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Adamantylidene revisited: flash photolysis of adamantanediazirine

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Abstract

Irradiation of 2-adamantane-2,3′-[3*H*]-diazirine (**1**) in isooctane at room temperature gives two primary photoproducts, 2-diazoadamantane and 2-adamantylidene (**Ad:**), with quantum yields of about 0.5 each. The fluorescence quantum yield of **1** is small, $\phi_f(\mathbf{1}) \approx 10^{-4}$. The reactivity of **Ad:** was studied by nanosecond laser flash photolysis; it is best described as that of a carbene equilibrating between the singlet ground state and a low-lying triplet state. **Ad:** reacts with the precursor diazirine **1**, pyridine, acetonitrile, tetramethylethylene, amines, water, and acetic acid with rate constants approaching the diffusion-controlled limit, as well as with molecular oxygen ($k_{O_2} = 2.3 \times 10^9$ M^{-1} s^{-1}). Reaction of **Ad:** with **1** ($k_X = 3.6 \times 10^9$ M^{-1} s^{-1}) gives an ylide, $\lambda_{max} = 290$ nm, which forms adamantanone azine as a stable product by a reaction having activation parameters $E_a = 15.5$ kcal mol^{-1} and $A = 2 \times 10^{12}$ s^{-1}. At low concentrations of **1** in thoroughly dry, degassed solvents, the lifetime of **Ad:** reaches ca. 225 ns in isooctane, 500 ns in perfluorodecalin, and 700 ns in benzene. Diazoadamantane forms azine by a second-order reaction with a half-life of several hours at 10^{-4} concentration.

Keywords: Carbenes; Laser flash photolysis; Absolute reaction rate constants; Ylides

1. Introduction

2-Adamantylidene (**Ad:**) is formed by irradiation of the readily available 2-adamantane-2,3′-[3*H*]-diazirine (**1**). **Ad:** has long been known [1] to be intrinsically long-lived, because its intramolecular rearrangements are impeded by geometrical constraints, which makes it an ideal candidate to study the intermolecular reactivity of a simple dialkycarbene. Morgan et al. [2] have investigated **Ad:** by laser flash photolysis (LFP) employing pyridine and thiophene as 'indicators' and, more recently with Bally et al. [3], by direct IR and optical detection following irradiation of matrix-isolated **1**. These authors concluded that the electronic ground state of **Ad:** is a singlet state on the basis that irradiation in solid glasses at low temperature failed to produce an EPR spectrum and that the transient kinetics of thiophene ylide formation from **Ad:** were not influenced by the presence of oxygen. That conclusion was reinforced by the observation of an electronic absorption band of matrix-isolated **Ad:** at 620 nm and by quantum chemical calculations.

We encountered some incompatibilities with the mechanistic interpretations of the previous LFP study in the course of recent work on the photorearrangement of dialkyl diazirines to the corresponding diazo compounds [4]. We do not challenge any of the experimental results reported in the previous LFP study, but additional investigations lead us to propose that the data need substantial re-interpretation. The main reactions studied in the present work are summarized in Scheme 1. Some related and consistent findings, which are reported in an accompanying paper, were reached independently by Pezacki et al. [5].

2. Experimental part

2.1. Flash photolysis, transient absorption spectra

For kinetic measurements performed in Bordeaux, excitation was provided by a frequency-tripled, mode-locked Nd:YAG laser (Quantel, TEM$_{00}$, 200 ps, 20 mJ/pulse at 355 nm). A crossed-beams arrangement with a 10:2 mm cell (detection:excitation) was used. The temperature of the sample could be varied from 5 to 50°C by a cell holder equipped with Peltier elements, or from room temperature down to −60°C by using a flow of cold nitrogen gas and a quartz

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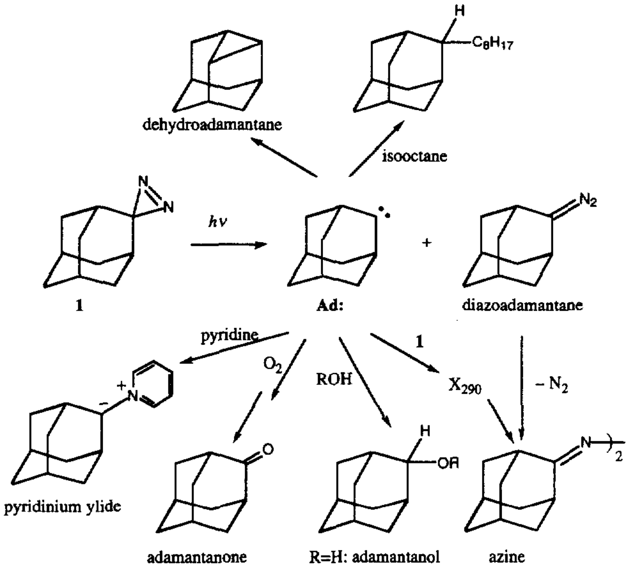


Scheme 1.

Dewar flask. Due to the low value of the absorption coefficient of diazirine **1** at 355 nm, this arrangement required concentrations of **1** in the range of 3–10 mM. A colinear-beams arrangement with optical paths up to 4 cm was used for studies of more dilute solutions ([**1**] ≈ 1 mM). The signal was recorded either with a Tektronix 7912AD transient digitizer (10 ns–1 ms) or with a digital oscilloscope (1 ms–10 s). Flushing with nitrogen, argon, oxygen or with mixtures of these gases was used to vary the oxygen content of the solutions, as indicated.

In Basel, transient kinetics were determined by excitation with an excimer laser operated on XeF (351 nm, 25 ns pulse width, 100 mJ/pulse). A pulsed Xenon arc was the source of monitoring light in a crossed-beams arrangement with a 5:1 cm sample cell (detection:excitation). Measurements were done at ambient temperature (ca. 22 ± 2°C). Solutions were degassed by the freeze–pump–thaw technique in evacuable quartz sample cells. To investigate the effect of oxygen on the transient kinetics, the solutions were equilibrated with air or oxygen at pressures controlled by a mercury barometer which was attached to the vacuum line.

The absorption spectra and kinetics of long-lived species ($\tau > 30$ s) at low temperature were recorded with a photodiode array spectrophotometer (HP-8452A) after excitation by a frequency-tripled, Q-switched Nd YAG laser (BMI laser, multimode, 5 Hz, 10 ns, 30 mJ/pulse at 355 nm) for several seconds. In these experiments, the excitation beam was passed through a ground glass diffuser held 2.5 cm in front of the sample cell, and the absorbance of the solution at 355 nm was limited to about 0.3 in order to achieve homogeneous excitation. Nevertheless, it was best to shake the cell for a few seconds between excitation and recording of the spectra in order to get reproducible absorbance decays.

2.2. Quantum yields

The quantum yield of photodecomposition of diazirine **1** was determined under irradiation by the 366-nm line of a mercury lamp (Philips HPK 125), isolated by a set of filters. The photon flux was determined using solutions of Aberchrome 640 [6–8] or azobenzene [9–11] as actinometers, and the rate of decomposition of **1** was measured by the decrease of the absorption at 366 nm.

2.3. Analysis of transient kinetic data [12]

Least-squares fitting of model functions was done using the data points in a form for which standard errors were assumed to be constant. Thus, absorbance decay traces were directly analyzed by nonlinear least-squares fitting of the appropriate rate law, usually a single exponential function. Similarly in Stern–Volmer analyses, values of $\log(k_{obs}/s^{-1})$ or amplitudes A of exponential growth or decay curves were used as data points, rather than k_{obs}/s^{-1} or $1/A$. Nonlinear least-squares fitting was thus preferred to the use of linearized model functions such as 'dual reciprocal plots', which tend to give excessive weight to poorly defined data points. Uncertainty intervals are quoted as standard errors.

