[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Photolysis of Azomethane

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In an investigation begun in this Laboratory it was hoped to use free methyl radicals formed in the photolysis of azomethane to induce chains in acetaldehyde at temperatures below that at which thermal decomposition could proceed. Inasmuch as previous investigators appeared to be quite certain of the mechanism of the decomposition of azomethane, it appeared likely that absolutely accurate information might be obtained about the length of chains initiated by free radicals.

According to Ramsperger[1] both the pyrolysis and the photolysis of azomethane proceed according to the over-all reaction

$$CH_3N{=}NCH_3 \longrightarrow C_2H_6 + N_2$$

with the latter having a quantum yield of about 2.0. Forbes, Heidt and Sickman[2] have challenged the latter figure and have produced evidence which, they claim, indicates that the quantum yield approaches 1.0 as an upper limit at pressures around 100 mm.; at higher pressures the quantum yield is reduced to a much lower figure by deactivating collisions. Heidt and Forbes[3] later published a statement on the products of pyrolysis and photolysis which indicated that methane was formed to a large extent in the later course of the decomposition. This conclusion was based upon pressure measurements at room temperature, −78.5, and −183°.

Leermakers[4] on the basis of experiments involving the simultaneous pyrolysis of lead tetraethyl and azomethane, concluded that neither decomposition affected the other and that consequently the ethyl radicals known to be produced in the decomposition of the former[5] were not initiating chains in the latter. It was suggested that, inasmuch as methyl radicals might be expected to behave similarly to ethyl radicals, methyl radicals likewise would not initiate chains at 270° and less. The work of Leermakers[6] and that of F. O. Rice and Evering[7] employing the mirror methods of Paneth[8] had shown that in all probability the reaction proceeded by a primary mechanism

$$CH_3N{=}NCH_3 \longrightarrow N_2 + 2CH_3$$

Consequently, Leermakers concluded that the decomposition of azomethane is not a chain reaction. O. K. Rice and Sickman[9] reached the same conclusion from their own work and that of Forbes, Heidt and Sickman.[2]

These conclusions of previous investigators seemed so decisive that it appeared only necessary to measure the nitrogen yield in the photolysis of azomethane in order to determine accurately the number of methyl radicals produced; the nitrogen determination was conducted because of the conclusions of Heidt and Forbes[3] that reaction 1 does not represent the over-all reaction.

The analyses conducted in this work changed the course of the investigation completely. It was found impossible to reconcile the amount of nitrogen formed with the proportions of the hydrocarbon products. The results of actual analyses given below indicate that many of the conclusions reached by previous investigators solely on the basis of pressure changes may require some modification. Pending the establishment of other data it does not seem feasible to use the photolysis of azomethane as a source of known quantities of methyl radicals.

Experimental Method

Azomethane.—The azomethane was prepared by the method of Ramsperger[1] except that the symmetrical dimethylhydrazine dihydrochloride was prepared according to the method of Hatt.[10] In our more recent preparations the mercury cut-offs recommended by Ramsperger were eliminated and large stopcocks were used. It was found that the yield of azomethane could be improved by reducing the pressure of the system initially to such a point that the azomethane would distil out of the preparation flask as soon as formed. As with previous investigators it was found that the principal impurities were probably moisture and air (perhaps nitrogen). Care must be taken that the former is not drawn from the drying tubes into the azomethane by the liquid air used for condensation. The entrapment of nitrogen in the condensed azomethane was best avoided by distilling toward the evacuating system from a dry-ice–toluene mixture to liquid air. In distilling

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(1) Ramsperger, THIS JOURNAL, **49**, 912, 1495 (1927).

(2) Forbes, Heidt and Sickman, *ibid.*, **57**, 1935 (1935).

(3) Heidt and Forbes, *ibid.*, **57**, 2331 (1935).

(4) Leermakers, *ibid.*, **55**, 4508 (1933).

(5) Paneth, *Ber.*, **62**, 1335 (1929); **64**, 2702, 2708 (1931).

(6) Leermakers, THIS JOURNAL, **55**, 3499 (1933).

(7) F. O. Rice and Evering, *ibid.*, **55**, 3898 (1933).

(8) *Cf.* F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," Johns Hopkins University Press, Baltimore, Md., 1935.

(9) O. K. Rice and Sickman, *J. Chem. Phys.*, **4**, 242 (1936).

(10) Hatt, "Organic Syntheses," John Wiley & Sons, Inc., New York, N. Y., **16**, 18 (1936).

backward through a stopcock to dry-ice–toluene the liquid air was removed and the system was opened to a large reservoir. This enabled most of the nitrogen to escape into the reservoir. The stopcock to the dry-ice–toluene receiver was then closed and the reservoir was opened to the pumping system. After this the azomethane was again distilled forward from the dry-ice–toluene to the liquid air. This operation was repeated about six times (after about fifteen other distillations). At the end it was concluded that various samples distilled from the approximately 6 cc. of azomethane so formed (using four times the quantities indicated by Ramsperger) were reasonably pure.

