792. *The Thermal Decomposition of Azomethane.*

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The thermal decomposition of azomethane has been reinvestigated in the temperature range 390—450° by the " toluene-carrier " flow technique. The rate constant for the decomposition in 15 mm. of toluene is given by $k = 10^{14}e^{-46,000/\boldsymbol{R}T}$ sec.$^{-1}$. The experiments provide strong evidence that the primary step in the decomposition is the splitting-off of a methyl radical. The reason for the discrepancy between these results and those obtained in static systems and the bond strengths in azomethane are discussed.

The thermal decomposition of azomethane has been investigated by several workers (Schumacher, " Chemische Gasreaktionen," Steinkopf, Dresden, 1938) because there was good evidence that it is a unimolecular reaction whose rate is dependent on the overall pressure in the reaction system, at pressures which are readily accessible to experiment. It has frequently been supposed that the azomethane molecule splits directly into an ethane and a nitrogen molecule, but this view receives no support from Riblett and Rubin (*J. Amer. Chem. Soc.*, 1937, **59**, 1537) who analysed the products formed in the decomposition and found considerable quantities of methane, some ethylene, and some unidentified involatile products. There are very few undoubtedly unimolecular reactions whose rates have been found to depend on the overall pressure and it is important to know if the decomposition of azomethane occurs so simply that it may be used to test theories of unimolecular reactions and of energy transfer.

There is a second point of interest in connection with this reaction : the rate constant has been given as $k = 3{\cdot}1 \times 10^{16} \exp(-52,000/\boldsymbol{R}T)$ sec.$^{-1}$ (Ramsperger, *ibid.*, 1927, **49**, 912; Kassel, " Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, 1932) and alternatively as $k = 8 \times 10^{15} \exp(-50,200/\boldsymbol{R}T)$ (Rice and Sickman, *J. Chem. Phys.*, 1936, **4**, 242); in either case the pre-exponential or *A* factor is very much larger than that which has been considered " normal " on theoretical grounds. It is understandable that such high *A* factors should be found for chain reactions and it has been suggested that this reaction is a chain decomposition.

By studying the decomposition in a flow system in the presence of toluene we hoped to isolate the initial step of the azomethane decomposition and so throw light on these matters.

Experimental

Materials.—*NN'*-Dimethylhydrazine dihydrochloride (Hatt, *Org. Synth.*, 1936, **16**, 18) was converted into the cuprous chloride addition compound of azomethane (Diels and Koll, *Annalen*, 1925, **443**, 262) which when heated at 120—140° yielded azomethane; the gas was purified by bulb-to-bulb distillation in a vacuum-system. The toluene was twice pyrolysed and distilled before it was used for kinetic experiments.

Apparatus.—This was of the type used by Sehon and Szwarc (*Proc. Roy. Soc.*, 1950, *A*, **202**, 263).

Procedure.—The products of the pyrolysis flowed through an ice–salt trap which removed the dibenzyl, then through liquid-nitrogen traps which removed the condensable products; the methane and nitrogen were pumped into a storage and analytical system. The proportion of methane in the non-condensable gases was found by burning the mixture in oxygen over a platinum filament and measuring the carbon dioxide formed. As the analytical system was not very suitable for the determination of ethane the amount formed was taken as equal to ($N_2 - \frac{1}{2}CH_4$). Ethane was identified by its vapour pressure in the system.

The toluene pressure in the flow system varied between 11 and 16 mm., the toluene : azomethane ratio between 10 and 30, and the contact time was between 1·2 and 1·4 sec. Between 10 and 50% of the azomethane was decomposed in a run. In calculating the results in the usual way on the basis of the nitrogen formed in the decomposition it was assumed that azomethane obeyed the perfect-gas laws.

