Quantum Yield of Formation of Diazo Compounds from the Photolysis of Diazirines

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Laser flash photolysis of diazirines has been widely used to produce carbenes "instantaneously" (within a few nanoseconds) which allows for kinetic information to be obtained on the intermolecular reactions of singlet carbenes as well as on their intramolecular rearrangement. In most cases, this rearrangement has yielded olefinic rearrangement products (ORP) which were first thought to result exclusively from a 1,2-H migration[1] in the primarily formed carbene. Frey[2a] and later Platz[2b] then proposed that rearrangement also occurs in the excited state of the diazirine, in a process (RIES) concerted with the extrusion of nitrogen. It has also been suggested[3] that ORP could be formed by thermal rearrangement, possibly acid catalyzed, of the ground state of a diazo compound. The formation of diazo compounds during the photolysis of diazirines is predicted by theoretical studies.[4] The photolysis of adamantyldiazirine, in hexane at room temperature, produces an absorption at 234.5 nm assigned to diazoadamantane,[5] and it gives a reddish color to cold pentane solutions[6] due to the weak absorption of diazoalkanes in the visible ($\epsilon_{max} \approx 3-10$; $\lambda_{max} = 450-495$ nm).[3a,7,8a] Some diazo compounds have also been detected by IR in rigid matrices[8] and even in *n*-heptane,[8a,d] but alkylchlorodiazomethanes expected from the alkylchlorodiazirines were never observed at room temperature, probably because of their rapid thermal decomposition.[9] These diazo compounds could be formed in high yield,[3a] and this might explain the low quantum yield of carbene formation in the photolysis of some diazirines, e.g. less than 10% in the case of the isopropylchlorodiazirine.[10] Furthermore, if their decomposition really yields appreciable amounts of ORP, this process would explain the excessive amount of ORP obtained when diazirines are decomposed in the presence of large concentrations of olefinic reactant.[11] The alternative (which we favored until now) is the existence of a carbene olefin complex (COC) as shown in Scheme 1. It is therefore important to quantify the yield of formation of such diazo compounds in the photolysis of diazirines.

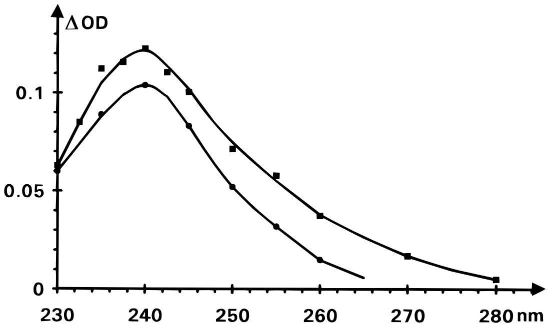
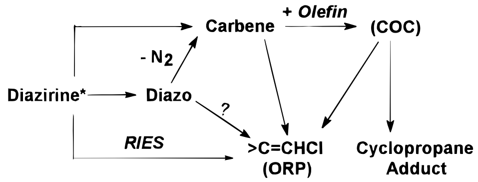
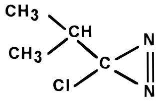


Figure 1. Transient absorption spectra assigned to diazomethanes **1b** (■) and **2b** (●) observed 1 μs after excitation of diazirines **1a** and **2a** in isooctane by a 355 nm, 200 ps pulse.

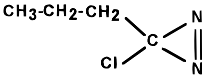
Scheme 1



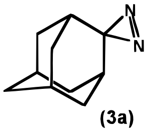
We wish to report the observation at room temperature in fluid solutions of metastable diazo compounds produced by the photolysis of diazirines, the kinetic parameters for their disappearance, and an evaluation of their yield of formation.



(1a)



(2a)



(3a)