2.4. Emission spectroscopy

A SPEX Fluorolog spectrofluorimeter equipped with a Hamamatsu R928 photomultiplier was used for the fluorescence measurements. Emission spectra were corrected for instrument response using a certified tungsten lamp; the stability of the response function was checked regularly with quinine sulfate solutions.

2.5. Product analysis by GC-MS

Irradiated solutions were concentrated by evaporation of the solvent and 1 μl-aliquots were injected into a Hewlett-Packard gas chromatograph (HP 5890) equipped with a 25-m dimethyl-silicone column. The temperature of the column was programmed to rise at a rate of 10°C/min from 70 to 270°C. Retention times were 8, 11, 12, 17, 22, and 25 min for **3**, **4**, adamantan-2-ol, isooctane addition products, bis-adamantyl ether, and azine **2**, respectively. Eluted products were analyzed by a mass spectrometer (HP 5971), that was coupled to the GC-outlet.

2.6. Materials

Diazirine **1** was prepared [13] from 2-adamantanone and purified by chromatography on a silica column. Three different batches, including one kindly provided by Prof. Platz for comparison purposes, gave the same results. Isooctane was used from several sources (SDS or Fluka, spectroscopy grade; Aldrich and Rathburn, HPLC grade) without noticeable differences in the results. However, the lifetime of **Ad:** strongly depended on the water content of the solvent, which increased on exposure of the solutions to moist air or glass. On the other hand, prolonged flushing of isooctane solutions with inert gases, which was done to remove O_2, appeared to reduce the water content of isooctane by evaporation. Thus, special care was required to use solvents of constant humidity in series of experiments designed to determine the effect of added reagents on the lifetime of **Ad:**. Where indicated, isooctane and benzene were dried with molecular sieves (Fluka, UOP, 4 Å) before use. Thiophene (Fluka or Aldrich, 99+% grade) was used within a few days following receipt from the supplier. GC analysis of perfluorodecalin (Aldrich, 95%) indicated a purity ≥98%. Pyridine of analytical quality was distilled and kept over KOH.

3. Results

3.1. Fluorescence of diazirine 1

Weak fluorescence emission from dialkyldiazirines, including **1**, has been reported some time ago [14], and a detailed investigation of the fluorescence spectrum and lifetime ($\tau_f = 0.24 \pm 0.01$ ns in various solvents at room temperature) of **1** was reported recently by Buterbaugh et al. [15]. These authors determined the fluorescence quantum yield for **1** in several solvents as $\phi_f = 1.2 \times 10^{-3}$ using 1,4-diphenyl-1,3-butadiene as a standard. In this work, an even lower quantum yield of about 1.5×10^{-4} was determined for **1** in isooctane using benzo[*c*]phenanthrene as a standard ($\phi_f = 0.12$ in degassed cyclohexane) [16]. The reason for the discrepancy is not clear, but it might simply reflect the uncertainty associated with measuring a very small fluorescence quantum yield vs. highly fluorescent standards. On the basis of the radiative constant, $k_f \approx 1.5 \times 10^6$ s^{-1}, estimated [17] from the intensity of the first absorption band of **1**, one calculates $\phi_f = k_f \tau_f \approx 4 \times 10^{-4}$, but the reliability of such estimates for weak transitions is questionable.

The fluorescence of **1** interfered with the transient absorption measurements in the range of 370–450 nm: kinetic traces exhibited ringing in the detection circuit which lasted for about 15 ns and precluded accurate analysis of transient absorptions during that time. This problem was alleviated by using lower concentrations of **1** and by optimizing the optical set-up of the detection system.

3.2. Measurements using the pyridinium ylide trapping technique

The absorption band of **Ad:** at 620 nm is very weak [3], and the carbene could not be detected directly by virtue of its absorption using flash photolysis. However, excitation of **1** (5–10 mM) in aerated isooctane solutions containing pyridine (3–100 mM) produced strong transient absorption, $\lambda_{max} = 385$ nm (inset of Fig. 1), which is attributed to the pyridinium ylide [2]. Despite the improved time resolution of the current set-up, it was difficult to resolve the formation of the pyridine ylide accurately because of the interfering fluorescence signal mentioned above. In degassed or argon-purged solutions, however, growth curves were substantially slower and well separated from the fluorescence signal (Fig. 1), which indicates that **Ad:** is quenched by oxygen.

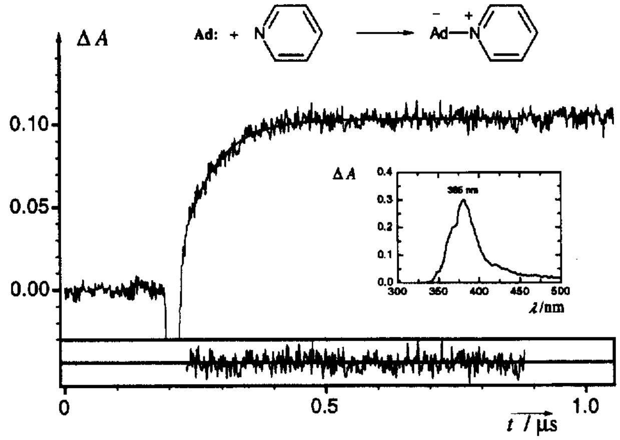


Fig. 1. Kinetic trace of the formation of the pyridinium ylide after flash photolysis of **1** (1 mM) at 351 nm in degassed isooctane containing 10 mM pyridine. The solid line corresponds to the best fit of a single exponential growth function observed at 385 nm, $k_{obs} = 1.53 \times 10^7$ s^{-1}. Inset: transient absorption spectrum of the pyridinium ylide observed with a delay of 1 µs after the laser pulse. Bottom trace: normalized residuals of the fit.

Growth curves of the pyridine ylide absorbance at 385 nm, determined by flash photolysis of **1** (1.05 mM) in argon-purged isooctane solutions, obeyed first-order kinetics, and the observed rate constants increased linearly with pyridine concentration (0.75–9.0 mM, 24 measurements; Eq. (1)).

$$1/\tau_{growth} = k_{obs} = k_0 + k_Y[\text{pyridine}] \qquad (1)$$

The second-order rate coefficient for the addition of **Ad:** to pyridine, $k_Y = (5.0 \pm 0.2) \times 10^9$ M^{-1} s^{-1}, and the first-order rate constant for the decay of **Ad:** in deoxygenated isooctane in the absence of pyridine, $k_0 = (1.2 \pm 0.2) \times 10^7$ s^{-1}, were determined by nonlinear fitting to the data points $\log(k_{obs}/\text{s}^{-1})$.

The products formed by the decay of **Ad:** in the absence of pyridine do not absorb at 385 nm. The amplitude of the 385-nm kinetic growth curves due to formation of the pyridinium ylide must then be proportional to the efficiency of the trapping reaction, $A_{385} = ak_Y[\text{pyridine}]/(k_Y[\text{pyridine}] + k_0)$, where the rate constants k_0 and k_Y are defined as in Eq. (1). The factor a depends on the quantum yield of formation of **Ad:**, the molar absorbance coefficient ε of the pyridinium ylide, and the amount of light absorbed by **1**. The observed amplitudes were corrected for pulse-to-pulse variations in the laser intensity (±10%). A plot of $1/A_{385}$ vs. $1/[\text{pyridine}]$ was indeed linear (Eq. (2)).

$$1/A_{385} = \frac{1}{a}\left\{1 + \frac{k_0}{k_Y[\text{pyridine}]}\right\} \qquad (2)$$

The parameters of Eq. (2) were determined by nonlinear least-squares fitting to the amplitudes A_{385} of the same set of kinetic traces that was used for analysis by Eq. (1) (0.75–9.0 mM, 24 measurements). The ratio of the intercept and slope of Eq. (2) gave $k_Y/k_0 = 550 \pm 150$ M^{-1}, which is consistent with the ratio $k_Y/k_0 = 417 \pm 71$ M^{-1} of the rate constants obtained from Eq. (1). A similar series acquired with aerated solutions of **1** (5 mM) in isooctane containing various amounts of pyridine (3–20 mM, 6 measurements) gave $k_Y/k_0 = 114 \pm 6$ M^{-1}. Using $k_Y = (5.0 \pm 0.2) \times 10^9$ M^{-1} s^{-1} from above, the lifetime of **Ad:** in aerated isooctane at [**1**] = 5 mM is calculated as $\tau_0 = 1/k_0 = 18 \pm 2$ ns.

