PHOTODECOMPOSITION QUANTUM YIELDS OF 3-CHLORO-3-METHYLDIAZIRINE IN THE GAS PHASE

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Summary

A careful integration technique has allowed the determination of photodecomposition quantum yields Φ_D of 3-chloro-3-methyldiazirine at several wavelengths using conventional equipment. The results obtained are

Φ_D (313 nm) = 0.87 ± 0.13
Φ_D (334 nm) = 0.90 ± 0.1
Φ_D (343 nm) = 0.96 ± 0.07

A change of collision frequency from 5.0×10^7 to 5.7×10^{10} does not alter the quantum yield which is also unaltered by oxygen. Our data are explained by a mechanism which includes two photodecomposition paths. The first is a direct photodissociation from the electronic state reached by the initial transition and the second involves methylchlorocarbene.

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1. Introduction

The photolysis of alkyldiazirines has been reviewed by Frey [1]. It is generally accepted that this photolysis generates the corresponding carbene; participation of triplet states has been mentioned [1, 2] but their identification in the photolysis experiments remains elusive.

3-Chloro-3-methyldiazirine was photolysed in the liquid phase by Moss and Mamantow [3]. They identified the products of insertion of the generated chloromethylcarbene into different olefins. The products of the gas phase photolysis have been reported by Jones *et al.* [4]. The influence of pressure on the product distribution has been described by Cadman *et al.* [5] and Figuera *et al.* [6].

Recently Frey and Penny [7] have re-interpreted the photolysis. In their opinion the photoisomerization 3-chloro-3-methyldiazirine → methylchlorodiazomethane plays a crucial role in the reaction mechanism. This type of isomerization has been described by Amrich and Bell [8] but their interpretation of the results was questioned by Moore and Pimentel [9] who

indicated that diazomethane was formed by insertion of methylene in nitrogen and not by isomerization. However, direct formation of the diazocompound has been observed in the *thermolysis* of 3-butyl-3-phenyldiazirine [10].

Although the participation of the carbene in the reaction seems to be unquestionable, the studies of product energy distribution require the involvement of more than one electronic surface in the reaction.

Participation of different electronically excited states has been reported in the gas phase photochemistry of azoethane and hexafluoroazomethane [11] and also in cyclic azo compounds [12]. In these cases changes of quantum yields with pressure, and other effects, have been observed. However, similar effects have been reported in the photolysis of azoisopropane [13] in which involvement of different vibrationally excited *cis* and *trans* ground states has been invoked.

In this work we have studied the quantum yields of 3-chloro-3-methyldiazirine photodecomposition at different pressures and conditions. Also we have irradiated the substrate at different vibronic transitions in order to deposit different amounts of vibrational energy in the initially "prepared" excited state.

It was expected that, according to the hypothesis of ref. 6, vibrationally excited 3-chloro-3-methyldiazirine would be formed and a substantial change of the quantum yield with the mentioned variables would be found.

2. Experimental

The preparation, purification, handling and analysis of 3-chloro-3-methyldiazirine and its photolysis products have been described previously [6].

2.1. Absorption spectra of 3-chloro-3-methyldiazirine

Routine spectra were mainly recorded using a Perkin–Elmer model 200. For higher resolution we built a single-beam spectrophotometer which used a Jarrell Ash 0.5 m grating monochromator. The maximum resolution of this apparatus was 0.02 nm. The bands irradiated in the photolysis experiments are shown in Fig. 1.