It was not practicable to obtain true vapor pressure data. With the small amounts of our samples it was found that traces of grease or other impurity present in the reservoirs, might cause one fraction to present two different vapor pressures in two different reservoirs. Different fractions of the same 6-cc. yield all had vapor pressures between 744 and 756 mm. at 0° in different reservoirs. All together the various readings indicated that the last fraction was substantially like the first.

Light Source.—The light source used throughout these experiments was a constricted mercury arc of the type described recently.[11] Unless otherwise noted there was interposed between the light source and the reaction system a Corning No. 534 blue nultra filter. According to the specifications this filter transmits only wave lengths longer than 3500 Å. In all the experiments except the one at −22.5° the arc was located 2.5 cm. from the reaction vessel; at −22.5° the arc was 3.3 cm. from the reaction vessel.

Reaction Vessel and Thermostat.—The reaction vessel was a Pyrex flask of 1015-cc. volume connected to the vacuum system, the manometer, and the gas analysis system by means of capillary tubing closed off with simple greased stopcocks. The thermostat was a Pyrex beaker to which the filter was affixed in most of the experiments. The temperature was maintained manually at 20° or (in one experiment) at −22.5°. The total thickness of Pyrex between the arc and the reacting gas was of the order of 2 mm. This thickness transmits only at more than 2900 Å., transmitting the 3130 mercury line and the 3020 and 2960 to a slight extent.

Gas Analysis.—A Fischer Scientific Co. Gas Analysis Apparatus was permanently connected to the reaction system, through a mercury gas buret, a Töpler pump, and a trap. The large volumes of azomethane used made possible analyses on a macro-scale. The products of the decomposition were separated into condensable and non-condensable portions in the liquid air trap, measured in the mercury buret, bubbled through an auto-bubbler pipet (of the type described by Burton and Davis[12]) containing hydrochloric acid, and measured again over water. The hydrochloric acid was removed for analysis after each experiment. Any azomethane residue was removed by acid stannous chloride solution in an auto-bubbler pipet. Other pipets contained potassium hydroxide (for removing carbon dioxide and other acid gases), chromous chloride, and potassium pyrogallate (for the direct determination of residual oxygen after the combustions). Hydrogen was determined by cupric oxide oxidation while the volume of paraffin gases and the average value of n in the formula C_nH_{2n+2} were determined by oxidation over a hot platinum wire with subsequent measurements of the volume before and after bubbling through potassium hydroxide. After the removal of the unused oxygen, the fraction of nitrogen in the sample was calculated from the volume of the residual gas. Corrections were made, of course, for the nitrogen initially present in the oxygen.

The procedure of dividing the gases into condensable and non-condensable portions made it possible to determine approximately the amounts of methane, ethane and propane in the original gas. Naturally, the amounts of ethane and propane may be in error. They involve the assumption that these gases are the only saturated hydrocarbons in the condensed gas sample, while the calculated n might actually be the average for a mixture of ethane and some much higher hydrocarbon. Furthermore, it will be shown below that even in the non-condensable gases there is the possibility that the presence of some other hydrocarbon may require a recalculation of the results.

Photolysis of Azomethane.—Ordinarily, the azomethane was stored in a small reservoir immersed in a dry-ice–toluene mixture. The reservoir and its contents were constantly shielded from the light except when the cooling mixture was deliberately removed to permit distillation of the sample. In fact, during the whole course of the investigation the room was darkened to avoid the entrance of daylight. Preceding each run a sample was distilled into the reaction vessel, which was maintained at a constant temperature of 20°, and the initial pressure was determined. The reaction vessel was exposed to the arc when the latter had become steady at 4 amperes with the arc stretched through the capillary as previously described.[11] At the conclusion of each run the gas was permitted to stand in the vessel for at least five minutes to obtain check readings. In a few cases the gas stood for as long as three days without affecting the pressure.

Successive samples were withdrawn through the liquid air trap where they were fractionated into condensable and non-condensable portions and analyzed as already described. The results of these analyses for different fractions decomposed and different initial pressures are summarized in Table I.

In both Tables I and II P_0 is the initial pressure of the gas in the reaction vessel in mm. and P_F the final pressure. ΔP is the pressure change during the photolysis. All ratios, for example, $\Delta P/P_0$, are expressed in per cent. V_A is the volume of gas in cc. measured over water after all azomethane or possible alkaline gas has been removed by successive treatments with hydrochloric acid, stannous chloride and potassium hydroxide (the latter to remove acid vapors). V_G is the calculated volume of di-acid (alkaline) gas in the sample based upon titration of the hydrochloric acid in the first auto-bubbler pipet. The values are extremely variable; the reason for the variation will be explained below. V is the volume of gas after the photolysis measured over mercury before any chemical treatment. Mention should be made of the fact that, except for V, volumes (in Table II) are given only for moist gases. The values for N_2/V as given in Table I are corrected for moisture in the nitrogen so that the percentage given is the true one. The other percentages involving

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[11] Burton, THIS JOURNAL, **58**, 1645 (1936).

