318. *The Photolysis of 3-Methyldiazirine (Cyclodiazoethane)*

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The photolysis of methyldiazirine has been investigated in the gas phase both alone and in the presence of various added gases. The volatile products were ethylene, acetylene, hydrogen, and nitrogen. The relative yields of these compounds were pressure-dependent. The results are explained in terms of two primary reaction paths, one giving rise to ethylene and nitrogen, the other to ethylidene and nitrogen. The ethylidene rearranges to yield an excited molecule of ethylene which can decompose to acetylene and hydrogen or be collisionally stabilised. The evidence for the intermediate formation of ethylidene rests on the comparison with analogous systems since attempts to obtain direct evidence for the presence of this radical were negative. The absorption spectrum and pyrolysis of methyldiazirine are reported. The results obtained in this work are compared with earlier investigations on the photolysis of diazoethane.

ETHYLIDENE has been postulated as an intermediate in the photolysis of diazoethane [1,2] and methylketene.[3] It has further been suggested that the mercury-photosensitised reactions of ethylene also involve this radical,[4] and there has been some discussion about the electronic state of the radical in this system. The properties of ethylidene appear to depend on the nature of its precursor, and, when this is diazoethane, also on the wavelength of the photolytic radiation. The photolysis of diazirine [5,6] has been shown to yield methylene in the same manner as the photolysis of diazomethane; it therefore seemed likely that the photolysis of methyldiazirine would be similar to that of diazoethane. This work was undertaken to study further the reactions of ethylidene and also to investigate the behaviour of highly vibrationally excited ethylene molecules.

EXPERIMENTAL

2,4,6-Trimethyl-1,3,5-triazabicyclo[2,1,0]hexane (I), m. p. 113—115°, was prepared from liquid ammonia, t-butyl hypochlorite, and acetaldehyde as described by Schmitz.[7] 3-Methyldiazirine was prepared by adding a solution of (I) in dilute sulphuric acid to an excess of sodium dichromate in dilute sulphuric acid at 40°. The methyldiazirine was swept out of the reaction vessel in a stream of nitrogen [8] and condensed in a trap cooled in solid carbon dioxide. The crude diazirine was freed from acetaldehyde by bubbling it, in a nitrogen stream, through concentrated potassium hydroxide solution, and then passing it over pellets of potassium hydroxide to remove moisture. The purified methyldiazirine was collected at $-78°$ as a colourless mobile liquid. It had infrared peaks at 1600 and 988 $cm.^{-1}$ characteristic of the diazirine ring. Gas chromatography on a silicone column gave only one peak. Throughout the work the methyldiazirine was stored as a liquid at $-78°$.

Apparatus.—A conventional high-vacuum system was used. Most photolyses were carried out in cylindrical Pyrex vessels whose volumes ranged from 10 to 250 ml. The light source for most of the work was an unfiltered medium-pressure mercury arc (Hanovia U.V.5 500). In photolyses using monochromatic radiation of 3130 Å, a 250w Osram ME/D high-pressure mercury lamp was used in conjunction with a chemical filter and an interference filter. In this case the reaction vessel was cylindrical with optically flat quartz end-windows. To avoid absorption errors, greaseless stopcocks with Viton A diaphragms were used throughout the vacuum system.

Analysis.—Analysis was by gas chromatography using a 25 ft. × 0·18 in. (i.d.) coiled copper

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[1] R. K. Brinton and D. H. Volman, *J. Chem. Phys.*, 1951, **19**, 1934.
[2] H. M. Frey, *J.*, 1962, 2293.
[3] G. B. Kistiakowsky and B. H. Mahan, *J. Amer. Chem. Soc.*, 1957, **79**, 2412.
[4] D. W. Setser, B. S. Rabinovitch, and D. W. Placzek, *J. Amer. Chem. Soc.*, 1963, **85**, 862.
[5] H. M. Frey and I. D. R. Stevens, *Proc. Chem. Soc.*, 1962, 79.
[6] M. J. Amrich and J. A. Bell, *J. Amer. Chem. Soc.*, 1964, **86**, 293.
[7] E. Schmitz, *Chem. Ber.*, 1962, **95**, 688.
[8] E. Schmitz and R. Ohme, *Chem. Ber.*, 1962, **95**, 795.

column containing di-2-cyanoethyl ether on 40—60 mesh Chromosorb P. The column was immersed in a large Dewar flask filled with crushed ice. Hydrogen was the flow gas and a Gow-Mac katharometer the detector. The input system to the chromatograph employed a multi-channel stainless steel valve of the type described by Pratt and Purnell.[9] The remainder of the analytical system has been described previously.[10]

RESULTS AND DISCUSSION

Absorption Spectrum of 3-Methyldiazirine.—The ultraviolet spectrum is highly characteristic of the diazirines as a class.[11] The maximum of the short-wavelength absorption occurs below 190 mμ (52,000 cm.$^{-1}$) and this band tails to about 240 mμ (41,500 cm.$^{-1}$). The long-wavelength absorption (Figure 1) consists of a series of well-defined maxima starting at about 292 mμ (34,200 cm.$^{-1}$), increasing in intensity to the highest maximum at 341 mμ (29,300 cm.$^{-1}$) (ε ~470), and then showing a sharp fall.

