thermal synthesis together with an abnormally large synthesis of hydrogen sulfide by ionization, gives rise to an effective M/N which decreases with increasing temperature.

3.   The ion cluster mechanism accounts satisfactorily for the observed characteristics of the decomposition reaction (neglecting back reaction), though it is not necessary to insist upon this as the only possible mechanism.

4.   The fact that the decomposition of hydrogen sulfide by alpha particle ionization is more efficient than its synthesis is probably due to the fact that the vapor pressure of sulfur is so small at the temperatures employed, thus limiting the efficiency with which the ionization energy may be utilized in the synthesis of hydrogen sulfide.
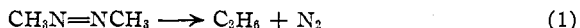
MINNEAPOLIS, MINNESOTA

THE CATALYTIC DECOMPOSITION OF AZOMETHANE, SYM.-DIMETHYLHYDRAZINE, AND MONOMETHYLAMINE: THE THERMAL DECOMPOSITION OF SYM.-DIMETHYLHYDRAZINE

BY P. H. EMMETT AND R. W. HARKNESS

A study of the catalytic decomposition of azomethane was undertaken for the two-fold purpose of learning more of the influence of catalysts upon various C–N linkages and of ascertaining whether the first order homogeneous gaseous reaction could be accelerated by the presence of proper catalysts.   It soon became apparent, however, that the final products of the catalytic reaction were principally ammonia, hydrogen and carbon, rather than nitrogen and ethane, which Ramsperger[1] has shown are produced by the thermal homogeneous decomposition

$$CH_3N=NCH_3 \longrightarrow C_2H_6 + N_2 \qquad (1)$$

Nevertheless, the catalytic studies were continued with a view to elucidating the steps by which compounds such as azomethane decompose over catalytic materials.   In the course of the azomethane studies it became desirable to investigate also the catalytic decomposition of dimethylhydrazine and monomethylamine, and the thermal decomposition of dimethylhydrazine.

Experimental

The catalytic and thermal decompositions were carried out in a static system.   The reaction vessel was kept at any constant temperature between 220 and 350° by a surrounding mercury vapor bath, the pressure of

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[1] Ramsperger, THIS JOURNAL, **49**, 912, 1495 (1927); **51**, 2134 (1929).

which was automatically regulated. The catalyst either as a gauze or in the form of 8–14 mesh particles supported in a platinum basket could be inserted into or removed from the reaction vessel magnetically. A mercury manometer and Toepler pump connected to the reaction vessel completed the essential parts of the apparatus.

The arrangement for inserting and removing the catalyst from the reaction vessel resulted in about 10–15% of the reacting gas being in side tubes at room temperature rather than at the temperature of the reaction vessel. In the experiments on the non-catalytic decomposition of dimethylhydrazine the catalyst tube itself was sealed off, leaving only the side tubes and traps which together contained 7–8% of the reacting gas.

The silver and platinum gauzes used as catalysts were 80 mesh and had an actual surface area of about 80 sq. cm. The iron catalyst used for most of the runs was a doubly promoted synthetic ammonia catalyst containing about 0.25% K_2O, and 1.05% Al_2O_3, and weighing 1.15 g. as oxide; it was reduced in hydrogen at 500°. In one experiment on dimethylhydrazine a pure iron wire having a surface area of 73 sq. cm. was used.

In each experiment the reaction vessel was filled to about 50 mm. with the gas to be studied. Pressure changes were followed manometrically from the instant at which the catalyst was lowered into the reaction vessel. When desired, the manometer could be lowered and samples of the gaseous mixture pumped out of the system by a Toepler pump and analyzed. Analyses of the gaseous products were carried out in a Bone and Wheeler gas analysis apparatus; hydrogen was determined by removing it with hot copper oxide, and the methane and ethane by combustion over a hot platinum wire in the presence of excess oxygen.

