function of [pyridine]. Individual solutions at each concentration of pyridine were prepared separately and degassed for the same length of time (5 min). A plot of the change in top OD as a function of [pyridine] showed that most of the adamantylidene is captured at about 0.1 M pyridine. Double reciprocal treatment of the data gave, after analysis, a value of $k_{pyr}\,\tau$ [11].

2.4. UV-LFP of 2-adamantane-2,3′-[3H]-diazirine (Columbus)

Laser flash excitations for kinetic studies were obtained with a Nd:YAG laser (Continuum PY62C-10, 150 ps, 25 mJ/pulse, 355 nm), which has been described previously [12b]. Transient absorption spectra were obtained by excitation of the sample with a Lumonics TE-861-4 excimer laser (351 nm) or Lambda Physic LPX-100 excimer laser (308 nm) and recorded with an EG and G Princeton Applied Research Model 1460 optical multichannel analyzer (OMA).

Stock solutions of AdN_2 were made with concentrations between 0.01–0.001 M. The stock solution (1 ml) was pipetted to a 2 ml volumetric flask and various amounts of either pyridine or thiophene (0.1 to 0.01 M) were added to each volumetric flask. The samples were transferred into quartz cuvettes and flushed with argon prior to photolysis. At least

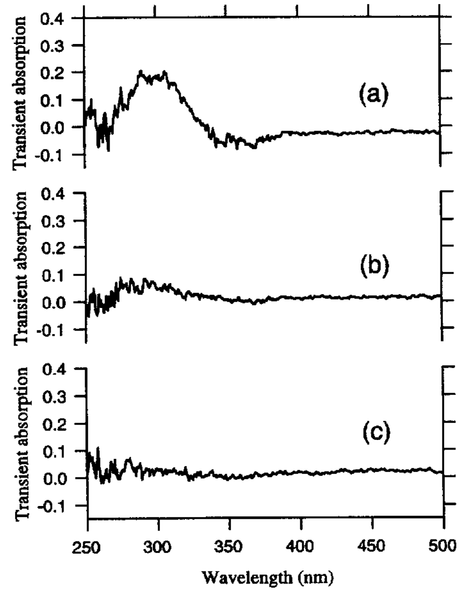


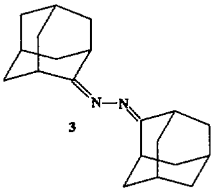
Fig. 1. Transient spectrum produced in argon purged benzene upon LFP (XeF excimer, 351 nm) of (a) 0.0111 M (b) 0.00224 M and (c) 0.00111 M adamantyldiazirine at ambient temperature.

two transient spectra were recorded and averaged for each data point.

3. Results and discussion

Laser flash photolysis (LFP) studies of oxadiazolines have recently been reported [13]. LFP (Nd:YAG, 355 nm, 150 ps, 35 mJ) of AdN_2 (0.01–0.08 M) in benzene produces a transient which absorbs at 290–300 nm (Fig. 1). It was possible to resolve the formation of this species following the laser pulse (Fig. 2). The formation of the transient was exponential and could be analyzed to deduce an observed rate constant of formation (k_{obs}). The observed rate constant of formation of the transient is linearly dependent on the concentration of diazirine precursor ($k = 1.1 \times 10^9\ M^{-1}\ s^{-1}$, Fig. 3) in benzene at ambient temperature. The lifetime of Ad: under these conditions in argon purged benzene at ambient temperature, extrapolated to infinite diazirine dilution is 69 ns.

We postulate that the 290–300 nm transient is an intermediate which eventually rearranges to form azine **3**, a common product formed upon decomposition of AdN_2 [14–16].