[12] Burton and Davis, *Ind. Eng. Chem., Anal. Ed.*, **9**, 139 (1937).

TABLE I

SUMMARY OF ANALYTICAL RESULTS

Experiment	22	16[c]	19	26	27	29	20	24	30[d]	31[e]	25	28
P_0	101.6	99.8	100.6	100.3	100.7	99.0	57.8	51.0	49.7	48.4	25.0	13.5
$\Delta P/P_0$	4.9	10.1	9.4	9.8	20.1	85.8	17.5	19.2	19.6	20.4	38.0	58.7
Unsat./V_A	0	0	0.7	0	0.5	0.4	0.7	0.8	0.8	0.4	0.8	0.9
CH_4/V_A	0	1.2	3.2	4.8	8.0	4.4	0.6	1.4	1.1	...	3.7	...
C_2H_6/V_A	41.0	44.8	40.9	40.0	39.0	36.8	45.3	42.1	44.7	...	42.2	...
C_3H_8/V_A[a]	1.5	0	0	0	0	7.9	0	0	0	...	0.3	...
N_2/V_A	58.2	55.5	54.8	56.3	53.8	52.0	53.9	56.6	53.1	55.4	53.2	53.3
Total	100.7	101.5	99.4	100.1	100.3	101.7	100.5	100.8	99.7	...	100.2	...
M or D[b]	M	M	M	M	M	D	D	D	D	M	M	M
V_G	33.9	...	...	2.9	2.7	0.45	3.7	14.5	1.1	0.85	1.7	0
$N_2/V = a$	5.4	11.5	10.1	10.2	18.1	47.8	16.1	18.0	17.3	18.3	28.6	38.1
$\Delta P/P_F = b$	4.7	9.2	8.5	8.9	16.7	46.2	14.9	16.1	16.3	17.0	27.3	36.9
a/b	1.15	1.25	1.19	1.15	1.08	1.03	1.08	1.12	1.06	1.08	1.05	1.03

N_2/V_A average = 54.7.

[a] This is an idealized figure presumed from the value of n in those cases where n has been determined on the residue condensed in liquid air. [b] N_2 by actual measurement = M; by difference = D. [c] In expt. 16 no effort was made to separate the product into condensable and non-condensable fractions by means of liquid air. [d] Expt. 30 was conducted with unfiltered light. [e] Expt. 31 was conducted at *ca.* −22.5° with unfiltered light.

TABLE II

DETAILED SUMMARY OF TWO ANALYSES

	28			31		
Experiment	F_N[a]	F_C[a]	Total	F_N	F_C	Total
P_0	..	...	13.5	..	...	48.4
$\Delta P/P_0$	..	...	58.7	..	...	20.4
V	11.4	17.5	28.9	15.2	66.2	81.4
V_A	11.0	10.2	21.2	14.5	13.1	27.6
Contraction	0.8	23.2		1.1	30.9	
Absorption	1.2	17.8		1.5	26.7	
n	?	1.865		?	2.28	
O_2 used, cc.	1.6	31.3		1.9	45.6	
N_2, cc.	10.3	1.0	11.3	14.1	1.2	15.3
CH_4, cc.		1.38			...	
C_2H_6, cc.		8.24			8.43	
C_3H_8, cc.		...			3.28	
Unsat./V_A			0.9			0.4
CH_4/V_A		6.5			...	
C_2H_6/V_A		38.8			30.5	
C_3H_8/V_A		...			11.9	
N_2/V_A			53.3			55.4
V_G			0			0.85

[a] F_N represents the fraction not condensed by liquid air; F_C represents the condensed fraction.

V_A are, of course, self-corrected. Although hydrogen was looked for in every experiment none ever was found.

It will be noticed that for experiments 28 and 31 data on the alkane content have been omitted. The detailed summary for those two is shown in Table II.