2.2. Incident light analysis

Photolysis wavelengths (obtained from a super high pressure mercury lamp, Osram HBO 200 W fed with d.c. current, and the xenon lamp mentioned before) were selected using a "high intensity" monochromator (Bausch and Lomb). In order to determine the quantum yields it was necessary to determine precisely the spectral distribution $I_0(\lambda)$ of this selected light. A single-beam spectrophotometer with slight modifications was used: the lamp was replaced by a combination of the high intensity monochromator and the lamp whose light output was going to be analysed, and the sample cell was removed. The results are given in Fig. 1.
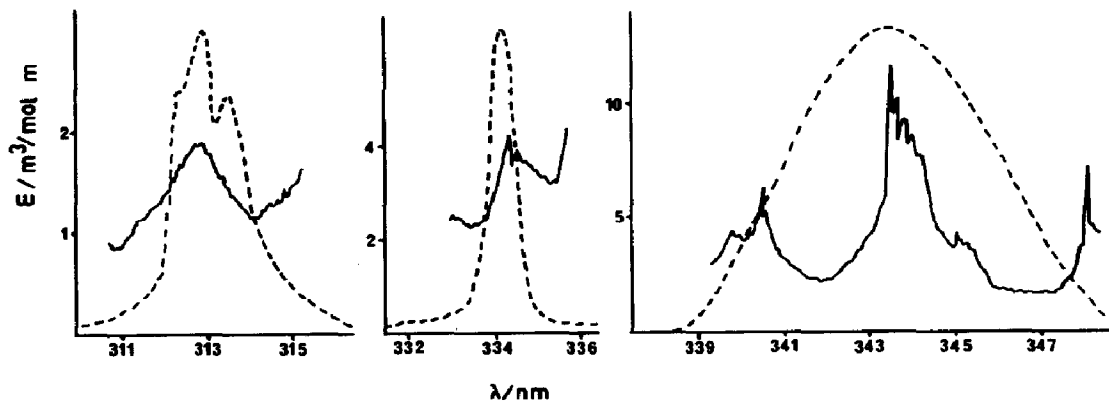
Fig. 1. The 3-chloro-3-methyldiazirine bands irradiated (——) and the photolysis light (------) in arbitrary units.

2.3. Actinometry

Ferrioxalate actinometry was used [14]. Only the light incident on the cells† was measured.

Assuming irreversible photodecomposition, the quantum yields Φ_D can be calculated using the equation [15]

$$\int_{c_0}^{c} dc \{\sum_{\lambda} I_0(\lambda) - \sum_{\lambda} I_0(\lambda) \times 10^{-\epsilon(\lambda)cl}\}^{-1} = \Phi_D t$$

where c is concentration and t the time. The first summation represents the incident light and the second the transmitted light. Plotting the left-hand term of the equation against time yields a straight line of slope Φ_D (Fig. 2).

The instability of the mercury lamps required the simultaneous measurement of the light and the decomposition of 3-chloro-3-methyldiazirine. For this purpose a known percentage of the light was reflected from the incident beam by a quartz plate and was absorbed in a cell containing the actinometer. The stability of the xenon lamp makes this procedure unnecessary.

3. Results

3.1. Irradiation with the mercury lamp (313 and 334 nm)

This lamp presents some positive features compared with the xenon lamp. The intensity output integrated over the monochromator-selected band is about 2×10^{-8} einstein s^{-1} at 313 nm and about 7×10^{-9} einstein s^{-1}

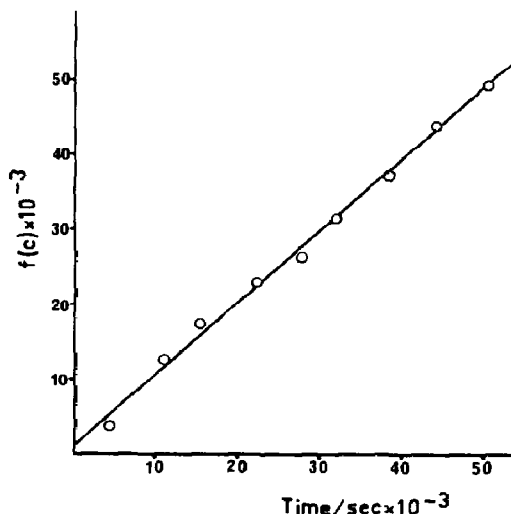† These cells were similar to those described in ref. 6.