Laser-flash photolysis of isopropylchlorodiazirine, **1a**, in isooctane at 25 °C, produces a transient absorption in the 230−250 nm region ($\lambda_{max} \approx 240$ nm), which decays with a "lifetime" of ca. 0.5 s. This transient absorption (Figure 1) is assigned to isopropylchlorodiazomethane, **1b**, due to its spectral similarity with the absorption of diazomethane ($\lambda_{max} = 220$ nm).[12] Similar results were obtained by photolysis of *n*-propylchlorodiazirine, **2a**, and of 2-adamantyldiazirine, **3a**, in isooctane. The lifetime of 2-diazoadamantane, **3b**, is long enough for recording its UV and IR absorption spectra with conventional spectrophotometers (HP 8452A, photodiode array detector, and PE Paragon 1000 FTIR). The kinetics of disappearance of the 234 nm and 2042 cm^{-1} absorptions were compared for isooctane solutions of **3a** (0.01 M) irradiated for a few seconds using the third harmonic of a Nd:YAG laser (5 Hz, 355 nm, 20 mJ/pulse). The spectra recorded in 1 mm cells, at regular time intervals during a 2 h period, gave similar decay times for the UV and IR absorptions, ca. 1 and 1.5 h, respectively. This similarity and the effect of acetic acid on the decay time at 234 nm in flash-photolysis experiments, yielding $k_q \approx 10^5$ M^{-1} s^{-1}, confirm the assignment of the 234 nm absorption to **3b**.

The absorption coefficient of **3b** at 2042 cm^{-1}, around 1000 M^{-1} cm^{-1}, and its quantum yield of formation, around 50%, were measured from the comparison of IR spectra of solutions in which acetic acid was added immediately after irradiation or before irradiation (the methodology is given in the supporting information). The absorption coefficient of **3b** at 234 nm is

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[1] Methyl, phenyl, Cl, ... may also undergo 1,2-shift at slower rates.

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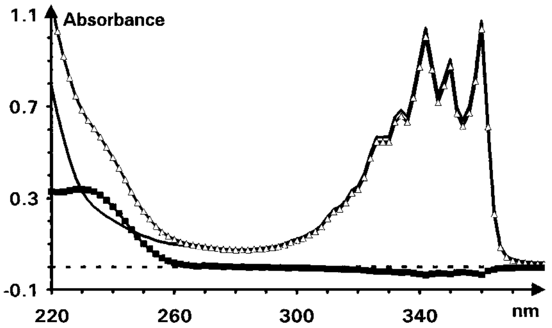

Figure 2. Absorption spectra of a solution of diazirine **1a** in isooctane at −30 °C, before (—) and after (−△−) irradiation. The differential spectrum (−■−) is assigned to diazomethane **1b**.

then calculated to be ~6500 M^{-1} cm^{-1}, similar to the value reported[12] for diazomethane at 220 nm, $\epsilon = 8300$ M^{-1} cm^{-1}.

Assuming that the UV absorption coefficient of diazomethanes **1b** and **2b** is, by analogy, also in the range of (6−8) × 10^3 M^{-1} cm^{-1}, the quantum yield of formation of these species, Φ_{diazo}, can be determined either by flash spectroscopy at room temperature or by conventional spectroscopy at −30 °C. In the first case, we used the relative actinometry technique,[13] with benzophenone triplet as standard. The relation $\Phi_{diazo} = (A_{240} \times \epsilon_{3BP})/(A_{530} \times \epsilon_{diazo})$, where A_{240} and A_{530} are the amplitudes of the transient absorptions at 240 and 530 nm produced by the excitation under the same conditions of solutions of diazirines and benzophenone, respectively, gives $\Phi_{diazo} \approx 0.10$ from both **1a*** and **2a***.[14]

At −30 °C, diazomethanes **1b** and **2b** have lifetimes of several minutes and can therefore be observed with a photodiode array UV−vis spectrophotometer after irradiation of the solution during 1 or 2 s by a frequency-tripled Nd:YAG laser running at 10 Hz. The decay of the diazo is negligible during the few seconds needed for excitation, shaking the cell to homogenize the solution, and recording of the spectrum. The absorption spectrum recorded immediately after irradiation shows (i) a decrease of the absorbance in the 330−370 nm region due to the photolysis of a fraction of the diazirine, the only species absorbing in this region, and (ii) an increase of the absorbance in the 210−260 nm region, due to the absorptions of the diazo and of the permanent products formed by the decomposition of the diazirine (chlorobutene and azine). The absorption spectrum recorded a few minutes later, when the diazo has disappeared, provides the contribution of these permanent products, plus those formed during the decomposition of the diazo. In the region 220−290 nm, this spectrum is identical to that recorded before irradiation because the absorption of the permanent products is negligible for $\lambda > 220$ nm: chlorobutene does not absorb strongly at $\lambda > 220$ nm and azine is a minor product, because the rearrangement of propylchlorocarbenes is fast.[15] Therefore, the difference between the spectra recorded immediately after excitation and a few minutes later (Figure 2) offers a good estimate, at least for $\lambda > 220$ nm, of the absorption of the diazos **1b** and **2b**.[16]

The yield of formation of the diazo is then given by the ratio between the concentrations of diazo formed, $(\Delta A_{230}/\epsilon_{diazo})$, and of diazirine decomposed, $(-\Delta A_{360}/\epsilon_{diazirine})$. With $\epsilon_{diazirine} = 100$ and $\epsilon_{diazo} = 7000$, this operation yields $\Phi_{diazo} \approx 0.13$ for **1a*** → **1b** and $\Phi_{diazo} \approx 0.10$ from **2a*** → **2b**.

