Thermal Decomposition of the Diazirines. Part III.[1] 3-Chloro-3-methyldiazirine

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The thermal decomposition of 3-chloro-3-methyldiazirine has been investigated. The products, vinyl chloride and nitrogen are formed quantitatively by a first order reaction which is probably unimolecular. The high pressure rate constants were determined at a series of temperatures by carrying out runs in the presence of added perfluoropropane whence $k_\infty = 10^{14 \cdot 135} \exp(-31,072/RT)$ sec.$^{-1}$. Arrhenius parameters were also measured at 4 torr at which pressure the rate constants have fallen to about a third of their high pressure limiting value, whence, $k_{4 \text{ torr}} = 10^{11 \cdot 708} \exp(-27,177/RT)$ sec.$^{-1}$. Rate constants were also determined at one temperature at various pressures from 6·3 torr to 0·025 torr. The fall-off curve may be fitted approximately by the Kassel integral with $s = 9$ or 10. The possible structures for the transition complex are discussed.

THE work reported in this paper represents a continuation of our efforts to determine the nature of the processes occurring in the thermal decomposition of diazirines. The evidence previously available suggested that these decompositions were unimolecular. The intermediate formation of a carbene seems probable, and such a postulate allows the thermal and photochemical decompositions to be related to one another but it must be emphasised that except in the case of diazirine itself there is no direct evidence for such an intermediate. The present study with 3-chloro-3-methyldiazirine was undertaken for two purposes. First to determine the effect of the electronegative chlorine atom on the energetics of the process and second to confirm that the decomposition was unimolecular by following the reaction in the fall-off region.

EXPERIMENTAL

Materials.—3-Chloro-3-methyldiazirine was prepared from acetamidine hydrochloride by oxidation with sodium hypochlorite in the presence of lithium chloride and carried out in a solution of dimethylsulphoxide. The method was essentially that described by Graham.[2] The product was swept from the reaction mixture in a stream of nitrogen, through a drying tube packed with sodium hydroxide pellets and collected in a trap cooled to −78°. Final purification was by repeated trap to trap distillations. For most of the work the 3-chloro-3-methyldiazirine was stored at −78°c. In the early part of the work this compound was stored (as a solid) in a trap cooled in liquid nitrogen. On one occasion the material exploded violently while so frozen. No subsequent explosions occurred when the compound was kept at −78°c, however it is clear that the 3-chloro-3-methyldiazirine should always be handled with caution.

Perfluoropropane was a commercial sample (Matheson C.P. grade) which was degassed before use.

Apparatus.—Two separate systems were used. For reactant pressures from 6 torr to 0·02 torr a kinetic apparatus coupled directly with a mass spectrometer was used. For reactant pressures above 50 torr another kinetic apparatus was used, and analysis was by gas chromatography. A few runs at lower reactant pressures were also carried out in the second apparatus.

Low Pressure Systems.—A conventional high vacuum system was used. Greaseless stopcocks with Viton A diaphragms were used throughout to minimise absorption problems associated with the use of greased stopcocks.

The reaction vessel was a cylindrical Pyrex bulb whose volume was approximately 1 litre (length : diameter ∼4 : 3). It was immersed in an oil thermostat whose temperature was controlled by an A.E.I. electronic regulator type RT3R. In some runs the thermostat fluid was a fused salt eutectic. Sample pressures above 1 torr were measured directly with a simple mercury manometer. Below 1 torr a McLeod gauge was used.

Analysis. This was by means of a modified A.E.I. M.S.10 mass spectrometer (permanent magnet). The contents of the reaction vessel were continuously sampled through a 10 micron capillary leak situated at the centre of the vessel. Peaks in the mass spectrum were scanned by varying the accelerating voltage and the signals were fed to a 10 mv potentiometric recorder. By using a reversible motor the scan could be restricted, so that one or two adjacent peaks could be scanned over short time intervals. This was considered more reliable than attempting to ' sit ' on a peak maximum. The times associated with peak maxima could be obtained directly from the recorder chart, but again it was felt in general to be more reliable to record these as they occurred using a stopclock. The parent peak of the reactant is rather small and the relative large peak at mass 55 (parent minus Cl) was used as a measure of the reactant concentration. A typical chart record of a run is shown in Figure 1.

High Pressure Apparatus.—Again a conventional high vacuum system was used. Reactant pressures were measured with a simple mercury manometer. The Pyrex reaction vessel was spherical with a volume of ∼150 ml. and was immersed in an Ultra-thermostat whose temperature could be maintained to ±0·1°c using a contact thermometer.