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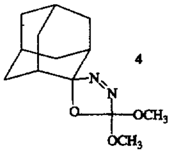

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LFP (308 nm, XeCl, excimer laser) of oxadiazoline **4** or AdN_2 in the presence of pyridine also forms a new transient with $\lambda_{max} = 380$ nm (Fig. 4). This transient is attributed to ylide **1** because its spectrum is similar to that of other carbene-pyridine ylides which have been reported [5,6]. Signifi-

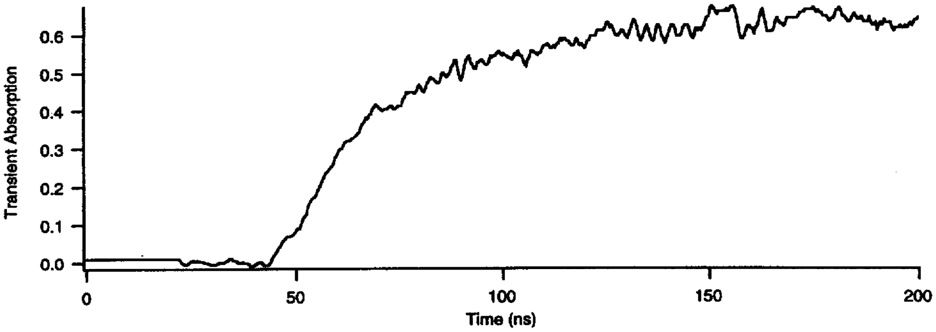

Fig. 2. The formation of the 290–300 nm absorbing transient upon LFP of adamantyldiazirine (0.016 M) in argon purged benzene at ambient temperature.

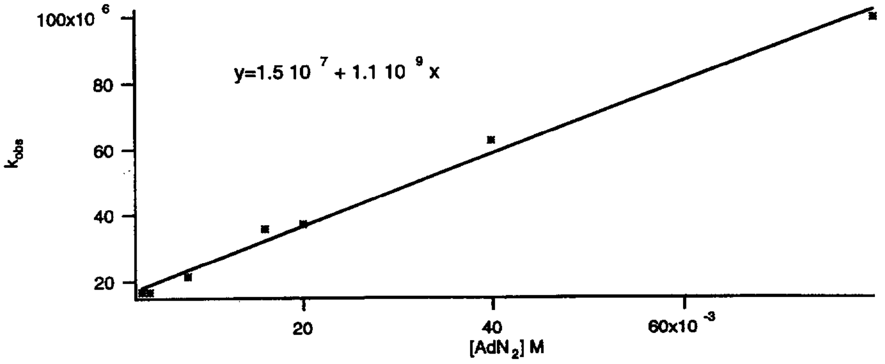

Fig. 3. A plot of the observed rate constant of formation of the 290–300 nm absorbing transient as a function of [adamantyldiazirine] in argon purged benzene at ambient temperature.

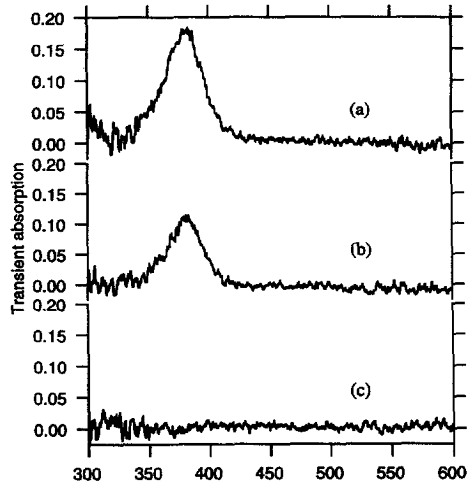

Fig. 4. The transient spectrum produced upon LFP of AdN_2 (0.002 M) at ambient temperature in the presence of (a) 0.062 M (b) 0.019 M and (c) O M pyridine in argon purged cyclohexane at ambient temperature.

cantly, LFP of **4** does not produce the intermediate absorbing at 300 nm, providing further evidence that this transient is derived from diazirine precursor AdN_2.

With AdN_2 it was possible to resolve the formation of **1** (Fig. 5) as a function of pyridine concentration. Analysis as before leads to values of k_{obs}, plots of k_{obs} versus [pyridine] (Fig. 6) and the following values in argon purged, rigorously dried solution: [1]

$$\tau(\text{Ad:}) = 553 \pm 15 \text{ ns}, k_{pyr} = 2.0 \times 10^9 \text{ M}^{-1} \text{s}^{-1} \text{ (benzene)}$$

$$\tau(\text{Ad:}) = 19 \pm 2 \text{ ns}, k_{pyr} = 2.6 \times 10^9 \text{ M}^{-1} \text{s}^{-1} \text{ (cyclohexane)}$$

These values of k_{pyr} are comparable to those of other simple carbenes [5,6], but the τ values of Ad: have not been corrected for the concentration of diazirine. The short lifetime of **1** in cyclohexane must be due to CH insertion reactions with the solvent [14–16].