RESULTS AND DISCUSSION

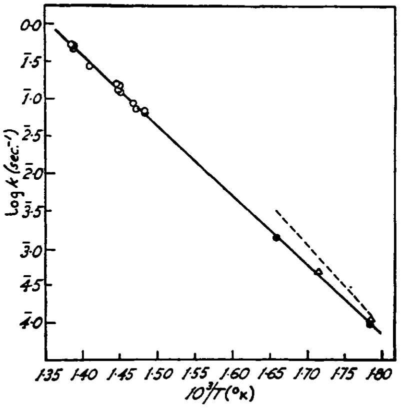
A plot of the logarithms of the rate constants against the absolute temperature is shown in the Figure. The solid line corresponds to the Arrhenius equation, $k = 10^{14} \exp(-46{,}000/\boldsymbol{R}T)$ sec.$^{-1}$. The amount of methane formed varied from 30% of the non-condensables at the lower temperatures to 50% at the higher. It must be supposed that all this methane is produced from methyl radicals released in the primary decomposition which abstract hydrogen atoms from the toluene carrier gas. The ethane found could be produced either by a partial initial split of the molecule into ethane and nitrogen or by the combination of methyl radicals. It is not possible to decide directly by which path it is formed but it can be shown that the rate of formation of ethane is such that it may readily be accounted for by the combination of methyl radicals present in the concentrations corresponding to the rate of production of methane. If the rate constant for the reaction of methyl radicals with toluene is given by $k = 1{\cdot}4 \times 10^{11} \exp(-8300/\boldsymbol{R}T)$ mole^{-1} c.c. sec.$^{-1}$ (Trotman-Dickenson and Steacie, *J. Chem. Phys.*, 1951, **19**, 329; Gomer and Kistiakowsky, *ibid.*, p. 85), then the concentration of methyl radicals in a typical experiment in the middle of the temperature range, at 417°, was $1{\cdot}07 \times 10^{-11}$ mole c.c.$^{-1}$ in the reaction zone. This corresponds to a rate of formation of ethane of $5{\cdot}73 \times 10^{-9}$ mole c.c.$^{-1}$ sec.$^{-1}$, which may be compared with the observed rate of $3{\cdot}2 \times 10^{-9}$ mole c.c.$^{-1}$ sec.$^{-1}$. This is certainly of the correct order of magnitude and the difference probably arises partly because the effective volume of the reactor for the reactions of methyl radicals is rather larger than the effective volume for the decomposition. The positions of the limits of the reaction zone are determined by the temperature profile in the furnace and consequently will be rather further from the hottest region for reactions with low activation energies. Because of this uncertainty and because the experimental errors in the determination of the methane : ethane ratio are rather large, a reliable value for the rate of reaction of methyl radicals with toluene cannot be calculated from our results, but the findings are strong evidence that all the ethane comes from the combination of methyl radicals.

Our results are compared with those of other workers and this is done in the Figure. The points for 15 mm. total pressure are taken from the smoothed curves obtained by the authors for the variation of rate constant with pressure at the different temperatures. It has been assumed that toluene and azomethane have approximately equal efficiencies for purposes of energy transfer; this has not been proved for azomethane but the efficiencies are very similar for toluene, and indeed all large molecules, with *cyclo*propane (Pritchard, Sowden, and Trotman-Dickenson, *Proc. Roy. Soc.*, 1953, *A*, **217**, 563) and *cyclo*butane (*idem, ibid.*, **218**, 416). The agreement between the three sets of results is excellent.

A reason may be suggested for the discrepancy between these results and those obtained at high pressures, and for the complexity of the products from pure azomethane. The near identity of the rates measured by us and those obtained by the workers in static systems suggests that the same process, which is the fission of a C–N bond, is rate-determining in each case. In pure azomethane, the methyl radicals will abstract hydrogen atoms from the substrate and will combine with the $\mathrm{Me{\cdot}N{:}N{\cdot}CH_2{\cdot}}$ radicals so formed. Ethyl radicals, and hence ethylene, may be formed by the subsequent decomposition of $\mathrm{C_2H_5{\cdot}N{:}NMe}$; the high-boiling products are probably formed by the addition of radicals to the nitrogen double bond (Taylor and Jahn, *J. Chem. Phys.*, 1939, **7**, 474). The higher activation energy found at high pressures is probably caused by the decomposition of some of the $\mathrm{Me{\cdot}N{:}N{\cdot}CH_2{\cdot}}$ radicals which are formed in greater numbers at high pressures. The rate of decomposition of this chain-carrying radical will be markedly temperature-dependent. The number decomposing cannot be large as the quantum yield for the photolysis of azomethane is only slightly dependent upon temperature (Burton, Davis, and Taylor, *J. Amer. Chem. Soc.*, 1937, **59**, 1989). This decomposition will explain the high activation energies which lead to the abnormal frequency factors.

The activation energy of a unimolecular reaction whose rate is a function of pressure is also dependent on pressure, but the dependence is not sufficiently marked to be the cause of the difference found here (Slater, *Phil. Trans.*, 1953, **246**, *A*, 57). Probably the best expression for the high-pressure rate constant is $k = 1{\cdot}5 \times 10^{14} \exp(-46{,}000/\boldsymbol{R}T)$ sec.$^{-1}$. In view of these results it seems that the dependence of the rate constants on pressure is real but that the shape of the pressure–rate-constant curve is influenced by factors other than energy transfer. Consequently this decomposition is not an ideal reaction on which to test theories of unimolecular reactions.