Both the azomethane and the dimethylhydrazine were made from dimethylhydrazine hydrochloride prepared by the method given by Thiele[2] and supplemented by Ramsperger.[1] The azomethane was formed by oxidizing dimethylhydrazine dihydrochloride with potassium chromate, while the dimethylhydrazine was prepared by dropping water on a mixture of dimethylhydrazine dihydrochloride and sodium hydroxide. The gases were dried thoroughly over soda lime; they were then condensed in a solid carbon dioxide–acetone bath and pumped free of ammonia and dissolved air. Azomethane was stored as a gas. Dimethylhydrazine has a boiling point of 81°; an approximate vapor pressure determination indicated the boiling points of the supply used in the present experiments to be 82.5 ± 2°. The methylamine was prepared by dropping 30% monomethyl-ammonium hydroxide on soda lime, condensing the evolved gas in a solid carbon dioxide trap and drying the product finally by passage through a soda lime tube.

[2] Thiele, *Ber.*, **42**, 2576 (1909).

Results

(a) The Catalytic Decomposition of Azomethane.—Negative results were obtained with both silver and platinum gauzes both before and after their activation by treatment with a hydrogen–oxygen mixture. The catalysts could be removed or inserted at will without influencing to any detectable amount the rate of decomposition at 280°. The rate curves of the homogeneous decomposition for initial pressure of about 50 mm. of azomethane are those of a first order reaction. The approximate constants calculated at 280° are, on an average, about 0.046, in good agreement with 0.052, obtained by Ramsperger at the same temperature and pressure.
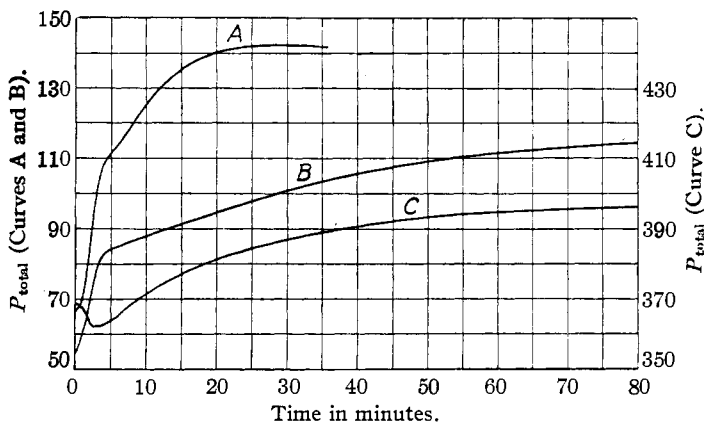

Fig. 1.—Catalytic decomposition of azomethane on iron synthetic ammonia catalysts: Curve A, azomethane at 280°; Curve B, azomethane at 250°; Curve C, azomethane + 310 mm. of hydrogen at 250°.

In the presence of an iron synthetic ammonia catalyst azomethane decomposes rapidly. Pressure changes during typical runs are illustrated by curves A and B in Fig. 1, for 280 and 250°, respectively. A rapid pressure increase equal to about 50% of the initial pressure occurs in the first five minutes; this is followed by a much slower increase, the final pressure being approximately 2.20 times the initial pressure of azomethane.

Analysis of the products of reaction showed that at the end of the catalytic runs the principal gaseous products were ammonia and hydrogen. In addition, small quantities of methane, ethane and nitrogen were present. In Table I are shown the partial pressures of each of the various products present at the end of typical runs. In some of the runs the catalyst was removed at the end of the first five minutes and the products analyzed. As can be seen by comparing runs 23 and 36 with 9, 11, 34 and 38, the principal change occurring after the first five minutes in the catalytic runs results in an increase in the partial pressure of water-soluble material and the partial pressure of hydrogen. At the end of the first five minutes prac-

tically all of the azomethane had disappeared.   This was evidenced by the fact that on heating all of the gaseous products at the end of the first five minutes to 360° for an hour, no appreciable pressure increase resulted. Runs 35 and 37 were of this type.

In the course of the work it was noticed that all of the nitrogen was not being accounted for by the products formed.   It seemed probable that some nitride might have been formed on the iron catalyst.   Accordingly, beginning with run 37, the iron catalyst was analyzed for nitrogen at the end of each run by admitting hydrogen, reducing the nitride to form ammonia, and noting the decrease in pressure resulting.   It is apparent from runs 37 and 38 that nearly all of the nitrogen of the original azomethane is accounted for by the summation of that in the nitride and that in the gaseous products.   The water-soluble product present at the end of the catalytic runs was principally ammonia; this was deduced from a comparison of the vapor pressure curve of the product, curve A,[3] Fig. 2, with that of ammonia, curve D, Fig. 2.

