2. During the rearrangement of the catechol esters small amounts of 3-acylcatechols are formed.
3. The 4-acylcatechols may be converted into the corresponding alkylcatechols.
4. The alkylcatechols are effective germicides. The phenol coefficient increases with the length of the alkyl chain.

GLENOLDEN, PENNA. RECEIVED AUGUST 10, 1937

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

The Photolysis of Azomethane. III. The Effect of Nitric Oxide and the Nature of the Primary Step[1,2]

BY THOMAS W. DAVIS, FRANCIS P. JAHN AND MILTON BURTON[3]

Hitherto it has been tacitly assumed[4] that azomethane decomposes almost entirely to form free methyl radicals and molecular nitrogen in one primary act. Patat and Sachsse,[5a] among others, have considered the possibility of a primary step yielding $N{=}NCH_3$ and CH_3. The $N{=}NCH_3$ radical has been assumed to be very unstable;[4a,5,6] although Patat and Sachsse[5a] have indicated the implications of an assumed stability, Patat[5b] has been inclined in favor of the assumption of the initial split into free radicals. In general, however, there has been no evidence for a valid conclusion as to the relative probabilities of the paths

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

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

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

Inasmuch as azomethane has been used as a source of free methyl radicals in estimating chain lengths,[4c] it is evidently important to have information as to the primary step.

Burton, Davis and Taylor[6,7] have shown that methyl radicals formed in the photolysis of azomethane do not disappear exclusively by the reaction

$$2CH_3 + M \longrightarrow C_2H_6 + M \qquad (15)$$

but that some probably disappear by an association reaction of the type

$$CH_3 + A \longrightarrow CH_3A \qquad (6)$$

where A is used to symbolize a molecule of azomethane. The product is itself a free radical.[8] The results obtained were consistent with the hypothesis that part of the primary step might be represented by reaction 1 as well as by reaction 2. Unfortunately, the evidence on this point was not conclusive.

One of us[9] discovered in a study of the pyrolysis of azomethane that nitric oxide almost completely inhibits any pressure change in the early stages of the reaction. Although such an observation is not directly interpretable[10] the result suggested the possibility of making use of a similar method for a direct determination of the nature of the primary reaction in the photolysis.[11]

Staveley and Hinshelwood[12] have made use of the assumption that nitric oxide reacts very rapidly with free radicals in order to detect the participation of radicals in reaction chains. In the work described below we have made use of the same assumption in determining the nature of the primary step in the photolysis of azomethane. Although we have attempted to avoid the pitfalls involved in kinetic studies dependent on pressure changes by studying the products of the photolyses analytically, it must be emphasized that our conclusions are based upon the assumption that

(1) Abstract from a thesis to be submitted by Francis P. Jahn to the Graduate School of New York University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Presented before the Division of Physical and Inorganic Chemistry at the Rochester Meeting of the American Chemical Society, Sept. 6, 1937.

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(4) *Cf.* (a) F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935, p. 140; (b) O. K. Rice and Sickman, *J. Chem. Phys.*, **4**, 242 (1936); (c) Allen and Sickman, THIS JOURNAL, **56**, 2031 (1934).

(5) (a) Patat and Sachsse, *Z. physik. Chem.*, **B31**, 105 (1935); (b) Patat, *Naturwissenschaften*, **23**, 801 (1935); *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, Fachgruppen II, [N. F.] **2**, 77 (1936).

(6) Burton, Davis and Taylor, THIS JOURNAL, **59**, 1038 (1937).

(7) Burton, Davis and Taylor, *ibid.*, **59**, 1989 (1937).

(8) The comparatively low probability of reaction 15 is well illustrated in the work on the alkyl halides (*cf.* Bonhoeffer and Harteck, "Grundlagen der Photochemie," Verlag von Theodor Steinkopff, Dresden, 1933, p. 172) and in the work on acetone [Spence and Wild, *J. Chem. Soc.*, 352 (1937)]. In the former case the yield of ethane is negligible; in the latter, analyses show that there is a high probability that methyl disappears by other reactions, particularly at low temperatures (~20°).

(9) Jahn, unpublished work.

(10) The work cited in references 6 and 7 indicates that failure to observe a pressure increase may be due to a multifold effect involving reactions such as 1, 2, 6, 16 and 18. *Cf.* Riblett and Rubin, THIS JOURNAL, **59**, 1537 (1937).

(11) *Cf.* (a) Linnett and Thompson, *Trans. Faraday Soc.*, **33**, 501 (1937); (b) Thompson and Linnett, *ibid.*, **33**, 874 (1937).

