THE THERMAL AND CATALYTIC
DECOMPOSITION OF METHYLHYDRAZINES

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ABSTRACT

The thermal decomposition of methylhydrazine (MMH), 1,1-dimethylhydrazine (UDMH) and trimethylhydrazine (TMH) using a Bendix time of flight mass spectrometer is discussed and the catalytic decomposition of MMH and UDMH over heated Shell 405, a spontaneous hydrazine decomposition catalyst, is also reported.

Both the catalyzed and uncatalyzed experiments were conducted using a heated quartz chamber directly preceding the leak to the mass spectrometer. The temperature range was from ambient to an upper limit of 1000°C.

The main products of the thermal degradation of the methyl derivatives of hydrazine are hydrogen cyanide (HCN), nitrogen (N_2), and ammonia (NH_3); in the catalytic decomposition the main products are N_2 and H_2, as the NH_3 originally formed is decomposed by Shell 405 to yield N_2 and H_2.

CONTENTS

1. Introduction

The thermal and catalytic decomposition of ammonia, hydrazine, and methoxylamine have been previsouly investigated and reported [1, 2]. Results are given in this report of the mass spectrometric study of the thermal decomposition of the three methylhydrazines; methylhydrazine (MMH), 1,1-dimethylhydrazine (UDMH), and trimethylhydrazine (TMH). The catalytic decomposition of MMH and UDMH with Shell 405 catalyst was also investigated and is reported herein. Only the Shell 405 catalyst was investigated because of its superior performance, when compared to other catalysts, in catalyzing the decomposition of hydrazine in actual small rocket engine firings.

The possible poisoning of the Shell 405 catalyst by the methyl compounds was considered before any experimentation was begun. However, it was believed, because of the large surface of the catalyst exposed to rather small amounts of the hydrazine derivatives, that the experimental results would not be affected by poisoning of the catalyst surface. Microscopic examination of the catalyst, before and after decomposition of the hydra- zine derivatives, showed negligible changes in the gross surface struc- ture of the catalyst. Rockenfeller [3] has investigated various tech- niques to determine poisoning of catalysts which were used to decompose carbon-containing monopropellants in small rocket engines.

The experimental procedures have been previously reported [1]. Commercially available MMH and UDMH were purified by distillation and gas chromatography. Trimethylhydrazine, because of the small amount available, was distilled but not chromatographed. It was synthesized by the method reported by Class [4].
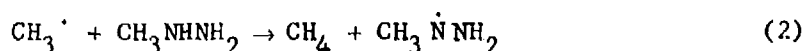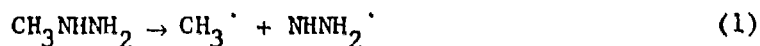
2. Thermal Decomposition of Methylhydrazine

Figure 1 is the mass spectrum of MMH at room temperature. The spectrum compares favorably with the one published by Dibeler et al. [5].

Figure 2 shows changes in the mass spectrum of MMH when it is passed through a reaction chamber maintained at various temperatures between 25°C and 980°C.

Eberstein [6] also investigated the adiabatic, pyrolytic decompo- sition of MMH at approximately 650°C. Mass analysis of the products of Eberstein's experiments showed a considerable amount of H_2, NH_3, and HCN. H_2, NH_3, and HCN were also the main degradation products of the present pyrolysis experiments.

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It is difficult to state with certainty whether any CH_4 was also present in these experiments because the CH_4 and NH_2 fragments have the same mass number in the spectrum (Table I). Ionization and appearance potentials were not determined in the present experiments but would have been of considerable aid in identification of certain fragments. One way to determine the presence of CH_4 is to study any change in the NH_3/NH_2 ratio with temperature variation. Since CH_4 adds to the mass 16 peak, a decrease in the NH_3/NH_2 ratio with respect to temperature would indicate the presence of CH_4, which could be obtained according to the following reactions:

$$CH_3NHNH_2 \rightarrow CH_3{}^{\cdot} + NHNH_2{}^{\cdot} \tag{1}$$

$$CH_3{}^{\cdot} + CH_3NHNH_2 \rightarrow CH_4 + CH_3\dot{N}NH_2 \tag{2}$$

However, the NH_3/NH_2 ratio could also be decreased by the presence of any NH_2 formed according to the following reaction:

$$CH_3NHNH_2 \rightarrow CH_3NH^{\cdot} + NH_2{}^{\cdot} \tag{3}$$
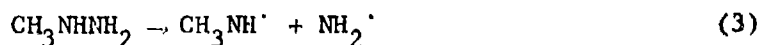
The formation of CH_4 is doubtful in these experiments as the conditions are not favorable for molecule-radical reactions.

Eberstein proposes a chain termination reaction to explain the formation of ethane, C_2H_6. Although a mass 30

$$CH_3{}^{\cdot} + CH_3{}^{\cdot} \rightarrow C_2H_6 \tag{4}$$

fragment is observed in the present studies, it is believed that this fragment is more likely to represent CH_3NH: (Reaction 3) than C_2H_6. The rise and decline in the mass 30 peak between 400° and 800°C (Figure 2) may seem anomalous but the same results were also obtained from the pyrolysis of UDMH (Figure 5).