The volume of oxygen used is that required for the oxidation of the hydrocarbon gases. The *contraction* is the decrease in volume in cc. due to water formation during the combustion and the *absorption* represents the volume of carbon dioxide formed at the same time. n is the calculated value in the hypothetical mixed alkane C_nH_{2n+2}. The figures given for the alkanes are evidently idealized; they are based on the assumption that only two gases are present in the sample analyzed: in the uncondensed fraction—methane and ethane, and in the condensed—ethane and propane. In both experiments 28 and 31 the values for the contraction and absorption in the uncondensed fraction are so unusual as to preclude the calculation of a significant value for n. The results are presented for what they are worth without an attempt at interpretation other than the remark that a compound such as acetylene might account for the effect; however, acetylene would not be expected to pass the bromine pipet. It is possible that the high value for n in the condensable fraction of expt. 31 may be due to the presence of such a gas and that the computed value for propane is consequently wrong. In any event, the percentage given for propane or the presence of an equivalently large quantity of such another gas would be enough to differentiate expt. 31 (which was conducted at −22.5°) from all the other experiments. Judging from the small volumes of the contraction and the absorption in both experiments it is apparent that even if the actual hydrocarbons in the uncondensed portion were known the percentages reported would be only slightly changed.

As Ramsperger, and Forbes, Heidt and Sickman, have noted, it was found that when the photolysis was conducted at shorter wave lengths, as in experiments 30 and 31, a solid deposit settled on the walls of the reaction vessel; the deposit in experiment 31 (at −22.5°) was much lighter than in experiment 30. When the reaction vessel was removed for cleaning, the deposit disappeared completely, probably due to oxidation by the inrushing air.

Photolysis of Azomethane plus Acetaldehyde.—In some early experiments, in which azomethane was photolyzed in the presence of acetaldehyde using the blue nultra filter, it was found that, in a time which later experience demonstrated was sufficient to cause about 20% pressure increase ($\Delta P/P_0$) in pure azomethane, no acetaldehyde was decomposed at 20° according to the analyses. This result was in line with the conclusions of Leermakers on chain lengths in the photolysis of acetaldehyde at low temperatures[13] and was, of course, expected. The formation of a fog in the reaction vessel during runs and the deposition of an extremely viscous, non-volatile material was, however, unexpected. In the case mentioned the results are summarized in Table III. The method of calculation is obvious from the table. The following were known by measurement at the end of the photolysis: the initial pressures of the acetaldehyde and the azomethane, the volume of the reaction vessel (1015 cc.), the weight of acetaldehyde in the deposit (determined by Ripper's method[14]) and the total pressure change. The value for N_2/V was determined by difference after analysis of the resultant gases. However, as is shown in Table III, there are sufficient data for a calculation of N_2/V on the assumption that the average value for a/b calculated in Table I for $\Delta P/P_0 = 20\%$ holds in this case also. The check between the observed and the calculated values for N_2/V is good. No allowance has been made in these calculations for a pressure decrease due to a loss of azomethane from the vapor phase by inclusion chemically or otherwise, in the deposit. This was not deemed necessary since the agreement between the observed and calculated nitrogen values would indicate that the deposit contained solely acetaldehyde. The conclusion may be drawn from Table III that, for every 3.3 molecules of nitrogen liberated, approximately two molecules of acetaldehyde are lost by an association reaction.

TABLE III

SUMMARY OF EXPT. 5. AZOMETHANE PLUS ACETALDEHYDE AT 20°

Initial pressure CH_3CHO, obsd., mm.	104.2
Initial weight CH_3CHO, calcd. = c, g.	0.255
Wt. CH_3CHO in deposit (by analysis) = d, g.	.042
d/c, %	16.5
ΔP_A (due to CH_3CHO) calcd., mm.	−17.2
$\Delta P_{\text{obsd.}}$[a], mm.	7.2
ΔP (due to CH_3NNCH_3) calcd., mm.	24.4
P_0 = initial pressure CH_3NNCH_3, obsd., mm.	106.3
$\Delta P/P_0$, %	22.9
$\Delta P/P_F$ (= b) from $\Delta P/P_0$, %	18.6
a/b from Table I (assumption)	1.08
N_2/V (= a) calcd., %	20.1
N_2/V by analysis (approximate), %	19.9
V (at 760 mm., 20°) calcd., cc.	173.8
N_2, calcd., cc.	35.0
CH_3CHO (at 760 mm., 20°) in deposit, cc.	21.2

[a] $\Delta P_{\text{obsd.}}$ is the final total pressure increase on prolonged standing after the completion of the run. The figure given is somewhat lower than that immediately at the completion of the run before the fog had a chance to settle. The value at that time was 11.6 mm.

It was noticed that the deposit had a faint musty odor similar to that of aldehyde ammonia and was quite readily soluble in water without change of odor. When a small amount of hydrochloric acid was added, the odor of acetaldehyde was quite strong.

The formation of the deposit is definitely linked to the photolysis of azomethane for blank runs with acetaldehyde alone were without effect and prolonged standing of mixtures of the two gases without illumination was also without results.

Rate of Photolysis of Azomethane.—With the exception of experiments 30 and 31 in which unfiltered light was used, the conditions of light intensity during the photolyses were fairly well reproduced in most experiments. The arc was maintained constant at 4.0 amperes and was cooled constantly with running water. The distance from the arc to the reaction vessel was rigidly fixed. While no photometer readings were taken there is no reason to expect a large order of variation between experiments on the basis of light intensity alone. Consequently, the pressure–time relationships during the photolyses of azomethane are of some significance if the different experiments are considered relatively to each other.