(12) Staveley and Hinshelwood, *Proc. Roy. Soc.* (London) **A154**, 335 (1936); *Nature*, **137**, 29 (1936); *J. Chem. Soc.*, 812 (1936).

nitric oxide reacts only with free radicals in the system studied.

Our results indicate that azomethane decomposes almost exclusively by reaction 2, that reaction 6 takes place quite readily and that ethane formed in the photolysis of azomethane probably does not result from reaction 15.

Experimental Method

The procedure employed was similar to that described by Burton, Davis and Taylor.[6,7]

Azomethane.—The method of preparation of azomethane was slightly modified. On theoretical grounds it appeared advisable to add the usual potassium chromate solution to the iced solution of dimethylhydrazine hydrochloride. It seemed to us that in this way the danger of formation of higher products of oxidation (*e. g.*, methyl nitrate) and the danger of explosion[13] both would be reduced and that the yield of azomethane would be correspondingly increased. We have found that the sole advantage of this procedure is that foaming is prevented until all the dimethylhydrazine hydrochloride has reacted. The yield is, as a matter of fact, reduced and a difficulty arises through the formation of a large quantity of low-boiling impurity (perhaps methyl nitrite) which is not removed conveniently. Our procedure has been to use the method of purification already described[6] and finally to use only the last fractions of evaporation of the condensed liquid. Samples so prepared had a v. p. of ~752 mm. at 0° and were considered satisfactory for use.

Nitric Oxide.—Nitric oxide was prepared by dropping mercury into a 25% solution of nitrosylsulfuric acid in sulfuric acid, prepared according to the method described by Biltz and Biltz.[14] Precautions were taken to remove residual air by repeated evacuation of the acid and by flushing out the system with nitric oxide before a sample was considered satisfactory for use.

Analytical Method.—The analytical method was modified to ensure the removal of residual nitric oxide preliminary to a determination of the reaction products. This usually was done by the introduction of oxygen before treatment of the product gases (as already described[6]) with bromine and potassium hydroxide. No effect was ever observed on subsequent absorption in potassium hydroxide; the oxygen added was removed quantitatively by chromous chloride and pyrogallol treatments.[6] Evidently any residual nitric oxide was always removed by the analytical treatment before this point of the procedure.

Procedure and Results.—The general procedure of the runs was similar to that already described.[6,7] The reaction vessel was opened to the nitric oxide reservoir and filled to the desired pressure. It was then shut off from the reservoir and the intermediate tubing was exhausted. Azomethane was then introduced slowly through a very slightly opened stopcock until the desired pressure was attained. In preliminary experiments it was established that in a few minutes the mixing was sufficient to yield the same results as after several hours of standing. The usual time was about five minutes.

In the work around 20° we used a water thermostat with filter and at higher temperatures an air thermostat with filter, the same as those already described. The Corning No. 534 blue nultra filter, transmitting only wave lengths longer than 3500 Å., was used in all the experiments except one. In experiment 19, as indicated in Table I, no filter was used. The thickness of Pyrex glass in that experiment transmits down to >2900 Å.

The runs were started by exposing the reaction vessel to the light from the constricted mercury arc[15] and stopped by interrupting the arc. The current in the arc was held at ~4.2 amperes during runs. Since the arc was not kept perfectly steady and since the arc distance in the 20° runs was much less than in the higher temperature experiments, no direct comparison of the precise slopes of the rate curves can be made. The general shapes of the curves, however, are interesting and will be discussed later.

The samples of gas were removed for analysis immediately after the conclusion of the runs and treated as previously described. The results of the analyses are summarized in Table I and the graphs of four typical runs are shown in Fig. 1, in which ΔP is the pressure change observed at any time.

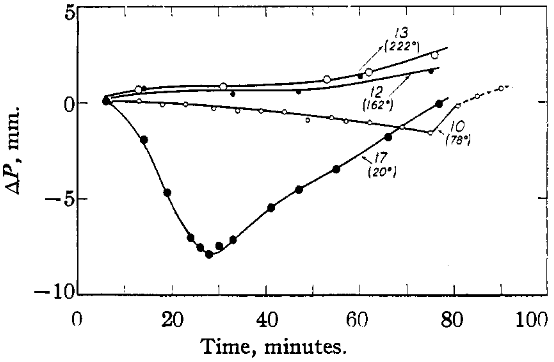

Fig. 1.—The course of pressure change in several experiments; the dotted portion of the curve for expt. 10 represents the pressure change after illumination had ceased.