Dimethylcarbene is predicted by theory [17–19] to have a singlet ground state. Carbenes with singlet ground states react rapidly with pyridine [5,6]. Carbenes with triplet ground states react slowly with pyridine to form singlet ylides because the reaction is formally spin forbidden. The rate of the spin forbidden reaction is controlled by the accessibility of the energy surface connecting the singlet carbene and pyridine with ylide [20,21]. The large value of k_{pyr} that is observed indicates that Ad: has a singlet ground state. This is consistent with the matrix spectroscopy of Ad: [22].

Values of k_{pyr} are more accurate than those of τ because slopes can be determined more accurately than intercepts. To check the validity of τ, determined in this manner, the yields of ylide **1** were measured as a function of [pyridine] in various solvents (Fig. 7). A double reciprocal plot of the data (Fig. 8) is linear [5,6]. The ratio of the intercept/slope of this plot is k_{pyr} τ. Values of τ determined by this method (Table 1) are in good agreement with the directly determined values using the k_{pyr} values of this work.

The lifetime of Ad: is longest in benzene. C–H insertion reactions are less favorable in benzene then in cyclohexane due to the increased strength of the C–H bond in the former solvent. It is also conceivable that Ad: is solvated to some

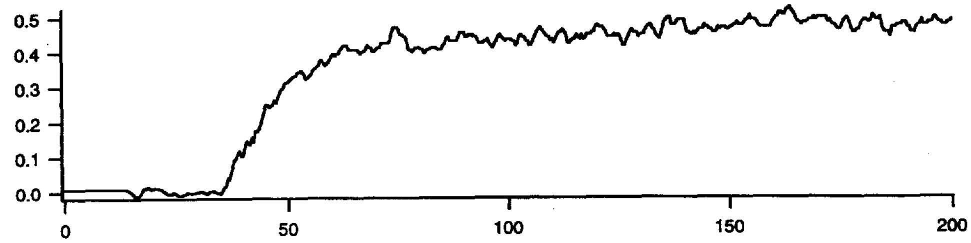

Fig. 5. The formation of ylide **1** following LFP of (0.0024 M) AdN_2 in argon purged benzene at ambient temperature.

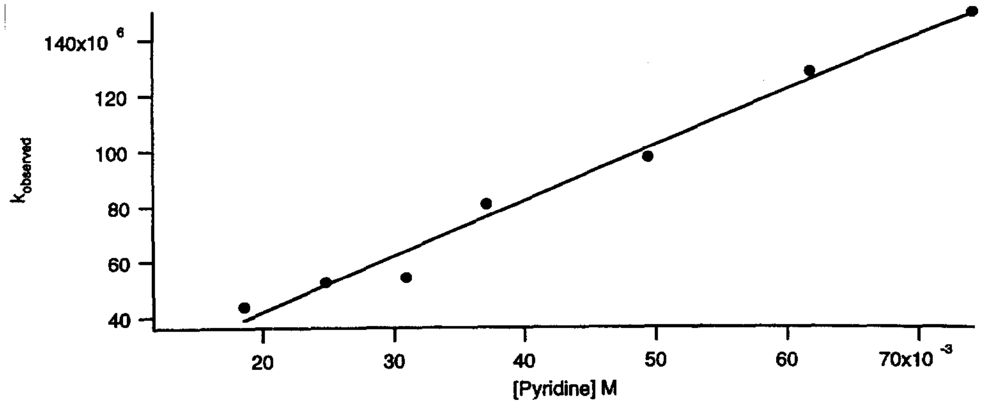

Fig. 6. A plot of k_{obs} of formation of **1** following LFP of 0.001 M AdN_2 in argon purged benzene at ambient temperature as a function of [pyridine].

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[1] The authors are indebted to Professor Wirz and Professor Bonneau for informing us of the extreme sensitivity of τ in this system to the presence of trace quantities of water.