Analysis. This was by gas chromatography using a Perkin-Elmer F11 equipped with a hydrogen flame detector and a gas sampling valve. The column (12 ft. stainless steel) was packed with 60—80 mesh Chromosorb P coated with 20% w/w of dinonyl phthalate. Signals from the detector amplifier were fed to a potentiometric recorder fitted with a ball and disc integrator.

Both undecomposed diazirine and vinyl chloride were thus measured. The system did not allow the detection of nitrogen (which was the carrier gas). No other products were detected. Use of an internal standard (pentane) showed that the reaction was quantitative (carbon balance). In one run the reaction was followed by following the pressure change using a pressure transducer. The analytical

[1] Part II, H. M. Frey and A. W. Scaplehorn, *J. Chem. Soc.* (*A*), 1966, 968.
[2] W. H. Graham, *J. Amer. Chem. Soc.*, 1965, **87**, 4396.

data and the pressure data yielded rate constants which differed by less than 0·7%. Reproducibility of duplicate analyses was better than 1%.
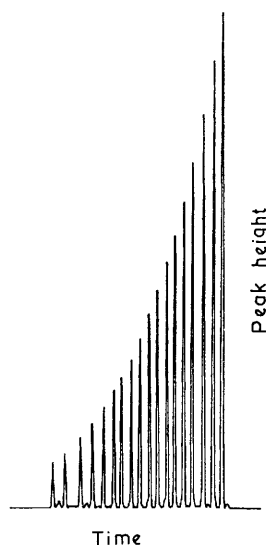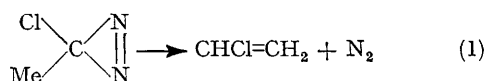

FIGURE 1   Intensity of mass 55 peak as function of time

RESULTS

In the temperature range 106—170°c, 3-chloro-3-methyl-diazirine undergoes a first order decomposition according to the equation:

$$\text{Cl, Me} \diagup C \diagdown \| \text{N, N} \longrightarrow CHCl=CH_2 + N_2 \qquad (1)$$

No other products were detected. First order kinetics were obeyed for well over 50% decomposition. In the low pressure system runs were carried out at an initial reactant pressure of 4 torr and at nine temperatures. The results are shown in Table 1. An Arrhenius plot of the

TABLE 1

Rate constants for decomposition at 4 torr

Temp. (°K)...	380·0	388·3	396·7	404·3	408·0
10^3k (sec.$^{-1}$)	0·123	0·266	0·530	1·04	1·40

Temp. (°K)...	420·2	430·1	437·7	443·1	
10^3k (sec.$^{-1}$)	3·50	8·18	13·80	20·89	

data in Table 1 yielded a good straight line from which the Arrhenius parameters were obtained by the method of least squares whence

$$k_{4\,\text{torr}} = 10^{11·708 \pm 0·104} \exp(-27,177 \pm 196/RT) \text{ sec.}^{-1}$$

Earlier work with diazirines has shown that their decompositions are unimolecular processes. For such reactions the rate constant decreases with pressure below a certain threshold value of the pressure. Addition of inert gas (perfluoropropane) showed that at 4 torr the decomposition of 3-chloro-3-methyldiazirine was already in the fall-off region. The pyrolysis was studied at 147°c at various pressures from 6·30 to 0·025 torr. The results are shown in Table 2 and plotted in Figure 2.

Rate constants obtained below 0·1 torr are less reliable than those obtained at higher pressures since under the low pressure conditions the signal-to-noise ratio of the mass

spectrometer was poor. Attempts to reach the high pressure limiting rate by the use of large pressures of inert gases were not successful since under these conditions the mass spectrometer output signal showed considerable instability. Use of high pressures of reactant alone sometimes resulted in thermal explosions at the highest reaction temperatures.

To obtain limiting high pressure rates decompositions were carried out in the second apparatus. In all cases the reaction mixture consisted initially of 50 torr of the diazirine with 300 torr of perfluoropropane. Preliminary experiments showed that higher pressures of inert gas did not lead to an increase in rate constant. Hence with this reaction mixture rates were being obtained in the limiting high pressure region. Rate constants were obtained at eight temperatures in the range 110—148°c and the data are in Table 3.