In the table, P_{NO} is the initial pressure of nitric oxide, expressed in mm.; P_{azo}, the initial pressure of azomethane; P_o, the initial total pressure; P_m, the minimum pressure attained during the experiment (when a minimum is actually observed); P_f, the final pressure; ΔP_m, the pressure change at minimum pressure (*i. e.*, $P_m - P_o$). $V_{calcd.}$ is the total calculated volume of gas, corresponding to P_f as given in the table, reduced to 0° and 760 mm. and expressed in cc.; $V_{obsd.}$ is the actually observed volume reduced to the same conditions; V_u is the volume under the same conditions of the dry undissolved product gases after bubbling through acid and alkaline solutions as already described. The significance of $\Delta P_m/P_{NO}$ is obvious. N_2/NO represents the ratio of volume of dry nitrogen produced to volume of nitric oxide originally present, the latter being calculated to the conditions of

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[13] *Cf.* Jahn, THIS JOURNAL, **59**, 1761 (1937).

[14] H. Biltz and W. Biltz "Laboratory Methods of Inorganic Chemistry," translated by Hall and Blanchard, John Wiley and Sons, Inc., New York, 1909, p. 204.

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

TABLE I

SUMMARY OF ANALYTICAL RESULTS[a]

Experiment	18[c]	16	17	19[d]	14	10[e]	11	12	13
Temp., °C.	20	20	20	20	20	78	78	162	222
P_{NO}	10.1	9.9	10.2	10.0	13.3	13.4	20.5	13.6	13.3
P_{azo}	39.7	100.5	102.2	102.9	74.8	97.7	103.3	103.5	105.1
P_o	49.8	110.4	112.4	112.9	88.1	111.1	123.8	117.1	118.4
P_m	41.7	102.0	104.5	106.8	77.3	109.5	...	...	...
P_f	42.7	103.9	112.3	107.0	77.6	111.8	120.0	118.7	120.8
$-\Delta P_m$	8.1	8.4	7.9	6.1	10.8	1.6	...	...	...
CH_4, %	0.7	0	3.7	4.8	0	0	0	0	3.7
C_2H_6, %	11.8	1.9	28.4	8.3	0.8	?	0.9	2.9	2.7
C_3H_8, %	0.9	4.7	0.5	0	1.3	0	.6	0.5	0
N_2, %	86.9	93.8	67.5	86.7	97.8	97.3	98.3	96.5	93.7
Total	100.3	100.4	100.1	99.8	99.9	...	99.8	99.9	100.1
M or D[b]	D	D	D	D	M	M	D	D	D
$V_{calcd.}$	53.2	129.3	140.0	133.2	95.9	116.2	124.8	99.5	89.0
$V_{obsd.}$	52.7	131.3	141.7	133.8	96.7	106.7	117.5	92.3	82.5
V_u	9.2	9.5	29.1	10.4	10.0	11.2	10.0	8.8	8.5
$-\Delta P_m/P_{NO} \times 10^2$	80	85	77	61	81	12	...	...	...
$N_2/NO \times 10^2$	64	72	152	83	59	78	46	74	80
$(N_2/NO)_m \times 10^2$	58	63	64	81	58	...	...	...	...

[a] The percentages are on the basis of gas not soluble in hydrochloric acid or stannous chloride. All symbols are explained under *Procedure and Results.* [b] N_2 by actual measurement = M; by difference = D. [c] In expt. 18 the products were heated for thirty-five minutes at 100°. The pressure at 20° after this heating was 51.3 mm. corresponding to $V_{calcd.}$, 64 cc. [d] Expt. 19 was conducted with unfiltered light. [e] In expt. 10 the pressure continued to increase after the arc was extinguished; P_f given is the last observed value before removal of the gas for analysis. P_f at the conclusion of illumination was actually 110.9 mm. corresponding to $V_{calcd.}$, 115.3 cc.

measurement of the volume of nitrogen. $(N_2/NO)_m$ is the ratio (calculated from the data) at the time when the pressure was a minimum. This was done simply by making the rough assumption that practically no alkane gas was produced before minimum pressure was attained. From the volume of alkane gas given off in the run the volume of nitrogen produced after attainment of the minimum was calculated on the basis of previously published data.[6] The general validity of the method is shown by the fairly good agreement of experiments 14, 16, and 17. The much higher value of $(N_2/NO)_m$ in experiment 19, conducted with unfiltered light, is presumably real.

Attention should be called to the fact that, although there was no indication of the formation of any solid or liquid product at 78° and above, deposition of some product took place at 20°. The amount of such deposition was almost imperceptible; however, when no filter was employed a fog appeared almost immediately during the photolysis. After the completion of this last experiment, the residue formed by the fog was examined. When the reaction vessel was opened to the air the residue appeared to diminish in amount; on examination under a hand lens it appeared to be made of many fine droplets of colorless liquid. The flask was set over a dry-ice container in order to draw the liquid into a drop which might be examined. After six hours of this treatment the residue had taken the form of a film and now appeared brown, oily and viscous. The vapors were tested before this treatment and found not alkaline—the odor was that of azomethane without olfactory evidence of formaldehyde. After the six-hour period the odor was practically imperceptible. Some of the residue was swabbed up on a piece of filter paper; a qualitative nitrogen test run by Mr. Werner H. Bromund was positive.