Fig. 2. Quantum yield determination at 343 nm of 2.7 Torr of 3-chloro-3-methyldiazirine plus 710 Torr of propane. Example of plots of the left-hand term $f(c)$ of equation (see text) against time.

at 334 nm. The xenon lamp output is only about 4×10^{-10} einstein s^{-1} at 343 nm.

Also the lamp output (see Fig. 1) had a relatively narrow bandpass (*i.e.* 0.59 nm FWHM at 313 nm and 0.38 nm at 334 nm for the mercury lamp in contrast with 2.8 nm at 343 nm for the continuous xenon lamp limited by the monochromator). The quantum yields obtained are plotted in Fig. 3 against the collision frequency.

The quantum yield seems to be independent of the collision frequency and of the gas used. Oxygen, propane, *cis*-butene-2 and the pure compound gave the same quantum yields within experimental error:

$$\Phi_{334} = 0.9 \pm 0.1$$
$$\Phi_{313} = 0.87 \pm 0.13$$

The errors include the deviations of I_0 which have been estimated as 15%. Possible changes in the composition of the photolysis products were not observed.

3.2. Irradiation with the xenon lamp (343 nm)

The use of this lamp is complicated by its low power output. The minimum usable bandwidth in order to obtain appreciable decomposition was 2.8 nm, with the undesirable feature that only a small fraction of it is absorbed by our sample (Fig. 1), *i.e.* this wavelength corresponds to a region of low extinction coefficient in the diazirine spectrum. Long irradiation times were necessary to determine precisely the fraction of the light absorbed.

A quantum yield at 343 nm of $\Phi_{343} = 0.96 \pm 0.07$ was finally obtained. The error, as for the mercury lamp, includes that associated with the deter-
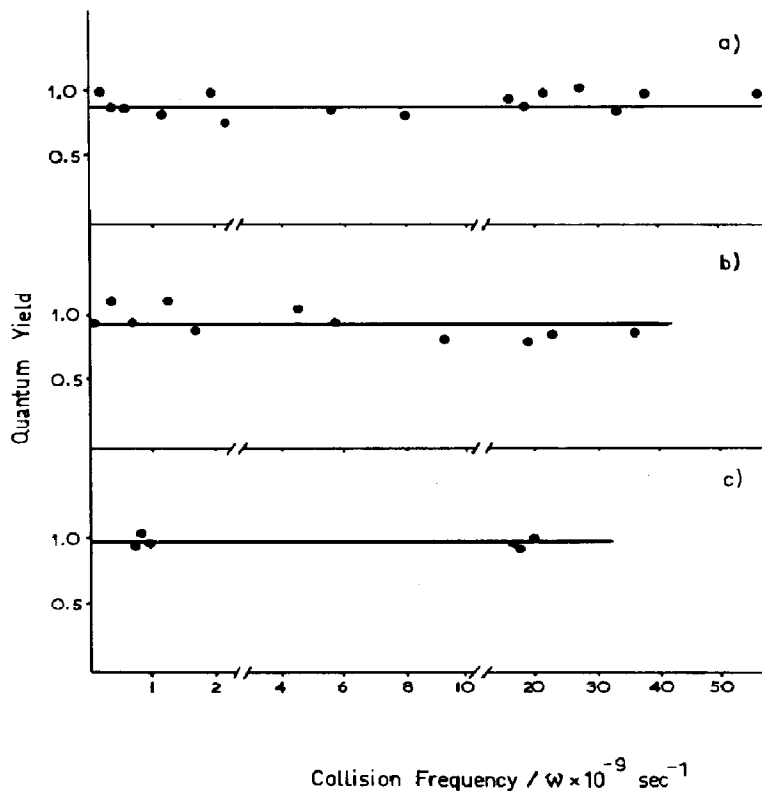
Fig. 3. Quantum yield of 3-chloro-3-methyldiazirine decomposition *vs.* collision frequency at (a) 313 nm, (b) 334 nm and (c) 343 nm.

mination of the incident light. The results obtained are plotted against collision frequency in Fig. 3.