Neglecting for the moment the effect of decreased light absorption by azomethane as the reaction proceeds, it is evident that the rate of change of partial pressure of azomethane may be represented by the equation

$$\mathrm{d}p/\mathrm{d}t = Kp$$

or

$$\ln P_0/p_t = Kt$$

where P_0 is the initial pressure of the system, p is the partial pressure of azomethane (when $t = 0$, $p = P_0$) and p_t is the partial pressure of azomethane at time t. Now, if $p_{N_2,t}$ be the partial pressure of nitrogen at time t

$$p_{N_2,t}/p_t = V_{N_2,t}/V_t$$

where P_t is the observed pressure and V_t the total measured volume at time t, while $V_{N_2,t}$ represents the volume of nitrogen as determined by actual analysis. But, from Table I, ($V_{N_2,t}/V_t$ and N_2/V are the same)

$$p_{N_2,t}/P_t = \frac{a}{b} \times \frac{\Delta P}{P_t}$$

and

$$P_{N_2,t} = \frac{a}{b} \times \Delta P$$

But

$$p_t = P_0 - P_{N_2} = P_0 - \frac{a}{b}\,\Delta P$$

Consequently

$$\ln \frac{P_0}{P_0 - a/b\ \Delta P} = Kt$$

In Fig. 1, a curve is plotted showing the relation between a/b and $\Delta P/P_0$ (see Table I) where the

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[13] Leermakers, THIS JOURNAL, **56**, 1537 (1934).

[14] *Cf.* Kolthoff and Furman, "Volumetric Analysis," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1929, pp. 450–452.

latter is indicated in per cent. The values of a/b, as taken from this curve, were used in plotting the rate curves in the three experiments illustrated in Fig. 2. It is seen that the initial portion of each curve follows a straight line, as may be expected, but that the rate later falls off. In experiment 28, where $P_0 = 13.5$ mm., this departure from linearity is evident sooner than in experiment 29, where $P_0 = 99.0$ mm. The values for K during the linear (initial) portions of the curves, as determined from Fig. 2 and similar plots, are summarized in Table IV.

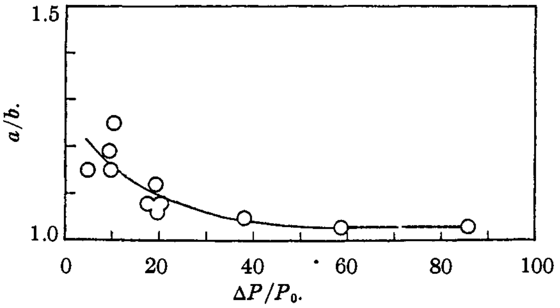

Fig. 1.—Relationship between a/b and $\Delta P/P_0$, the latter being expressed in per cent.

TABLE IV

Experiment	P_0	$K \times 10^3$
21	100.7	1.66
22	101.6	1.69
23	101.0	1.63
26	100.3	1.40
27	100.7	1.57
29	99.0	1.38
20	57.8	1.65
24	51.0	1.67
25	25.0	1.85
28	13.5	1.88

There appears to be a slight drift toward higher K values at lower initial pressures. This is in the direction which might be expected on the basis of relative probabilities of light absorption and confirms the measurements of Goldfinger.[15]

Discussion of Results

The analyses reported here are the first complete ones recorded in the literature of azomethane since those of Thiele,[16] who examined the products both of explosion and of complete decomposition in a hot tube.

The most significant feature to be observed at the outset is that the percentage of nitrogen in the yield of gases insoluble in acid, averages 54.7% regardless of the stage of reaction at which the analysis is made. This excess of nitrogen over that expected from a simple decomposition of azomethane suggests that azomethane may be removed from the system by some means other than decomposition to yield nitrogen. Hence the use of the amount of nitrogen as a measure of the azomethane disappearing may be invalid. Such an assumption was actually made in calculating the data in Table IV. Furthermore, the use of pressure change observed during reaction, as a measure of the azomethane decomposed, also requires further consideration.

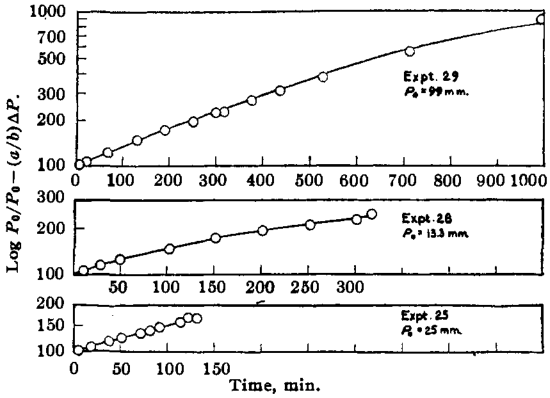

Fig. 2.—Rate of photolysis according to equation 1.

