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Thermal Decomposition of Hexamethylene Tetramine

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In order to get information about the mechanism of the thermal decomposition of hexamethylene tetramine (hexa), hexa was decomposed thermally in a vacuum vessel, and the composition of the gas thus produced was determined with a mass spectrometer. The main products found were ammonia and a carbon-rich solid residue. The carbon in the carbon-rich residue seems to act as a catalyst for the decomposition.

In a thermal decomposition product of phenol resin, one of the present authors (T. T.) has found an appreciable amount of ammonium compounds.¹⁾ The origin of the compounds was inferred to be the hexamethylene tetramine (hexa) which is added to resol or novolak, the precursory products of the resin, as a hardening reagent of the resin. The purpose of the present study is to confirm the origin of the ammonium compounds mentioned above and to clarify the thermal decomposition mechanism of hexa.

Stranski *et al.*²⁾ reported on the thermal decomposition of hexa. They investigated the total pressure of the decomposition gas produced in the presence (180—250°C) and in the absence (250—

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1) H. Hoshino, N. Wasada and T. Tsuchiya, This Bulletin, **39**, 1809 (1966).

2) I. N. Stranski, G. Klipping, A. F. Bogenschurtz, H. J. Heinrich and H. Maennig, *Advances in Catalysis*, **9**, 409 (1957).

500°C) of the solid phase, and found that in both systems the decomposition has similar characteristics and that the ratio of the final pressure to the initial pressure increases with the temperature. They did not study the compounds produced by the decomposition.

Experimental

The hexa was a G. R.-grade substance obtained from the Tokyo Kasei Kogyo Co., Ltd. The hexa was heated in a vacuum ampoule. Figure 1 shows the hard glass ampoule used for thermal decomposition. About 0.5 g of hexa was into the ampoule, A, through the side tube, B. After the ampoule had been evacuated for about an hour at room temperature with a diffusion pump, it was sealed off at C. The volume of the ampoule was about 13 *ml*. In each of the pyrolysis experiments, the furnace was first preheated to the required temperature. Then the ampoule containing the sample was placed in the furnace up to the dotted line, D (Fig. 1), for an hour. At the end of this period the furnace was quickly evacuated and cooled. After cooling, the ampoule was attached to a mass spectrometer through the common joint, E, for analysis. The experiments were carried out at temperatures of 200, 270, 300 and 400°C.

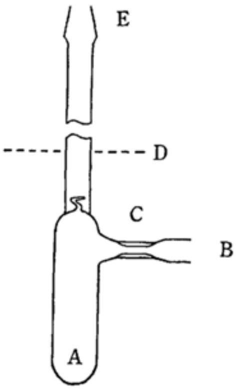

Fig. 1. Ampoule for thermal decomposition.

As the amount of ammonia, which is the main component of the products, as is shown in Table 1, reached a nearly constant value after about an hour of heating at 300°C, we fixed the heating time at one hour in the following experiments.

Besides the gaseous products, the samples treated at temperatures higher than 300°C gave a dark carbonaceous product. The gas products were analyzed with a CEC 21-103C mass spectrometer. The gaseous fraction was cooled in a liquid nitrogen trap. The gaseous and the trapped materials at a certain temperature were analyzed separately. The accuracy of analysis was better than ±5%. The total amount of gas produced was measured with a gas burette and a mercury manometer. The residue obtained in pyrolysis at temperatures higher than 270°C was out-gassed thoroughly, washed with water and alcohol, dried, and weighed. The treated residue was inferred, from its color and for a reason which shall be discussed later, to consist in the main of carbon and shall be referred to as "residual carbon."

Results and Discussion

Figure 2 shows the amount of residual carbon and total gas produced as functions of the decomposition temperature. The figure indicates that hexa begins to decompose at approximately 270°C. At 400°C, the weight percentages of the products are: residual carbon, 60%; gaseous compounds, 33%, and water- or alcohol-soluble material, 7%. Table 1 shows the amount of gaseous products formed per mole of hexa on thermal treatment. Because the *m*/*e* 28 peak was rather weak and because accurate analysis from *m*/*e* 14 and *m*/*e* 12 was impossible, we assumed that the peak is composed of CO^+ and of N_2^+ ions. Each of the gas products at various temperatures (P-T curve) is shown in Fig. 3.