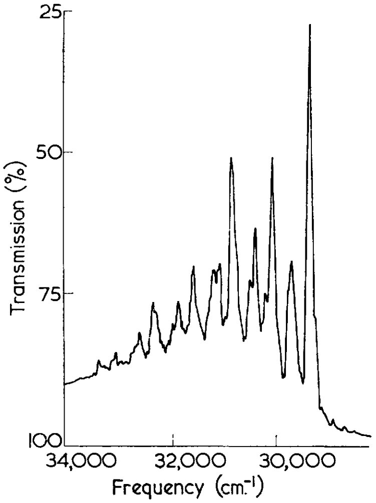

FIGURE 1. Absorption spectrum of 3-methyldiazirine (7 mm. pressure)

Photolyses of 3-methyldiazirine were carried out at various temperatures between 0 and 60° in Pyrex reaction vessels. Under these conditions the product ratios were independent of temperature. In the majority of experiments no attempts were made to filter the light from the medium-pressure mercury lamp, but from the absorption spectrum of the methyldiazirine it can be seen that the effective radiation was from the mercury lines between 2900 and 3340 Å, with the greatest contribution from the lines at 3130 Å. Runs were carried out at various initial pressures of methyldiazirine in the range 1—250 mm. The only volatile products observed were ethylene, acetylene, and nitrogen. Hydrogen, which from the stoicheiometry of the reaction one would expect to be formed, could not be detected since it was being employed as the flow gas in the chromatograph. However, one run was analysed (initial pressure ~10 mm.) using nitrogen as the flow gas, when the presence of hydrogen was confirmed (" negative " peak in air position on chromatogram).

After a large number of runs, especially with initial pressures above 10 mm., a thin film of non-volatile material was deposited on the walls of the reaction vessel. This could only be removed by strong heating, when it charred without melting. In addition, when photolysing methyldiazirine at pressures above about 50 mm., minute oily drops of a non-volatile liquid were formed, which could not be removed by pumping the reaction vessel at room temperature. After photolysing four samples of the methyldiazirine at an

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[9] G. L. Pratt and J. H. Purnell, *Analyt. Chem.*, 1960, **32**, 1213.
[10] H. M. Frey and I. D. R. Stevens, *J.*, 1962, 3865.
[11] H. M. Frey and I. D. R. Stevens, *J.*, 1963, 3514.

initial pressure of 200 mm., the liquid was removed from the reaction vessel using a small quantity of acetone. Most of the acetone was allowed to evaporate, the remaining mixture gave a positive (though weak) test for nitrogen.

It was not possible to determine the carbon balance in the volatile products directly, since relative and not absolute measurements of the products were determined chromatographically. For a few runs the following procedure was therefore adopted. Gas mixtures of methyldiazirine and cyclopentane were prepared with a ratio of about 10 : 1. These mixtures were made up in the same apparatus as was used to prepare test samples for standardisation purposes. After photolysis of the mixture for a time sufficient to cause virtually complete decomposition of the methyldiazirine, the relative yields of ethylene plus acetylene to cyclopentane were determined. The results showed some scatter, but indicated that the ethylene and acetylene constituted not less than 85% of the carbon in the diazirine, with a mean value of 92%.

The ratio of ethylene to acetylene depended on the initial pressure of 3-methyldiazirine, but was almost independent of the amount of methyldiazirine decomposed in the range 25—95% (see Table 1).

TABLE 1

Ratio of ethylene to acetylene at 16 mm.

% Decomposition	25	40	54	71	80	95
$C_2H_4 : C_2H_2$	2·84	2·81	2·86	2·88	2·98	2·95

A series of photolyses was carried out with different initial pressures of methyldiazirine in the range 0·9—230 mm. In all cases photolysis was continued for a time sufficient to allow almost complete decomposition of the diazirine. The yields of acetylene and ethylene are shown in Table 2.