When diethyl amine (DEA) was added to the solution, competition between the reactions of **Ad:** with pyridine and with DEA reduced the amplitude of the pyridinium ylide signal, A_{385}. In aerated isooctane containing 4.5 mM pyridine, the decrease of A_{385} as a function of DEA concentration obeyed the expected Stern–Volmer relationship, Eq. (3), namely, $1/A_{385}$ increased linearly with DEA concentration at constant pyridine concentration.

$$1/A_{385} = \frac{1}{a}\left\{1 + \frac{k_0 + k_{\mathrm{DEA}}[\mathrm{DEA}]}{k_Y[\mathrm{pyridine}]}\right\} \qquad (3)$$

Nonlinear fitting to the amplitudes A_{385} ([DEA] = 2–100 mM, 8 measurements) gave the parameters for the slope, $k_{\mathrm{DEA}}/(ak_Y[\mathrm{pyridine}])$, and the intercept, $(k_0 + k_Y[\mathrm{pyridine}])/(ak_Y[\mathrm{pyridine}])$, of Eq. (3). Their ratio, $k_{\mathrm{DEA}}/(k_0 + k_Y[\mathrm{pyridine}])$, is 49 ± 5 M^{-1}; using the values $1/k_0 = 18 \pm 2$ ns and $k_Y = (5.0 \pm 0.2) \times 10^9$ M^{-1} s^{-1} from above, one obtains the rate coefficient $k_{\mathrm{DEA}} = (3.8 \pm 0.5) \times 10^9$ M^{-1} s^{-1} for the reaction of **Ad:** with DEA. No absorption attributable to an ammonium ylide was observed, even with large amounts of DEA.

3.3. Measurements using diazirine (1) as an indicator for adamantylidene

Formation of a transient absorption was observed in the range 270–330 nm, $\lambda_{\max} = 290$ nm, at low concentrations or in the absence of pyridine and DEA in isooctane solution. The absorption spectrum of this species, henceforth denoted as X_{290}, is shown in Fig. 2. The growth of this absorbance, A_{290}, was accurately resolved and obeyed a first-order rate law. Diazirine **1** does not give fluorescence emission at 290 nm. The growth rate k_{obs} depended on the concentration of **1** in aerated isooctane, $\tau_{\mathrm{growth}} = 1/k_{\mathrm{obs}} = (18 \pm 1)$ ns for [**1**] = 5 mM and (25 ± 2) ns at [**1**] = 0.85 mM. From these two points one obtains $k_X = (3.7 \pm 1.5) \times 10^9$ M^{-1} s^{-1} and $k_0 = (3.7 \pm 0.5) \times 10^7$ s^{-1} assuming a linear relationship with the concentration of **1**, Eq. (4).

$$k_{\mathrm{obs}} = k_0 + k_X[\mathbf{1}] \qquad (4)$$

More accurate data were obtained using degassed isooctane (20 measurements, [**1**] = 1–5 mM). The observed rate constants increased linearly with the concentration of **1**, and $k_X = (3.6 \pm 0.2) \times 10^9$ M^{-1} s^{-1} and $k_0 = (8.8 \pm 0.6) \times 10^6$ s^{-1} were determined by nonlinear fitting to $\log(k_{\mathrm{obs}}/\mathrm{s}^{-1})$.

The lifetime of **Ad:** extrapolated to [**1**] = 0 M was thus $\tau_0 = 1/k_0 = 113 \pm 8$ ns in this series. This limiting lifetime is somewhat different from that determined from Eq. (1), $\tau_0 = 85 \pm 15$ ns. Moreover, earlier measurements of the concentration dependence of **1** not reported here had given a slope consistent with the above, but a significantly different intercept. Varying exposure of the solvent to moisture was found to be the origin of these discrepancies. The limiting lifetime in degassed isooctane solutions saturated with water was $\tau_0 = 90 \pm 10$ ns. On the other hand, τ_0 increased to 225 ± 15 ns after prolonged drying of the solvent with molecular sieves.

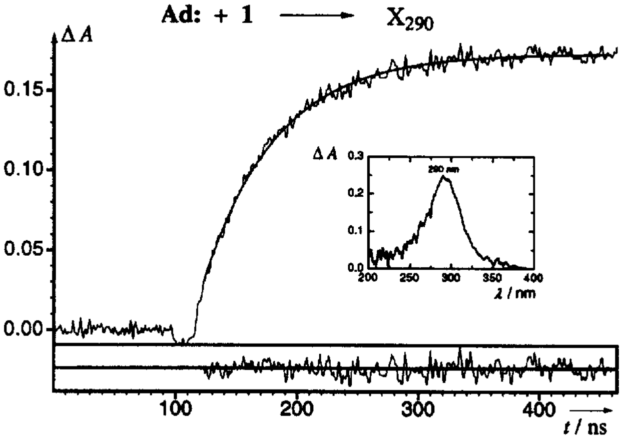


Fig. 2. Kinetic trace of the formation of ylide X_{290} following flash photolysis of **1** (2 mM) at 351 nm in degassed isooctane. The solid line corresponds to the best fit of a single exponential growth function observed at 290 nm, $k_{\mathrm{obs}} = 1.62 \times 10^7$ s^{-1}. Inset: transient absorption spectrum of ylide X_{290} observed with a delay of 1 μs after the laser pulse. Bottom trace: normalized residuals of the fit.

The linear dependence of the growth rate of X_{290} on the concentration of **1**, Eq. (4), suggests that X_{290} is formed by reaction of **Ad:** with excess **1** and that the rate coefficient k_X is the bimolecular rate constant of this reaction (Scheme 1). This hypothesis is further supported by the observations described below.

(i) Addition of DEA to aerated isooctane solutions of **1** (3 mM) and pyridine (1.4 mM) reduced the amplitudes of the absorption of X_{290}, A_{290}, and of the pyridinium ylide, A_{385}, in the same proportion. The inverse of the amplitudes A_{290} and A_{385} were linearly related to [DEA] (aerated isooctane, 5 concentrations of DEA in the range of 5–50 mM) with slope:intercept ratios of $k_{\mathrm{DEA}}\tau = 70.6 \pm 4$ and 76.5 ± 4 M^{-1}, respectively. Hence, the limiting lifetime $\tau([\mathrm{DEA}] \to 0)$ of the reactive intermediate responsible for the formation of X_{290} is the same, within the limits of error, as that forming pyridinium ylide.

(ii) Addition of pyridine (5 concentrations in the range of 3–30 mM) reduced the yield of X_{290}, and the inverse of the amplitude A_{290} was linearly related to pyridine concentration with a slope:intercept ratio of $k_Y\tau = 114 \pm 7$ M^{-1}. With $\tau = 1/(k_0 + k_X[\mathbf{1}]) = 21 \pm 2$ ns for [**1**] = 3 mM one obtains $k_Y = (5.4 \pm 1.2) \times 10^9$ M^{-1} s^{-1} in good agreement with the value determined from the kinetics of pyridinium ylide formation.