A considerable rise in the peaks representing H_2, NH_3, N_2, and HCN is very noticeable at temperatures greater than 500°C. The rise in HCN can be explained by the following reactions:

$$CH_3NHNH_2 \rightarrow CH_3N^{\cdot} + NH_3 \tag{5}$$

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Table I. Mass Peaks in the Decomposition of MMH, UDMH, and TMH

Mass Peak	Possible Fragment
1	H^+
2	H_2^+
12	C^+
13	CH^+
14	N_2^{++}, CH_2^+
15	NH^+, CH_3^+
16	NH_2^+, CH_4^+
17	NH_3^+
18	NH_4^+
26	$C_2H_2^+$, CN^+
27	$C_2H_3^+$, HCN^+
28	N_2^+, $C_2H_4^+$
29	CH_3N^+, N_2H^+, $C_2H_5^+$
30	$N_2H_2^+$, $C_2H_6^+$, CH_4N^+
31	$N_2H_3^+$
32	$N_2H_4^+$
41	CHN_2^+
42	$CH_2N_2^+$
43	$CH_3N_2^+$, $C_2H_5N^+$
44	$C_3H_8^+$, CH_4N_2 + $C_2H_6N^+$
45	$CH_5N_2^+$
46	$CH_6N_2^+$
59	$C_2H_7N_2^+$
60	$C_2H_8N_2^+$
71	$C_3H_7N_2^+$
72	$C_2H_8N_2^+$
73	$C_3H_9N_2^+$
74	$C_3H_{10}N_2^+$

$$CH_3N^{\cdot} \rightarrow \left[CH_2 = NH \right] \rightarrow HCN + H_2 \qquad , \qquad (6)$$
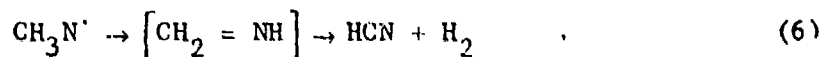
It is interesting to note from Figure 2 that whereas the parent peak, mass 46, begins to decrease at 250°C, most of the fragment peaks between masses 15 and 31 remain constant to about 700°C when they rapidly decrease.

3.   Catalytic Decomposition of Methylhydrazine with Shell 405 Catalyst

Figure 3 represents the catalytic degradation of MMH over Shell 405 catalyst maintained at several temperatures. A comparison of Figures 2 and 3 shows the differences in the thermal degradation of· MMH and the decomposition over a heated catalyst. First, it can be seen from Figure 3 that the N_2 peak, mass 28, accounts for a considerable portion of the sum of all peaks at temperatures greater than 600°C. Secondly, the marked increase of the H_2/H ratio, when compared to Figure 2, indicates the complete degradation of MMH according to the overall reaction:

$$2CH_3NHNH_2 \rightarrow N_2 + 5H_2 + 2HCN \qquad . \qquad (7)$$
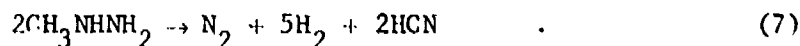
These experimental results are again substantiated by the results previously reported for N_2H_4 and CH_3ONH_2 [1, 2].

The behavior of the HCN moiety, mass 27, between 600° and 850°C is rather perplexing (Figure 3). One would expect the HCN to constantly increase with temperature and to account for all of the carbon element of the MMH. However, in the catalytic experiments, HCN decreases at a temperature higher than 600°C, thus indicating that HCN is decomposed over the heated catalyst according to the following reaction:

$$2HCN \rightarrow N_2 + H_2 + 2C \qquad . \qquad (8)$$

In the catalytic experiments, the deposition of carbon, both in the quartz reactor and on the gold leak leading to the ionization chamber of the mass spectrometer is evidence for the occurrence of Reaction 8. The same results, with respect to HCN were obtained from the decomposition of CH_3ONH_2 over Shell 405 and Phillips catalyst (Figures 3 and 4, reference 2). The disappearance of HCN in the catalyst experiments has been encountered too many times to be considered spurious. It cannot be ascribed to any experimental variations.

The NH_3/NH_2 ratio is again maintained at approximately 1.5 throughout the whole range of temperatures indicating that the NH_2 is formed from NH_3. Both the NH_3 and NH_2 peaks increased when the catalyst temperature was raised to about 400°C and then began decomposing according to the equation:

$$2NH_3 \rightarrow N_2 + 3H_2 \qquad . \qquad (9)$$

Again, previous results with both NH_3 and N_2H_4 support the present conclusions.

4. Thermal Decomposition of 1,1-Dimethylhydrazine

Figure 4 is the mass spectrum of UDMH. Figure 5 shows the mass spectrum of UDMH over the temperature range of 25° to 980°C. UDMH begins to decompose at temperatures between 200° and 300°C, as evidenced by the decrease in the parent peak, mass 60. The parent peak is no longer present at 800°C, again indicating that complete decomposition had occurred.

The slight variation in the H_2/H ratio indicates that most of the hydrogen is not evolved as H_2, but is eliminated in combination with other elements. Very little H_2 abstraction occurs in the thermal degradation.

Again, as in the previous experiments with MMH and CH_3ONH_2, the major products of the high temperature pyrolysis were HCN, N_2, and NH_3.

Gray [7] also found that UDMH is rapidly decomposed at temperatures in the 400° to 500°C range. He reported the half life of UDMH to be 2.5 minutes at 420°C and 1.5 minutes at 460°C.

Fisher [8] also investigated the pyrolysis of UDMH and reported the presence of the $(CH_3)_2N \cdot$ radical at 800 C by determining its ionization potential. He also reported the appearance potentials of the $(CH_3)_2NH$ (mass 45) and $CH_3N = CH_2$ (mass 43) fragments. These fragments were present in extremely small quantities in the pyrolysis reaction.
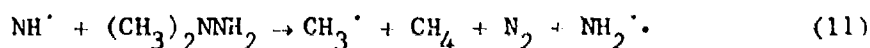
Cordes [9] also investigated the pyrolytic decomposition of UDMH at 400°C in a flow reactor. The products of decomposition were mostly N_2 and CH_4 with smaller quantities of C_2H_6, C_3H_8, and H_2. No HCN was reported by Cordes at these low temperatures.

