197. *Kinetics of the Thermal Decomposition of Azomethane.*

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The kinetics of the thermal decomposition of pure azomethane have been reinvestigated in a static system between 0·2 and 800 mm. and 229° and 321° by measuring the rate of production of nitrogen. The effect of added gases shows that the high-pressure reaction involves short chains that may be initiated and terminated at the surface of a reaction vessel. The rate constant of the homogeneous reaction fully inhibited by propene is given by:

$$\log k\ (\text{sec.}^{-1}) = (15{\cdot}7 \pm 0{\cdot}15) - (51{,}200 \pm 250/2{\cdot}303\boldsymbol{R}T)$$

The study of the thermal decomposition of azomethane played an important part in the development of modern theories of unimolecular reactions.[1,2] Most decompositions of organic compounds that were first thought to be unimolecular and to have rate constants that fell at low pressures have since been shown to be partially chain processes. They were therefore unsuitable for the experimental verification of theories of unimolecular reactions and the dependence of their rates on energy transfer. The decomposition of azomethane was still believed to be unimolecular. The investigations of this reaction are, however, unsatisfactory by modern standards. Most of the kinetic information was obtained by following the change in pressure in a static system. It was assumed that the reaction might be represented by $CH_3{\cdot}N{:}N{\cdot}CH_3 = C_2H_6 + N_2$; the observed change in pressure was in accord with this assumption. More recently, Riblett and Rubin [3] showed that the products of the decomposition are complex. Furthermore much information on the reactions of the methyl radicals initially formed in the decomposition [4] has been obtained from the photolysis of azomethane at lower temperatures.[5] Hence it is now certain that side reactions involving methyl radicals yield methane and high-boiling products. We have followed the thermal decomposition by determining the rate of formation of nitrogen because a molecule of nitrogen is probably formed each time an N–C bond is broken.

[1] Kassel, " Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, 1932.
[2] Trotman-Dickenson, " Gas Kinetics," Butterworths, London, 1955.
[3] Riblett and Rubin, *J. Amer. Chem. Soc.*, 1937, **59**, 1537.
[4] Page, Pritchard, and Trotman-Dickenson, *J.*, 1953, 3878.
[5] Jones and Steacie, *J. Chem. Phys.*, 1953, **21**, 1018.

There are still only a few unimolecular reactions whose rates have been observed to depend upon the rate of energisation by collision. Only a small fraction of these can be studied in the presence of a wide range of chemically inert gases. Such studies are of value because they provide information on the relative rates of transfer of energy on collision. The isomerisation of *cyclo*propane and the decomposition of *cyclo*butane occur at such high temperatures that the number of interesting compounds that are sufficiently stable not to disturb the chemical processes is limited. The reactions of the nitrogen oxides and their derivatives often occur at low temperatures, but the reactants, products, and intermediates all react readily with most organic substances. Experiments must therefore be confined to some inorganic gases, the rare gases, and a few fluorocarbons. Studies of a greater range of additives would be very desirable. Unfortunately the present work has shown that the decomposition of azomethane, which appeared promising, is also unsatisfactory.

EXPERIMENTAL

Azomethane.—*sym*-Dimethylhydrazine hydrochloride was prepared by Hatt's method [6] and dissolved in excess of sodium hydroxide to yield the free base. This solution was added slowly and with constant stirring to a suspension of mercuric oxide [7] (rapid addition once led to a minor explosion). The azomethane was distilled off on a water-bath and collected in a solid carbon dioxide trap (yield 60—70%). The gas was dried (P_2O_5 and KOH), degassed, and stored at liquid-nitrogen temperature. Its purity was confirmed by gas chromatography. No evidence of *cis*- and *trans*-isomers was found although the analytical system distinguished clearly between the but-2-enes.