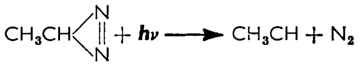
TABLE 2

Percentage yields of acetylene and ethylene at various initial pressures of 3-methyldiazirine

Pressure (mm.)	0·93	1·4	2·05	2·8	3·4	5·6	7·0	9·5	11·9	16
C_2H_2	53·8	50·2	46·7	43·8	39·7	36·3	32·5	29·0	27·8	25·3
C_2H_4	46·2	49·8	53·3	56·2	60·3	63·7	67·5	71·0	72·2	74·7
Pressure (mm.)	31	39	71	105	139	166	173	205·5	232	
C_2H_2	20·9	21·0	17·4	14·8	14·1	12·2	12·6	10·9	11·1	
C_2H_4	79·1	79·0	82·6	85·2	85·9	87·8	87·4	89·1	88·9	

It will be observed that the yield of acetylene increases as the pressure decreases.

By analogy with the photochemical decomposition of diazoethane and methylketen the following mechanism seemed probable:

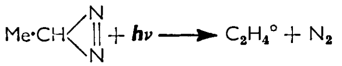

(1)

$$CH_3CH \xrightarrow{k_2} C_2H_4^* \quad (2)$$

$$C_2H_4^* \xrightarrow{k_3} C_2H_2 + H_2 \quad (3)$$

$$C_2H_4^* + M \xrightarrow{k_4} C_2H_4 + M \quad (4)$$

The absence of any butenes in the products indicates that any reaction between the ethylidene (or the excited ethylene molecule) and the methyldiazirine is unimportant. In view of the chemical stability of the diazirine this is not surprising. The mechanism suggested leads to the prediction that at sufficiently low pressures the yield of acetylene should extrapolate to 100%. However, a plot of the yield of acetylene as a function of pressure extrapolates to only *ca.* 60·2%. The results are shown plotted in Figure 2. This suggests that there is an additional reaction leading to the formation of ethylene which has insufficient energy to decompose into acetylene plus hydrogen. We therefore add formally to the mechanism



$$\text{Me·CH}\langle N_2 \rangle + h\nu \longrightarrow C_2H_4^{\circ} + N_2 \qquad (5)$$

Reactions (1)—(5) lead directly to the equation

$$(C_2H_4 - C_2H_4^{\circ})/C_2H_2 = k_4M/k_3 \qquad (6)$$

Since the composition of the products was, within experimental error, largely independent of the percentage decomposition it appears that the efficiency for stabilisation of the excited ethylene molecule [reaction (4)] by ethylene plus nitrogen, or by acetylene plus hydrogen plus nitrogen, must be approximately the same as by the methyldiazirine from which they were derived. This is not unreasonable since conventional unimolecular studies in the "fall-off" region have shown that nitrogen and hydrogen are very inefficient in energy-transfer processes. Further, in general the relative efficiency of a molecule to activate or deactivate seems to increase with increasing molecular complexity. Thus, we may write for the relative efficiencies of molecules in reaction (4), methyldiazirine > ethylene > acetylene $\gg$ nitrogen and hydrogen. Accordingly, a plot of the left-hand side of equation (6) against the initial pressure of methyldiazirine should yield a straight line passing through the origin with a slope of k_4/k_3. Such a plot is shown in Figure 3.