Eberstein [6] investigated the UDMH pyrolysis at 640°C and found H_2, NH_3, CH_4, and HCN as his main degradation products.
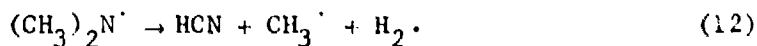
All three investigators postulate the initiation reaction in the decomposition of UDMH as follows:
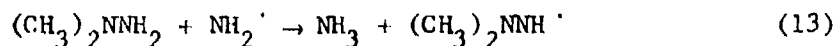
$$(CH_3)_2NNH_2 \rightarrow NH_2^{\cdot} + (CH_3)_2N^{\cdot} \tag{10}$$
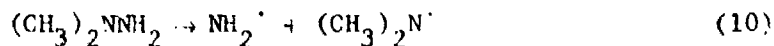
and the formation of CH_3, CH_4, and N_2 from:

$$NH^{\cdot} + (CH_3)_2NNH_2 \rightarrow CH_3^{\cdot} + CH_4 + N_2 + NH_2^{\cdot}. \tag{11}$$

Also the formation of HCN is postulated as occurring from the reaction:

$$(CH_3)_2N^{\cdot} \rightarrow HCN + CH_3^{\cdot} + H_2. \tag{12}$$

The formation of NH_3 is believed to occur according to:

$$(CH_3)_2NNH_2 + NH_2^{\cdot} \rightarrow NH_3 + (CH_3)_2NNH^{\cdot} \tag{13}$$

or

$$N_2H_4 + NH_2 \rightarrow N_2H_3^{\cdot} + NH_3. \tag{14}$$
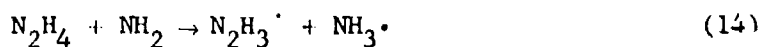
The N_2H_4 of Reaction 14 was formed from the following propagation reaction:

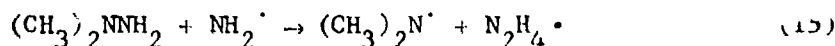$$(CH_3)_2NNH_2 + NH_2^{\cdot} \rightarrow (CH_3)_2N^{\cdot} + N_2H_4. \tag{15}$$

Figure 5 does not indicate any rise in the mass peaks of fragments with a molecular weight greater than 40, at any temperature. Such a rise would definitely indicate the presence of free radicals. An interesting observation is the constant level of the mass 15 peak (CH_3). The constant level, especially at the elevated temperatures, would indicate the possible pressure of $CH_3^{\cdot}$ free radicals. Another interesting result, not previously observed in the MMH and CH_3ONH_2 experiments, is the ratio of the 17/16 peaks ($NH_3/NH_2 + CH_4$). This ratio appears to be in error if the same results were expected for UDMH as from the results of the MMH experiments. Where the 17/16 ratio was always found to be about 1.5 with MMH and CH_3ONH_2, the 17/16 ratio was found to be less than one with

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UDMH. This ratio alteration could be accomplished by either of the two possible mechanisms already discussed (Reactions 10 and 11). The formations of $NH_2\cdot$ by Reaction 10 or that of CH_4 by Reaction 11 would result in an increase of the mass 16 fragment without affecting the one at mass 17. Thus, the ratio would be reduced. Reaction 11 would also explain the constant CH_3 level.

The small increase in the H_2/H ratio, even at the elevated temperatures, indicates that there is very little hydrogen abstraction in the thermal decomposition of UDMH. A rise in the mass 30 fragment (N_2H_4 or C_2H_6) between 600° and 750°C is again evident as it was found in the MMH experiments.

Again, a determination of the ionization or appearance potentials of the decomposition products, by the optional incremental capability of the mass spectrometer, would have been of considerable aid in determining the most plausible reaction mechanism.

5.   Catalytic Decomposition of 1,1-Dimethylhydrazine with Shell 405

Figure 6 represents the catalytic decomposition of UDMH over Shell 405 at temperatures between 25° and 750°C. Some unexpected experimental results were obtained. First, the HCN peak (mass 27) rose over the entire temperature range studied rather than rising and then falling as previously found with MMH and CH_3ONH_2 under the same experimental conditions. Second, the 17/16 ratio becomes less than one at approximately 400°C. Third, the mass 15 rises to a peak at a temperature of about 250°C, then rapidly declines rather than remaining constant as previously found.

In the present experiment, the HCN kept rising and was by far the prevalent degradation product in the UDMH catalytic decomposition. It is possible, but highly unlikely, that the Shell 405 catalyst could have been poisoned more extensively by the presence of the second CH_3 group of UDMH.

The anomalous behavior of the 17/16 ratio and of the mass 15 peak cannot be explained without further experimental data.

It appears that Reactions 8 and 12 are the predominant reactions in the catalytic decomposition of UDMH. These reactions would account for most of the N_2, H_2, HCN mass peaks which were detected. The decomposition to carbon was evident by the black deposits on the walls of the reaction chamber and on the gold leak leading to the ionization chamber of the mass spectrometer. The H_2/H ratio again increased to a larger value indicating a considerable amount of hydrogen abstraction from UDMH.

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6. Thermal Decomposition of Trimethylhydrazine

Figure 7 is the mass spectrum of TMH and Figure 8 represents its thermal decomposition. The spectrum of Figure 7 corresponds to the one furnished by Dibeler [5]. The fragments at masses 59 and 42 were the largest ones; the parent peak at mass 74 was 50 to 60 percent as large as either of the other two.

The following results were observed from the thermal decomposition of TMH over the temperature range of $25°$ to $900°C$. HCN, instead of N_2 as in other thermal degradations studied, is the most prominent peak at the higher reaction chamber temperatures.