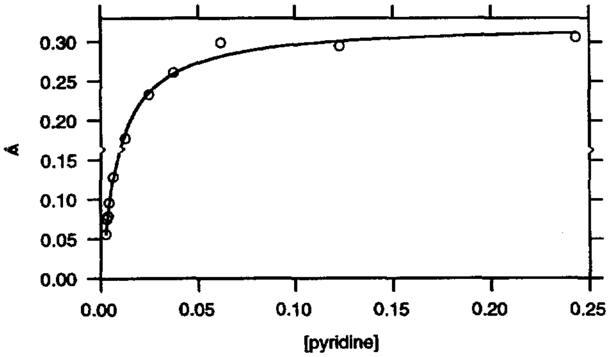

Fig. 7. The yield of ylide **1** as a function of [pyridine] produced by LFP of AdN_2 (0.0016 M) in argon purged benzene at ambient temperature.

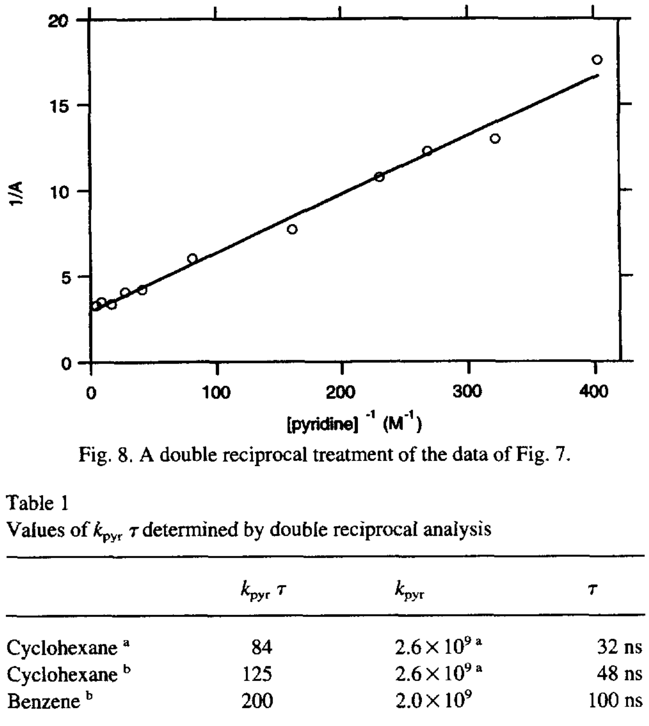

Fig. 8. A double reciprocal treatment of the data of Fig. 7.

Table 1
Values of k_{pyr} τ determined by double reciprocal analysis

	$k_{pyr}\tau$	k_{pyr}	τ
Cyclohexane [a]	84	2.6×10^9 [a]	32 ns
Cyclohexane [b]	125	2.6×10^9 [a]	48 ns
Benzene [b]	200	2.0×10^9	100 ns

[a] AdN_2 precursor, YAG laser, 351 nm (Columbus).

[b] Oxadiazoline precursor **4**, XeCl excimer laser, 308 nm (Ottawa).

extent by the π system of benzene. Effects of this type have been discovered by Khan and Goodman [23], by Moss and co-workers [24] and by the Jones group [25].

LFP of **1** (0.011 M) in benzene containing 0.51–1.26 M thiophene produces the transient first reported by MJP [1]. This transient was formed in an exponential process which was analyzed to yield an observed rate constant of formation (k_{obs}). A plot of k_{obs} as a function of [thiophene] is linear with a slope of $2.9–3.2 \times 10^6$ M^{-1} s^{-1} which is k_T, the absolute rate constant for reaction of an intermediate with thiophene. The inverse of the intercept of this plot is τ, the lifetime (5–7.5 μs) of the species which reacts with thiophene to form this transient. These results are in reasonable agreement with MJP who reported values of τ of 2.2 μs and k_T of $1.75 \pm 0.6 \times 10^6$ M^{-1} s^{-1}.

Different results are obtained with thiophene when rigorously dried and deoxygenated benzene or cyclohexane is employed. LFP of AdN_2 under these conditions again produces a transient absorption at 320 nm (Fig. 9). The observed rate constant of formation of this transient is again linearly dependent on [thiophene] (Fig. 10). However, the slope of this plot is 1.8×10^9 M^{-1} s^{-1} in benzene and is 2.5×10^9 M^{-1} s^{-1} in cyclohexane. The intercept of each plot is $1/\tau$ where τ is the lifetime of the species reacting with pyridine.