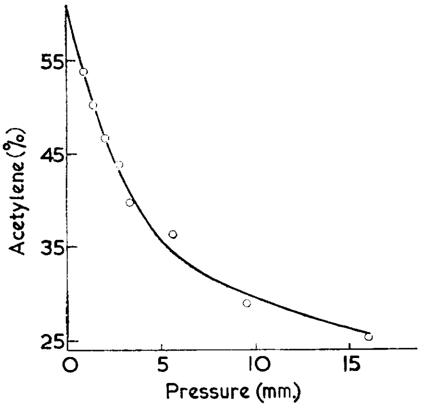


FIGURE 2. Percentage yield of acetylene as a function of pressure

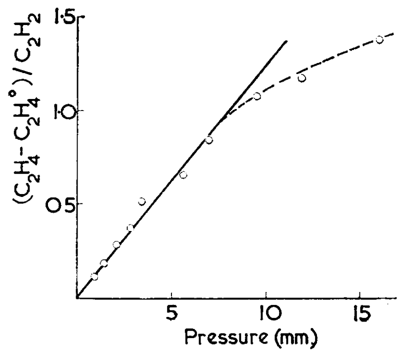


FIGURE 3. Plot of $(C_2H_4–C_2H_4^{\circ})/C_2H_2$ as function of pressure

At pressures below about 10 mm. the plot is linear and passes through the origin. This is the region where 50% or more of the excited ethylene molecules formed according to reaction (2) subsequently decompose to yield acetylene and hydrogen. If k_4M is assumed to have a value of 5 × 10^9 sec.$^{-1}$ at 1 atm. (equivalent to assuming that the methyldiazirine has unit collisional deactivation efficiency), then in the low-pressure region $k_3 = 5{\cdot}4 \times 10^7$ sec.$^{-1}$, *i.e.*, the lifetime of the excited ethylene molecule is of the order of 10^{-8} sec. The curvature of the plot shown in Figure 3 at pressures above 10 mm. indicates that the value of k_3 is not constant, *i.e.*, there is a spectrum of values for this rate constant. This in turn implies that the excited molecules of ethylene are formed with a spectrum of energy values. Such a variation is to be expected and arises from several causes. First, the molecules of methyldiazirine have a range of energies corresponding to the Maxwell–Boltzman distribution at the temperature of the photolyses. Secondly, since monochromatic light was not employed, whilst the light at 3130 Å in the mercury spectrum was responsible for the major proportion of the decomposition, there was some contribution from nearby lines in the mercury spectrum. This will lead to different energy contents of the ethylidene formed in the photolytic step. Finally, it is possible that in this initial step the nitrogen molecule may be formed with varying amounts of vibrational (and kinetic) energy which will mean that the ethylidene can also contain varying amounts of excess of energy. These three factors will all lead to ethylidene, and hence ethylene, with a range of energies. This effect has already been noted in studies with methylene [12] and has recently been noticed [13] in the photolysis of 2,3-diazabicyclo[2,2,1]-hept-2-ene.

In earlier studies on ethylidene it was found that the radical reacted with propene by addition to the double bond (to yield 1,2-dimethylcyclopropane) but did not react with saturated hydrocarbons. Since in these systems the isomerisation of the ethylidene is a unimolecular process in competition with the addition to propene which is a bimolecular process, the latter reaction is favoured by high pressures of propene. However, even at propene pressures of about 1000 mm., 90% of the ethylidene rearranged to ethylene, compared with about 10% which added to the double bond. In addition, ethylidene from diazoethane was found to be much less indiscriminate than methylene, and no reaction with but-2-ene was observed.

To try and confirm the intermediacy of ethylidene in the present work, methyldiazirine was photolysed in the presence of large excesses of ethylene, propene, and allene. In no case was any evidence for the occurrence of an addition reaction obtained. The added gases did however help in stabilising the ethylene molecules initially produced and this resulted in a reduction in the yield of acetylene. Thus, photolysis of 60 mmole methyldiazirine with 587 mmole propene gave $C_2H_2/C_2H_4 = 0{\cdot}05$. A similar value was obtained with 53 mmole methyldiazirine and 565 mmole allene. These values are subject to a rather large experimental error because in the chromatograms the acetylene peak occurred in the " tail " of the propene, since the latter was present in very large excess. In the case of the experiments with allene, where the acetylene preceded the allene, the overlap of peaks only allowed the use of peak heights rather than peak areas. In the case of reactions carried out with a large excess of ethylene this ratio could not be determined, since under these conditions the signal for ethylene was well outside the linear range of the detector. Finally, photolysis of methyldiazirine in cyclohexene at —20° showed no addition to the double bond. In this experiment no acetylene was detected. Under these experimental conditions it is thought that if the ratio of acetylene to ethylene were as high as 0·01, the acetylene would have been detected.

A few pyrolyses of the methyldiazirine were carried out in the gas phase at pressures between 2 and 50 mm. at about 190°. In all cases the only volatile products were ethylene and nitrogen. Runs carried out at 151° with 50 mmole of methyldiazirine (using pressure measurements) showed that the thermal decomposition followed first-order kinetics.

In the proposed mechanism we have assumed the intermediate formation of ethylidene. It must, however, be pointed out that exactly the same kinetics would result if the excited molecule of ethylene, postulated as formed from the ethylidene, actually arose from the methyldiazirine directly. We favour the two-stage process, though the evidence for the intermediacy of the ethylidene rests largely on analogy with the photochemical decomposition of diazoethane and methylketen. (It should also be added that the postulation of the intermediate formation of carbenes in the pyrolysis of toluene-*p*-sulphonylhydrazones and in the photolysis of other diazo-compounds and diazirines, has resulted in a unification of many diverse reactions and has helped in predicting the composition of the hydrocarbon products which result from the subsequent rearrangements of the carbenes.)