The 17/16 ratio is considerably smaller than in any of the previous experiments. There is no doubt that the increase at mass 16 is due to the increase of CH_4. The 15 peak, most likely CH_3, also shows a corresponding increase at the elevated temperatures before peaking at approximately $600°C$.

The large peak at mass 59 began a corresponding decline along with the parent peak, mass 74, at about $250°C$. However, the other large peak, mass 42, remained fairly constant to about $750°C$ and then declined very rapidly.

7. Conclusions

It is difficult to attempt to derive any sensible reaction mechanism when the presence of certain reaction products has not been definitely established.

It has been shown in most cases studied, that the main products of the thermal degradation of the methyl derivatives of hydrazines are HCN, N_2, and NH_3; in the catalytic degradation, the main products are N_2 and H_2, as the NH_3 initially formed is decomposed by Shell 405 to yield N_2 and H_2.

In conclusion, the present experiments have demonstrated the usefulness of the mass spectrometer to study chemical reactions of propellants.
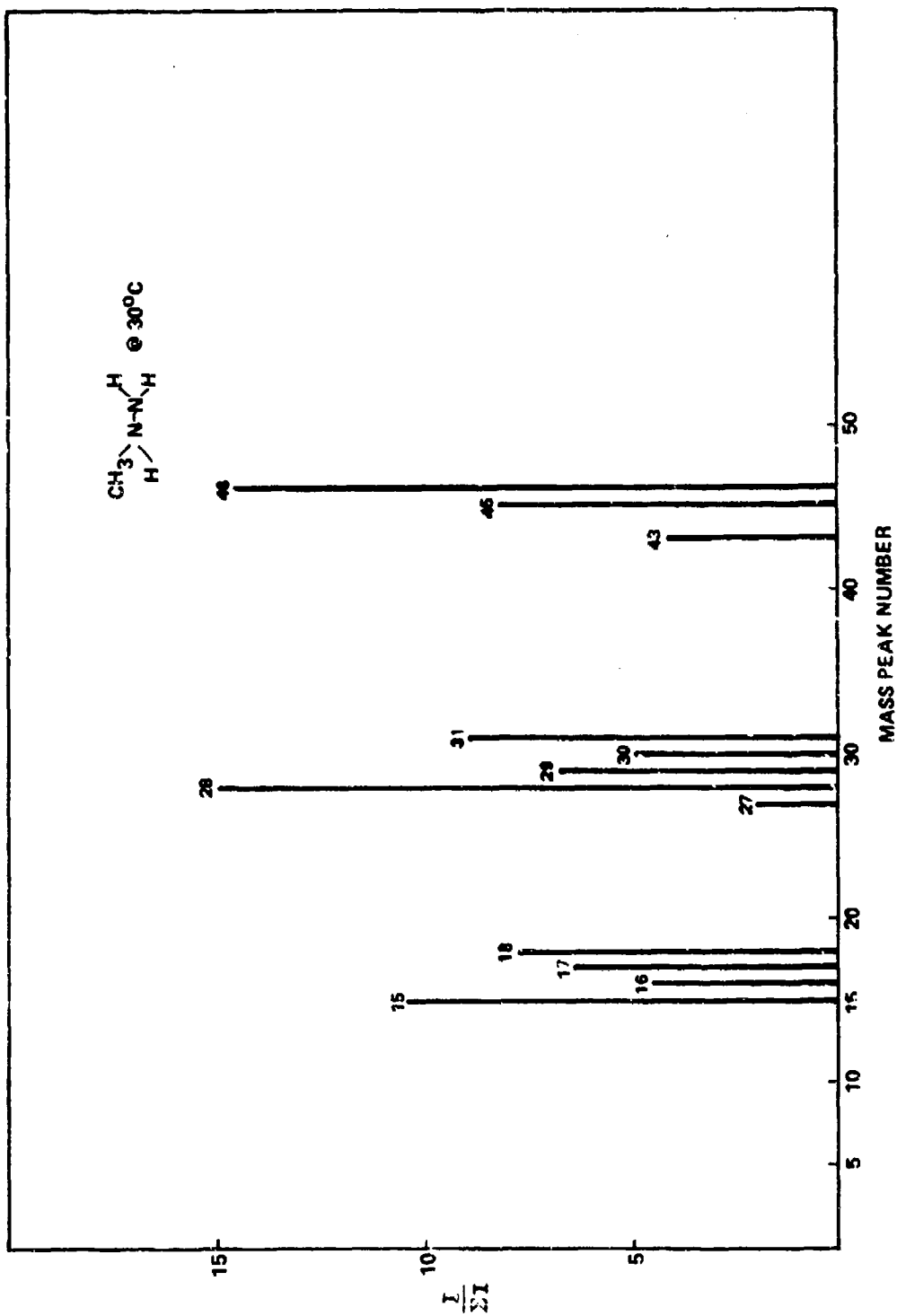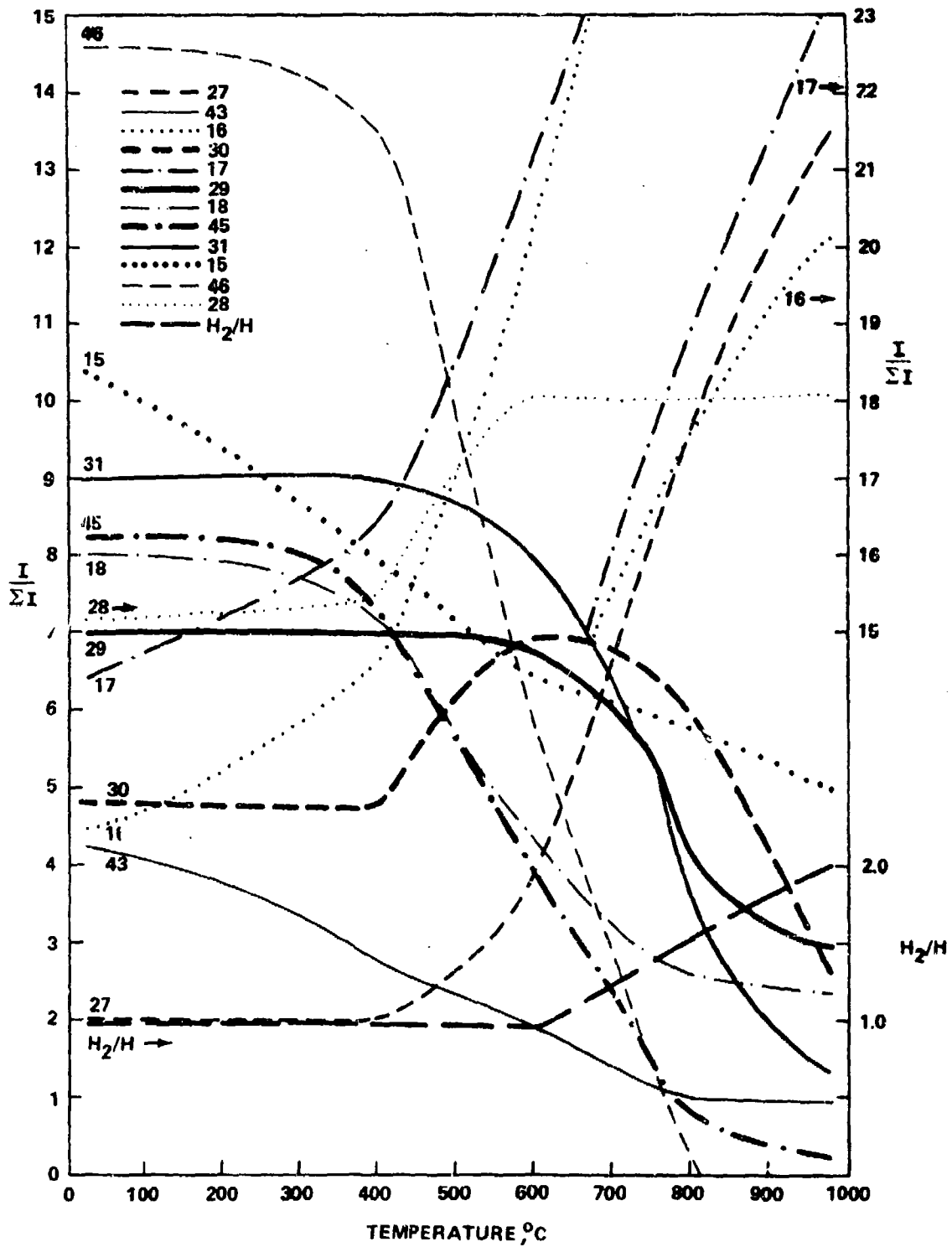
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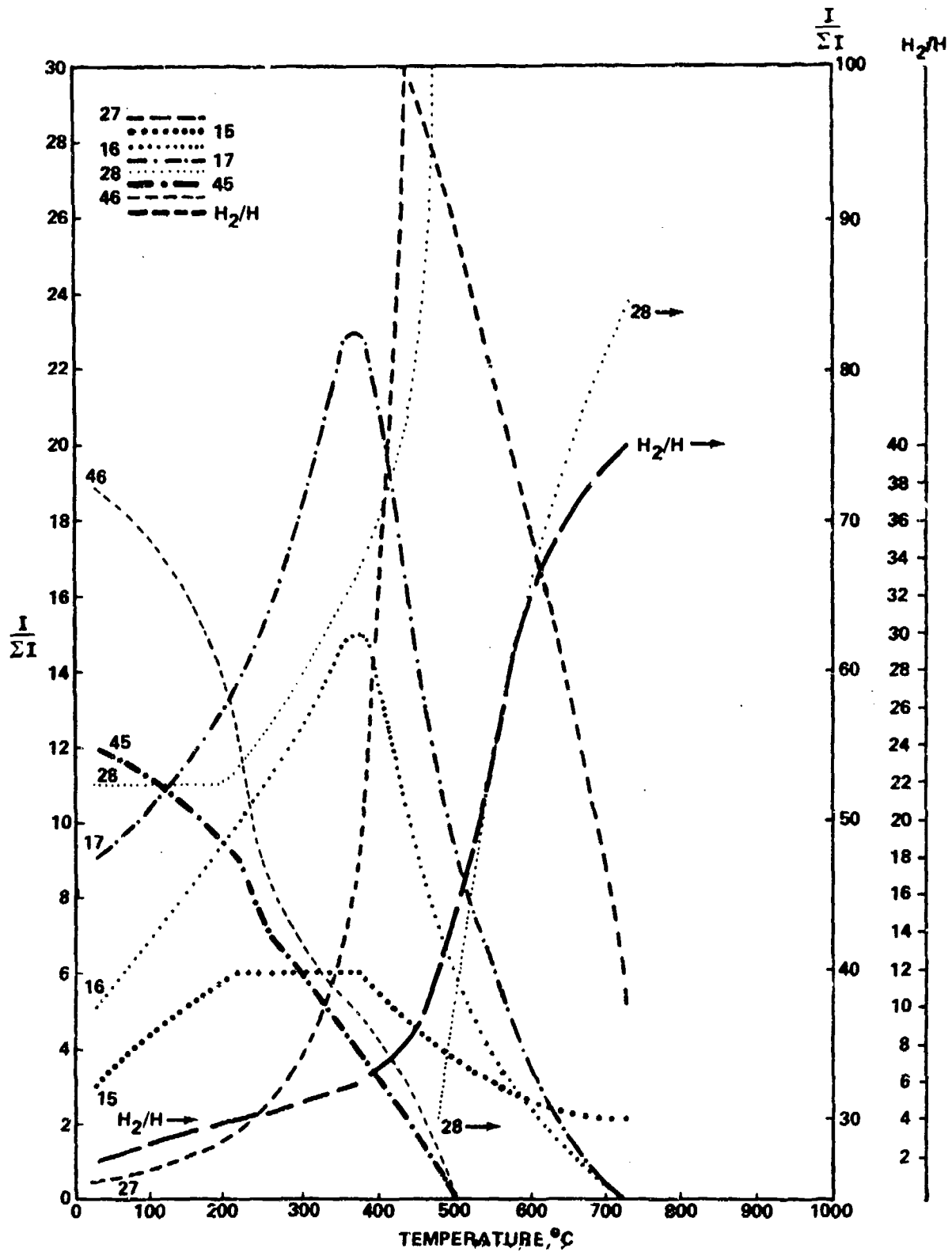Figure 1. Mass Spectrum of MMH