Since the use of high pressures of reactant at the highest temperatures leads to thermal explosions in the 'low pressure' apparatus it is clear that self-heating might give rise to appreciable errors in the high pressure apparatus. This did not appear to be the case. Thus the use of higher pressures of inert gas (above 300 mm.) did not affect the

TABLE 2

Rate constants as a function of pressure at 147·0°c

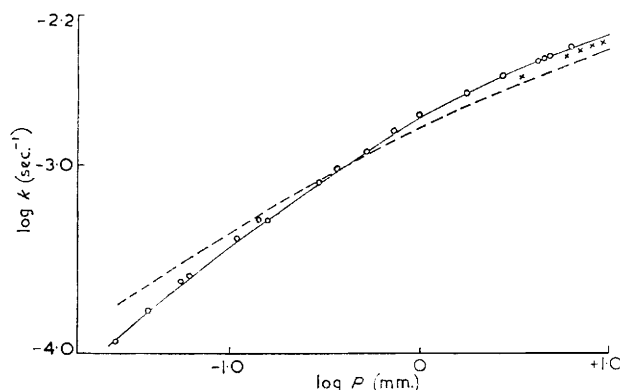| Pressure (torr)	6·30	4·88	4·55	4·25	2·75	1·77
10^3k (sec.$^{-1}$)	4·26	3·88	3·75	3·65	3·03	2·44
Pressure (torr)	0·998	0·729	0·523	0·368	0·296	0·158
10^3k (sec.$^{-1}$)	1·82	1·52	1·17	0·960	0·813	0·509
Pressure (torr)	0·142	0·109	0·061	0·055	0·037	0·025
10^3k (sec.$^{-1}$)	0·512	0·408	0·258	0·234	0·168	0·114

FIGURE 2   Variation of rate constant with pressure
○ Rate data determined by mass spectrometry.   × Rate data determined by gas chromatography.   – – – – Kassel curve with $s = 9$, $\sigma = 6$ Å

rate constant. If self heating were important a reduction in rate should have been observed owing to a dilution effect. Further, the highest temperature rates which would be most susceptible to this self heating do not deviate from the Arrhenius equation. The difference between the observations in the two apparatuses may easily be rationalised. In the high pressure apparatus a six fold excess of perfluoropropane was always present and this acts as a thermal sink. Also, the surface to volume ratio of the small (high pressure) reaction vessel was greater than that of the large reaction vessel so thermal equilibration with the walls was faster. Finally no attempt was made to obtain rate constants in the high pressure apparatus at

temperatures above 430°K since it was only above these temperatures that explosions had been observed in the low pressure system.

TABLE 3

Rate constants for decomposition at 'high' pressure

Temp. (°K)	383·8	384·5	389·0	394·5
$10^3 k$ (sec.$^{-1}$)	0·282	0·296	0·472	0·830
Temp. (°K)	399·1	405·0	412·4	421·4
$10^3 k$ (sec.$^{-1}$)	1·32	2·30	4·65	10·6

An Arrhenius plot of the data in Table 3 gave a good straight line from which the Arrhenius parameters were calculated by the method of least squares whence:

$$k_\infty = 10^{14\cdot135 \pm 0\cdot060} \exp(-31{,}072 \pm 109/RT) \text{ sec.}^{-1}$$

(all error limits are standard deviations).
Some experiments were carried out using gas chromatographic analysis in the pressure range 3·5—9 torr. The rate constants obtained (shown in Figure 2) were about 5% lower than those obtained using the low pressure apparatus. This agreement is acceptable in view of the two different techniques being employed. It should also be noted that the high pressure apparatus was not designed for work in the low pressure region and pressures in this case could not be measured precisely. There may therefore be a small systematic error in these pressure measurements.

The high pressure limit could also be reached by the addition of other inert gases to the diazirine. In particular the addition of a large excess pressure of ethylene to a lower pressure of the diazirine raised the rate constant to its limiting value. No new reaction products were observed under these conditions.
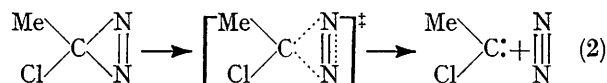
DISCUSSION