In a few experiments sufficient hydrogen was added initially to prevent the formation of any iron nitride.   In such experiments as shown by curve C, Fig. 1, a pressure decrease

Fig. 2.—Vapor pressure determination of water-soluble constituents.

occurred during the first five minutes followed by a long gradual increase. At the end of these runs, no nitride was present on the iron catalyst.   The pressure decrease is presumably, therefore, associated with the reduction of the iron nitride by the excess hydrogen to form ammonia.

(b)   **Thermal Decomposition of Sym.-dimethylhydrazine.**—In determining the thermal behavior of dimethylhydrazine, some approximate data were obtained on its decomposition at 320 and 250°.   In Table II are shown the times for one-eighth, one-fourth and one-half decomposition,
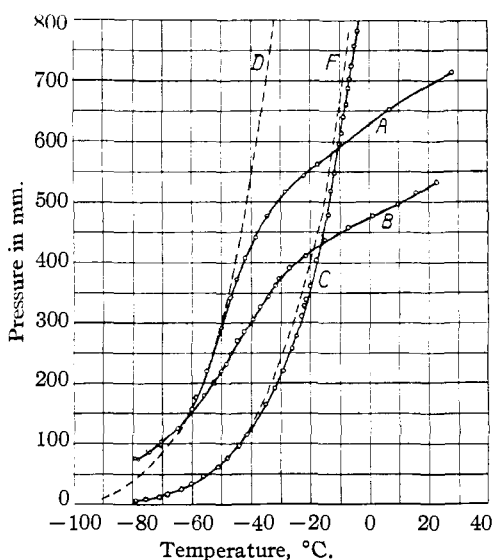
[3] It should be noted that curves A and B, Fig. 2, are, strictly speaking, vapor-pressure curves over only those portions lying below about −50 and −30°, respectively. The upper parts of these curves represent a region in which because of the small quantity of material used, the liquid phase was not present.   Curves D and F were plotted from data in the "International Critical Tables."

TABLE I
RESULTS OF EXPERIMENTS

	Catalytic azomethane decomposition, 250°						To "break," catalytically. Then thermally to 350°		Dimethylhydrazine decomposition		Catalytic to "break," 220°	Catalytic to "break." Then thermal to 350°		Thermal, 350°		Catalytic decomposition of monomethylamine at 250°
	To completion				To "break"				Catalytic to completion, 250°							
Run number	9	11	34	38	23	36	35	37	46	63	59	58	69	45	49	70
Duration of catalyst run, minutes	135	130	125	182	15	6	5	10	575	665	43	14	1?	177	354	120
Initial pressure of reactant, mm.	47.5	47.0	55	53.0	97.0	52.5	54	51.5	52.0	52.5	51.5	53.5	50.0	72.0	49.0	77.5
Pressure after removing catalyst, mm.	...	...	...	...	...	..	79.0	71.5	...	...	..	80.0	73.0	...	...	...
Final pressure, mm.	104.5	102.5	117.5	104.5	128.5	77.0	82.0	73.0	158.5	149.0	76.5	96.0	86.5	172.0	114.0	151.5
Mm. of water-soluble product	54.3	56.3	57.7	60.5	75.5	42.3	35.8	38.2	83.2	81.2	63.2	51.8	48.6	29.2	20.3	73.7
Mm. of ammonia from Fe_4N	...	...	...	41.0	...	..	...	45.0	7.0	...	...	..	8.0	...	...	5.0
Mm. of hydrogen	34.1	38.2	41.9	26.9	46.3	19.5	19.8	15.0	60.0	47.5	0.2	0.2	0.9	0.0	0.0	73.3
Mm. of methane	9.4	7.6	10.9	12.0	2.1	4.8	15.8	11.6	3.5	6.0	5.4	18.4	19.8	66.0	45.7	...
Mm. of ethane	4.8	1.3	1.9	2.3	4.0	4.2	2.2	2.9	4.3	3.1	0.8	3.6	1.7	17.6	8.7	1.7
Mm. of unsaturated hydrocarbons	...	...	...	0.0	...	0.8	1.9	2.0	...	...	..	..	..	0.0	...	...
Mm. of nitrogen (by difference)	1.8	0.0	5.2	2.8	0.6	5.4	6.6	3.4	7.7	11.2	7.0	22.0	15.5	59.2	39.3	2.8
Percentage of nitrogen accounted for assuming one nitrogen atom per mole of water-soluble product (a) neglecting Fe_4N	60.9	59.8	61.8	62.3	64.8	50.5	45.0	43.8	94.8	98.7	75.0	89.5	79.7	...	...	...
(b) including Fe_4N	...	...	...	100.0	...	..	..	87.5	102.0	...	..	..	87.6	103.0	101.0	...
Percentage of hydrogen accounted for (a) Water-soluble (calculated as NH_3)	104.0	100.0	95.4	93.4	60.3	67.8	71.2	70.0	98.4	90.8	..	..	..	79.5	75.4	...
(b) Water-soluble as CH_3NH_2	...	...	...	...	86.3	94.8	93.2	94.7	...	...	83.2	83.0	78.8	89.3	86.0	...