Figure 2. Thermal Decomposition of MMH

Figure 3. Catalytic Decomposition of MMH Over Shell 405
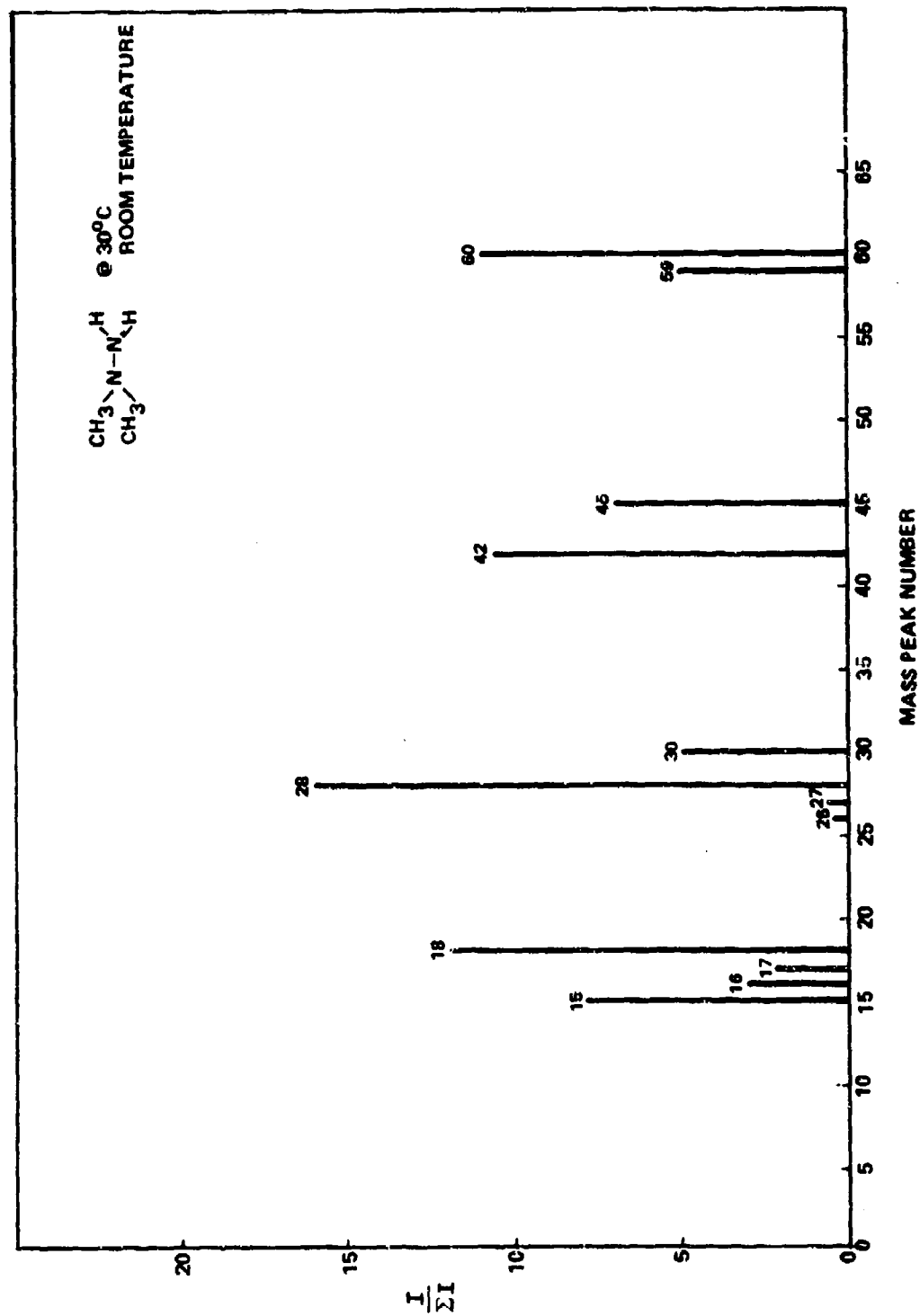
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