The simplest assumptions of the primary step in the decomposition appear to be either

$$CH_3N{=}NCH_3 + h\nu \longrightarrow C_2H_6 + N_2 \quad (1)$$

or

$$CH_3N{=}NCH_3 + h\nu \longrightarrow 2CH_3 + N_2 \quad (2)$$

the one yielding stable molecules of nitrogen and ethane by a rearrangement of the suitably activated azomethane; the other yielding free radicals by disruption of C–N bonds. Such a reaction as

$$CH_3N{=}NCH_3 + h\nu \longrightarrow CH_3 + N{=}NCH_3 \quad (3)$$

has little probability,[17] although not denied, it will not be further considered here, as the ultimate fate of the radical $NNCH_3$ would be pure conjecture. Furthermore, in the hydrolysis of azomethane Thiele[16] finds the principal products to be formaldehyde and methylhydrazine, which result would suggest a possible isomeric form of azomethane of the type $CH_2{=}N{-}NH{-}CH_3$. The decomposition of such an isomeric form might be expected to give readily a radical with an ability to confer definite basic properties

$$CH_2{=}N{-}NH{-}CH_3 + h\nu \longrightarrow CH_2N{-}NH + CH_3 \quad (4)$$

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[15] Goldfinger, *Compt. rend.*, **202**, 1502 (1936).

[16] Thiele, *Ber.*, **42**, 2575 (1909).

[17] *Cf.* Patat, *Naturwissenschaften*, **23**, 801 (1935).

TABLE V

COMPARISON OF ALKANE YIELD AND PRESSURE INCREASE

Expt.	P_0	V	V_{Alk}	V_0 (calcd.)	$V-V_{Alk}$	V_{Alk}/V_0, %	$V_{Alk}/(V-V_{Alk})$, %	$\Delta P/P_0$, %
22	101.6	141.4	5.6	135.9	135.8	4.1	4.1	4.9
16	99.8	143.3	13.6	133.2	129.7	10.2	10.0	10.1
19	100.6	148.0	12.0	134.5	136.0	8.9	8.8	9.4
26	100.3	144.6	11.8	134.1	132.8	8.8	8.9	9.8
27	100.7	160.1	25.3	134.5	134.3	18.8	18.8	20.1
29	99.0	252.8	113.5	132.2	139.3	86.0	81.5	85.8
20	57.8	89.9	12.4	77.3	77.5	16.0	16.0	17.8
24	51.0	79.7	11.0	68.2	68.7	16.1	16.0	19.2
30	49.7	78.7	11.8	66.5	66.9	17.7	17.6	19.6
25	25.0	45.6	11.2	33.4	34.4	33.5	32.6	38.0

The fate of the methyl radicals produced in any of the above reactions is likewise as doubtful as the primary step for azomethane. The simplest course would be the production of ethane. The possibility nevertheless exists of such a chain reaction as

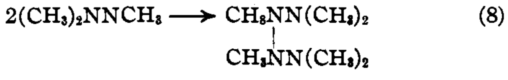
$$CH_3 + CH_3N{=}NCH_3 \longrightarrow C_2H_6 + N_2 + CH_3 \quad (5)$$

even though the work of previous investigators indicates its improbability. On the other hand, an addition of CH_3 to azomethane seems never to have been considered

$$CH_3 + CH_3N{=}NCH_3 \longrightarrow (CH_3)_2NNCH_3 \quad (6)$$

$$CH_3 + (CH_3)_2NNCH_3 \longrightarrow (CH_3)_2NN(CH_3)_2 \quad (7)$$

or



$$2(CH_3)_2NNCH_3 \longrightarrow \begin{array}{c} CH_3NN(CH_3)_2 \\ | \\ CH_3NN(CH_3)_2 \end{array} \quad (8)$$

The only definite statement that can be made is that the reaction may be much more complicated than has been assumed previously.

Of the above reactions, 8 is the only one which would involve a pressure decrease and does not appear highly probable. In the other reactions, the pressure either increases or is unchanged. It may be concluded therefore that the pressure increase occurring during the decomposition is due to the formation of alkane molecules. The data in Table V substantiate this.

P_0, V and ΔP have the significance previously indicated. V_{Alk} is the total volume of dry alkane gases as determined by analysis. V_0 is the initial volume of azomethane calculated to 760 mm. and 20° approximately the conditions at the time of the gas analysis. The correspondence between V_0, a calculated value, and $V-V_{Alk}$, a measured one, indicates that the pressure increase is to be accounted for by the alkane produced. It is, however, apparent that in some cases there is a discrepancy between the ratios in the last three columns, especially in the values of $\Delta P/P_0$. The only satisfactory explanation of this appears to lie in the doubtful accuracy of ΔP which, involving as it does a difference, frequently small relative to P_0, is correspondingly less accurate. This error, however, does not affect the validity of any of the calculations reported above.