It also should be mentioned that a white deposit appeared in the Töpler pump and traps in the early experiments and increased in amount as the investigation proceeded. When this deposit was exposed to the air no change was observed.

Discussion

The Nature of the RNO Compounds.—The normal course of the photolysis of azomethane involves a pressure increase.[6] Table I shows that when nitric oxide is present at 20° a pressure decrease occurs. The usual assumption[11,12] is that a reaction takes place between nitric oxide and any free radical, although there is as yet no definite information in the literature as to the precise nature of the compounds. The conclusions to be derived concerning the mechanism depend largely on what we may say concerning the volatility of these RNO compounds.

There are at least three possible reactions by which nitric oxide may disappear from the reaction mixture. Considering what we know of the photolysis of azomethane, none of the following appear utterly improbable.

$$CH_3 + NO \longrightarrow CH_3NO \qquad (16)$$
$$CH_3N{=}N + NO \longrightarrow CH_3N{=}NNO \qquad (17)$$
$$CH_3A + NO \longrightarrow CH_3ANO \qquad (18)$$

It should be noted that there is no attempt to elucidate the nature of these products. CH_3NO is isomeric with formaldoxime, b. p. 84°, and with formamide, b. p. 210.7°. Whether an RNO product formed actually isomerizes to one of these compounds cannot be stated. However, the known properties of nitroso compounds[16a] would indicate a ready isomerization of CH_3NO to $CH_2{=}NOH$ although the reverse reaction would not be expected to occur. There is also the possibility of formation of a polymer; formaldoxime forms a termolecular polymer with great ease.[16b]

A satisfactory interpretation of the work of Thompson and Linnett,[11b] who studied the photolysis of a mixture of mercury dimethyl and nitric oxide, requires that CH_3NO be formed and that it or its isomer subsequently precipitated. Furthermore, the CH_3NO or its isomer must have been stable to light of $\sim$2537 Å. As to the properties of the other hypothetical products shown in reactions 17 and 18, we are without definite information.

The Stability of the Products.—It has been mentioned that when the reaction mixture was permitted to stand after the completion of experiment 10 at 78°, the pressure slowly increased, indicating the decomposition of one of the products of the reaction. No such effect was noted at 20°, indicating the stability of the products at that temperature. When, as in experiment 18, the products were heated to $>100°$ for thirty-five minutes and allowed to cool to the original temperature, a distinct pressure increase was noted. In fact, the pressure attained was higher than the initial pressure. However, the volume of gas as measured over mercury corresponded not to that pressure but to the pressure immediately after the completion of the photolysis and before the heating operation. Obviously, most of the products formed by decomposition were condensed out in the Töpler pump.[17] The depolymerization of condensed RNO compounds would account for most of this result. The RNO molecule itself apparently decomposes but slightly, if at all; the total volume of alkane gas in this experiment was 1.2 cc. The significance of the values for N_2/NO and $(N_2/NO)_m$ will be discussed later.

The Effect of Wave Length.—Apparently, whatever the products are, they are stable (apart from possible polymerization) to light of 3500 Å. This may be concluded particularly from experiment 17 which was continued past the point of minimum pressure until the pressure had returned to approximately its original value. Burton, Davis and Taylor[6] have indicated that in the initial stages of the photolysis of azomethane, at the approximate temperature and pressure of experiment 17, the ratio of nitrogen to carbon atoms in the product is $\sim$1.25, when only the insoluble products are considered. When the amount of nitrogen formed after minimum pressure is calculated on this basis and the value of $(N_2/NO)_m$ is calculated from the result, it is found that the value so obtained agrees very well with similar ones for experiments 14 and 16. It should be noted that the agreement between $V_{\text{calcd.}}$ and $V_{\text{obsd.}}$ in this experiment is good, indicating that no condensation of products took place during compression prior to analysis. Consequently, it appears that any RNO product formed during the process of pressure decrease is not decomposing or dissociating (or otherwise interfering with the normal course of the photolysis) during the period of pressure increase, when presumably all the nitric oxide has been used up, and that the RNO compounds are stable at 3500 Å. This is not surprising in view of the results of Thompson and Linnett.[11b]