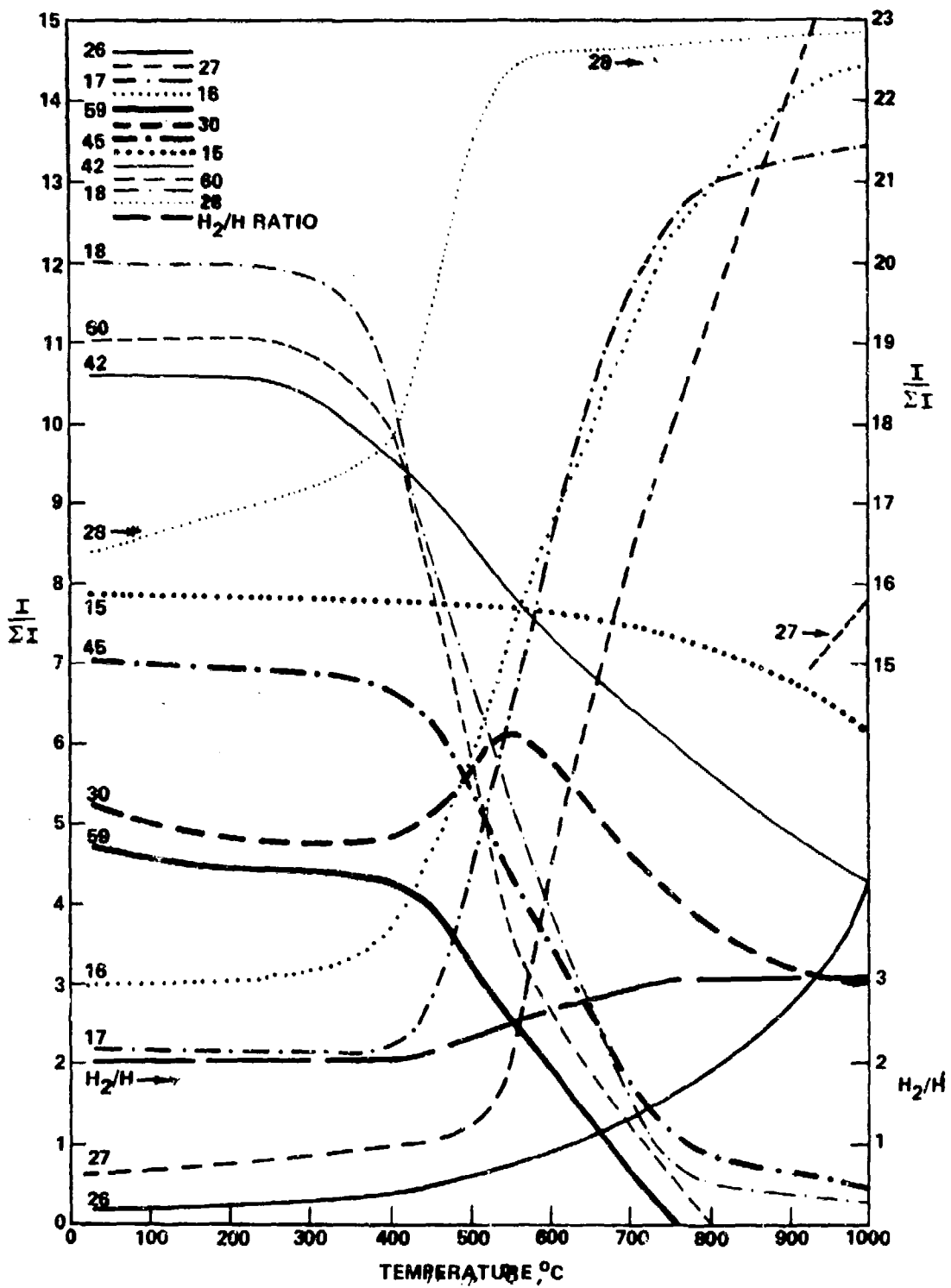Figure 4. Mass Spectrum of UDMH
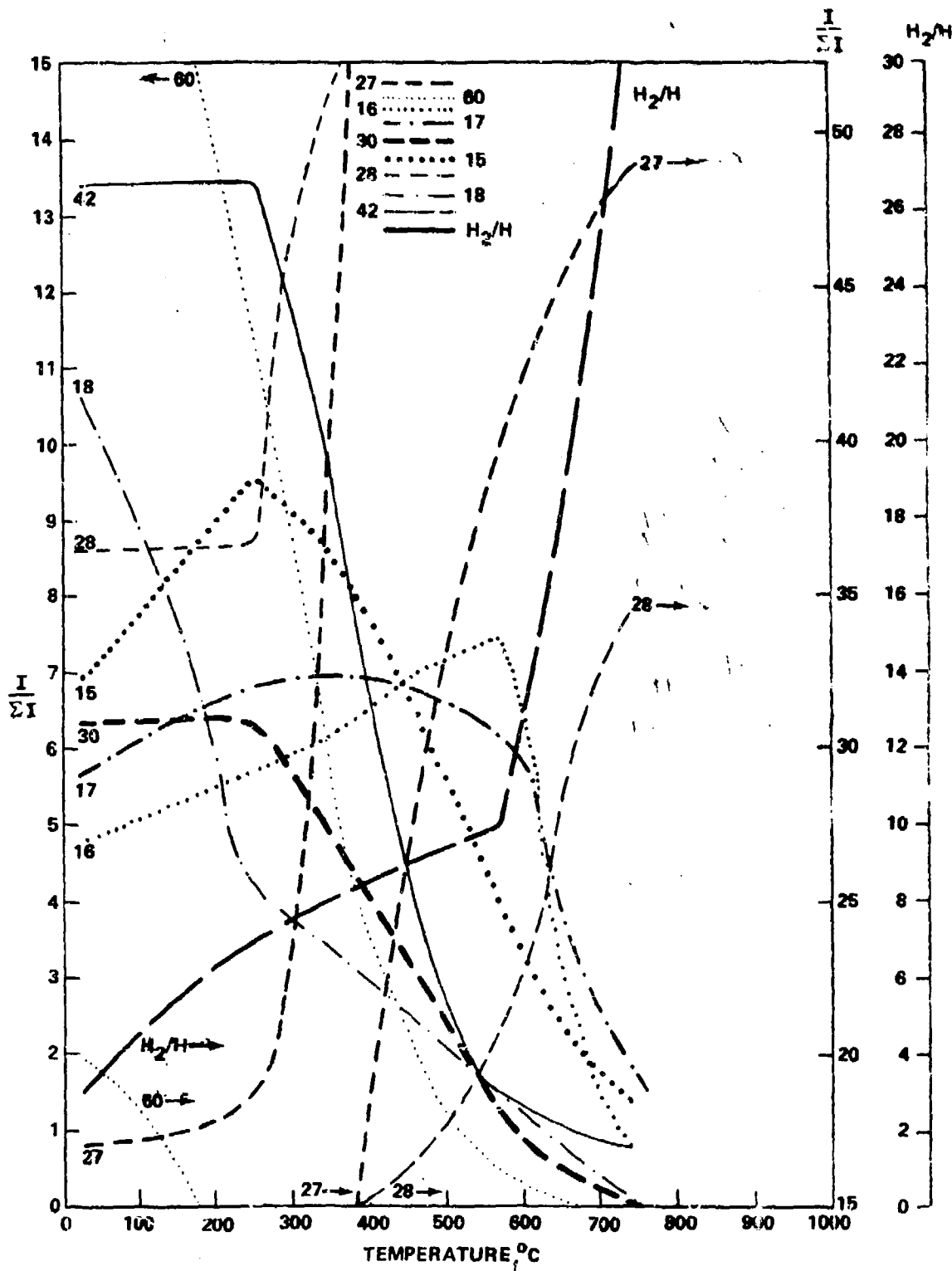
Figure 5. Thermal Decomposition of UDMH