Comparing now those cases of small decomposition, where $\Delta P/P_0$ is no greater than 20%, the nitrogen formed averages 55.3% while the alkane formed, calculated as ethane, averages 44.4%. Evidently some compound is produced during the reaction which has a higher carbon to nitrogen ratio than that in azomethane. Reaction 7 above presents such a possibility. Assuming that such a possibility requires free methyl radicals it would appear that out of five molecules of azomethane *decomposing* to give nitrogen, only four give alkane and hence *at least* one of them must have yielded methyl radicals.

Turning to the results in Table III on the photolysis of azomethane in presence of acetaldehyde, it is seen that for every two molecules of acetaldehyde precipitated (presumably as a polymer) 3.3 molecules of nitrogen were produced from the azomethane. If every methyl radical is assumed involved in the polymerization of two aldehyde molecules, it would appear that of every 6.6 molecules of azomethane decomposed, one decomposed yielding free methyl radicals.

It should be realized that the latter figure of one in 6.6 would tend to be a maximum ratio, while the former 1 in 5 is a minimum. The agreement is by no means perfect but is sufficiently significant to suggest that azomethane may not decompose entirely into nitrogen and free methyl radicals.

With regard to the possible existence of some compound formed with azomethane and methyl radicals, reference to Table I will show values of V_G, the volume of gas, assumed di-acid, calculated from the titration of the hydrochloric acid used in the first absorption pipet. As already stated the values are extremely variable since it was not at first realized that the hydrolysis of azomethane was rapid enough to cause interference. The values for the later experiments were obtained as rapidly as possible after the exit gases from the decompositions had been washed with the acid, the time of contact between the undecomposed azomethane and acid being as short as practicable. The results definitely indicate some basic material present. In experiments 28 and 29, corresponding to over 50 and 80% decomposition, the amount of this basic material is very small and the values of V_G may be due simply to azomethane hydrolysis. It should be noted further that in precisely these experiments the discrepancy between nitrogen and alkane produced is by no means as large as that discussed above for decompositions amounting to less than 20%. In experiment 29 the nitrogen value is 52% while the alkane calculated as ethane is approximately 51%. In addition to this evidence, is the formation of the deposit during photolysis at shorter wave lengths. The observation already mentioned that the deposit disappeared immediately on contact with air is in line with the known easy oxidation of many hydrazines.[18]

The belief that methyl radicals are without effect on azomethane rests largely on Leermakers' study of the simultaneous thermal decomposition of azomethane and lead tetraethyl.[4] Leermakers calls attention to the falling off in the rate constant for the decomposition of lead tetraethyl of some 25% at 260° in presence of azomethane. This is calculated from the over-all pressure change observed assuming the azomethane pressure change to be found in pure azomethane. No interpretation is offered of the falling off since Leermakers' primary object was to discover the presence of chains initiated by the ethyl radicals from the lead tetraethyl in the azomethane. Such chains would have caused a rising constant. An examination of his data at 275° shows a similar 10 to 15% falling off. The decrease in rate constant finds a ready explanation on the basis of one conclusion from this study, namely, that ethyl radicals could disappear by addition to azomethane whereas Leermakers assumes the ultimate fate of all the ethyls to be butane. Two possibilities, however, present themselves: either, all the lead tetraethyl decomposes into free radicals and only a part of them combine with azomethane, or, part of the lead tetraethyl decomposes to form butane directly. If the latter were true, it would be expected that the proportion of lead tetraethyl decomposing into radicals would be greater the higher the temperature and that therefore the greater would be the effect of azomethane. Actually, however, the effect of azomethane is less at 275 than at 260°. Hence it must be concluded that not all of the ethyl radicals react with azomethane at these temperatures. Such a result is not necessarily true at lower temperatures though it would appear reasonable to conclude that there also some of the methyl radicals may actually combine to give ethane and hence that our results do not prove decisively that azomethane does decompose to give nitrogen and ethane directly. Allen and Sickman[19] in studying the azomethane induced decomposition of acetaldehyde came to the conclusion that the chain length varied between 500 at 244.8° and 22 at 328.7°. If the conclusion be derived from our work that azomethane does not decompose exclusively by a free radical mechanism it appears that the calculated figures for the chain length may be considerably too low, since fewer but longer chains would not be required to explain the effects observed. This would be in line with Leermakers' estimate[13] of quantum yields of about 300 in acetaldehyde at 309.5°. In the latter case also, the chain length based upon free radical production would be higher than the figure given because it would be expected that during photolysis most of the acetaldehyde decomposes by a rearrangement mechanism.[20] It now appears that in many of those reactions where clear-cut rupture into free radicals or alternatively clear-cut rearrangement to form stable molecules was thought to be occurring, actually both processes might have been taking place. Formic acid dissociates into stable molecules[21] but acetic acid apparently gives both stable molecules[22] and free radicals.[11] Formaldehyde gives stable molecules[23]; acetaldehyde apparently dissociates in

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[18] Taylor and Ditman, *J. Chem. Phys.*, **4**, 214 (1936).

