



JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

J. Am. Chem. Soc., 1996, 118(30), 7229-7230, DOI:[10.1021/ja9613217](https://doi.org/10.1021/ja9613217)

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Supporting Information :

The IR absorption spectrum of isooctane containing known concentrations (10 to 30 mM) of the diazirine (1574 cm^{-1}), the parent ketone (1724.7 & 1733.4 cm^{-1}), the related azine (1646.2 cm^{-1}), the 2-adamantylacetate (1740.6 cm^{-1}) and acetic acid (1717 cm^{-1}) were recorded in the region $1550 - 2100\text{ cm}^{-1}$ and the corresponding absorption coefficients were determined. The azine, prepared from adamantanone (Aldrich) and hydrazine and recrystallized from hot hexane, shows an intense UV absorption band at 214 nm ($\epsilon = 25000\text{ M}^{-1}\text{cm}^{-1}$) with a shoulder at 234 nm . The 2-adamantylacetate was prepared from the 2-adamantanol (Aldrich).

The IR spectrum of a solution of diazirine (10.3 mM) recorded 3 minutes after irradiation at 355 nm during a few seconds, shows the bands of the diazirine (5.45 mM), the azine (1.4 mM), the adamantanone* (0.2 mM) and a new band at 2042 cm^{-1} (absorbance = $1.697/\text{cm}$) assigned to the diazo. The balance between diazirine lost and products formed indicates that $[\text{diazo}] < 1.85\text{ mM}$ so that $\epsilon_{2042} > 917\text{ M}^{-1}\text{cm}^{-1}$. The IR spectrum of the same solution recorded every ten minutes during 2 hours show a slow decrease of the diazo absorption concomitant with an increase of the azine absorption and a decrease of the diazirine absorption. After complete disappearance of the diazo, the azine and adamantanone formed accounts for 85% of the diazirine decomposed as shown by the following balances: diazirine = 4.42 mM (1.03 mM additional lost); azine = 2.22 mM (0.82 mM additional); adamantanone = 0.50 mM (0.3 mM additional); other products = 0.94 mM (16% of the diazirine lost). The formation of 0.82 mM azine and 0.3 mM ketone during the decomposition of the diazo requires that $[\text{diazo}]$ was at least 1.12 mM (possibly more if some azine is produced from two diazo molecules and if some other products are formed). Therefore $\epsilon_{2042} < 1515\text{ M}^{-1}\text{cm}^{-1}$.

In a second type of experiment, acetic acid ($\approx 6\text{ mM}$) was added to a solution of diazirine (10 mM). After irradiation during a few seconds, the concentration of the diazirine had decreased by 35% and azine** and acetate were formed in concentrations accounting for 11% and 38% of the diazirine consumed. The absorption of the diazo was not observed. On further irradiation (up to 80% decomposition of the diazirine), the ratio azine/acetate decreased, but only slightly. We found that the total amounts of azine and acetate formed account for about 15% and 41%, respectively, of the diazirine decomposed. This leaves us with about 44% of the diazirine decomposed being transformed into products X that do not absorb in the investigated IR region. Then, another solution of diazirine was

irradiated up to 63% decomposition and its IR spectrum, showing the absorption bands due to diazo, azine and to the remaining diazirine, was recorded. The IR spectrum was recorded again after addition of acetic acid (6 mM) to the solution: the diazo had completely disappeared, the azine and diazirine were unchanged and the acetate absorption appeared on the side of the strong band of acetic acid. The concentration of acetate was obtained from the absorbance at 1740 cm^{-1} , after correction for the absorption due to acetic acid. Assuming that the decomposition of the diazo in the presence of the added acetic acid gives the same distribution of products as in the previous experiment (acetate : **X** \approx 41 : 44), the concentration of diazo, formed during the irradiation and lost after addition of acid, is given by: $[\text{Diazo}] = [\text{Acetate}] + [\text{X}] = [\text{Acetate}] \times 2.07$. The absorption coefficient of the diazo, obtained from the absorbance at 2042 cm^{-1} before the addition of acid, $\epsilon_{2042} = 970\text{ M}^{-1}\text{cm}^{-1}$, is within the range 917 - 1515 deduced from the first type of experiment.

The quantum yield of formation of the diazo is then calculated from the results of the first experiment. The balance of products, 3 minutes after irradiation, was: diazirine lost : 4.85 mM; diazo formed : 1.7 mM; adamantanone formed : 0.2 mM; azine formed : 1.4 mM (i.e 2.8 mM monomeric species); other products, not seen by IR : 0.15 mM. If the diazo and the carbene **Ad:** are the only primary products obtained from the diazirine excited state (the RIES process is negligible in this case) and if the azine, adamantanone and other products are exclusively formed from, or *via*, **Ad:** (the decomposition of the diazo during 3 minutes is negligible), the diazo and **Ad:**, must be produced in the ratio $1.7 / (1.4 + 0.2 + 0.15) = 0.97$. Taking into account the few percents decomposition of the diazo during 3 minutes, raises the value of this ratio up to 1.07. Within experimental incertitudes, the diazo and **Ad:** are formed with a 50% quantum yield.

