660. *The Photolysis of Dimethyldiazirine.*

By H. M. Frey and I. D. R. Stevens.

The photolysis of dimethyldiazirine has been investigated in the gas phase. At pressures above ~180 mm., propene and nitrogen constitute more than 99% of the products and are formed in equimolar amounts. At pressures below 60 mm. increasing quantities of other hydrocarbons are formed and the ratio of propene to nitrogen falls. Addition of nitrogen (1 atm.) causes the ratio to return to unity and suppresses the formation of the other hydrocarbons. The yields of many of the hydrocarbon products were determined in the pressure range 1—60 mm. The primary step in the photolysis is thought to be the production of dimethylcarbene and nitrogen. The carbene rapidly rearranges to yield a " hot " molecule of propene. The products formed at low pressures are explained in terms of decomposition of the " hot " propene in competition with its collisional stabilization.

Thermal decompositions and photolyses of some diazirines have recently been reported.[1-3] The product ratios obtained by the pyrolysis of ethylmethyldiazirine were found to differ from those obtained by the photolysis of this compound.[3] These differences were tentatively attributed to the intermediate formation of a carbene which may contain excess energy. The present work was undertaken to test this postulate and follows the reported studies on the pyrolysis of dimethyldiazirine.

Experimental

The preparation of dimethyldiazirine has been described previously.[1]

Apparatus.—A conventional high-vacuum system was used. Photolyses were carried out in cylindrical Pyrex vessels whose volumes ranged from 10 to 250 ml. These were fitted with Fluon–glass diaphragm valves to reduce the absorption errors which occur when conventional greased stopcocks are used. The light source was an unfiltered medium-pressure mercury arc (Hanovia U.V.S. 500).

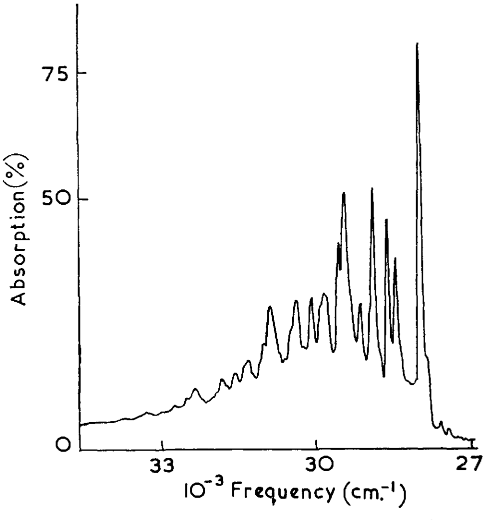

Fig. 1. Long-wavelength absorption band of 3,3-dimethyldiazirine.

Analysis.—Analysis was by gas chromatography, through a 30 ft. × 0·18 in. coiled copper

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[1] Frey and Stevens, *J.*, 1962, 3865.

[2] Frey and Stevens, *Proc. Chem. Soc.*, 1962, 79.

[3] Frey and Stevens, *J. Amer. Chem. Soc.*, 1962, **84**, 2647.

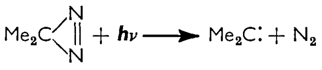
column containing either hexane-2,5-dione or di-2-cyanoethyl ether on 40—60 mesh Chromosorb P. The hexane-2,5-dione was used at 0° and the ether column at room temperature. All runs were analysed in duplicate through both columns. The remainder of the analytical system has been described earlier.[1] Hydrocarbons used for calibration were obtained from commercial sources when available; others were prepared by normal synthetic procedures.

Absorption Spectrum of 3,3-*Dimethyldiazirine.*—The ultraviolet spectrum is highly characteristic of the diazirines as a class and is similar to those of other compounds containing strained nitrogen–nitrogen double-bonds, *e.g.*, 2,3-diazabicyclo[2,2,1]hept-2-ene. The maximum of the short-wavelength absorption occurs below 190 mμ ($\varepsilon \sim 6000$) and this band tails to about 240 mμ. The long-wavelength absorption (Fig. 1) consists of a series of well-defined maxima starting at about 295 mμ, increasing in intensity to the longest-wavelength peak about 360 mμ ($\varepsilon \sim 180$) and showing a sharp fall after it. The spacings in this multiplet show a series of 3 or 4 band progressions which will be discussed in a later communication.