[19] Allen and Sickman, THIS JOURNAL, **56**, 2031 (1934).

[20] Blacet and Roof, *ibid.*, **58**, 278 (1936); Rollefson, *J. Phys. Chem.*, **41**, 259 (1937); Burton, *ibid.*, **41**, 322 (1937).

[21] Gorin and H. S. Taylor, THIS JOURNAL, **56**, 2042 (1934); Burton, *ibid.*, **58**, 1655 (1936).

[22] Farkas and Wansbrough-Jones, *Z. physik. Chem.*, **B18**, 124 (1932).

[23] Locker and Patat, *ibid.*, **B27**, 431 (1934).

both ways.[20] The results of this work indicate that azomethane may resemble acetaldehyde and acetic acid in its tendency to suffer both rupture and rearrangement.

Forbes, Heidt and Sickman[2] showed that the quantum yield of decomposition of azomethane (based upon pressure measurements) approached a value of unity at low pressures (*i. e.*, in the neighborhood of 100 mm.) and apparently decreased both at longer wave lengths (about 3660 Å.) and with increasing pressure. Their measurements appear to have been made on only three or four different samples of azomethane; several runs at different wave lengths and successively decreasing partial pressures of azomethane were made with the same sample. Our results would indicate that the partial pressures of azomethane as calculated by them were too high and that a correction should be made for azomethane disappearing in an association reaction with methyl. This would tend to bring up the quantum yields. Whether it would bring the quantum yields up to unity we do not know; however, there is not very much concordance between their various results. The quantum yields as reported by them do decrease with successive runs on the same sample and our results indicate the reason why. Also, our work indicates a deposit of some product even at >3500 Å.; perhaps it is the formation of such a product which might account for the extremely low quantum yields they report in certain runs.

In conclusion, some mention should be made of our results both at low temperatures and in protracted runs. In both cases (experiment 31 at −22.5° and experiments 28 and 29 for long runs) it may be seen in Tables I and II that the propane yields (as idealized from the *n* values) are high. The explanation in the long runs is that the methyl radicals combine with some of the products to form the higher carbon compounds. In no case is there a simple replacement reaction such as

$$CH_3 + C_2H_6 \longrightarrow C_3H_8 + H \qquad (10)$$

for no hydrogen has been found in the analyses. To be sure, the reaction

$$CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5 \qquad (11)$$

followed by

$$CH_3 + C_2H_5 \longrightarrow C_3H_8 \qquad (12)$$

or

$$2C_2H_5 \longrightarrow C_4H_{10} \qquad (13)$$

would account for the result. However, such considerations lie entirely in the realm of conjecture. Suffice it to say that the probability of that general type of reaction increases as the relative concentration of azomethane decreases.

Similarly, as the temperature is lowered, the probability of methyl radical adding on to azomethane by such a reaction as 7 decreases. Reactions such as 12 and 13 would then be favored; the analysis of Table II is in agreement with such an hypothesis.

Conclusion.—Methods heretofore used depending exclusively on pressure measurement for the calculation of the amount of azomethane decomposed photolytically have been in error. There is a greater amount of azomethane decomposed than is represented by the pressure increase. The amount of nitrogen formed for small decompositions exceeds the hydrocarbons produced. The evidence appears to indicate that azomethane decomposes by a rearrangement mechanism as well as by rupture into free radicals, which latter has hitherto been thought to be the exclusive path.

Summary

1. The results of a number of analyses of the products of the photolysis of azomethane have been reported.

2. In general, the amount of nitrogen produced exceeds the amount of hydrocarbon gas. The amount of higher hydrocarbon produced (expressed as propane) increases with degree of decomposition and at reduced temperatures. No hydrogen and but a small smount of unsaturated hydrocarbons are produced.

3. The results of some preliminary work with azomethane photolyzed in the presence of acetaldehyde are also reported. This work is being continued.

4. The results obtained are consistent with an hypothesis that azomethane does not decompose exclusively by rupture but that it may also decompose by a rearrangement mechanism to form stable molecules.

5. The hypothesis that some of the free methyl radicals formed react with azomethane to form an addition compound is consistent both with the results reported here and with the results of previous investigators.

6. The rates of the photolyses are in approximate agreement with what might be expected from the hypotheses offered as to the mechanism of the reactions.

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