3.3. Further check on the invariance of the quantum yield with pressure, i.e. with collision frequency

The data at 313 and 334 nm are affected by the errors involved in the determination of the incident light. These errors could obscure some trend in the quantum yield. In order to avoid these problems three series of experiments were performed.

(1) In a cell of path length 10 cm we introduced 5 Torr of 3-chloro-3-methyldiazirine, and in a similar cell the same amount of 3-chloro-3-methyl-diazirine plus 710 Torr of propane. The cells were irradiated alternately for 5 min each for a total of 12 h. According to the definition of quantum yield

$$\Phi_D = -\frac{dc/dt}{I_{abs}/V}$$

the decay of the initial substrate should be equal for two samples that have identical Φ_D and similar absorption. In Fig. 4 we have plotted the decay of the absorbance (*i.e.* substrate concentration) against time. The identical
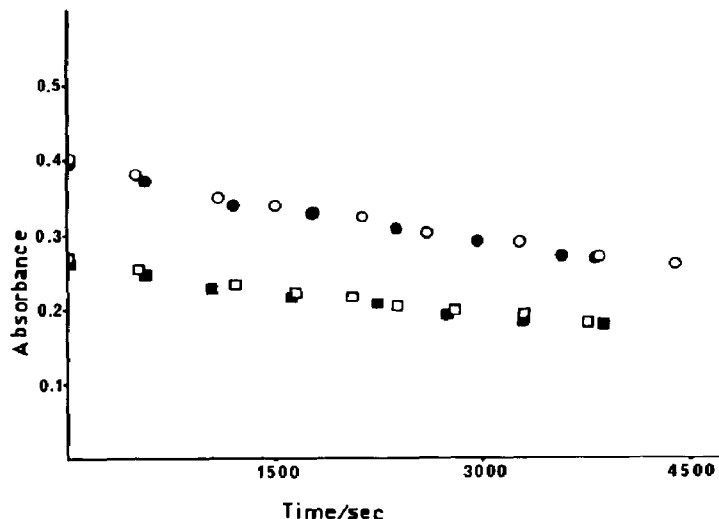
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Fig. 4. Decay of two samples of 3-chloro-3-methyldiazirine that absorb the same fraction
of the incident light: O,●, runs at 334 and □, ■, at 343 nm. The filled symbols indicate
the sample pressurized with 710 Torr of propane. The xenon lamp was used.

behaviour of the two samples shows that the pressure does not influence Φ_D.
The experiment was run at 334 nm with the xenon lamp.

(2) We confirmed these results by photolysing, alternately, 5 Torr of
3-chloro-3-methyldiazirine in a 10 cm cell and 50 Torr of 3-chloro-3-methyl-
diazirine in a 1 cm cell. As expected (Fig. 5) the decays of the absorbance of
the two samples were the same and therefore also the quantum yields. In this
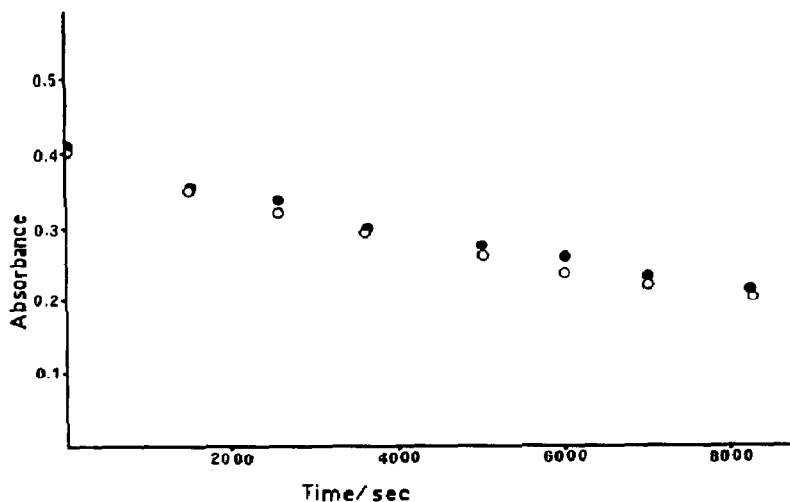case we used the mercury lamp as λ = 313 nm.