RESULTS AND DISCUSSION

Photolyses of dimethyldiazirine were carried out at various temperatures between 15° and 60° in Pyrex reaction vessels. Under these conditions the product yields were independent of temperature. No attempt was made to filter the light, but from the absorption spectrum of the diazirine it is clear that the effective radiation was from the bands between 3000 and 3660 Å in the mercury spectrum, the largest contributor to the decomposition being the band at 3130 Å. Runs were carried out at various pressures from 1 to 250 mm. Above about 180 mm. the photolysis affords equimolar amounts of propene and nitrogen with less than 1% of other products, results identical with those of thermal decomposition. At pressures below 60 mm. increasing quantities of other hydrocarbons are formed and the propene : nitrogen ratio falls below unity. In this pressure range the extent of decomposition was varied from 10% to 90%, photolysis being continued in most cases until 75% of the diazirine had been decomposed. The relative yields were insensitive to the percentage decomposition in the range studied. The major hydrocarbon products detected (other than propene) in the low-pressure range were ethane, ethylene, propane, but-1-ene, 2,3-dimethylbutane, 4-methylpent-1-ene, and biallyl (hexa-1,5-diene). Small quantities of acetylene, cyclopropane, and isobutane were also found. Traces of several other hydrocarbons were detected (see below). Hydrocarbons formed in small quantities with retention times longer than biallyl would not have been detected with the analytical procedure employed, and neither methane nor hydrogen could be measured. The yields of ethane and isobutane could be estimated only semi-quantitatively.

The following mechanism accounts for most of the major products.



$$\mathrm{Me_2C{:}} \xrightarrow{k_1} \mathrm{Me{\cdot}CH{=}CH_2^*} \tag{1}$$

$$\mathrm{Me{\cdot}CH{=}CH_2^* + M} \xrightarrow{k_2} \mathrm{Me{\cdot}CH{=}CH_2 + M} \tag{2}$$

$$\mathrm{Me{\cdot}CH{=}CH_2^*}\left\{\begin{array}{lr}\xrightarrow{k_{3a}} \mathrm{CH_2{=}CH{\cdot}CH_2{\cdot} + H{\cdot}} & \text{(3a)}\\ \xrightarrow{k_{3b}} \mathrm{CH_2{=}CH{\cdot} + Me{\cdot}} & \text{(3b)}\\ \xrightarrow{k_{3c}} \mathrm{CH{\equiv}CH + CH_4} & \text{(3c)}\end{array}\right.$$

$$\mathrm{H{\cdot} + Me{\cdot}CH{=}CH_2} \xrightarrow{k_4} \mathrm{Me_2CH{\cdot}} \tag{4}$$

$$\mathrm{2CH_2{=}CH{\cdot}CH_2{\cdot}} \xrightarrow{k_5} \text{Biallyl} \tag{5}$$

$$CH_2{=}CH{\cdot}CH_2{\cdot} + Me_2CH{\cdot} \xrightarrow{k_6} Me_2CH{\cdot}CH_2{\cdot}CH{:}CH_2 \qquad (6)$$

$$2Me_2CH{\cdot} \xrightarrow{k_7} Me_2CH{\cdot}CHMe_2 \qquad (7)$$

$$2Me_2CH{\cdot} \xrightarrow{k_8} C_3H_6 + C_3H_8 \qquad (8)$$

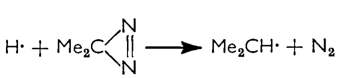
$$2Me{\cdot} \xrightarrow{k_9} C_2H_6 \qquad (9)$$

$$Me{\cdot} + CH_2{:}CH{\cdot}CH_2{\cdot} \xrightarrow{k_{10}} CH_3{\cdot}CH_2CH{=}CH_2 \qquad (10)$$