The kinetics of disappearance of the diazos **1b**−**3b**, measured by their UV absorption and strongly temperature dependent, were studied from room temperature ($\tau \approx 0.6$ s) down to −31 °C ($\tau \approx 210$ s) for **1b** and down to −20 °C ($\tau \approx 170$ s) for **2b** and from room temperature up to 60 °C for **3b**. Decays are first order for **1b** and **2b**, and Arrhenius plots, $\ln(1/\tau)$ *vs* $1/T$, give the following kinetic parameters: $A = 10^{12.7\pm0.3}$ s^{-1} and $E_a = 16.8$ and 17.5 kcal/mol for **1b** and **2b**, respectively. The "decay time" of **3b** decreases from ~50 min at 25 °C to ~7 min at 49 °C, but the kinetic parameters derived from the Arrhenius plot of the data obtained on this small temperature range, $E_a \approx 15$ kcal/mol and $\log A \approx 7.5$, do not seem reliable because: (i) the decay of the UV absorption of **3b** does not fit exactly a first-order kinetics; this may be due to some second-order process or, more probably, owing to the overlap of the diazo and azine absorptions as the fit with first-order kinetics is much better for the decay of the IR absorption at 2042 cm^{-1} where **3b** is the only absorbing species; (ii) the decay of **3b** is so slow that reaction(s) with impurities, even in trace amounts, either initially present or produced during the photolysis, may be nonnegligible. This may also explain the 50% difference between the decay times measured by IR and UV.

Several conclusions may be drawn from this study. First, the formation of **1b** with a quantum yield of approximately 10−15% is not responsible for the very low yield of carbene formation from **1a***. Platz's hypothesis[2] of an efficient RIES process in the case of this compound seems to offer the best explanation, but this should be confirmed by analysis of the products obtained under photolysis and thermolysis in the presence of various amounts of a reactive olefin at various temperatures, as was done for the chloromethyl- and *n*-propylchlorodiazirines.[17]

Second, the frequency factor for the disappearance of **1b** and **2b** is in agreement with the reaction diazo → carbene + N_2 being the major (if not the only) disappearance pathway. A rearrangement concerted with N_2 extrusion, which certainly requires a specific transition state, would probably be unfavored by a large negative $\Delta S^\ddagger$ term and would have a frequency factor lower than $10^{12.7}$ s^{-1}. An acid-catalyzed process involving protonation of the diazo (traces of HCl are observed in the photolysis of alkylchlorodiazirines), N_2 elimination, and deprotonation cannot have a $10^{12.7}$ s^{-1} preexponential factor because its first step is a bimolecular reaction with a pseudo-first-order rate constant $k = k_2$ [HCl], where k_2 is limited by diffusion and [HCl] < 10^{-5} M.

Third, the diazo compound cannot be responsible for the excess of rearrangement products observed when alkylchlorodiazirines are decomposed by photolysis or thermolysis in the presence of olefins. For example, the decomposition of **2a** in the presence of tetramethylethylene (TME) gives a mixture of chlorobutene and cyclopropane where the percentage of chlorobutene, extrapolated to [TME] = ∞, is ~38% under thermolysis at 80−100 °C and ~52% under photolysis at 10−55 °C, the difference between these numbers being due to RIES.[17] In contrast, the quantum yield of formation of **2b** is approximately 10%, and, most probably, the decomposition of **2b** gives mainly the carbene so that the yield of formation of chlorobutene *via* an hypothetic rearrangement of **2b** bypassing the carbene should not exceed a few percent.

Supporting Information Available: Experimental procedure for the determination of the UV and IR absorption coefficients of diazoadamantane; IR and UV spectra of solutions of 2-adamantyldiazirine at various time delays after irradiation (3 pages). See any current masthead page for ordering and Internet access instructions.

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