as well as the values of the first order constant k_1, calculated for successive two-minute intervals by the formula

$$k_1 = \frac{2.303}{t_2 - t_1} \log_{10} \frac{P_1}{P_2}$$

and expressed as reciprocal seconds.   Runs 54 and 55 were made with the reaction vessel packed with fire-glazed Pyrex tubes sufficient to increase the surface to volume ratio about five-fold.   The calculated first order constants were reasonably constant between about 15 and 80% decomposition in all runs except 55, where for some unknown reasons the constants increased steadily to a maximum and then decreased.   The values of the constants for percentage decompositions less than 15% and greater than 80% were smaller than those in the interval 15–80%.   The average value 1.97 for run 55 was taken over the range 20–80% decomposition.   The change in reaction rate with temperature shown in Table II corresponds to an energy of activation of about 57,000 calories per mole.

The products of the thermal decomposition indicated a very complex reaction.   They were principally methane and nitrogen, together with considerable quantities of ethane, and of some water-soluble material. A vapor pressure determination on this water-soluble material as represented by curve B, Fig. 2, is rather inconclusive, apparently indicating, however, the presence of both ammonia and monomethylamine.   The analyses of runs 45 and 49 shown in Table I illustrate the relative amounts of the various products formed.

The data shown in Table II are considered to indicate that the thermal decomposition of dimethylhydrazine is a homogeneous first order reaction. However, because the reaction vessel contained, as already pointed out, only 92% or so of the gas in the reaction system, and because runs at only a limited number of pressures and temperature were taken, these conclusions must be regarded as tentative.   Because of the apparently complex nature of the thermal decomposition, further experiments were not carried out.

TABLE II

RATE OF THERMAL DECOMPOSITION ON DIMETHYLHYDRAZINE

Run	T. °C.	Initial pressure, mm.	Ratio of final to initial pressure	Time (minutes) for fractional decomposition			$k_1 \times 10^3$ (seconds)$^{-1}$
				$^1/_8$	$^1/_4$	$^1/_2$	
45	350	72	2.42	3.5	6.0	11.5	1.31
49	350	49	2.42	3.0	5.2	10	1.39
50	350	22	2.69	3.2	6.0	12.5	1.04
54[a]	350	45.5	2.27	3.3	6.0	12.5	1.04
55[a]	350	58.5	2.24	4.0	6.5	10.8	1.97
51	320	56	2.37	31.5	56	105	0.130

[a] In runs 54 and 55 the surface and volume ratio was increased about five-fold by packing the reaction vessel with glass rods.

(c) The Catalytic Decomposition of Dimethylhydrazine.—The catalytic decomposition of dimethylhydrazine over iron catalysts at 250° is illustrated by curve A in Fig. 3. The curve is similar to those for the catalytic decomposition of azomethane since it indicates a rapid 50% pressure increase in the first few minutes followed by a much slower pressure increase for several hours.