$$Me{\cdot} + Me_2CH{\cdot} \xrightarrow{k_{11}} Me_3CH \qquad (11)$$

The primary production of dimethylcarbene $Me_2C{:}$ is to be expected from the results obtained in the photolysis of other diazirines.[2,3] This is followed by the fast hydrogen-atom transfer to yield propene. This type of hydrogen shift occurs with numerous other substituted carbenes, the simplest case being the rearrangement of ethylidene to ethylene.[4,5] Initially the propene must possess considerable excess energy. The actual magnitude of this excess energy is uncertain for two reasons: (*a*) the fraction of the energy of the light quantum responsible for the initial decomposition which is associated with the nitrogen molecule is unknown, and (*b*) the heat of formation of the dimethyldiazirine is unknown. However, the heat of formation of the diazirine must be appreciably greater than that of propene, so the propene may be formed with energy well in excess of 90 kcal./mole (the energy of the 3130 Å light quantum). If the excited propene does not lose energy rapidly by collision with another molecule in the system (reaction 2), then it may decompose by one of the suggested routes (reactions 3a, b, or c). On energetic grounds the decomposition to yield an allyl radical and a hydrogen atom is favoured over that yielding methyl and vinyl radicals. While the decomposition to yield methane and acetylene involves the smallest ΔH it does not appear to be an important reaction, presumably because of the strain associated with the four-centre transition state. Direct evidence that the basic mechanism involves the decomposition or deactivation of excited propene molecules comes from the pressure-dependence of the yields of the various hydrocarbons. The yields of all products associated with the decomposition of propene increase as the total pressure is lowered. Further, the addition of an inert gas (one atmosphere of nitrogen was used) reduces the yields of these products (by stabilizing the "hot" propene). In one run argon was used in the place of nitrogen and was equally effective.

The hydrogen atoms produced by reaction (3a) add to propene to give isopropyl radicals. There is considerable evidence for the occurrence of this reaction and also for the virtual absence of a reaction yielding n-propyl radicals.[6,7] Evidence that reaction of hydrogen atoms with dimethyldiazirine to yield isopropyl radicals, *i.e.*,



$$H{\cdot} + Me_2C\langle{}^{N}_{N}\| \longrightarrow Me_2CH{\cdot} + N_2 \qquad (12)$$

is not important in the present system will be given later.

Reactions (5)—(11) are all simple radical reactions for which there is ample evidence in the literature.

The yields (expressed as a percentage of the total hydrocarbons measured) of the major products as a function of pressure are shown in Figs. 2—5. They are clearly in qualitative agreement with the suggested mechanism. All the products of the mechanism were detected except methane (which could not be separated from nitrogen with the analytical

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[4] Frey, *J.*, 1962, 2293.

[5] Kistiakowsky and Mahan, *J. Chem. Phys.*, 1956, **24**, 922; *J. Amer. Chem. Soc.*, 1957, **79**, 2412.

[6] Bradley, Melville, and Robb, *Proc. Roy. Soc.*, 1956, *A*, **236**, 339.

[7] Jackson and McNesby, *J. Chem. Phys.*, 1962, **36**, 2272.

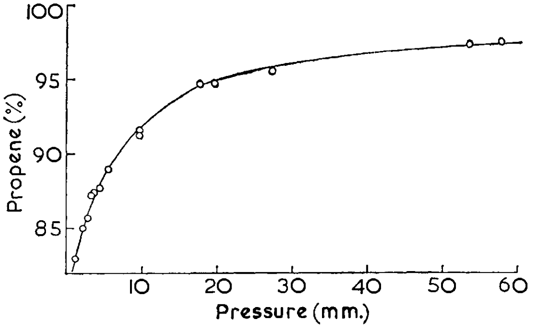


FIG. 2. Yield of propene as a function of pressure.

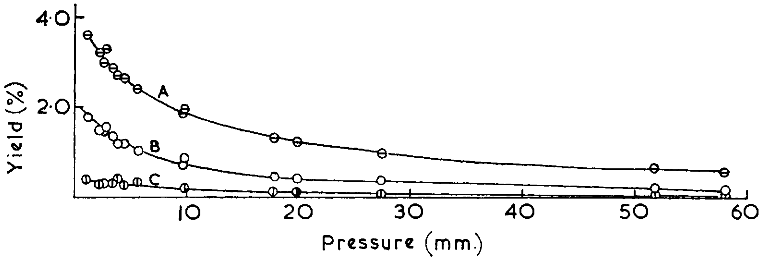


FIG. 3. Yields of (A) but-1-ene, (B) ethylene, and (C) acetylene.