The UV absorption coefficient of the diazo was determined by using a solution containing a known concentration of diazo (determined by IR) and measuring the absorbance at 234 nm before and after addition of a trace of acetic acid to decompose the diazo without giving products absorbing at 234 nm.

* this solution was aerated

** The yield of formation of the azine, around 6%, is compatible with i) the carbene lifetime in the absence of acid, $\tau \approx 20\text{ns}$, ii) the rate constant of quenching of the carbene by acetic acid ($k_q = 5 \times 10^9\text{ M}^{-1}\text{s}^{-1}$) and iii) the formation of azine by a reaction (carbene + diazirine) with a rate constant $k_{az} \approx 10^9\text{ M}^{-1}\text{s}^{-1}$.

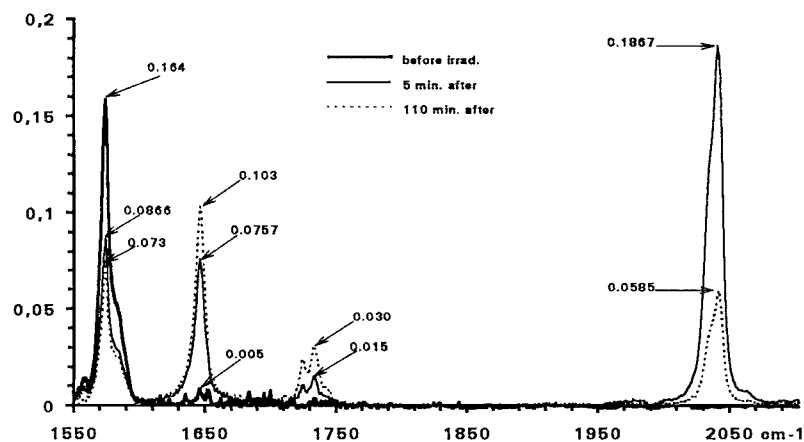


Figure 1 (Sup.Mat.) IR spectra of a solution of diazirine **3a** in isooctane, at room temperature and without acid, before, 3 min. and 110 minutes after irradiation

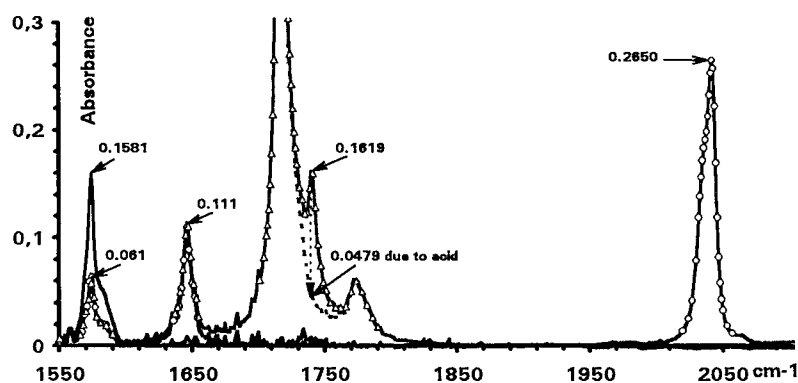


Figure 2 (Sup. Mat.) IR spectra of a solution of diazirine **3a** in isooctane, at room temperature, before irradiation, after irradiation and after addition of acetic acid.

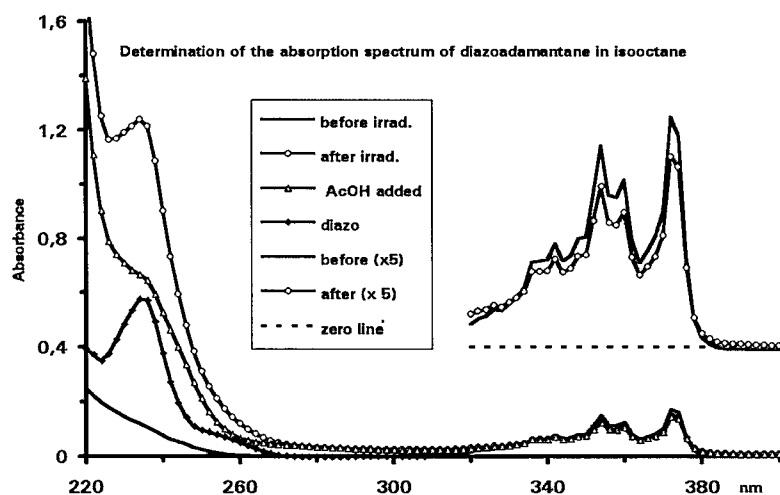


Figure 3 (Sup. Mat.) UV spectra of a solution of diazirine **3a** in isooctane, at room temperature, before irradiation, after irradiation and after addition of acetic acid. Differential spectrum assigned to diazoadamantane.