The final products of the catalytic decomposition are ammonia and hydrogen, principally, with small percentages of ethane, nitrogen and methane. Typical analyses are shown in Table I for runs 46 and 63.
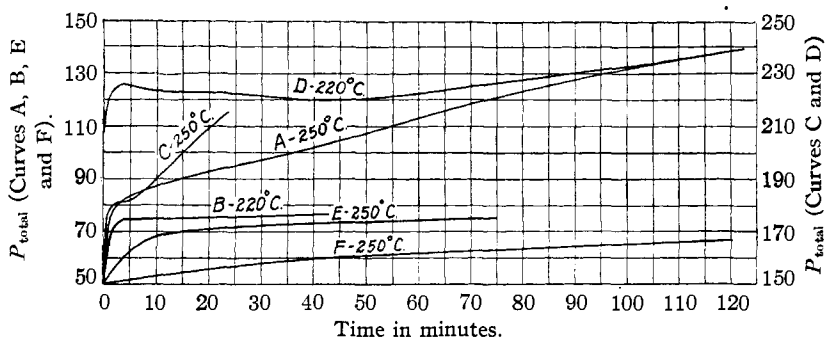

Fig. 3.—Catalytic decomposition of dimethylhydrazine: Curves A and B, pure dimethylhydrazine; Curves C and D, dimethylhydrazine + excess hydrogen; Curve E, dimethylhydrazine with iron wire catalyst; Curve F, dimethylhydrazine with platinum gauze catalyst.

In order to study more fully the reactions occurring during the catalytic processes, some decomposition experiments were carried out at 220°. The initial rapid reaction was found to occur as at 250°, in about two or three minutes, giving again a 50% pressure increase. The slower subsequent decomposition occurring at 250° was, however, practically entirely absent at 220°. A typical rate curve is shown in Fig. 3, curve B.

Analysis of the products of the reaction at 220° showed principally a water-soluble product together with smaller quantities of nitrogen and methane and a trace of ethane. The water-soluble constituent present was definitely identified as monomethylamine. Its vapor pressure curve is shown by curve C, Fig. 2, compared to that of pure monomethylamine in curve F. Run 59, Table I, illustrates the composition of the final products. When these were heated thermally to 350°, a decrease occurred in the partial pressure of water-soluble material and an increase in methane, nitrogen and ethane, as well as in the total pressure. This change in composition can probably be attributed to the decomposition of some dimethylhydrazine, diffusing out of some of the side tubes of the reaction vessel, since the latter as already pointed out was so designed for the catalytic work as to leave about 15% of its contents outside the heated zone.

In two runs excess hydrogen was added initially. The influence on the rate is shown by curves C and D in Fig. 3. In the presence of the excess hydrogen the initial pressure rise in the first two minutes was followed by a slight decrease and then a final increase that was definitely faster than in the absence of the excess hydrogen.
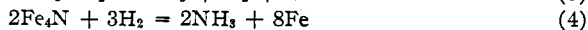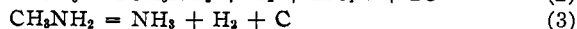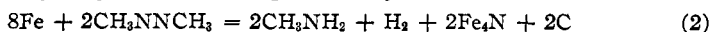
At the completion of the catalytic runs on the decomposition of dimethyl-hydrazine over iron synthetic ammonia catalysts, the activities of the iron wire catalyst and of a platinum gauze were determined. The rates of decomposition over these catalysts at 250° are shown in Fig. 3, curves E and F. The rate over platinum was sufficiently small to have warranted its being neglected in the work with synthetic ammonia catalysts supported in platinum baskets. The nature of the curve on unactivated iron wire suggests that the same qualitative type of decomposition is occurring at a rate considerably slower than on the active catalyst. The initial rapid pressure rise represents an increase of only about 35% instead of 50% in pressure. No analyses of the products of these two runs were made.

(d) **Catalytic Decomposition of Monomethylamine.**—Several experiments on the decomposition of monomethylamine over iron synthetic ammonia catalysts were carried out at 250°. The rate of decomposition is similar to that occurring after the first few minutes in the decomposition runs on both azomethane and dimethylhydrazine. The analysis of the final products formed in run 70 is shown in Table I. The monomethylamine apparently decomposed practically quantitatively into ammonia, hydrogen and carbon. Monomethylamine was found to be stable in a Pyrex vessel at 350° in the absence of a catalyst.