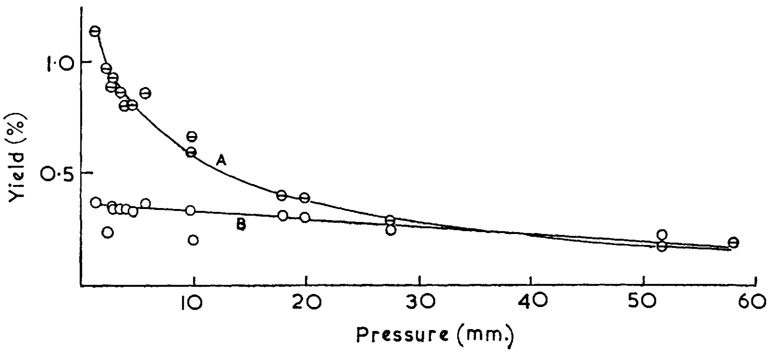


FIG. 4. Yields of (A) propane and (B) cyclopropane.

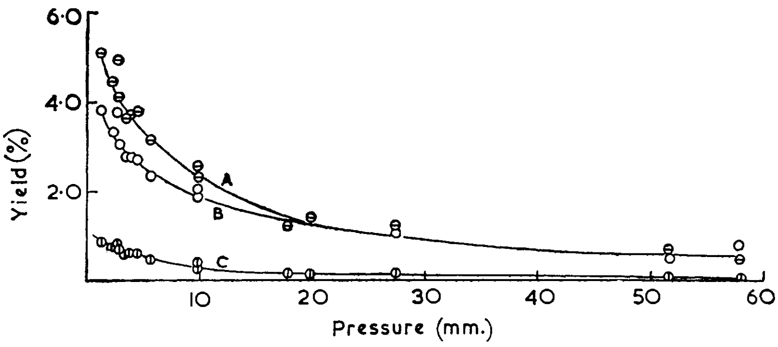
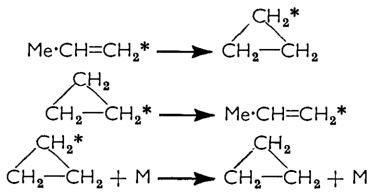


FIG. 5. Yields of (A) 4-methylpent-1-ene, (B) biallyl, and (C) 2,3-dimethylbutane.

system used). Also, while both ethane and isobutane were detected, they could not be estimated quantitatively, owing to " peak overlap."

In addition to the compounds expected from reactions (1—11) appreciable quantities of ethylene were formed as well as small quantities of cyclopropane. The yield of cyclopropane, which was independent of the pressure in the range 1—60 mm. averaged about 0·3%. It may be formed by the reverse of the normal thermal isomerization of cyclopropane to propene, *i.e.*,



(13a)

(13b)

(14)

There is certainly no objection to this reaction on energetic grounds, and the small yield of cyclopropane is consistent with the large entropy decrease in the transition state for the forward reaction. It is interesting that very recently methylcyclopropane has been observed as a product in the mercury-photosensitized decomposition of but-1-ene.[8]

Ethylene which constitutes nearly 2% of the total product at 1 mm. is probably formed by an abstraction reaction of the vinyl radicals, resulting from the decomposition of propene by reaction (3b). That appreciable decomposition of the excited propene occurs with the formation of $Me\cdot + CH_2{=}CH\cdot$ is clearly indicated by the high yield of but-1-ene (reaction 10). The vinyl-radical abstraction is almost certainly reaction (15).

$$CH_2{=}CH\cdot + Me\cdot CH{=}CH_2 \xrightarrow{k_{15}} CH_2{=}CH_2 + CH_2{=}CH\cdot CH_2\cdot \qquad (15)$$

Since no buta-1,3-diene was detected, dimerization of the vinyl radicals is not important in this system. As the decomposition of the hot propene to methyl and vinyl is the only source of these radicals, the reaction mechanism presented yields the balances:

$$[CH_3\cdot CH_2\cdot CH{=}CH_2] + [Me_3CH] + 2[C_2H_6] = [C_2H_4]$$
$$[CH_3\cdot CH_2\cdot CH{=}CH_2] < [C_2H_4]$$