It is more difficult to explain the results with unfiltered light. Burton, Davis and Taylor[6] have already shown that the use of unfiltered light is practically without effect on the nitrogen yield in the photolysis of pure azomethane. In experiment 19 the nitrogen yield was much higher, although $-\Delta P_m$ was smaller, than in the experiments with filtered light at 20°; evidently, the result is traceable to the effect of nitric oxide. The same phenomenon is probably responsible for both observations; *e. g.*, the formation of an RNO product causes pressure decrease, the decomposition of such a product (or dissociation of its polymer) causes a pressure increase. Light of wave length between 3500 and 2900 Å. is apparently sufficient to effect such a decomposition and thus to cause the pressure decrease to be less than would be the case with filtered light. This is not contradictory to the results of Thompson and Linnett;[11b] it merely indicates that it is probably a different RNO compound with which we are

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[16] Sidgwick, Taylor and Baker, "The Organic Chemistry of Nitrogen Compounds," Oxford University Press, Oxford, 1937, (a) pp. 169, 204, (b) p. 172, (c) p. 167.

[17] It should be noted that all the analyses were conducted at about 30°.

dealing in this case. Inasmuch as nitrogen appears to be produced in this photodecomposition it seems likely that the compound is either $CH_3N{=}NNO$ or $(CH_3)_2NNCH_3NO$. $-\Delta P_m$ in this experiment was 6.1 mm.; in other similar experiments at 20° the average value of $-\Delta P_m$ was 8.1 mm. If we assume that the difference of 2 mm. is caused by the formation of nitrogen as a result of RNO decomposition, we could calculate an "ideal" value of $(N_2/NO)_m$, not including the amount of nitrogen so formed, of 0.60. This is slightly below the value of 0.63 for experiments 16 and 17 and indicates that part of the 2 mm. difference is probably attributable to the formation of some alkane gas, but a smaller amount than is usually associated with the formation of nitrogen.[18] If, instead of calculating on the basis of the $-\Delta P_m$ variation, the figure for $(N_2/NO)_m$ had been computed on the basis of the usual nitrogen–carbon ratio,[6] as was done in experiment 17, then the value would have been ~0.69, which is much higher than the usual average. There consequently appears to be little doubt that the excess nitrogen originates in an RNO compound and not in azomethane itself. Judging from the work of Thompson and Linnett, this cannot be CH_3NO. It will be shown below, in the discussion of the path of reaction, that the formation of CH_3NNNO is improbable. It may therefore be inferred that CH_3ANO is the RNO compound involved.

The Effect of Concentration.—In experiments 18, 16, 17 and 14 at 20° the ratios of the initial concentrations of nitric oxide and azomethane were varied. The greater the P_{NO}/P_{azo} ratio, the greater would be the chance of reaction 16 occurring before reaction 6. It is evident from Table I that the values of $(N_2/NO)_m$ decrease slightly with increase of P_{NO}/P_{azo}.[19] Inasmuch as the nitric oxide : azomethane ratio decreases during the photolysis a great variation in $(N_2/NO)_m$ could not be expected. The significance of the variation is discussed later.

The Effect of Temperature.—It has been shown above that increase of temperature is probably effective in dissociating an RNO polymer but that it seems to have but a slight further effect in decomposing the RNO molecule itself. It was noted in experiment 18 that the observed increase in pressure at 20°, after heating the products of the photolysis, was unrelated to the volume as measured over mercury. It was assumed consequently that the RNO, dissociated from the polymer, reprecipitated at atmospheric pressures. Obviously the decrease of volume noted in this way should not exceed the initial volume of nitric oxide, V_{NO}, corrected to 0° and 760 mm. In Table II the differences in the calculated and observed volumes are compared with V_{NO} for five experiments. It is clear that in none of the experiments did $V_{calcd.} - V_{obsd.}$ approach the maximum allowable according to this hypothesis. The nearest approach was in the case of experiment 18 where the products were heated after the completion of the photolysis.

TABLE II

CORRELATION OF VOLUME DATA

Expt.	18[a]	10	11	12	13
Temp., °C.	....	78	78	163	222
$V_{calcd.} - V_{obsd.}$	11.3	9.5	7.3	7.2	6.5
V_{NO}	12.6	14.0	21.3	11.4	9.8

[a] The value of $V_{calcd.}$ used in expt. 18 is that corresponding to a pressure of 51.3 mm. See Table I, note *c*.

It may be noted from Table I that increase of temperature is without considerable effect on the nature of the products. The comparison is best made among experiments 14, 11, 12 and 13, covering the range 20–222°. In experiment 14 the minimum point was just passed at the completion of the run; *i. e.*, the nitric oxide was just consumed. In the other experiments the time of the run was presumably insufficient to consume all the nitric oxide. It may be seen that at the lower temperatures practically no alkane is produced as long as any nitric oxide may be presumed to be present. The amount of alkane produced, although small, increased steadily at 168 and 222°.