Fig. 5. Decay of two samples that absorb the same fraction of the incident light at
313 nm but contain different 3-chloro-3-methyldiazirine concentrations. The mercury
lamp was used.

(3) Finally we made use of the beam splitter in order to irradiate simultaneously two samples. In the first experiment we introduced 4.3 Torr of 3-chloro-3-methyldiazirine in one cell and 17 Torr of 3-chloro-3-methyl-diazirine in the other similar cell. The cells were interchanged each 5 min for a total photolysis time of 2.5 h. The experiment was repeated with 6.5 Torr of 3-chloro-3-methyldiazirine in one cell and 8.7 Torr of 3-chloro-3-methyl-diazirine plus 1 atm of propane in the second cell. The ratio of quantum yields for the two cells was 0.91 for the first experiment and 0.95 for the second, *i.e.* both values were within the error limits for equal Φ_D. The photolysis was carried out at 313 nm using the mercury lamp.

These experiments show that Φ_D is independent of pressure in the range 1.4 - 1.6 $\times 10^3$ Torr at 313, 334 and 343 nm.

4. Discussion

Contrary to our expectations the quantum yield of 3-chloro-3-methyl-diazirine decomposition is invariant with pressure. From 5.0×10^7 to 5.7×10^{10} collisions s^{-1} no alteration of Φ_D is observed. These data rule out the intervention of vibrationally excited states as reaction intermediates. In order to be unaffected by deactivating collisions the lifetime of the inter-mediates involved would have to be of the order of 10^{-12} s.

The participation of radicals and triplet states is very unlikely. High oxygen pressures did not change Φ_D. This is not really meaningful as Φ_D is close to unity; unless the oxygen were to permit new reaction pathways Φ_D should not exceed unity. In contrast — and this is more significant — the product distribution is not changed, indicating the absence of radical and triplet states.

The quantum yield is invariant to wavelength in the range studied. The band at 343 nm leads to excitation of the first level of the symmetric C—C stretching vibration, while the band at 333 nm excites the overtone of this vibrational mode. Light of 313 nm takes the system to a combination level made up of the mode mentioned plus an overtone of the symmetric N=N stretch [16]. These different excitations, which "deposit" very different vibrational energies in the excited molecule (9.6 kJ mol^{-1} at 343 nm, 19 kJ mol^{-1} at 334 nm and 43 kJ mol^{-1} at 313 nm), gave the same decomposition quantum yield (see also Fig. 3):
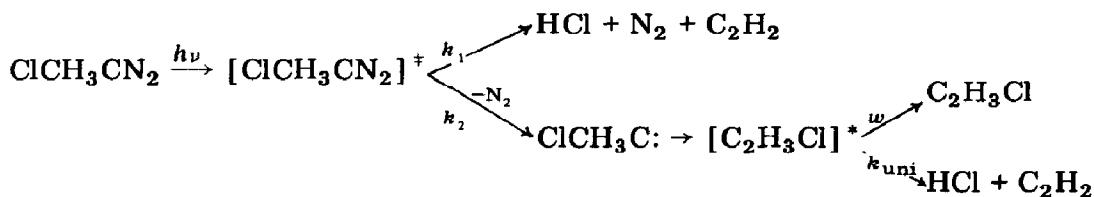
$$\Phi_D \ (313 \ nm) = 0.87 \pm 0.13$$
$$\Phi_D \ (334 \ nm) = 0.9 \ \ \pm 0.1$$
$$\Phi_D \ (343 \ nm) = 0.96 \pm 0.07$$

The tendency towards lower Φ_D at shorter wavelengths may be real but it is extremely difficult with our experimental methods to reduce the errors in order to make the differences relevant. Another approach seems neces-sary. However, the effect already reported [6] for vinyl chloride excess energy is clear: the more energy deposited the higher the decomposition rate.