The failure to detect reactions between the ethylidene and propene, etc., in the present work cannot be considered as strong evidence for the absence of this radical. Even in the photochemical system involving diazoethane the addition reaction was of minor importance. In the present system the failure to observe any addition may result from the ethylidene radical being produced in a highly vibrationally excited state. (This would favour the

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[12] H. M. Frey, *Proc. Roy. Soc.*, 1959, *A*, **250**, 409.

[13] C. Steel, *J. Phys. Chem.*, 1963, **67**, 1779.

reaction yielding ethylene and thence acetylene rather than the addition reaction.) A consideration of the energetics of this system compared with that involving diazoethane shows that considerably more energy is available for this excitation. The heat of formation of methyldiazirine is expected to be appreciably greater than that of diazoethane (in the case of diazirine and diazomethane [14] the difference amounts to 30 kcal./mole). Also, the mean energy of the photolytic radiation is greater in the case of the diazirines then in the case of the diazo-compounds. It is also possible that the ring structure of the diazirines compared with the linear diazo-group results in a larger fraction of the exciting light quantum being converted into vibrational energy.

Further evidence to support the postulated existence of ethylidene radicals with varying energy contents and hence varying chemical reactivity comes from the work of Magee [15] on the vacuum ultraviolet photolysis of methane. Here the presence of ethylidene radicals has been suggested, and these radicals have been found to undergo insertion reactions with carbon–hydrogen bonds. Magee rationalises the occurrence of this reaction in his system (in contrast with its absence in the photolysis of diazoethane in the presence of paraffins) in terms of the production of " cool " ethylidene, *i.e.*, ethylidene with a higher value for the ratio of kinetic to vibrational energy. This is in line with the explanation for the non-reactivity of ethylidene towards olefins suggested here.

The evidence for the intermediate formation of ethylidene in the pyrolytic systems is less certain. Here the ethylene may certainly be formed directly (or *via* the normal diazo-compound) but it clearly does not contain sufficient energy for subsequent formation of acetylene.

We turn now to consider the photolytic formation of ethylene with insufficient energy to decompose and which is formally written in our mechanism as reaction (5). If we assume that the decomposition of the methyldiazirine leads directly to ethylene, then it might be thought that a single step, resulting in the formation of ethylene molecules with a range of energies, some greater and some less than the energy of activation of reaction (3), could encompass all the experimental results. However, such a range of energies would result in extreme curvature in the plot shown in Figure 3 over the entire pressure range and would not yield any linear portion. It therefore seems necessary to suppose that the reaction leading to C_2H_4 is quite distinct from that yielding ethylidene or C_2H_4. It may be that this reaction occurs through another excited state of the methyldiazirine (first triplet?) or that the two reaction paths are those suggested by equations (1) and (5), and that in the latter case the nitrogen carried a very large fraction of the available excess of energy. Certainly, the initially formed excited molecule has an appreciable lifetime as shown by the considerable vibrational structure of the absorption spectrum, and a transition to the excited triplet state must be a possibility. Further work is required before any firm theories about this particular aspect of the system can be substantiated.

One more possible reaction needs to be considered. This concerns the photoisomerisation of diazirines to diazo-compounds. In the case of diazirine itself, by using monochromatic light of 3200 Å (which is not appreciably absorbed by diazomethane) Amrich and Bell [6] were able to show that about 10% of the primary photochemical reaction was an isomerisation to diazomethane. In the case of some diazirines prepared from cyclic ketones this photoisomerisation has been found to be of considerable importance.[16] In the present work the absence of any but-2-ene in the reaction products suggested that if the photoisomerisation did occur it could only be a minor reaction path. To investigate this possibility further, photolyses were carried out using monochromatic light of 3130 Å (not appreciably absorbed by diazoethane). After approximately 10, 30, 50, and 90% of the methyldiazirine had been decomposed the ultraviolet absorption spectrum of the mixture was recorded. No evidence was obtained for the presence of diazoethane. We therefore

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[14] G. S. Paulett and R. Ettinger, *J. Chem. Phys.*, 1963, **39**, 825.

[15] E. M. Magee, *J. Chem. Phys.*, 1963, **39**, 855.

[16] W. B. L. Evans and I. D. R. Stevens, unpublished results.

conclude that either the photoisomerisation reaction is negligible or that under our experimental conditions the diazoethane (which must initially be formed in a highly excited state) rapidly reacts further. In this respect it is possible that the nitrogen-containing " oil " formed by the photolysis of methyldiazirine at relatively high pressures may be an azine resulting from reactions of the diazoethane. Direct evidence for such a reaction has been obtained in other systems.[16]

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