Other Gases.—Propene was prepared by the dehydration of propan-2-ol. *trans*-But-2-ene and *cyclo*pentane were standard samples from the National Chemical Laboratory. Carbon dioxide was obtained by evaporation of Drikold. Sulphur-free toluene was purified by partial pyrolysis and distillation as for use in kinetic studies by the carrier technique. No impurity was detected in these gases by chromatography. *cyclo*Propane contained a trace ($<0{\cdot}1\%$) of propane, and *n*-pentane 0·05% of *iso*pentane.

Apparatus.—A Pyrex reaction vessel (609 ml.) was used for most of the runs; one of 50·2 ml. was used for pressures above 100 mm. The vessels were contained in an electric furnace kept constant to ±0·1° by a gas-thermometer controller.[8] The temperatures were measured to 0·05° with a two-junction thermocouple in a well inside the reaction vessel. Both vessels were seasoned either by carrying out several preliminary decompositions of azomethane or by decomposing allyl bromide which deposits an inert carbonaceous film.

Procedure.—In experiments with azomethane alone below 100 mm., the volume of reactant was measured in a gas burette from which it was injected into the reaction vessel at the beginning of the run. At the end of the run the products were pumped through traps cooled to −196° or below. The non-condensable methane and nitrogen were circulated through an oxidising furnace (powdered CuO 98·2%, Fe_2O_3 1·8%; 610°) and through a trap system. The nitrogen was then measured in a second gas burette. Rate constants were calculated for a first-order reaction, it being assumed that the vapours behaved as ideal gases. For the runs at 170 mm., the azomethane was admitted directly from the storage bulb to the reaction vessel and measured on a mercury manometer. Above 600 mm. the azomethane was first condensed into a small storage bulb so that an ample pressure was available. When needed, gases were added to the reaction vessel after the azomethane had been injected. The total pressure was read on a butyl phthalate or mercury manometer.

RESULTS AND DISCUSSION

Pyrolysis of Azomethane.—A series of runs at 530° and between 5 and 25 mm. showed that the rate constant for the decomposition, *k*, was independent of the amount of azomethane decomposed to nitrogen if the conversion was kept between 1 and 10%. The experiments were among the first to be carried out and the reproducibility was not as good

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[6] Hatt, *Organic Syntheses*, 1936, **16**, 18.

[7] Renaud and Leitch, *Canad. J. Chem.*, 1954, **32**, 545.

[8] Taylor and Sickman, *J. Amer. Chem. Soc.*, 1932, **54**, 602.

as was subsequently achieved. Nevertheless, the point was clearly established. Thereafter all decompositions were retricted to less than 10%.

Approximately 100 successful runs were carried out, grouped round six azomethane pressures. The rate constant for the decomposition at a particular pressure was then found by a short interpolation. This procedure was followed because it proved difficult to measure an exact quantity of gas. Runs were performed at three or four different temperatures for each pressure. The results obtained are expressed in terms of the Arrhenius parameters determined by a least-squares treatment. They are listed in the Table together with the rate constant for a temperature lying towards the centre of each group of determinations. The reaction vessel used at the highest pressures may not have been properly seasoned: little weight should be attached to these results.

Rate constants and Arrhenius parameters for the pyrolysis of azomethane.

$(CH_3N)_2$ (mm.)	log *k* (290°)	log *A*	*E* (kcal. mole^{-1})
	(sec.$^{-1}$)		
0·2	$\bar{5}$·19	13·12	46·2
1·0	$\bar{5}$·50	13·94	47·5
5·0	$\bar{5}$·79	15·23	50·1
20·0	$\bar{4}$·01	16·03	51·6
158·5	$\bar{4}$·20	16·38	52·0
794·3	$\bar{4}$·29	16·82	52·9
Various with C_3H_6	$\bar{5}$·8	15·7	51·2
Infinite [9]	$\bar{4}$·2	16·5	52·5
Infinite [10]	$\bar{4}$·4	15·9	50·2

The variation of the rate constant with pressure is in reasonably good agreement with the effect reported by Ramsperger [9] and by Rice and Sickman.[10] The high-pressure Arrhenius parameters also agree well with those obtained by previous workers, as shown in the Table.