Referring to Fig. 1, it may be seen that at the lower temperature (20°) there is a rapid decrease of pressure in the initial stages. At higher temperatures (78°) this rate decreases. At 163° the initial pressure increase may be due to a slight Draper effect; however, there is a small but definite pressure increase throughout the run. At 222° the rate of pressure increase is somewhat greater.

The Path of the Reaction. *Path 1.*—The failure to observe an appreciable amount of alkane

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(18) It can be shown by a simple calculation that in order for the "ideal" value for $(N_2/NO)_m$ to be 0.63, the ratio of nitrogen and carbon atoms in the gas produced in the decomposition of the R-NO compound would have to be ~5.25.

(19) In experiment 18 $(N_2/NO)_m$ was calculated on the assumption that all the nitrogen originated during the photolysis; the amount produced during the period of pressure increase was then calculated on the basis of the data of Burton, Davis and Taylor[6] and the value for $(N_2/NO)_m$ determined to be 0.58. Had it been calculated on assumptions similar to those involved in the similar calculation of experiment 19 (see above), it would have been found to be ~0.51. Evidently, the value of 0.58 is a maximum estimate.

gas in the early stages of the photolysis definitely excludes reaction 1 as a possible primary process.

Path 2.—Assume CH_3NO completely involatile or polymerized to an involatile compound, as seems more likely. If the path of the photolysis and subsequent steps be exclusively by reactions 2 and 16, a decrease of pressure would be observed. $-\Delta P_m$ would exactly equal P_{NO}. If the photolysis be continued for exactly the time required to consume all the nitric oxide, then N_2/NO should be 0.5. Neither the effect of temperature on pressure change nor the magnitude of the N_2/NO ratios is consistent with the hypothesis that this path constitutes the exclusive mechanism.

Path 3. *a*.—If the path were by reactions 3, 16 and 17 there would be no nitrogen produced. This is contrary to the observations. The possibility that the paths 2 and 3 occur simultaneously is immediately ruled out by the fact that the N_2/NO ratios observed greatly exceed any value expected on the basis of this assumption.

b.—The assumption that the CH_3NNNO formed in reaction 17 subsequently decomposes,

$$CH_3NNNO \longrightarrow CH_3NO + N_2 \qquad (17a)$$

yielding nitrogen, is by itself inadequate to explain the results obtained. The assumption of immediate decomposition (*i. e.*, merely momentary existence) of CH_3NNNO is formally equivalent to path 2. Thus, if path 2 (as will appear later) is an adequate representation of part of the reaction, path 3*b* may likewise be. Since nothing is known of the properties of the hypothetical CH_3NNNO, there can be no definite conclusion on this point.

c.—There is the possibility that CH_3NNNO is not formed at all but that an alternative reaction occurs

$$CH_3NN + NO \longrightarrow CH_3NO + N_2 \qquad (17b)$$

This path also is formally equivalent to path 2. It is quite evident that it cannot be said that reaction 3 does not occur. It can only be stated that, if it does, the subsequent reactions are such as to conceal that fact.

Path 4. *a*.—Assume CH_3ANO to be volatile. The path by way of reactions 2, 6, 18 and

$$CH_3ANO \longrightarrow N_2 + (CH_3)_3NO \qquad (19)$$

with the rate of the last reaction dependent on temperature, is inadmissible. Experiment 18, when compared with the other experiments at 20°, clearly shows that if CH_3ANO is formed it certainly does not undergo reaction 19 at 100° to any measurable extent.

b.—Assume CH_3ANO to be volatile. If the path be by way of reactions 2 and 6 followed alternatively by 18 or the competing reaction

$$CH_3A + NO \longrightarrow N_2 + (CH_3)_3NO \qquad (18a)$$

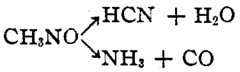
the pressure changes and the $N_{2,t}/NO$ ratio (where $N_{2,t}$ represents the volume of nitrogen produced in the time required to consume all the nitric oxide) would be related to the temperature. If it be assumed that the energy of activation of reaction 18a is higher than that of 18, low temperatures favor 18 and high temperatures favor 18a. At sufficiently low temperatures, the $N_{2,t}/NO$ ratio would be 0.5 and the maximum pressure decrease would equal P_{NO}. As the temperature is raised, reaction 18a would become more rapid; the yield of nitrogen would increase so that $N_{2,t}/NO$ becomes greater than 0.5. Simultaneously, the ratio $-\Delta P_m/P_{NO}$ would decrease to a value less than 1.0. At a sufficiently high temperature all the CH_3A may react according to reaction 18a. However, at such a temperature reaction 20 would also be expected.[16c]

$$(CH_3)_3NO \longrightarrow HCHO + (CH_3)_2NH \qquad (20)$$

Thus, at high temperatures $N_{2,t}/NO$ may approach 1.5 and the pressure would actually increase an amount equal to P_{NO} in the same time. At intermediate temperatures (assuming equal probabilities of reactions 18 and 18a), $N_{2,t}/NO$ would be 1.0 and there would be no initial pressure change. At 163 and 222° the pressure increases while N_2/NO is still less than 1.0. This path cannot, therefore, be the exclusive mechanism.