(iii) The ratio A_{290}/A_{385} was measured for solutions containing a constant amount of pyridine (3.4 mM) and various amounts of **1** (2.2–8.4 mM, 4 concentrations). It was found to be a linear function of [**1**] (intercept = 2.2 ± 6.6, slope = 135 ± 11 M^{-1}) in agreement with Eq. (5), which holds if both X_{290} and the pyridinium ylide are formed by reaction of **Ad:** with **1** and pyridine, respectively (Scheme 1).

$$A_{290}/A_{385} = \varepsilon_X \Phi_X / \varepsilon_Y \Phi_Y = (\varepsilon_X/\varepsilon_Y)(k_X[\mathbf{1}]/k_Y[\text{pyridine}]) \qquad (5)$$

(iv) Finally, A_{290} was measured in aerated isooctane without pyridine as a function of the concentration of **1** and corrected for the amount of exciting light absorbed in the analyzed volume. Variations of the laser pulse intensity were monitored with an Laser Precision energy meter (Rk-3230) using a beam splitter. The absorbances of the samples with varying concentrations of **1** were determined on a spectrophotometer. Bleaching by the laser pulse was negligible due to the low absorption coefficient of **1** at the excitation wavelength. The inverse of the amplitude A_{290} was linearly related to the inverse of [**1**], and the ratio of the slope and the intercept of the correlation gave $k_X\tau_0 = 125 \pm 20$ M^{-1}, τ_0 being the lifetime of **Ad:** when [**1**] → 0. With $\tau_{\text{growth}} = 18 \pm 1$ ns when [**1**] = 5 mM, and $1/\tau_{\text{growth}} = 1/\tau_0 + k_X[\mathbf{1}]$ (Eq. (4)), one obtains $k_X = (4.3 \pm 0.7) \times 10^9$ M^{-1} s^{-1} in good agreement with the more accurate value determined from the reaction kinetics.

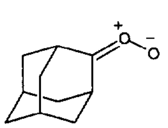
Irrespective of the nature of X_{290}, the risetime and amplitude of its absorption can be used to monitor the lifetime and reactivity of **Ad:**, just as pyridinium ylide has been used for the same purpose. Rate constants for the reaction of **Ad:** with acetic acid (0.1–4 mM) and tetramethylethylene (1–10 mM) were determined in this way from the slopes $k_r\tau_0$ of Stern–Volmer plots of the decrease of A_{290} as a function of the concentration of added reactants. With $\tau_0 = 18 \pm 1$ ns, the reaction rate constants are $k_{\text{AcOH}} = (5.1 \pm 1.0) \times 10^9$ and $k_{\text{TME}} = (2.4 \pm 0.5) \times 10^9$ M^{-1} s^{-1}, respectively.

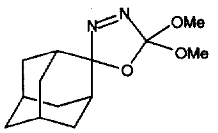
3.4. Effect of oxygen

Lifetimes for the formation of X_{290} in isooctane that was dried over molecular sieves were measured after flushing with argon, with mixtures of N_2 and O_2 containing 20, 35 and 50% of oxygen, and with pure oxygen. The values of τ_{growth} ([**1**] = 3.5 mM, $\lambda_{\text{obs}} = 290$ nm, time resolution 2 ns) were 46, 35, 31, 27, and ≈ 20 ns, respectively. The inverse of these values, $k_{\text{obs}} = 1/\tau_{\text{growth}}$, was linearly related to the oxygen concentrations that were calculated using oxygen solubility data for isooctane [18]. Non-linear least squares fitting of $\log(k_{\text{obs}}/s^{-1})$ vs. $[O_2]$ gave a slope $k_{O_2} = (1.8 \pm 0.1) \times 10^9$ M^{-1} s^{-1} and an intercept of $(2.2 \pm 0.1) \times 10^7$ s^{-1}. The latter value is consistent with that calculated from Eq. (4). Another series of measurements was done by equilibrating degassed solutions of **1** (1.1 mM) in isooctane with air (250, 280, 760 Torr) or pure oxygen (60 Torr). This series gave $k_{O_2} = (3.1 \pm 0.2) \times 10^9$ M^{-1} s^{-1} (14 measurements). The systematic difference between these measurements probably arises from the difficulty to avoid changes in the water content of the solvent with either preparation technique. The weighted average of these measurements is $k_{O_2} = (2.3 \pm 0.4) \times 10^9$ M^{-1} s^{-1}. The bimolecular quenching constant k_{O_2} is about one-tenth that of a diffusion-controlled reaction with oxygen, which suggests that the triplet state of the carbene ^{3}**Ad**: is substantially populated at room temperature.

Qualitative GC-MS data indicate that adamantanone is the final product formed by oxygen trapping of **Ad:**. The decay of the intermediate X_{290} yields adamantanone azine (cf. Section 3.7). Hence, the overall yield of azine is expected to diminish as an increasing amount of **Ad:** is intercepted by oxygen. The yield of azine was determined as a function of $[O_2]$ from the absorbance change at 214 nm after photolysis of about 10% of the diazirine (measured from the absorbance change at 354 nm) for solutions flushed with argon, air, neat oxygen and a 1:1 mixture of O_2 and N_2. Analysis according to Eq. (2) (replace k_Y by k_{O_2}) gave $k_{O_2}\tau_0 = (153 \pm 10)$ M^{-1}. With $\tau_0 = 47 \pm 1$ ns for the lifetime of **Ad:** at [**1**] = 3.5 mM in the absence of O_2, one gets $k_{O_2} = (3.3 \pm 0.3) \times 10^9$ M^{-1} s^{-1}, in acceptable agreement with the value determined more directly from the observed reaction kinetics.

The formation of adamantanone by the reaction of **Ad:** with molecular oxygen is expected to proceed via a carbonyl oxide intermediate which should also absorb around 300 nm. Such a transient was not observed, but it may well have been buried by the unavoidable formation of the transient X_{290} formed by the addition of **Ad:** to **1**. Attempts to detect the carbonyl oxide by flash photolysis the oxydiazoline precursor of **Ad:** used by Pezacki et al. [5] gave an extremely weak transient absorption, $\lambda_{\text{max}} = 280$ nm, with a lifetime of about 1 μs in oxygen-saturated isooctane that was not formed in the degassed solvent.


carbonyl oxide



oxadiazoline

3.5. Solvents other than isooctane

Benzene behaves as a relatively inert solvent towards **Ad:**, but due to the high solubility of water in benzene, the lifetime of the carbene is particularly sensitive towards adventitious moisture in this solvent. A series of measurements was done with solutions of **1** (0.7–5.4 mM) in degassed benzene that had been dried over molecular sieves. The growth rate of the X_{290} transient was linearly related to [**1**] (Eq. (4)), and nonlinear fitting to $\log(k_{\text{obs}}/s^{-1})$ gave a slope $k_X = (1.73 \pm 0.05) \times 10^9$ M^{-1} s^{-1} and an intercept $k_0 = (1.38 \pm 0.08) \times 10^6$ s^{-1}, $\tau_0 = 725 \pm 40$ ns (10 measurements). Formation of X_{290} was not detectable in water-saturated benzene.

A similarly long lifetime of **Ad:** was found in argon-flushed perfluorodecalin. The slope of a linear plot of $1/\tau_{\text{growth}}$ of X_{290} vs. [**1**] (2.2–7.0 mM, 4 concentrations) gave $k_X = (2.0 \pm 0.3) \times 10^9\ M^{-1}\ s^{-1}$ for the rate constant of the formation of X_{290} by addition of **Ad:** to **1**. From the intercept, the lifetime of **Ad:** at zero concentration of **1** was found to be 500 ± 50 ns.