Pyrolysis of Azomethane with Added Gases.—A series of 25 runs was carried out at 288°, 281·5°, and 261·5° in which the azomethane pressure was between 0·4 and 2·8 mm. Some of the runs were for the purpose of calibration and no gas was added, but between 20 and 60 mm. of carbon dioxide was added to the majority. The presence of the carbon dioxide raised the rate constant. Its effect is conveniently expressed in terms of a constant α defined by: $\alpha =$ (Amount of azomethane that would have to be added to yield the observed rate constant)/(Amount of carbon dioxide added). The numerator was found by inspection of the plot of azomethane pressure against rate constant. It was found that $\alpha = 0{\cdot}20 \pm 0{\cdot}05$ and within the rather large experimental error was independent of the pressure of azomethane and carbon dioxide. This figure agrees with Rice and Sickman's.

Experiments were then carried out in which *n*-pentane and *cyclo*pentane were added. With azomethane at 0·4—0·5 mm. and the pentane between 15 and 22 mm., $\alpha = 0{\cdot}44 \pm 0{\cdot}2$. This seemed low because it was expected that a molecule of the complexity of *n*-pentane would have at least the efficiency of azomethane in energy transfer. Similar experiments were therefore tried with *trans*-but-2-ene which should have $\alpha = 1$ because its mechanical properties are almost identical with those of azomethane. Its measured efficiency was less than that of carbon dioxide. Further experiments with *n*-pentane showed that the value of α decreased at high pentane pressures and was lower at higher azomethane pressures for the same pressure of pentane. These findings could be explained if the decomposition of azomethane involves short free-radical chains that increase in importance as the pressure is raised.

Extended series of experiments were then carried out in the presence of toluene and propene. Toluene was selected because of its proved ability to stop chain reactions; propene because it is widely believed to have the same property, at least under some conditions, is readily available, and is volatile. The results, shown in Figs. 1 and 2, can be interpreted if the added gas both accelerates the reaction at low pressures by increasing the rate of energisation and reduces the rate, particularly at high pressures, by inhibiting a short chain reaction. The chain reaction becomes more important as the pressure of

[9] Ramsperger, *J. Amer. Chem. Soc.*, 1927, **49**, 912, 1495.

[10] Rice and Sickman, *J. Chem. Physics*, 1936, **4**, 239, 242.

azomethane is increased. This is shown by the inhibition effected by propene at higher azomethane pressures. At low pressures of azomethane only the acceleration due to the added gas can been seen. Since the same limiting rate constant is obtained for all azomethane pressures with propene above about 100 mm., this rate can be identified with the rate of the initial step in the decomposition of azomethane (1). The decomposition of the radical (2) is exothermic by some 29 kcal. mole^{-1},[4] and therefore probably occurs very rapidly. Arrhenius parameters for the fully inhibited decomposition in the presence of 130—170 mm. of propene were determined with azomethane pressures of 0·93 mm. (261°, 276°, 295°, 300°), 4·7 mm. (239°, 251°, 275°, 295°), and 19·7 mm. (253°, 276°, 295°). The rate constants at all the pressures can be expressed by

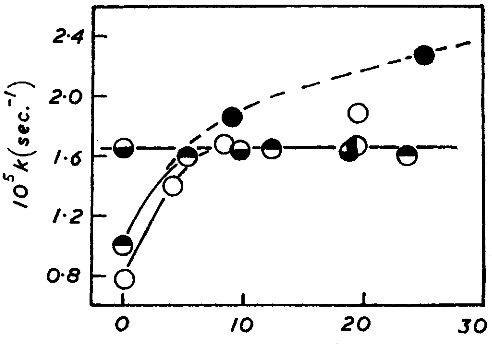

FIG. 1. *Rate constants at* 276·3° *for the decomposition of azomethane in the presence of toluene and carbon dioxide.*

Azomethane pressure: ○ 0·45 mm., ◓ 0·94 mm., ◐ 1·32 mm., ◒ 2·75 mm. (added gas, toluene); ● 0·94 mm. (added gas, carbon dioxide).