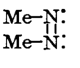
The heat of formation of azomethane is not known, but the heat of combustion of azo*iso*propane, Pr^{i}·N:N·Pr^{i}, has been found (Coates and Sutton, *J.*, 1948, 1187) to be ΔHf(Pr^{i}·N:N·Pr^{i},gas) = 19·4 ± 0·8 kcal./mole. Comparison with the substitution heats for olefins ("Selected Values of Properties of Hydrocarbons," Nat. Bur. Stand., Circular No C461, Washington, 1947) leads to the value ΔHf(Me·N:N·Me,gas) = 43·2 kcal./mole, an estimate which is unlikely to be in error by much more than ±2 kcal./mole. If ΔHf(CH_3,gas) = 32·6 kcal. (Mortimer, Pritchard, and Skinner, *Trans. Faraday Soc.*, 1952, **48**, 220) is then used, this leads to a value of $D_1 + D_2$ (*i.e.*, the heat of the process Me·N:N·Me $\longrightarrow$ N_2 + 2Me) of 22 kcal./mole. Making the usual assumptions (Szwarc, *Chem. Reviews*, 1950, **47**, 75), we identify the activation energy of 46 kcal. with D_1. The situation where D_1 is very much greater than D_2 exists in the alkylmercury series (Mortimer, Pritchard, and Skinner, *loc. cit.*), where, for example, $D_1 + D_2$ for $HgMe_2$ is 57 kcal., D(Me–HgMe) being 51 kcal./mole (Gowenlock, Polanyi, and Warhust, *Proc. Roy. Soc.*, 1953, *A*, **218**, 269). Azomethane is the only known case in which D_1 is greater than $D_1 + D_2$; however, this extreme result is not entirely unexpected in view of the very large amount of energy required to raise the nitrogen molecule to a bivalent state from its zero-valent ground state. The lowest triplet state of N_2 is $A^3\Sigma_u^+$ which is 143·5 kcal. above the ground state (Herzberg, "Diatomic Molecules," Van Nostrand, New York, 1950) and it is reasonable to assume that the valency state is not far removed from this level. We can form an estimate of this excitation energy from the thermochemical data in the following way: the strength of a normal C–N single bond is approximately 83 kcal./mole (Roberts and Skinner, *Trans. Faraday Soc.*, 1949, **45**, 339), so that $D_1 + D_2$ for azomethane should be 166 kcal. if no excitation energy were regained by N_2 in returning to its zero-valent state; the actual value of $D_1 + D_2$ is 22 kcal., so that the excitation energy involved is 166 − 22 = 144 kcal./mole, which is very close to the spectroscopic estimate, although this agreement is probably fortuitous.



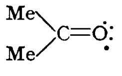
Arrhenius plot for the decomposition of azomethane in a system at approx. 15 mm. total pressure.

○ This work.
● Ramsperger (*loc. cit.*).
△ Sickman and Rice (*loc. cit.*).
– – – – Ramsperger's results (*loc. cit.*) at infinite pressure.

It is possible that the molecule does not initially lose one methyl group closely followed by a second, but that both methyl groups split off simultaneously. It has hitherto not been necessary to postulate such a mechanism for any other reaction and it can be shown by thermochemical argument that it is not necessary in this case either. Compare the bond strengths in the two analogous molecules



$$\begin{array}{l} \text{Me–N:} \\ \quad\ \| \\ \text{Me–N:} \end{array}$$



$$(\text{Me})_2\text{C=}\ddot{\text{O}}\text{:}$$

To the first approximation the Me–N dissociation energy in azomethane should be 83 kcal., and the Me–C dissociation energy in acetone should be 84 kcal. (Roberts and Skinner, *loc. cit.*); however, the C–C dissociation energy in acetone is only 73 kcal.; this weakening of 11 kcal. may be ascribed to a three-electron bond formed by conjugation of the free electron on the carbon atom with one of the lone pairs on the oxygen atom in the Me·CO· radical. That this resonance energy is of the correct order of magnitude may be seen from a study of the annexed Table, in which the relevant dissociation energies (in kcal./mole) are collected; they are all based on the values given by Gaydon (" Dissociation Energies," 2nd edn., Chapman and Hall, London, 1953) which, although they may not be correct, are internally consistent. The strengthening due to three-electron bond resonance in CO^+ relative to $>CO$ in acetone is 16 kcal., which is of the same order of magnitude as the stabilisation of the Me·CO· radical (the stabilisation of Me·CO· is about two-thirds of that in CO^+). In the azomethane case, the stabilisation by three-electron bond resonance of N_2^+ with respect to $-N{=}N-$ in azomethane itself is 119 kcal. If again we take two-thirds of this as the stabilisation energy of the Me·N⁚N· radical, we get 80 kcal., leaving the dissociation energy D(Me–N⁚N·Me) of the order of $83 - 80 = 3$ kcal./mole. This calculation merely serves to show that 46 kcal./mole is not an unreasonably low value for the dissociation energy of this single C–N bond: no significance should be ascribed to the exact calculated value.

Azomethane	Acetone
$D(-N{=}N-) = 82$ [a]	$D(>C{=}O) = 178$ [a]
$D(-N{=}N^+) = 201$ [b]	$D(-C{=}O^+) = 194$ [b]
$D(N{\equiv}N) = 225$ [b]	$D(C\overset{\equiv}{\leftarrow}O) = 256$ [b]

[a] Thermochemical estimate. [b] From Gaydon, *op. cit.*

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