In argon-flushed solutions with [**1**] $\approx$ 2.5 mM, the amplitudes A_{290} (normalized to the same excitation energy) in perfluorodecalin, isooctane, cyclohexane and decalin were 0.135, 0.100, 0.022 and $\approx$ 0.012, respectively, and the values of τ_{growth} were $\approx$ 140, 60 and 15–20 ns for the first three solvents. The fast rise of the weak signal obtained with decalin was not resolved. Clearly, lifetimes of **Ad:** and the amplitudes A_{290} are correlated. If the absorbance coefficient of X_{290} is the same in these four non-polar solvents, then the observed amplitudes A_{290} are proportional to the yield of X_{290} in these solvents. The limiting lifetimes are relatively short in alkane solvents, and this is associated with low yields of X_{290}. One may conclude that **Ad:** reacts with the alkane solvents, probably by C–H insertion. Several addition products of **Ad:** to isooctane were in fact detected by GC-MS analysis of the photoproduct mixture obtained after exhaustive irradiation of **1** (1.5–5 mM) at 366 nm in isooctane. The inverse of the limiting lifetime of **Ad:** in degassed, dry isooctane, $\tau_0 = 225 \pm 15$ ns, is an upper limit for the rate of insertion of **Ad:**, $k_{\text{i-oct}} < 5 \times 10^6\ s^{-1}$. The large amount of isooctane addition products observed by GC-MS indicates that $k_{\text{i-oct}}$ is not much below that limit. The limiting lifetime of **Ad:** in degassed, dry cyclohexane is much shorter, $\tau_0 \approx 20$ ns. This suggests that the rate of insertion is an order of magnitude faster in this solvent, and indeed GC-MS analysis showed that the yield of azine was reduced at least 10-fold in favor of solvent addition products compared to the product distribution obtained by irradiation in isooctane.

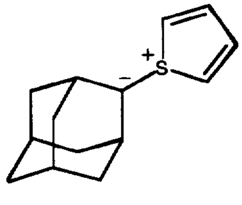
The growth of absorbance at 290 nm in degassed acetonitrile was beyond our time resolution of about 20 ns. This suggested rapid reaction of **Ad:** with the solvent, but in this case the intensity of the 290-nm transient was quite strong, about half as strong as that observed with high concentrations of **1** in isooctane solutions. Pyridine trapping was used to estimate the lifetime of **Ad:** in acetonitrile solutions of **1** (2.5 mM). Very high concentrations of pyridine (0.035–0.82 M) were required to generate the pyridinium ylide transient, $\lambda_{\max} = 385$ nm. Using the same method of analysis as above (Eq. (2)), the ratio of intercept and slope was $k_Y/k_0 = k_Y\tau_0 = 3.3 \pm 0.4\ M^{-1}$. Assuming that the rate of addition of **Ad:** to pyridine is the same as in isooctane, $k_Y = (5.0 \pm 0.2) \times 10^9\ M^{-1}\ s^{-1}$, the lifetime of **Ad:** in acetonitrile is calculated as $\tau_0 \approx 0.16$ ns.

Such a short lifetime is quite inconsistent with the assumption that the 290-nm transient formed in acetonitrile is X_{290}, despite the similarity of its absorption spectrum to that of X_{290}: the transient absorbances at 290 nm are of comparable intensity in acetonitrile and in isooctane, whereas the limiting lifetime τ_0 of **Ad:** is three orders of magnitude less in acetonitrile. A rate constant $k_X > 10^{12}\ M^{-1}\ s^{-1}$, well in excess of the diffusion limit, would be required to give such a high yield of X_{290} by addition of **Ad:** to **1** in acetonitrile. Moreover, the 290-nm transient decayed rapidly, $k = 3.6 \times 10^4\ s^{-1}$, much faster than the decay of X_{290} in isooctane ($k = 7\ s^{-1}$, cf. Section 3.7). By analogy with previous work on fluorenylidene and other carbenes [19,20], we propose that **Ad:** forms an ylide by addition to acetonitrile.

The bimolecular rate constant for the reaction of **Ad:** with acetonitrile was determined by measuring τ_{growth} at 290 nm in degassed isooctane containing small amounts (9.5–30.4 mM) of acetonitrile. The observed growth rate depended linearly on acetonitrile concentration, and nonlinear least-squares fitting to $\log(k_{\text{obs}}/s^{-1})$ gave $k_{\text{MeCN}} = (4.5 \pm 0.2) \times 10^8\ M^{-1}\ s^{-1}$ for the rate constant of the reaction of **Ad:** with acetonitrile. Under these conditions it became particularly evident that the 290-nm transient formed in the presence of acetonitrile was different from X_{290}: the decay of the 290-nm absorbance was clearly bi-exponential at low acetonitrile concentrations, where both X_{290} and the acetonitrile ylide are formed. The rate constant of the fast decay, $k_1 = (2.3 \pm 0.2) \times 10^5\ s^{-1}$, was comparable to that observed in neat acetonitrile, whereas the slow component, $k_2 = (7 \pm 1)\ s^{-1}$, was similar to that of X_{290} in neat isooctane (cf. Section 3.7).

3.6. Measurements using thiophene as an indicator for adamantylidene

In their original study, Morgan et al. [2] used thiophene (0.1–0.3 M) as a trapping agent for **Ad:** and observed the time-resolved formation of a transient absorption at 320 nm in benzene solution. The rate of formation of this transient was found to increase linearly with thiophene concentration, and a rate coefficient of $k_q = 1.75 \times 10^6\ M^{-1}\ s^{-1}$ and limiting lifetime of $\tau_0 = 2.2\ \mu s$ were determined from the slope and intercept of the dilution plot. The 320-nm transient was assigned to the thiophene ylide shown below. In repeating some of these experiments, we found that the formation of the 320-nm transient was much slower than the decay of **Ad:** determined by other means (cf. Sections 3.2 and 3.3). From this and the results reported in the accompanying paper [5] it is now quite clear that the original assignment must be revised. The 320-nm transient was not further studied, but it must arise from secondary reaction of an intermediate or intermediates other than **Ad:** with thiophene.



thiophene ylide

Yet, a bona fide thiophene ylide is formed by trapping of **Ad:** with thiophene in dry benzene solution, but its rate of formation is much faster, $k_T = (8.6 \pm 0.3) \times 10^8\ M^{-1}\ s^{-1}$, and its absorption lies at shorter wavelengths, $\lambda_{max} \approx 290$ nm, than the 320-nm transient. The second-order trapping constant k_T was determined from the linear increase of the absorbance growth rate at 290 nm with thiophene concentration (0.002–0.025 M, 14 measurements). The fast trapping of **Ad:** by thiophene to form the 290-nm transient has, presumably, escaped the attention of previous workers because the absorption spectrum of this transient is again quite similar to that of the transient X_{290} formed by addition of **Ad:** to **1** in the absence of thiophene.

3.7. Decay of the transient X_{290}

The decay of X_{290} obeyed a first-order rate law with a lifetime $\tau_X \approx 150$ ms in either air-saturated or nitrogen-flushed isooctane at room temperature. The temperature dependence of τ_X was measured from 15 to 50°C using the same solvent. An activation energy $E_a = 15.5 \pm 2.0$ kcal mol^{-1} and a pre-exponential factor $A = 10^{(12.3 \pm 0.8)}\ s^{-1}$ were determined by linear regression of an Arrhenius plot (Fig. 3). The lifetime τ_X at −40°C is predicted to be several minutes by extrapolation of the Arrhenius equation. Absorption spectra of cooled isooctane solutions were therefore recorded at regular time intervals on a diode array spectrophotometer (HP-8452A) following irradiation during a few seconds by a frequency-tripled Q-switched Nd YAG laser running at 5 Hz. In the first spectrum, recorded a few seconds after irradiation, there was a slight decrease of the diazirine absorption between 330 and 380 nm (hardly noticeable in Fig. 4), and three new absorption bands appeared. The first one, $\lambda_{max} = 286$ nm, corresponds to that of X_{290} measured by flash photolysis at room temperature (Fig. 2 and inset of Fig. 4); it disappears with a lifetime of 66 s at −33°C and of 94 s at −37°C, in good agreement with the lifetimes calculated by extrapolation of the Arrhenius equation as shown in Fig. 3. The second, $\lambda_{max} = 214$ nm, is due to the azine: its absorbance grows as X_{290} disappears, and this growth kinetically matches the decay of the absorption at 286 nm, as shown in Fig. 5, which indicates that X_{290} rearranges to azine. Both UV and IR measurements indicate that azine is the main product formed by the decay of X_{290}. Hence, the activation parameters measured for the disappearance of X_{290} can be assigned to the reaction $X_{290} \rightarrow$ azine. The third band, $\lambda_{max} = 234$ nm, is mainly due to diazoadamantane [4], and its intensity remains nearly constant during the decay of X_{290}. The small absorbance increase at this wavelength is attributed to spectral overlap with azine absorption.