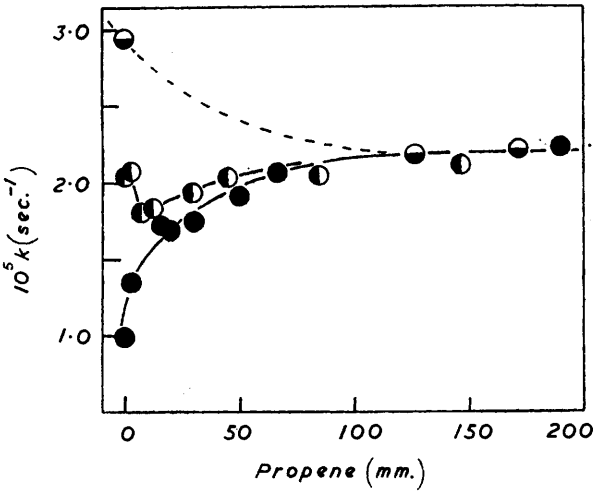

FIG. 2. *Rate constants at* 276·3° *for the decomposition of azomethane in the presence of propene.*

Azomethane pressure: ● 0·9 mm., ◐ 4·7 mm., ◒ 19·7 mm.

$$\mathrm{Me{\cdot}N{:}N{\cdot}Me = Me + N{:}NMe} \qquad (1)$$

$$\mathrm{N{:}NMe = N_2 + Me} \qquad (2)$$

$$\log k_1\ (\text{sec.}^{-1}) = (15{\cdot}7 \pm 0{\cdot}15) - (51{,}200 \pm 250/2{\cdot}303\boldsymbol{R}T)$$

The standard errors are for each individual pressure. They are reduced if the results are treated as one group. The unusually high *A* factor is clearly established. These Arrhenius parameters are to be preferred to those of Page, Pritchard, and Trotman-Dickenson;[4] later experiments have shown that their method of injection of azomethane into the gas stream is of doubtful efficacy.

Surface Effect.—The importance of the proper seasoning of the reaction vessel to obtain reproducible results has already been stressed. The treatment is necessary because very high rates are found in clean vessels, owing either to chains starting at the walls or to a molecular reaction on the surface. When the vessels had been properly conditioned, the rate constants measured in the large reaction vessel (surface/volume = 0·85 cm.$^{-1}$) were some 1·8 times those in the small vessel (surface/volume = 2·1 cm.$^{-1}$). However, if a large excess of propene was added to the system, the rates in the large and in the small vessel were the same. At an azomethane pressure of 10 mm., the rate constant in the small vessel in the presence of 580 mm. of propene was about 1·5 times that in the absence of propene. These facts can be understood if it is supposed that chains can be ended at the wall even in seasoned reaction vessels. There are few examples of chain termination at the walls of reaction vessels except in oxidations involving molecular oxygen.

Conclusion.—Because of the complications of the decomposition that have been found in these investigations, it is not well suited to yield information on energy transfer and the behaviour of unimolecular reactions at low pressures. Furthermore, little can be said about the elementary reactions that constitute the chain. Ramsperger's conclusion that the decomposition exhibited quasi-unimolecular behaviour is, however, probably correct. The rate constant almost certainly falls off below 100 mm. owing to the restricted rate of energisation. Moreover, some of the observed decline of the activation energy below the value of 51·7 kcal. mole^{-1} is probably real. At low pressures the chains contribute little to the reaction rate. This is one of the first reactions that have been found to exhibit the decline that is predicted by the theory of unimolecular reactions.

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[11] Taylor and Jahn, *J. Chem. Physics*, 1939, **7**, 474.