From the data given in Table 1 and Fig. 2, the overall composition of the products at 400°C, other than the gaseous species shown in Table 1, is estimated to be $C_{5.9}H_{6.1}N_{2.1}$. About 12% of

TABLE 1. COMPOSITION OF GASES PRODUCED FROM 1 mol OF HEXAMETHYLENE TETRAMINE AT VARIOUS DECOMPOSITION TEMPERATURES

Component	200°C	270°C	300°C	400°C
Trimethylamine	1.75×10^{-4}	5.43×10^{-3}	1.31×10^{-2}	2.12×10^{-3}
Dimethylamine	—	—	1.80×10^{-2}	9.67×10^{-3}
Methylamine	—	—	1.11×10^{-1}	3.67×10^{-2}
Propionitrile	—	—	—	4.05×10^{-5}
Acetonitrile	4.66×10^{-5}	2.18×10^{-3}	1.64×10^{-3}	5.93×10^{-3}
Ethylene imine	4.51×10^{-5}	2.18×10^{-3}	—	—
Water	3.74×10^{-3}	5.43×10^{-3}	8.18×10^{-3}	9.67×10^{-3}
Ammonia	1.26×10^{-3}	1.056	1.447	1.806
Methane	4.01×10^{-5}	1.53×10^{-2}	3.64×10^{-2}	4.08×10^{-2}
Hydrogen	—	2.19×10^{-3}	3.62×10^{-3}	4.13×10^{-3}
Carbon dioxide	5.23×10^{-4}	2.87×10^{-6}	—	1.35×10^{-5}
Nitrogen and carbon monoxide	2.87×10^{-4}	3.86×10^{-3}	2.71×10^{-3}	6.88×10^{-3}

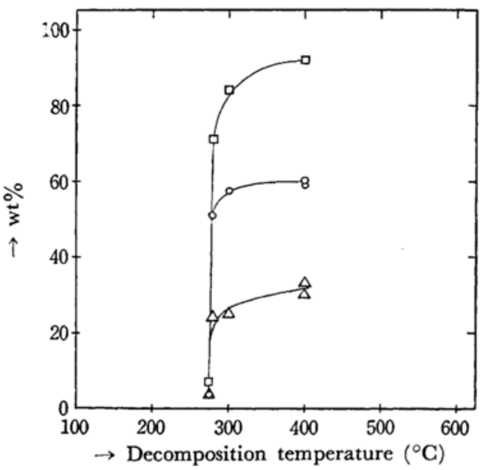

Fig. 2. Decomposition temperature *versus* gas product and residual carbon.
○ Residual carbon, △ Gas products,
□ Summation of residual carbon and gas products.

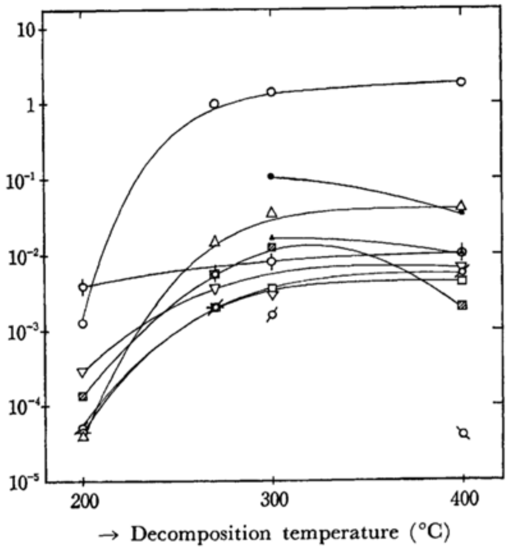

Fig. 3. Amount of gases produced from 1 mol of hexa *versus* decomposition temperature.
○ Ammonia, △ Methane, □ Hydrogen,
● Methylamine, ▲ Dimethylamine,
▨ Trimethylamine, ⦵ Ethylene imine,
ø Acetonitrile, ⏀ Water, ▽ Nitrogen and carbon monoxide, ⍉ Propionitrile.

the $C_{5.9}H_{6.1}N_{2.1}$ is soluble in water or in alcohol; the remaining 88% was inferred to be residual carbon. The hydrogen atom is considered to be present in the main in the soluble substances. The main component of the residual carbon is, therefore, the carbon atom, though it is shown from the material balance that at least 24% of the weight of the residual carbon is composed of hydrogen and nitrogen atoms. We assume that at least a part of the residual carbon is bulk carbon.