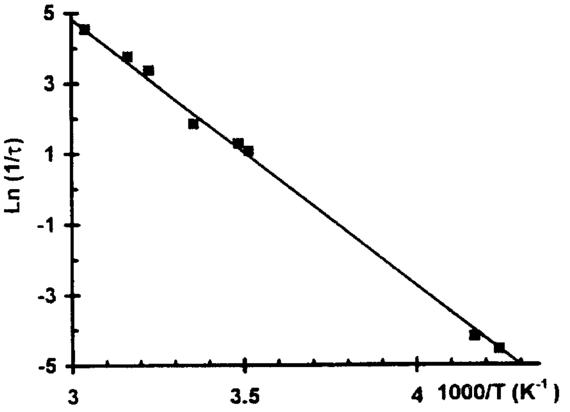


Fig. 3. Arrhenius plot for the decay of the ylide X_{290} in aerated isooctane. Lifetime measurements were made by laser flash photolysis for temperatures in the range of 11–56°C, and using a photodiode array spectrophotometer for −33 and −37°C.

The absorption bands at 234 nm and 214 nm were persistent on a time scale of hours at temperatures below 0°C. At room temperature the absorption at 234 nm disappeared very

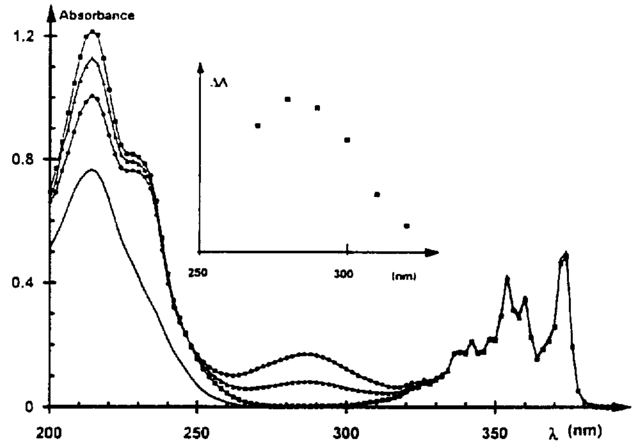


Fig. 4. Absorption spectra of a solution of diazirine **1** in isooctane, recorded at −35°C on a photodiode array spectrophotometer: before irradiation (———), 4 s (-●-●-), 2 min (-▲-▲-), and 10 min (-■-■-) after excitation by a frequency tripled Nd:YAG laser running at 5 Hz, during a 2-s interval. Inset: absorption spectrum of a long-lived transient species (≈ 150 ms), recorded by laser flash photolysis of diazirine **1** in isooctane at room temperature.

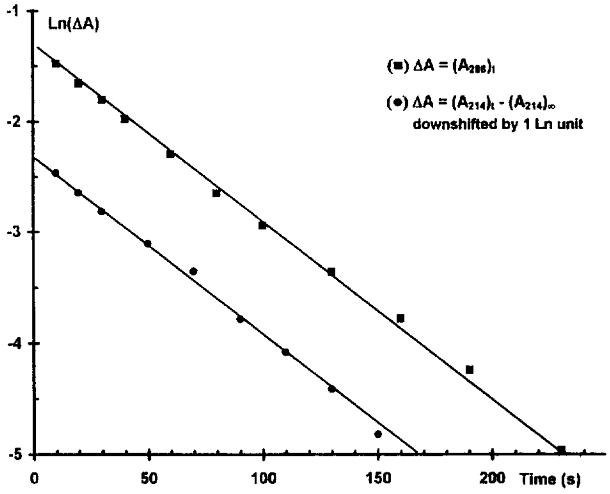


Fig. 5. First-order analysis of the transient absorbance decay at 286 nm (A_{286}, -■-■-) and of the absorbance growth at 214 nm (A_{214}, -●-●-) recorded in aerated isooctane, at −33°C, with a photodiode array spectrophotometer.

slowly while the absorption at 214 nm increased on the same time scale (see Section 3.8).

3.8. Decay of 2-diazoadamantane

Depending on the concentration of diazirine **1** and on the nature and purity of the solvent, the kinetics of the decay of diazoadamantane were found to be largely second-order, first-order, or a mixture of both, with half-lives ranging from a day to a few minutes. The yield of azine formed during the decay of diazoadamantane also varied from ≈0.5 to nearly zero, the larger yields being associated with predominantly second-order decays and long half-lives. In all cases, the concentration of diazirine remained unchanged during the decay of diazoadamantane (usually, only about 10% of the diazirine with an initial concentration of 2 mM was converted by irradiation).

In order to determine the amount of azine formed during the decay of diazoadamantane from the absorbance changes, knowledge of the absorption spectra of both species was required. An authentic sample of azine was prepared from adamantanone and hydrazine and purified by repeated crystallization. The molar absorbance coefficients of azine in isooctane at 214 and 234 nm were determined as $\varepsilon_{214} = 25{,}000$ and $\varepsilon_{234} = 7750\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$. For diazoadamantane, a value of $\varepsilon_{234} = 6500\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ has been determined from combined UV and IR measurements [4], but an absorption spectrum was not given. In cyclohexane, formation of azine is minimized because **Ad:** reacts efficiently with the solvent. Furthermore, in cyclohexane containing traces of acetic acid (ca. 1 mM), diazoadamantane decayed within a few minutes after irradiation, and no azine was formed, as shown in Fig. 6. The absorbance coefficient of diazoadamantane, $\varepsilon_{214} = 1500\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$, was then estimated by assuming that these changes in the absorption spectrum reflect the decay of diazoadamantane to a transparent product.

Based on the absorbance coefficients given above, it was possible to determine the stoichiometry of the reaction from the slow absorbance changes occurring after irradiation. The decay of diazoadamantane (initial concentration ca. 0.2 mM) in degassed or argon-flushed dry isooctane at 20°C was monitored over several half-lives. It obeyed a second-order rate law with $k_{\mathrm{obs}}/\Delta\varepsilon_{234} \approx 10^{-3}$ cm s^{-1}. With $\Delta\varepsilon_{234} = 5250\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ ($2 \times \varepsilon_{\mathrm{diazo}} - \varepsilon_{\mathrm{azine}}$), the bimolecular rate constant for the self-condensation of diazoadamantane is estimated as 5 $\mathrm{M}^{-1}\ \mathrm{s}^{-1}$, and the yield of azine was nearly quantitative, i.e., about half of the initial amount of diazo compound. Little if any diazirine was consumed during this process; the absorbance in the 320–380 nm region remained unchanged within the detection limits of the spectrophotometer (0.001 absorbance units, which corresponds to less than 5% of the initial change in absorbance due to the photolysis).

At 10-fold lower concentrations of diazoadamantane in dry isooctane, formation of azine by the reaction of the diazo compound with **1** became predominant. Under these conditions, the first half-life of the diazo decay decreased from about 20 h at [**1**] = 0.6 mM to 20 min at [**1**] = 10 mM.

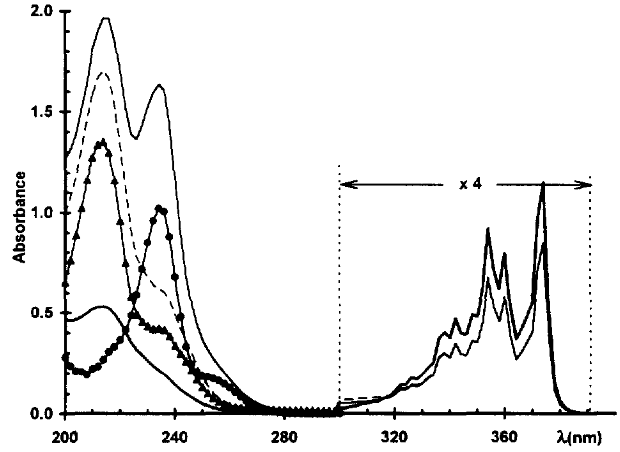


Fig. 6. UV absorption spectra of a solution of diazirine **1** in isooctane with ≈1 mM acetic acid before irradiation (———), a few seconds after irradiation (———), and 1 h later (- - -). The difference between the latter two is attributed to the absorption spectrum of diazoadamantane (-●-●-). The absorption spectrum of an authentic sample of the adamantanone azine is also shown (-▲-▲-). Absorbances in the range of 300–375 nm are amplified by a factor 4.

