760. *The Thermal Unimolecular Decomposition of Dimethyldiazirine.*

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The thermal decomposition of dimethyldiazirine in the temperature range 124—174° has been investigated and shown to be a first-order reaction giving propene and nitrogen. The reaction is homogeneous and does not show evidence of any radical-chain component. Below 100 mm. pressure, the first-order rate constant decreases with pressure, but at 100 mm. it has virtually reached its high-pressure limit. At a pressure of 4 mm. the measured rate of decomposition is accurately fitted by the Arrhenius equation

$$k_{4\ \text{mm.}} = 10^{13\cdot89} \exp\left(-33{,}165/\boldsymbol{R}T\right)\ \text{sec.}^{-1}.$$

The evidence indicates that the reaction is a true unimolecular transformation.

OWING to their instability, the thermal decomposition of aliphatic diazo-compounds in the gas phase has been little investigated. Recently[1] various substituted diazirines (cyclic diazo-methanes) have been prepared, and these appear to be somewhat more stable than the corresponding diazo-compounds. Here we report studies on the thermal decomposition of dimethyldiazirine; we hope later to report its photochemical decomposition.

EXPERIMENTAL

Dimethyldiaziridine was prepared from acetone (50 ml.), liquid ammonia (100 ml.), and hydroxylamine-*O*-sulphonic acid (35·5 g.; 96% pure) by Schmitz and Ohme's method.[1] After distillation from solid potassium hydroxide it formed crystals (6·2 g.), m. p. 40—43°, b. p. 102—104° (Schmitz and Ohme[1] give m. p. 44°; Abendroth[2] gives b. p. 106°).

Dimethyldiazirine was prepared in 80% yield by oxidation of the diaziridine with alkaline silver nitrate as described by Schmitz and Ohme.[1] The diazirine was swept out of the reaction vessel in a stream of nitrogen and condensed in a trap at −80°. The resultant colourless liquid was then distilled in a nitrogen stream over solid potassium hydroxide and stored at −80°.

Apparatus.—The conventional "static" high-vacuum system used in this work has been described previously.[3]

Analysis.—Analysis was by gas chromatography, through a 30 ft. × 0·18 in. coiled copper column containing hexane-1,4-dione on 40—60 mesh Chromosorb. Hydrogen was the carrier gas, and a Gow-Mac tungsten-filament katharometer was the detector. Signals from the detector were fed, *via* a variable attenuator, to a 0—1 mv Speedomax recorder fitted with a retransmitting slide-wire. Signals from this slide-wire were integrated by using a Perkin-Elmer model 194 instrument. The analytical precision was better than ±0·3%. Calibration mixtures were prepared in a specially designed vacuum-system in which Polythene-brass diaphragm valves were used rather than conventional stopcocks, to avoid absorption of vapours in stopcock grease.

Procedure.—Dimethyldiazirine was admitted to the reaction vessel from a gas pipette. At the appropriate time, the reaction vessel was opened to a large evacuated storage vessel, and the reaction mixture was allowed to flow into it for 5 sec. The storage vessel was then isolated from the reaction vessel, and its contents were transferred by Toepler pump to the analytical system. The path between the reaction vessel and the storage vessel was made short to avoid any "fractionation" effects. By mounting a Fluon-glass diaphragm valve connected to the reaction vessel immediately outside the furnace, the "dead space" was reduced to less than 0·2% and no correction was made for dead space in the calculations of the rate constants.

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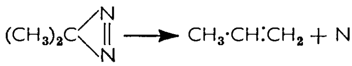
[1] Schmitz and Ohme, *Chem. Ber.*, 1961, **94**, 2166.

[2] Abendroth, *Angew. Chem.*, 1959, **71**, 283.

[3] Flowers and Frey, *Proc. Roy. Soc.*, 1960, *A*, **257**, 122.

RESULTS

In the temperature range 124—174° dimethyldiazirine undergoes a first-order decomposition according to the equation:



No other products were detected. No departure from first-order kinetics was observed even in runs carried to more than 80% decomposition. Table 1 shows the results obtained at 145·1° with an initial pressure of 4 mm. of dimethyldiazirine.

TABLE 1.

Time (min.)	10	15	20	30	40	46	64
Undecomposed (%)	80·87	73·55	65·2	53·6	43·5	38·37	26·36
10^4k (sec.$^{-1}$)	3·53	3·41	3·56	3·46	3·47	3·47	3·47

Rate constants were determined at eight temperatures in the range investigated, and at each temperature they were computed by the method of least squares from the results of at least six and usually more than eight runs. The values obtained, which all refer to an initial pressure of 4 mm. of dimethyldiazirine, are shown in Table 2:

TABLE 2.