As is seen in Fig. 3, the P-T curves of various products may be divided into two types, *i. e.*, those which show a tendency toward saturation (Type 1; the curves for ammonia, methane and hydrogen), and those which have a maximum (Type 2, the curves for methylamines). We will ignore the behavior of carbon dioxide, because its amount is very small. The compounds of Type 1 are considered to be the final products of the decomposition because they show saturation and because they are stable, low-molecular-weight compounds. The compounds of Type 2 are inferred to be intermediate products which can decompose further when heated to higher temperatures.

As the decomposing temperature increases, the molecular weight of the gaseous products tends to drop (Table 1). This phenomenon suggests the possibility that the compounds produced will decompose further into compounds of lower molecular weights as the temperature rises. The shape of the P-T curves of Type 2 is compatible with this inference. In order to check it, each of the compounds of a higher molecular weight in Table 1, *i. e.*, trimethylamine, dimethylamine, methylamine, propionitrile, acetonitrile, and ethylene imine, was heated individually and the decomposition products were investigated. The three amines were obtained from the Tokyo Kasei Kogyo Co., Ltd., as a 40% aqueous solution, and were dried with caustic potash and distilled under reduced pressure. The two nitriles and the imine were guaranteed reagents obtained from the same company as the amines, and were used without further purification. About 0.1 m*l* of each of these reagents was directly distilled under reduced pressure into the glass ampoule shown in Fig. 1; the ampoule was then treated just as in the case of hexa, and each reagent was decomposed at 300°C for an hour. The compositions of the gaseous compounds produced are shown in Table 2. The 1st column in the table shows the samples treated, and the 1st row shows the decomposition products. Though trimethylamine and propionitrile were not decomposed, the other compounds were more or less decomposed into lighter compounds. The common products from all the reagents were ammonia and methane. Other than these products, acetonitrile and ethylene imine gave hydrogen and nitrogen. In addition to these products, ethylene imine gave hydrogen cyanide and an appreciable amount of methylamine.

From Table 2, it may be seen that some of the compounds, for instance, ethylene imine, produced from hexa under lower decomposition temperatures (Table 1) decompose further, when heated to higher temperatures, into compounds of a lower molecular weight. The behavior of ethylene imine, for instance, which was found at temperatures below 270°C but which could not be detected

TABLE 2. DECOMPOSITION PRODUCTS OF REAGENTS (DECOMPOSED AT 300°C, WITHOUT ACTIVE CARBON)

Component	Reagent					
	Trimethylamine	Dimethylamine	Methylamine	Propionitrile	Acetonitrile	Ethyleneimine
Trimethylamine	100	—	—	—	—	—
Dimethylamine	—	97.5	—	—	—	—
Methylamine	—	—	89.9	—	—	66.0
Propionitrile	—	—	—	100	—	—
Acetonitrile	—	—	—	—	96.5	—
Ethyleneimine	—	—	—	—	—	6.1
Ammonia	—	1.5	9.2	—	0.8	11.5
Methane	—	1.0	0.9	—	0.2	5.4
Hydrogen	—	—	—	—	1.4	3.2
Nitrogen	—	—	—	—	1.1	5.2
Hydrogen cyanide	—	—	—	—	—	2.6

TABLE 3. DECOMPOSITION PRODUCTS OF REAGENTS (DECOMPOSED AT 300°C, WITH ACTIVE CARBON)

Component	Reagent					
	Trimethylamine	Dimethylamine	Methylamine	Propionitrile	Acetonitrile	Ethyleneimine
Trimethylamine	1.9	—	—	—	—	—
Propionitrile	—	—	—	65.1	—	—
Acetonitrile	—	—	—	14.6	96.4	—
Ammonia	20.9	20.2	58.9	1.0	—	54.6
Methane	33.8	44.4	23.9	—	—	10.4
Hydrogen	5.5	8.8	1.5	—	—	2.7
Nitrogen	17.9	8.6	7.6	15.0	3.6	8.7
Ethane	20.0	18.0	8.1	—	—	23.7
Ethylene	—	—	—	4.3	—	—

at temperatures higher than 300°C, can be elucidated by the results given in Table 2.

On the other hand, trimethylamine, which tends to decrease from 300°C with an increase in the temperature (Table 1), does not decompose at 300°C (Table 2). However, as has been described, residual carbon was obtained when hexa was treated above 270°C. The primary products produced under a lower heating temperature may decompose further in the presence of residual carbon. In order to estimate the influence of the catalytic action of the residual carbon on the decomposition reaction, the following experiment was carried out.