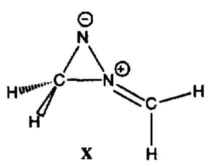
The product distribution obtained by irradiation of **1** was briefly investigated by GC-MS. The main products formed by 366-nm irradiation of **1** (1–5 mM) in isooctane were adamantanone azine (**2**), 2,4-dehydroadamantane (**3**), addition products of **Ad:** to isooctane (at least two isomers), adamantan-2-ol (formed by reaction of **Ad:** with traces of water), bis(2-adamantyl) ether (formed, presumably, by reaction of **Ad:** with adamantanol), and, in aerated solution, adamantan-2-one (**4**). Products corresponding to the addition of one and two solvent molecules to **Ad:** were found by GC-MS analysis of the photoproduct mixture formed by irradiation of **1** in acetonitrile.

3.9. Quantum yield of disappearance of diazirine 1

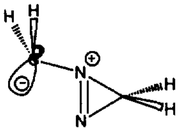
After the thermal decomposition of diazoadamantane, none of the photoproducts absorbs significantly at wavelengths $\lambda > 320$ nm. Hence, the amount of **1** decomposed by irradiation at 366 nm in aerated isooctane at room temperature was measured spectrophotometrically by the decrease of the absorption by **1** ($\varepsilon_{354} = 146\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$). The quantum yield of disappearance, ϕ_{-1}, increased with increasing concentrations of **1**, as was to be expected from the observation that **Ad:** reacts with **1** (cf. Section 3.2). Values of $\phi_{-1} \approx 1$ were measured with [**1**] = 1 mM using an azobenzene actinometer, whereas values measured using the Aberchrome 540 actinometer ranged from about 1.45 at [**1**] = 3 mM up to about 1.8 at [**1**] = 27 mM. The quantum yields were reproducible within ± 10%, but a systematic error of + 10 to 20% is likely for measurements done by reference to a sealed sample of Aberchrome which had been recycled many times, a procedure no longer recommended [7,8]. Of interest here is the systematic increase of ϕ_{-1} with increasing concentration of **1**, which has been established.

3.10. Ab initio calculations for X_{290}

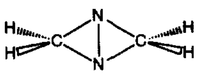
Neither the UV spectrum nor the Arrhenius parameters for its transformation to azine provide much information about the structure of the intermediate X_{290}. The reaction path for the addition of methylene (CH_2:) to diazirine (CH_2N_2) and the formation of azine ($CH_2{=}N{-}N{=}CH_2$) was calculated by various methods (Becke 3LYP/6-31 + G* + ZPVE, MP2(fc)/6-31 + G** + ZPVE, and G2) [21]. Several possible structures for the intermediate are shown below (**X**, **Y** and **Z**). The calculations indicate that (i) **Z** is a stable structure but is not on the lowest-energy reaction path leading to azine (it is also not expected to absorb at 290 nm), (ii) **Y** is an unstable transition state about 50 kcal mol^{-1} higher in energy than **X**, and (iii) the formation of azine occurs via an intermediate **X** which decays to azine by passing over a transition state that is 18–20 kcal mol^{-1} (14.7 kcal mol^{-1} in the case of Me_2C: + Me_2CN_2) [G.V. Shustov, private communication] higher in energy than **X**. Since the measured activation energy for the disappearance of X_{290} is 15.5 kcal mol^{-1}, it seems reasonable to assign structure **X** to the observed transient X_{290}.



X



Y



Z

A singlet ground state is predicted for **Ad:** with a singlet–triplet splitting $\Delta E = 2.82$ kcal mol^{-1} at the RHF/6-31G(d) and Becke 3LYP/6-31 + G(d) levels for ^{1}**Ad:** and UHF/6-31G(d), ROHF/6-31G(d) and UBecke 3LYP/6-31G(d) levels for ^{3}**Ad:**. Geometries were fully optimized, and vibrational frequencies were determined at the DFT (Becke 3LYP/6-31 + G(d)) level to make the zero-point corrections using a scale factor of 0.95.

4. Discussion

4.1. Re-interpretation of previous results [2]

Adamantylidene (**Ad:**) exhibits absorption in the visible (620 nm) [3], which is, however, too weak for the direct detection of this carbene by flash photolysis in solution. Morgan et al. [2] have used pyridine as a trapping agent for **Ad:**, which forms an ylide with strong absorption at 385 nm. Resolution of the growth rates of the pyridinium ylide was impeded by fluorescence emission of **1** in the same wavelength region.

As an alternative, Platz et al. used thiophene as trapping agent, which produced a transient with $\lambda_{max} = 320$ nm and a bimolecular rate constant $k_q = 1.75 \times 10^6$ M^{-1} s^{-1}. This value, as well as the other rate constants determined for the reactions of **Ad:**, were surprisingly low in comparison with more recent work on related carbenes. For example, rate constants for the formation of pyridinium ylides, k_Y, were found to be in the range of 10^9–10^{10} M^{-1} s^{-1} for benzyl and alkyl halocarbenes, 10^8–10^9 M^{-1} s^{-1} for aryl chlorocarbenes, and 10^6–10^8 M^{-1} s^{-1} for phenyl oxacarbenes. Few values are available for dialkyl carbenes, but one around 10^9 M^{-1} s^{-1} was reported for singlet dicyclopropyl carbene [22]. Ge et al. [23] stated "[dialkylcarbenes] react so rapidly with pyridine that it has become customary to take $k_Y \geq 10^9$ M^{-1} s^{-1}". It is now clear that the 320-nm transient observed by flash photolysis of **1** in the presence of high concentrations of thiophene is a secondary product. The addition of **Ad:** to thiophene is nearly diffusion-controlled and the resulting thiophene ylide absorbs at shorter wavelengths, $\lambda_{max} = 290$ nm. Because Platz et al. had determined the rate constants for the reaction of **Ad:** with other trapping agents by measuring their effect on the 320-nm transient, these values are also subject to revision. Consistent conclusions are reached on different grounds in the accompanying paper by Pezacki et al. [5].

4.2. Formation and trapping of Ad:

The primary photoproducts of diazirine **1**, **Ad:** and diazoadamantane, are formed with a quantum yield of about 0.5 each and within the time resolution of the faster set-up used in this work (2 ns). It is likely that the excited singlet state of **1**, which has a lifetime of 0.24 ns [15], is their direct precursor.

Trapping of **Ad:** by diazirine **1** produces transient X_{290}, $\lambda_{max} = 290$ nm, which in this work was used primarily to monitor the lifetime of **Ad:**. Based on ab initio calculations for the model reaction methylene + diazirine, this transient is attributed to an ylide which results from the addition of **Ad:** to one of the nitrogen atoms of diazirine (structure **X**). The ylide slowly rearranges to azine ($E_a = 15.5$ kcal mol^{-1} and $A = 2 \times 10^{12}$ s^{-1}). UV spectra recorded at −35°C within a few seconds after irradiation (i.e., when less than 7% of X_{290} has disappeared) show a small absorption band at 214 nm, where the azine absorbs, which then grows further as X_{290} disappears. The initial absorption at 214 nm is attributed to the overlapping absorptions of diazoadamantane and, possibly, X_{290}.