In fact, the yield of but-1-ene is greater than that of ethylene. While there are several possible reactions which could lead to this result, the most probable explanation is that the vinyl radicals undergo an addition as well as an abstraction reaction,

$$CH_2{=}CH\cdot + Me\cdot CH{=}CH_2 \xrightarrow{k_{16}} \cdot CHMe\cdot CH_2\cdot CH{=}CH_2 \qquad (16)$$

The formation of $\cdot CHMe\cdot CH_2\cdot CH{=}CH_2$ (reaction 16) which has been postulated to account for the high yield of but-1-ene leads to another set of radical-combination reactions. Most of these will yield hydrocarbons which would not have been detected with the analytical technique employed owing to their large retention volumes. The only product likely to have been formed in appreciable yield which would have been detected is 4 methylpent-1-ene formed by reaction (17)

$$\cdot CHMe\cdot CH_2\cdot CH{=}CH_2 + Me\cdot \longrightarrow Me_2CH\cdot CH_2\cdot CH{:}CH_2 \qquad (17)$$

The formation of this compound by a route not involving reactions (5)—(7) must lead to a value greater than 2 for the " cross " ratio ($k_6/k_5^{\frac{1}{2}}k_7^{\frac{1}{2}} = 2{\cdot}88 \pm 0{\cdot}09$).

In the absence of analytical data for the higher hydrocarbons formed by the reactions of a radical $\cdot CHMe\cdot CH_2\cdot CH{=}CH_2$, it is not possible to obtain a quantitative value for

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[8] Cvetanović and Doyle, *J. Chem. Phys.*, 1962, **37**, 543.

k_{15}/k_{16}; it is, nevertheless, clear from the discrepancies in the yields of ethylene and but-1-ene that $k_{15} < k_{16}$, *i.e.*, vinyl radicals add to propene faster than they abstract hydrogen from it. A small peak on the chromatograms had the same retention time as penta-1,4-diene, presumably formed by reaction (18):

$$CH_2{=}CH\cdot + CH_2{=}CH{\cdot}CH_2\cdot \longrightarrow CH_2{=}CH{\cdot}CH_2{\cdot}CH{=}CH_2 \qquad (18)$$

No peak corresponding to 3-methylbut-1-ene was present (to be expected from vinyl + isopropyl). The very small yield of penta-1,4-diene and the absence of 3-methylbut-1-ene and buta-1,2-diene indicate that vinyl radicals react considerably faster with propene than do alkyl radicals.

A few runs were carried out in the presence of about 5% of oxygen. The only new product then detected was carbon dioxide (any carbon monoxide formed would not have been distinguished from nitrogen). The yield of propene was only slightly affected but the yields of all the other hydrocarbons were considerably reduced. These results are consistent with the reaction of the radicals with the oxygen.

Photolysis of the dimethyldiazirine in the *liquid phase* in the presence of cyclohexene as solvent showed that no addition of the dimethylcarbene to the double bond took place. Hence, this addition is considerably slower than the hydrogen transfer leading to propene.

Evidence that $k_4 \gg k_{12}$ and that reaction (12) is relatively unimportant was obtained by photolysis of equimolar mixtures of dimethyldiazirine and ethylene for times such that between 5% and 10% of the dimethyldiazirine underwent decomposition. Considerable quantities of n-butane and pent-1-ene were formed, and biallyl was still produced. No 2,3-dimethylbutane was detected. This implies that, while there are appreciable concentrations of ethyl and allyl radicals in the system, virtually no isopropyl radicals are formed. Thus reaction (19) must be much faster than reaction (12). Since

$$H\cdot + C_2H_4 \longrightarrow \cdot C_2H_5 \qquad (19)$$

reaction (19) is known [9] to be about 4 times faster than reaction (4) the absence of isopropyl radicals is to be expected, and this also implies that $k_4 \gg k_{12}$.

Dimethylcarbene is thought to be produced by the photolysis of dimethylketen.[10] The experimental results obtained in that work can be explained by a reaction scheme which is essentially identical with that suggested in this paper.[11]

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[9] Trotman-Dickenson, " Gas Kinetics," Butterworths Scientific Publns., London, 1955, p. 287.
[10] Holroyd and Blacet, *J. Amer. Chem. Soc.*, 1957, **79**, 4830.
[11] Frey, " Progress in Reaction Kinetics," Vol. II, Pergamon Press, Oxford, in the press.