Instead of residual carbon, a commercial active carbon was used. The active carbon powder obtained from Takeda Yakuhin Kogyo (pure grade "Shirasagi") was heated at 360°C for 2 hr in a vacuum obtained with a diffusion pump. The sample substance (0.05 m*l*) was distilled, under a reduced pressure, into an ampoule which contained 0.1 g of the treated carbon at room temperature; then the system was heated by just the same procedure as has been described before, and the gas produced was analyzed. The temperature of the furnace was 300°C. All of the sample materials studied were found to have been decomposed thermally into ammonia, methane, hydrogen, nitrogen, and ethane. The results are shown in Table 3. We can see that trimethylamine and propionitrile, which were not decomposed at 300°C without active carbon, decompose when treated with active carbon. Ethane and ethylene are detected in the decomposition products when samples are heated with active carbon (Table 3), while the two compounds were not found in the case of a reaction without active carbon (Table 2). We cannot decide from this experiment whether or not the decomposition mechanism differs essentially according as active carbon is present during the decomposition, because the production of ethane or ethylene can depend on the degree of decomposition. The actual experimental conditions of the thermal decomposition of hexa are considered to be intermediate between the two extreme conditions, under which the results of Table 2 and Table 3 have been obtained.

Figure 4 shows the potential pathways of the thermal decomposition of hexa deduced from Table 2 and Table 3. The actual pathways of the production of lighter substances, such as nitrogen, methane, ammonia, and hydrogen, produced at higher temperatures may not necessarily follow the course suggested. They can be produced, for instance, directly from hexa. However, at least a part of these lighter compounds can legitimately be considered to be produced *via* intermediate products, such as trimethylamine and dimethylamine, because all these compounds, except for ethylene imine, are contained in the decomposition product of hexa at higher temperatures and can be shown to decompose into the lighter substances at these temperatures.

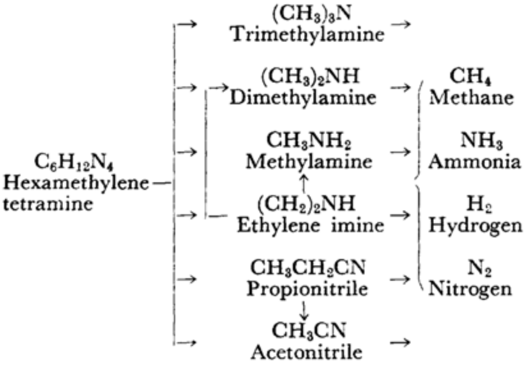

Fig. 4. Potential pathway of thermal decomposition of hexa.

We cannot expect to obtain direct information about the mechanism of the decomposition reaction of hexa itself from the results of the present experiment, because the primary thermal decomposition products of hexa react further with each other under the present experimental conditions and the information we get is the overall result of these primary and secondary reactions.

Based on these experimental results, however, the following possible profile of the reactions can be inferred. When heated to 200°C, a part of the hexa is decomposed and small amounts of ammonia, trimethylamine, acetonitrile, ethylene imine and methane are produced. The amounts of the last three substances are just the same. This suggests that their formations are closely related to each other. At 270°C, the amount of ammonia increases markedly, and hydrogen comes out for the first time. The carbon-rich solid phase is produced, it acts more or less as a catalyst for the following reactions, again promoting the production of the solid phase itself. At 300°C, the P-T curves for ammonia and methane are nearly saturated, monomethylamine and dimethylamine appear for the first time, ethylene imine disappears completely, and the trimethylamine curve reaches its maximum. The appearance of methylamine and dimethylamine and the disappearance of ethylene imine seem to have some interrelation. Ethylene imine gives methylamine, as is shown in Table 2, and the reaction of ethylene imine with hydrogen, which is detected at this temperature, as is shown in Fig. 3, would probably give dimethylamine at this stage of the reaction. Between 300 and 400°C, methylamine, dimethylamine and trimethylamine decrease, while ammonia and methane increase slightly. The increments of the latter compounds are approximately equal to the amounts of those substances expected, from Table 3, to be produced from the decrements of the former compounds.

The amount of water detected is about 0.1% of the weight of the charged hexa. Much should not be inferred from this result, because water molecule is known to be adsorbed on various parts of the gas-handling manifold and of the mass spectrometer. However, from the amount detected and its behavior, the water appears to originate mainly from that adsorbed on the hexa. The small *m/e* 28 peak is considered to be due mainly to nitrogen, as there is no source of carbon monoxide.

From the present results, the hexa, dipped in phenol resin, may be considered to be the origin of the ammonium compounds found in the thermal decomposition product of the resin.