Concerning the formation of methylchlorodiazomethane [7] we have observed in previous work on the photolysis of diazobutane [17] that the presence of oxygen fundamentally alters the process. A reaction of diazobutane with the oxygen similar to that reported in the photolysis of diazoethane [18] seems to take place. However, the effect of 1.2×10^3 Torr of oxygen in the 3-chloro-3-methyldiazirine photolysis is that of an inert gas. The same distribution of products as that found with nitrogen was obtained. The formation of a diazo compound seems to be incompatible with these results.

Eliminating the possibilities mentioned earlier we may tentatively write the mechanism

$$ClCH_3CN_2 \xrightarrow{h\nu} [ClCH_3CN_2]^{\ddagger} \overset{k_1}{\underset{k_2}{\lessgtr}} \begin{array}{l} \nearrow HCl + N_2 + C_2H_2 \\ \\ \searrow ClCH_3C: \xrightarrow{-N_2} [C_2H_3Cl]^* \overset{w}{\underset{k_{uni}}{\lessgtr}} \begin{array}{l} \nearrow C_2H_3Cl \\ \searrow HCl + C_2H_2 \end{array} \end{array}$$

where $\ddagger$ and $*$ denote electronic and vibrational excitation respectively.

The rate constants k_1 and k_2 must be very fast (about 10^{11} s^{-1}) for the reaction to be unaffected by pressure. The diazirine radiative lifetime calculated from the absorption spectrum is about 1 μs; the absence of fluorescence in the gas phase (we estimated that $\Phi_D < 0.0001$) indicates that the processes that compete with fluorescence (i.e. k_1 and k_2) are at least 10^4 times faster, or in other words $k_1 + k_2 > 10^{10}$ s^{-1} in good agreement with the pressure effects.

Alternatively, if the electronically excited 3-chloro-3-methyldiazirine had been converted to vibrationally excited ground electronic diazirine we would have expected some collisional deactivation and some decrease of the photodecomposition quantum yield at high pressure. In fact this result was not found and this hypothetical internal conversion can be ruled out.

Another point which deserves some discussion concerns the origin of the reaction paths corresponding to the rate constants k_1 and k_2. Have these paths a common origin or do they originate from two different electronic states? First of all we should consider the possible occurrence of these states. We discuss exclusively the singlet manifold as the results with oxygen ruled out the triplet. Robertson and Merrit [16] mentioned the possible presence of a second electronic system slightly to the red of the 0–0 band of the main n → π^* transition. This interpretation is strongly questionable [19, 20]. However, for the sake of the following discussion we are going to admit these two states. According to the theory of radiationless transitions it seems likely that the relative population of the states would depend on the vibrational mode excited. Assuming that each electronic state presents a different reactivity, one state would produce acetylene directly and the other would form acetylene via the carbene intermediate and subsequent vinyl chloride decomposition. If this were the case we would expect that the ratio

of the acetylene formed via the two different reaction channels would depend on the population of the states that are the initial points of the different routes (hence on the wavelength of irradiation). Experimentally [6] the ratio of the rates of acetylene formation at high pressure (direct channel) and low pressure (direct + indirect channels) is not sensitive to wavelength. This evidence suggests the active presence of a unique excited state in agreement with our previous discussion. According to the spectroscopic studies and calculations cited earlier this state should be the first electronically excited state, *i.e.* nπ^*.

The intermediacy of the carbene is in part a problem of semantics. The barrier for hydrogen migration from the methyl group to the divalent carbon atom is probably non-existent in the gas phase [21] and the carbene is merely a point in the descending surface that connects electronically excited diazirine and vinyl chloride.

The scheme described is in our view the most reasonable explanation of 3-chloro-3-methyldiazirine photolysis.

Acknowledgments

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