The rate constant for the reaction of **Ad:** with **1**, $k_X = (3.6 \pm 0.2) \times 10^9$ M^{-1} s^{-1}, is at least an order of magnitude larger than previous values reported in the literature for rate constants of reactions of carbenes with their diazirines precursors. For *t*-butyl–C–Cl, $k_X = 2 \times 10^6$ M^{-1} s^{-1} [24]. The long lifetimes of several other alkylhalocarbenes, e.g., 330–740 ns for Me–C–Cl, > 1 μs for cyclopropyl–C–Cl, and 7 μs for cyclopropyl–C–F, observed by photolysis of solutions containing the parent diazirine at concentrations ≈ 10 mM or larger, indicate that $k_X < 10^7$ M^{-1} s^{-1} in these cases

[25–29]. The value of this rate constant may have been underestimated in previous studies, and several unusual features observed in the studies of the rate of 1,2 H migration in alkylchlorocarbenes, such as low frequency factors or nonlinear Arrhenius plots, might be explained by assuming that at low temperature the lifetime of these carbenes was limited by reaction with the parent diazirine [30] instead of reaction with the solvent [31] or tunneling [32]. Further work is required to resolve this question.

The rate constants for the reaction of **Ad:** with various reagents other than **1** are collected in Table 1. The rate constants determined here are much larger than those reported previously [2], but they compare well with those measured for the corresponding reactions of other singlet carbenes [33,34].

4.3. Reactions of 2-diazoadamantane

Concerning the fate of diazoadamantane in dry isooctane at low concentrations of diazirine **1**, recall that no diazirine is consumed during the decay of diazoadamantane, that the decay largely obeys a second-order rate law, and that two equivalents of diazoadamantane give one of azine. The yield of azine is strongly diminished by trace amounts of acid. These results are in accord with the first of three processes that have been proposed [35–39] for the formation of azine from diazoadamantane: (i) 2 diazo → azine + N_2, (ii) diazo + diazirine → azine + N_2, and (iii) diazo → carbene + N_2 followed by carbene + diazirine → azine. We do not exclude that other reactions may prevail under different reaction conditions.

4.4. Lifetime of adamantylidene in various solvents

The lifetime of **Ad:** in relatively inert solvents such as isooctane is highly sensitive to adventitious impurities. While data collected on a given day indicated accurate reproducibility, and dilution series gave rate constants whose dependence on the concentration of trapping agent was accurately linear, the limiting lifetimes of **Ad:** determined by extrapolation to zero concentration of trapping agent were sometimes substantially different between the two laboratories or at different times (with different solvent batches or slightly different preparation techniques). Of the conceivable candidates responsible for these problems, moisture was identified as the most likely. Lifetimes of **Ad:** were shorter in water-saturated isooctane solutions and longest after drying the solvent with molecular sieves. Moreover, it was eventually realized that changes in the water content were inadvertently introduced by the degassing procedures. Thus, freezing of an aerated solution prior to degassing may capture substantial amounts of water in the solution depending on the volume and the humidity of the air contained in the evacuable sample holder. On the other hand, flushing of isooctane with dry inert gases results in the preferential evaporation of water and produces relatively dry samples, depending on the intensity and duration of flushing. We note explicitly that the longest lifetimes determined as intercepts of dilution plots must be taken as lower limits for the 'true' lifetimes in the absence of adventitious impurities. The bimolecular rate constants reported in this work (Table 1) are considered reliable.

Carbene **Ad:** reacts rapidly with most reagents and solvents. In contrast, the intramolecular rearrangement of **1** to dehydroadamantane is rather slow: limiting lifetimes of **Ad:** in degassed 'inert' solvents approach 1 μs, such that the rate constant for intramolecular rearrangement must be less than $1\times10^6\ s^{-1}$. This explains why high yields of dehydroadamantane are obtained only when the intermolecular reactions of **Ad:** are impeded by shielding the carbene in a cyclodextrin or zeolite cage [40,41]. The current values of the bimolecular rate constants of **Ad:** (Table 1) are in a normal range when compared to those published previously for several other singlet, or predominantly singlet, carbenes.

4.5. Reaction of adamantylidene with molecular oxygen

Carbene **Ad:** is quenched by molecular oxygen with a rate constant $k_{O_2} = (2.3\pm0.4)\times10^9\ M^{-1}\ s^{-1}$ which is about an order of magnitude below the diffusion-controlled limit. The quenching rate by oxygen is, nevertheless, surprisingly high, considering that singlet carbenes are usually rather 'inert' towards oxygen. *p*-Nitrophenylchlorocarbene reacts with oxygen to give a carbonyl oxide [42] with a rate constant around $2\times10^7\ M^{-1}\ s^{-1}$, and that value was considered to be

Table 1
Rate constants for reactions of **Ad:** with various reagents in isooctane

Reagent	Symbol	Rate coefficient	Product
Diazirine **1**	k_X	$(3.6\pm0.2)\times10^9\ M^{-1}\ s^{-1}$	X_{290} (ylide)
Pyridine	k_Y	$(5.0\pm0.2)\times10^9\ M^{-1}\ s^{-1}$	ylide
Thiophene	k_T	$(8.6\pm0.3)\times10^8\ M^{-1}\ s^{-1}$	ylide
Diethylamine	k_{DEA}	$(3.8\pm0.5)\times10^9\ M^{-1}\ s^{-1}$	ylide
Tetramethylethylene	k_{TME}	$(2.4\pm0.5)\times10^9\ M^{-1}\ s^{-1}$	cyclopropane adduct
Acetic acid	k_{AcOH}	$(5.1\pm1.0)\times10^9\ M^{-1}\ s^{-1}$	2-adamantyl acetate
Oxygen	k_{O_2}	$(2.3\pm0.4)\times10^9\ M^{-1}\ s^{-1}$	carbonyl oxide(?), adamantanone
Acetonitrile	k_{MeCN}	$(4.5\pm0.2)\times10^8\ M^{-1}\ s^{-1}$	ylide
Solvent	$k_{i\text{-}oct}$	$\approx2\times10^6\ s^{-1}$	insertion products

exceptionally large. Carbenes such as diphenylcarbene or fluorenylidene have been reported to give carbonyl oxides by reaction with O_2 with rate constants in the range of $1–5 \times 10^9$ M^{-1} s^{-1} [43,44], but that was attributed to thermal population of the low-lying triplet state of these carbenes. Calculations reported in this work and by Bally et al. [3] suggest that the ground state of **Ad:** is a singlet, but that the energy of the triplet state is higher by just a few kcal mol^{-1}. This is consistent with the reported absence of an EPR signal in matrices or glasses containing **Ad:** at low temperature [2]. If, for the sake of argument, the energy gap ΔE between ^{3}**Ad**: and ^{1}**Ad**: is taken to be $= 1.7$ kcal mol^{-1}, the fraction of ^{3}**Ad**: calculated from $[^3\mathbf{Ad}:]/[^1\mathbf{Ad}:] = 3 \exp(-\Delta E/RT)$, is 14% at 23°C, 0.005% at 77 K, and negligible at 4 K. The sensitivity of the EPR spectrometer was probably not sufficient to detect an 0.005% population of **Ad:** in the triplet state. Trapping of **Ad:** by oxygen results in the formation of adamantanone, which was observed by GC-MS as one of the major products (along with azine) of the photolysis of aerated or oxygen-saturated solutions.

5. Conclusion

This study offers substantial revisions concerning the reactivity of adamantylidene (**Ad:**). Reactions with acetic acid, water, tetramethylethylene, diethyl amine, pyridine, acetonitrile, thiophene, and even with the diazirine precursor (**1**) are close to the diffusion-controlled limit. **Ad:** is also quenched rapidly by oxygen, indicating substantial population of a low-lying triplet state at room temperature. By contrast, intramolecular rearrangement of **Ad:** is relatively slow: the lifetime of **Ad:** is nearly 1 μs in carefully dried and degassed 'inert' solvents.

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