Discussion and Conclusions

In the present experiments it has not been found possible by either silver, platinum or iron catalysts to catalyze the decomposition of azomethane into nitrogen and ethane according to equation (1) above. It is true, of course, that in all catalytic azomethane runs over iron catalysts both nitrogen and ethane were produced in quantities larger than would have been produced thermally at the same temperature. However, the catalytic reaction was so complex a process that the small quantities of both nitrogen and ethane might easily have been formed by some side reactions rather than by the speeding up of reaction (1).

The decomposition of azomethane by iron catalysts into ammonia, carbon and hydrogen can be explained by the successive reactions

$$8Fe + 2CH_3NNCH_3 = 2CH_3NH_2 + H_2 + 2Fe_4N + 2C \qquad (2)$$
$$CH_3NH_2 = NH_3 + H_2 + C \qquad (3)$$
$$2Fe_4N + 3H_2 = 2NH_3 + 8Fe \qquad (4)$$

Reaction (2) occurs rapidly, accounting for the rapid pressure increase during the first five minutes and is followed by reactions (3) and (4) which

proceed somewhat more slowly and are responsible for the more gradual increase in pressure extending over a period of several hours. The production of small quantities of methane, ethane and nitrogen in addition to the primary products ammonia, carbon and hydrogen occurs by some side reactions the nature of which is not known. The occurrence of Reactions 2, 3 and 4 has been deduced from and is consistent with the following observations, most of which have been mentioned in connection with the experimental results: (1) a pressure increase of about 50% occurs within the first five minutes. (2) At the completion of this rapid initial pressure rise, no azomethane remains undecomposed. (3) The final gaseous products at the end of the catalytic runs are principally hydrogen and ammonia in addition to small quantities of methane, ethane and nitrogen. (4) Methylamine is thermally stable at 350° in the absence of a catalyst; in the presence of iron synthetic ammonia catalysts at 250° it decomposes at a rate that is in good agreement with that obtained in the last slow pressure increase of the catalytic azomethane runs. (5) The assumption that the water-soluble product formed during the first five minutes of the catalytic azomethane decomposition is monomethylamine accounts for about 95% of the hydrogen present in the original sample compared to 70% that would be accounted for by assuming this product to be ammonia. (6) During the portion of the catalytic run occurring after the first five minutes, the partial pressures of both the water-soluble material and of hydrogen increase. (7) The presence of an excess of hydrogen in the original reaction mixture prevents the initial, rapid, 50% pressure increase from occurring. It is apparent that if reactions (2) and (4) are added in such a way as to eliminate the formation of iron nitride, the resulting equation is for a reaction entailing no volume change. Actually a pressure decrease of from 1 to 12 mm. resulted within the first five minutes during these excess hydrogen runs. The nature of the reaction causing this decrease is uncertain. (8) The final ammonia–hydrogen ratios conform closely to those that would be found at similar pressures in equilibrium with $Fe–Fe_4N$. The agreement of the values of $K = (NH_3)^2/(H_2)_3$ found in the present experiments with the equilibrium curve for the system $Fe–Fe_4N–NH_3–H_2$[4] extrapolated from 400° down to 250° is shown in Fig. 4.

Between 50 and 75% of the products of the thermal decomposition of dimethylhydrazine can be accounted for by the reaction

$$CH_3NHNHCH_3 = 2CH_4 + N_2 \qquad (5)$$
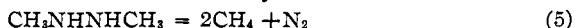
The excess nitrogen, the water-soluble product, and the ethane formed in the homogeneous decomposition are presumably the results of some side reactions. Possibly the occurrence of short chain reactions between various gaseous radicals such as suggested by F. O. Rice[5] for certain organic

[4] Brunauer, Jefferson, Emmett and Hendricks, THIS JOURNAL, **53**, 1778 (1931).

[5] F. O. Rice, *ibid.*, **53**, 1959 (1931).

decompositions accounts for the products formed. However, no simple reaction has been devised that will explain the formation of products other than those indicated by reaction (5) above.