Temp.	124·4°	131·3°	137·1°	145·1°	151·6°	159·5°	166·9°	174·2°
10^4k (sec.$^{-1}$)	0·463	0·917	1·65	3·47	6·77	13·8	27·1	47·2

These results are fitted by the Arrhenius equation $k_{4\ \mathrm{mm.}} = 10^{13\cdot89} \exp\left(-33{,}165/\boldsymbol{R}T\right)$ sec.$^{-1}$. The probable error in the activation energy calculated by the normal statistical procedures is ±6 cal. It is clear that little if any significance can be attached to this value. In this context the only conclusion that can be drawn from a very small value for the probable error is that the data are highly reproducible. This may easily be verified by computing a new value for E by using only seven of the eight rate constants. It will be found that the values for ΔE are in general considerably *greater* than the probable error. In fact, temperature uncertainties limit the accuracy with which the activation energy has been determined and result in the possibility of an error of ±300 cal.

The pyrolysis of dimethyldiazirine was studied at 145·1° in a packed reaction vessel which had a surface to volume ratio 8·4 times larger than the reaction vessel employed in all other experiments. The rate constant obtained, $3{\cdot}50 \times 10^{-4}$ sec.$^{-1}$, is the same (within experimental error) as that obtained in the normal reaction vessel. The reaction is, therefore, entirely homogeneous.

At sufficiently high pressures the rate constant of any unimolecular transformation must be independent of the pressure. This is no longer true at pressures where the rate of transformation of " energized " molecules approaches the rate of collisional activation. In this pressure-region " fall off " of the rate constant is expected theoretically, and has been observed experimentally in several cases. For dimethyldiazirine this region of fall-off is expected to occur at pressures below ~100 mm. While the apparatus employed was not constructed for determining rate constants over a wide pressure range with great precision, a few runs were carried out at various initial pressures at 159·5°. In each case the reaction time was 10 min. and rate constants were computed from these single values. The results are plotted in the Figure. The particular function of the pressure chosen has no theoretical significance, but does yield a more nearly linear plot than the conventional one for unimolecular reactions.[4]

From the Figure it is clear that at a pressure of 4 mm. the reaction is already in the

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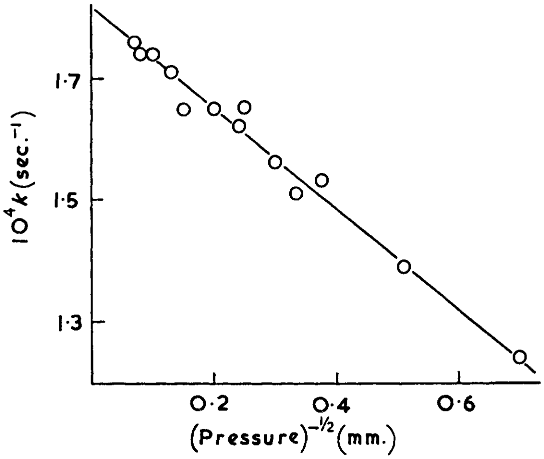
[4] Rabinovitch and Michel, *J. Amer. Chem. Soc.*, 1959, **81**, 5065.

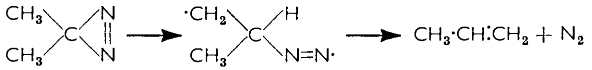
" fall-off " region. At 159·5°/4 mm. the first-order rate constant is ~30% less than the infinite pressure limit. Since the pressure at which fall-off occurs is dependent on the temperature, the Arrhenius constants corresponding to the values of k_∞ will be a little larger than those in the equation computed for the values of $k_{4\ \text{mm.}}$. The effect is, however, small and will not alter the activation energy by more than a few hundred calories. More extensive studies of the effect of pressure on the rate constant are being undertaken and will be reported in a later paper. Since in the runs at 4 mm. the reaction is of the first order even in runs carried to 80% completion, the sum of the efficiencies of nitrogen and propene must be approximately equal to that of the parent molecule, in maintaining the Maxwell–Boltzmann distribution of energy.

Propene is known to be a powerful inhibitor of radical-chain reactions. Since the rate of decomposition of dimethyldiazirine is not affected by the accumulation of propene in the system it is most unlikely that any chain reaction is involved. Hence all the available evidence strongly suggests that the decomposition is a true unimolecular transformation.



Decomposition of dimethylazirine at 159·5°.

Two possible mechanisms need to be considered for this decomposition. The first involves the movement of a hydrogen atom to form propene and a nitrogen atom *via* a diradical, *i.e.*,



The other possible mechanism involves the intermediate formation of dimethylcarbene,

$$(CH_3)_2CN_2 \longrightarrow (CH_3)_2C\!: + N_2$$

$$(CH_3)_2C\!: \longrightarrow CH_3{\cdot}CH{:}CH_2$$

The first mechanism seems highly improbable on energetic grounds. The second mechanism is consistent with the photochemical decomposition of dimethyldiazirine (to be reported later) and the known properties of isopropylidene.[5] The possibility that this mechanism involves the intermediate formation of dimethyldiazomethane is unlikely but cannot be ruled out at this stage. In this respect it is interesting that the thermal decomposition of diazomethane involves [6] an activation energy of 35 kcal. mole^{-1} for the reaction $CH_2N_2 \longrightarrow CH_2 + N_2$.

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The University, Southampton. [*Received, March* 19*th*, 1962.]

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[5] Holroyd and Blacet, *J. Amer. Chem. Soc.*, 1957, **79**, 4830.
[6] Setser and Rabinovitch, personal communication.