Work on the pyrolysis of diazirines has produced strong evidence that they decompose by unimolecular pathways.[1,3] This is supported by the present study. While there is no certainty about the reaction mechanism we have chosen to believe that the decompositions proceed via the formation of a carbene. The formation of some cyclopropanes in the pyrolysis of 3,3-diethyldiazirine and 3-t-butyldiazirine[4,5] is perhaps the strongest evidence for a carbene intermediate. It is to be expected that substitution in the 3-position of a chlorine atom should lead to some stabilization of the resulting carbene as compared with its hydrogen or alkyl analogue. It is therefore of interest to compare the energy of activation obtained for 3-chloro-3-methyldiazirine with that for 3,3-dimethyldiazirine. For the latter compound a value of 33·16 kcal./mole has been reported for decompositions carried out at 4 torr. At this pressure the rate constant has fallen to about 75% of its high pressure value. Hence the value of the energy of activation corresponding to k_∞ is likely to be a little higher than 33·16 and may well be ~34 kcal./mole. This compares with 31 kcal./mole obtained in the present study and would indicate a very appreciable stabilizing effect of the chlorine atom. Unfortunately comparison with the results obtained on the

pyrolysis of 3,3-diethyldiazirine yield a stabilization of only 800 cal./mole. It is unlikely that there is an appreciable difference in the stabilities of dimethyl and diethyl carbene so the discrepancy between these two sets of values is probably a reflection of the combined experimental errors. However a mean value for the stabilization effect of circa 2 kcal./mole does not seem unreasonable.
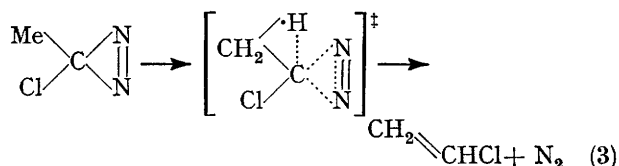
The differences between the Arrhenius parameters for the high pressure studies and those at 4 torr are striking. At 4 torr the rate constant for the decomposition has dropped to about 35% of its limiting high pressure value, thus the reaction is not far into the fall-off region, yet the energy of activation is some 4 kcal./mole below the high pressure value and the A-factor has fallen by more than two orders of magnitude. These big changes are in agreement with theoretical expectations based on either RRK or RRKM theories which show that there is a relatively rapid decrease in the Arrhenius parameters with pressure for unimolecular reactions when they enter the fall-off region.[6] This finding has important consequences in many other studies. Thus the determination of bond strengths by use of the toluene carrier or aniline carrier techniques, which are normally carried out at relatively low total pressures, can be seriously in error even if the reactions are only just in the pressure dependent region.

The fall-off curve plotted in Figure 2 shows that in the range 6·3—0·025 torr the rate constant falls from $4·3 \times 10^{-3}$ sec.$^{-3}$ to $0·11 \times 10^{-3}$ sec.$^{-1}$. The calculated high pressure value is $9·4 \times 10^{-3}$ sec.$^{-1}$. Thus at the lowest pressure studied the rate constant has fallen to less than 1·2% of its limiting high pressure value.

The A-factor of $10^{14\cdot135}$ indicates that the decomposition has a relatively small entropy of activation. This suggests that in the transition complex no new free rotations have developed. Various possibilities for the structure of the transition complex are consistent with this finding. The reaction may proceed in the formation of the normal diazo-compound which subsequently decomposes to the carbene or the carbene may be formed directly via a complex of the type depicted below:

$$\underset{Cl}{\overset{Me}{\diagdown}}C\underset{N}{\overset{N}{\diamond}} \longrightarrow \left[\underset{Cl}{\overset{Me}{\diagdown}}C\underset{N}{\overset{N}{\diamond}}\right]^{\ddagger} \longrightarrow \underset{Cl}{\overset{Me}{\diagdown}}C: + \underset{N}{\overset{N}{\diamond}} \quad (2)$$

Alternatively it is quite possible to suggest a transition complex which leads directly to the product without the intervention of a carbene:

$$\underset{Cl}{\overset{Me}{\diagdown}}C\underset{N}{\overset{N}{\diamond}} \longrightarrow \left[\underset{Cl}{\overset{CH_2 \cdots H}{\diagdown}}C\underset{N}{\overset{N}{\diamond}}\right]^{\ddagger} \longrightarrow \underset{CH_2}{\overset{}{\diagdown}}CHCl + N_2 \quad (3)$$

[3] H. M. Frey and I. D. R. Stevens, J. Chem. Soc., 1962, 3865.
[4] H. M. Frey and I. D. R. Stevens, J. Chem. Soc., 1965, 3101.
[5] E. Schmitz, D. Habish, and A. Stark, Angew. Chem., 1963, 75, 723.
[6] H. M. Frey, to be published.

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We will not reiterate the arguments for the intermediate formation of a carbene here; we will note that work on other substituted chlorodiazirines which will be reported later adds no support for this last complex. While in some photochemical systems evidence has been produced to show that in some cases part of the reaction proceeds by the formation of the diazo-compound no such similar evidence is available from pyrolytic studies. We therefore accept the complex depicted in equation (2) as the simplest representation of the situation at present.