c.—Assume CH_3ANO to be involatile. As before, the $N_{2,t}/NO$ ratio would be 0.5 at very low temperatures. $\Delta P_m/P_{NO}$ would then be -2.0. However, at high temperatures the behavior would be similar to that of path 4b. At an intermediate temperature corresponding to $N_{2,t}/NO = 1.0$ there would be a pressure decrease unless the CH_3ANO volatilized, which case has been considered above as path 4b. Thus 4c cannot be the exclusive mechanism.

Combination: Paths 2, 4b and 4c.—The assumption here is that azomethane decomposes exclusively by reaction 2 and that the methyl radicals may then disappear via reactions 6 and 16 forming CH_3A and CH_3NO. The former would react via 18 or 18a to give CH_3ANO or N_2 and $(CH_3)_3NO$. CH_3NO probably polymerizes during the photolysis as already mentioned; at the higher temperatures the polymer probably dissociates, possibly forming formaldoxime which would be volatile and might itself dissociate to some extent.[11b,20]



$$CH_3NO \begin{cases} \rightarrow HCN + H_2O \\ \rightarrow NH_3 + CO \end{cases} \qquad (21)$$

As for CH_3ANO it may or may not be volatile at room temperature. Evidently, there are not enough data with which to decide the precise course of the reaction steps, particularly since the fate of the RNO products can only be roughly surmised.

Combination Including Path 3.—The substitution of path 3a for path 2 in the above combination would result in a nitrogen deficiency unless we assume at the same time a high probability of reaction 18a in comparison with reaction 18. However, this seems unlikely if reaction 17 is faster than 17b, as it would have to be were path 3a to occur. It thus appears that, if any of the reaction is by path 3a, it is but a very small fraction. On the other hand, paths 3b or 3c may be substituted for path 2 in the above combination without adding any new hypotheses or conclusions; no difficulties are introduced and none are explained. The assumption of such paths may be correct but it is not necessary.

It seems that the most reasonable assumptions as to the course of the reaction are:

1. Reaction 1 occurs to a very limited extent if at all.
2. Reaction 2 does occur. If reaction 3 takes place at all it is either followed so rapidly and so inevitably by reaction 22

$$CH_3NN \longrightarrow CH_3 + N_2 \qquad (22)$$

or so well masked by subsequent reactions that it cannot be distinguished from reaction 2.

3. Methyl radicals disappear either by reaction 16 or by reaction 6 followed by 18 or 18a. The relative amounts of the reactions 16 and 6 and the ultimate fate of the products cannot be determined with the data at hand.

It should be noted that the variation of $(N_2/NO)_m$ with concentration is in agreement with this type of path. Evidently, the greater the relative amount of nitric oxide, the greater the probability of reaction 16 in comparison with reactions 6 and 18 or 18a. This would decrease the amount of nitrogen produced by reaction 18a, in line with the results reported.

The Source of Ethane in the Photolysis of Azomethane.—The experiments of Burton, Davis and Taylor[6] at 20° indicate that one out of every five methyl radicals formed in the primary step of the photolysis of azomethane disappears permanently through the step 6. The other four radicals ultimately appear as ethane molecules. The ethane cannot be formed by step 15 for, although no ethane is formed in the presence of nitric oxide, reaction 6 appears to take place nevertheless and is evidently a much faster reaction than 15. The production of ethane in such large quantities in the photolysis of pure azomethane must therefore be attributed to some subsequent reaction of the radical CH_3A or a compound formed from that radical. Such an assumption might also account for the production of methane and propane already reported.[6,7]

Effect of the NO Product on the Course of the Photolysis.—In considering the effect of wave length it has been shown that the product formed with nitric oxide does not interfere with the normal course of the photolysis. Consequently, the conclusions at which we arrive, based on the assumption that nitric oxide (and not any RNO compound) alone reacts with the products of the photolysis of azomethane, are not unreasonable.

Conclusion.—Work of previous investigators founded on the assumption that azomethane decomposes almost exclusively into free methyl radicals and molecular nitrogen appears to be justified by our photochemical results. There is a possibility, however, that their calculations may be somewhat distorted because of the fact that methyl radicals appear to combine rather readily with azomethane molecules. Complex molecules so formed appear to be the source of ethane and other alkane gas noted in the photolysis of azomethane. It seems likely that practically no ethane is produced by the direct combination of methyl radicals formed during the photolysis of azomethane.