Under these conditions we find that $\tau = 173$ ns and 20 ns in benzene and cyclohexane respectively. The thiophene trapping rate constants and lifetimes are similar to the values for Ad: obtained with pyridine. Thus, the species absorbing at 320 nm under rigorously dried conditions is associated with carbene-thiophene ylide **2**.

Although Morgan, Jackson and Platz [1] observed a species absorbing at 320 nm it cannot have been ylide **2** as the reactivity of the species trapped in that work is much too low. We speculate that the species observed by MJP is derived from reaction of thiophene with a secondary species derived from Ad:, perhaps the 290 nm transient formed by reaction of carbene with AdN_2. It is an unfortunate coincidence that this secondary species and thiophene ylide **2** have similar transient spectra. Thus, the carbene lifetimes and absolute rate constants of Ad:, reported earlier by MJP, are retracted [1].

4. Conclusions

Photolysis of AdN_2 releases adamantylidene (Ad:). Ad: reacts rapidly with AdN_2 ($k = 1.1 \times 10^9$ M^{-1} s^{-1}) in benzene to form an intermediate which absorbs at 290–300 nm and is likely to be a species which eventually rearranges to form

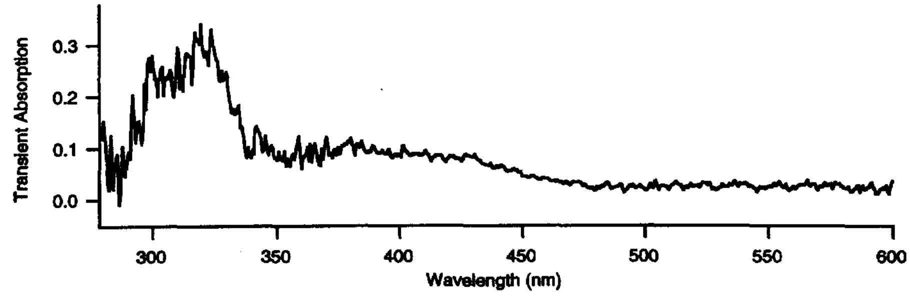

Fig. 9. The transient spectrum produced upon LFP of AdN_2 (0.020 M) in rigorously dried benzene at ambient temperature in the presence of 1.63 M thiophene.

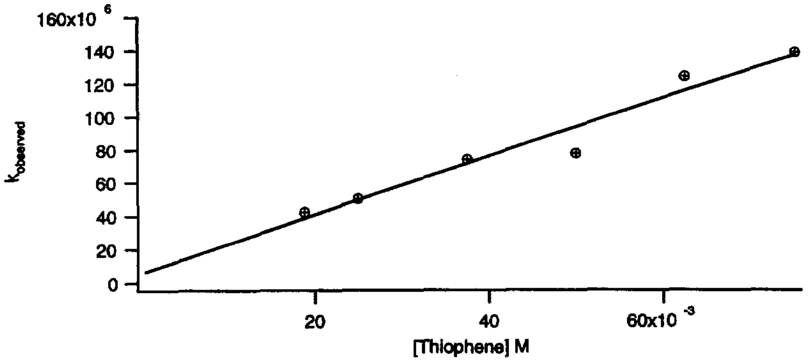

Fig. 10. A plot of k_{obs} of formation of **2** following LFP of (0.00213 M) AdN_2 in argon purged, rigorously dried benzene (ambient temperature) as a function of thiophene concentration.

azine product "3". The lifetime of Ad: in argon purged, rigorously dried benzene at ambient temperature is at least 553 ns. Ad: reacts rapidly with pyridine ($k_{pyr}=2.6\times10^9\ M^{-1}\ s^{-1}$) in cyclohexane and in benzene ($2.0\times10^9\ M^{-1}\ s^{-1}$). It is clear that a previous study [1] of this system was misinterpreted. The results of this study are consistent with those of Bonneau, Liu, Hellrung and Wirz (accompanying paper) where they overlap.

5. Abbreviations

Ad	adamantylidene
AdN_2	2-Adamantane-2,3^1-[3H]-diazirine
BLHW	Bonneau, Liu, Hellrung and Wirz
LFP	Laser flash photolysis
MJP	Morgan, Jackson and Platz
MSP	Matthew S. Platzobs, observed
pyr	pyridine
SM	Scott Morgan

Acknowledgements

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