The catalytic decomposition of dimethylhydrazine probably resembles closely that of azomethane. The one striking difference is that at the end of the initial rapid pressure rise monomethylamine and methane, but no
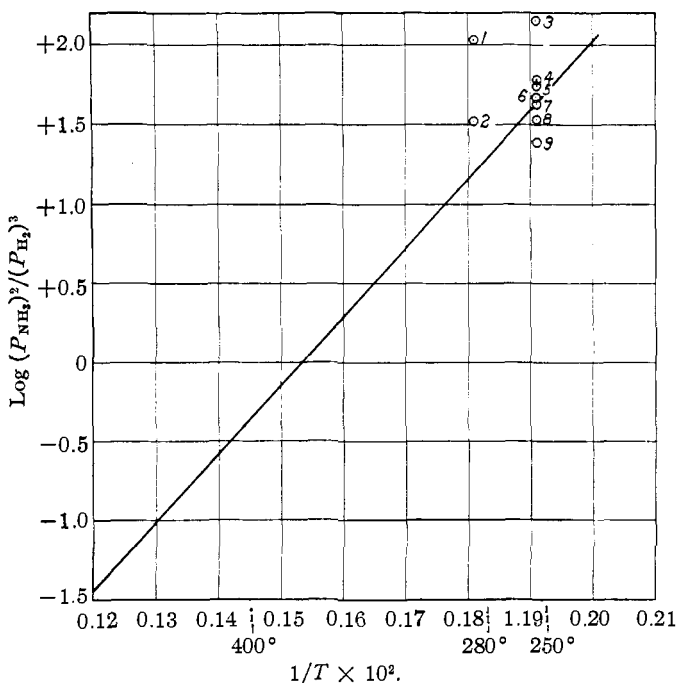

Fig. 4.—Composition of final NH_3–H_2 mixtures in catalytic azomethane and dimethylhydrazine decomposition over iron catalysts: 1, 2, 3, 4, 5, 7, 8, from azomethane runs; 6, 9, from dimethylhydrazine runs.

free hydrogen, are present in the gaseous products. The analysis of the products at this point agrees fairly well, in fact, with the empirical equation

$$16Fe + 8CH_3NHNHCH_3 = 12CH_3NH_2 + CH_4 + 4Fe_4N + 3C \qquad (6)$$

Reactions (3) and (4) above are presumably responsible for the gradual pressure increase occurring after the first few minutes.

In the presence of excess hydrogen, it might be expected that no Fe_4N would form and that the pressure increases would correspond to the combination of reactions (6) and (4), to give

$$8CH_3NHNHCH_3 + 6H_2 = 12CH_3NH_2 + CH_4 + 4NH_3 + 3C \qquad (7)$$

Run 72, shown as curve C, Fig. 3, made with 56 mm. of dimethylhydrazine

and excess hydrogen seems to be in approximate agreement with equation (7).

The catalytic decomposition of methylamine according to reaction (3) above is particularly interesting in that it demonstrates the ability of nitrogen over iron catalysts at 250° to not only detach itself from a linkage with carbon but to break the C–H bonds, with the formation of ammonia and hydrogen.

No attempt was made to determine definitely the form in which the carbon was deposited on the catalysts used in the various catalytic decompositions.

The authors wish to express their thanks to Dr. W. E. Kuentzel for starting the experimental work and conducting the earlier part of the work on azomethane.

Summary

Azomethane has been found to decompose rapidly at 250° over iron synthetic ammonia catalysts, the final gaseous products being principally ammonia and hydrogen, with small amounts of methane, ethane and nitrogen. The reaction apparently takes place in two steps, the first resulting in the formation of monomethylamine, hydrogen, Fe_4N and carbon; the second in the decomposition of the monomethylamine and the partial reduction of the Fe_4N by hydrogen. Dimethylhydrazine in a somewhat similar manner decomposes into ammonia, hydrogen and carbon, together with some methane, ethane and nitrogen. Monomethylamine decomposes quantitatively into hydrogen, ammonia and carbon, at 250° on iron catalysts. Dimethylhydrazine has been found to decompose thermally at 320 to 350° as a homogeneous first order gas reaction. It has an energy of activation of about 57,000 calories per mole. About 60% of the products of the homogeneous reaction can be accounted for by the equation $CH_3NHNHCH_3 = 2CH_4 + N_2$. However, considerable amounts of some unidentified water-soluble product, nitrogen and a small amount of ethane not accounted for in the above equation are also formed.