Summary

1. Analyses are reported of the products formed by the photolysis of azomethane in the presence of nitric oxide.
2. When nitric oxide is present during the photolysis of azomethane, practically no alkane gas is produced.
3. The photolysis of azomethane seems to proceed almost exclusively by a path involving the formation of free methyl radicals and nitrogen molecules in the primary act.

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(20) Dunstan and Bossi, *J. Chem. Soc.*, **73**, 353 (1898).

4. The methyl radicals subsequently combine with azomethane molecules yielding more complicated radicals and molecules.

5. The ethane and other alkane gas produced during the photolysis of azomethane results from a decomposition reaction involving the more complicated radicals and molecules. Practically none of the ethane formed results from a combination of the methyl radicals; methyl radicals do not combine readily at ordinary temperatures to form ethane.

6. Some compound formed by the interaction of nitric oxide and the products of the photolysis of azomethane is thermally unstable, yielding mainly substances which are soluble in acid solution.

7. Some compound so formed is more stable to light than is azomethane. When it is decomposed by light, nitrogen and a small amount of alkane gas are among the products.

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Freezing Points of a Number of Pure Hydrocarbons of the Gasoline Boiling Range and of Some of their Binary Mixtures

BY J. SMITTENBERG, H. HOOG AND R. A. HENKES

The freezing point or melting point is one of the most useful physical properties in the identification of chemical substances and in the verification of their degree of purity.

For this reason we started an investigation of the freezing points of a number of hydrocarbons of the gasoline boiling range, which were available in our laboratory. Since it was desirable to have some idea of the effect of impurities upon the behavior of the hydrocarbons when freezing, a number of binary hydrocarbon mixtures were also tentatively examined.

1. Preparation and Purification of the Hydrocarbons.—Nearly all the hydrocarbons were prepared synthetically, some in our laboratory and some in the laboratory for organic chemistry of the University of Amsterdam under the guidance of Professor Dr. J. P. Wibaut.

As a rule the hydrocarbons were purified by sharp rectification with a fractionating column of about 22 theoretical plates. Each preparation was separated into at least ten fractions and only those fractions whose boiling points differed by less than 0.2° and whose refractive indices differed by less than 0.0002 were accepted as "pure."

The preparation and examination of these hydrocarbons will be described shortly *in extenso* in a separate article. The provisional results of the determinations of the boiling point, the refractive index and the freezing point and/or melting point are given in Table I. A number of other physical properties are at present being determined.

2. Apparatus and Methods for the Determination of Freezing and Melting Points.—A platinum resistance thermometer, consisting of about 85 cm. of platinum wire 0.033 mm. in diameter and made to De Leeuw's pattern,[1] was used for most of the determinations. The total length of this thermometer, S, was 20 cm., its diameter 0.8 cm., and the volume of the actual measuring part, 1.5 cc.

In some instances a larger thermometer, L, was used, consisting of 100 cm. of platinum wire 0.05 mm. in diameter. The total length of this thermometer was 50 cm., its diameter 1.2 cm. and the volume of the measuring part 5 cc.

A Wheatstone bridge was used to measure the resistance; the values of the deflections of the galvanometer were calibrated with the aid of standard resistances, which could be placed in the bridge instead of the thermometer.

Four or five fixed points were used for the temperature standardization of the resistance thermometers, as follows

Fixed point no.	Substance	Accepted temp., °C.		Resistance of thermometer in ohms	
				S	L
1	Ice	M. p.	0.00	99.06	45.38
2	Mercury	F. p.	− 38.87	84.85	38.45
3	*n*-Heptane	F. p.	− 90.8	65.65	29.08
4	*n*-Pentane	F. p.	−129.73	50.82	21.87
5	Oxygen	B. p.	−183.0	30.7	

The *n*-heptane was a commercial product, obtained from the California Chem. Co., the freezing point of which is guaranteed by the National Bureau of Standards to be −90.8°. The *n*-pentane was a synthetic product which, according to its physical constants and cooling curve, was very pure. The value given by Mair[2] was accepted for its freezing point.

The following procedure was adopted for rapid conversion of intermediate resistances to the corresponding temperatures.

For each thermometer the constants a and b of the formula

$$t = aR - b \tag{1}$$

were calculated from the fixed points 2 and 3. In this formula t represents the fixed temperature in degrees centi-

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(1) De Leeuw, *Z. physik. Chem.*, **77**, 304 (1911).

(2) B. J. Mair, *Bur. Standards J. Research*, **9**, 457 (1932).