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Figure 6.   Catalytic Decomposition of UDMH Over Shell 405
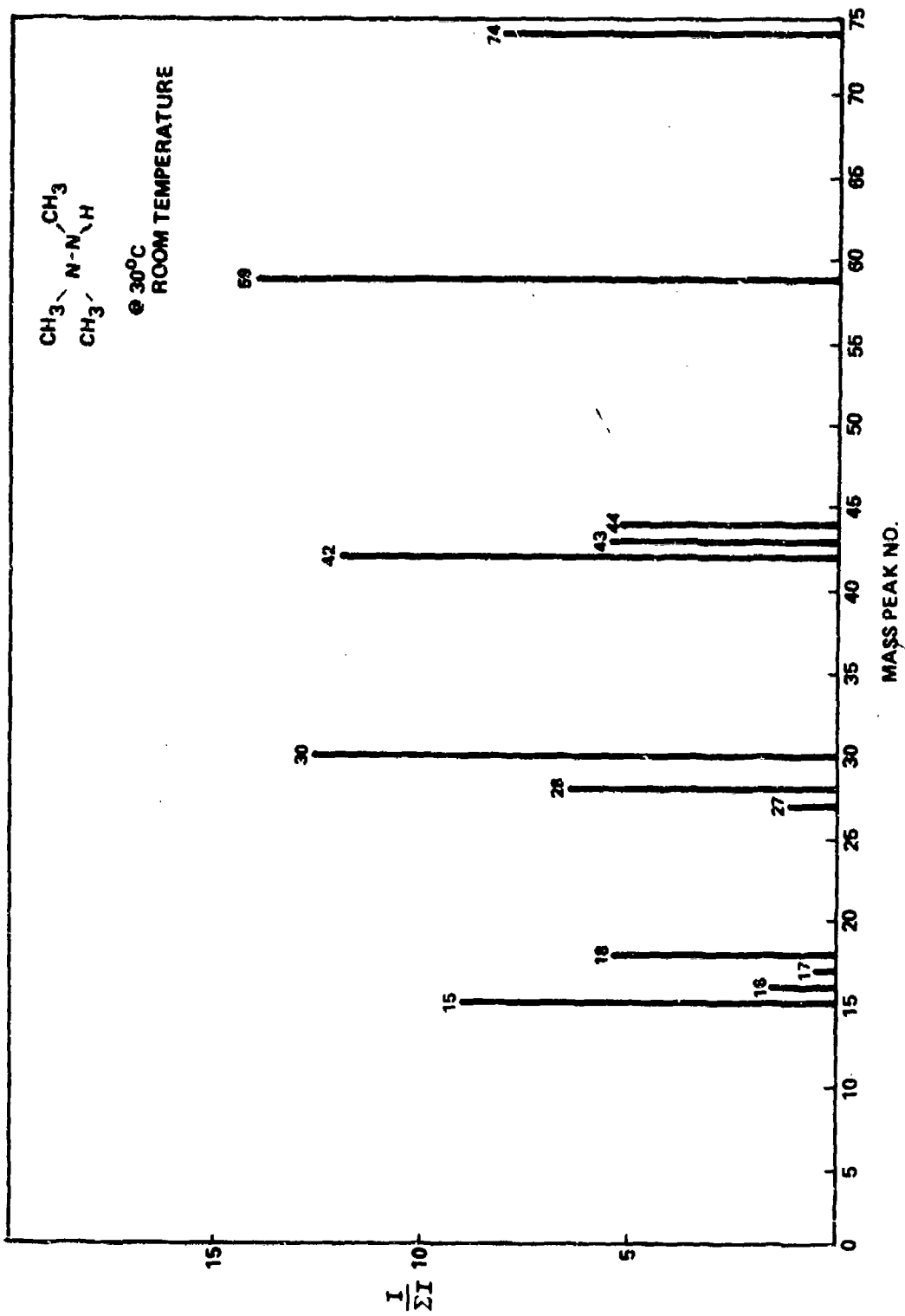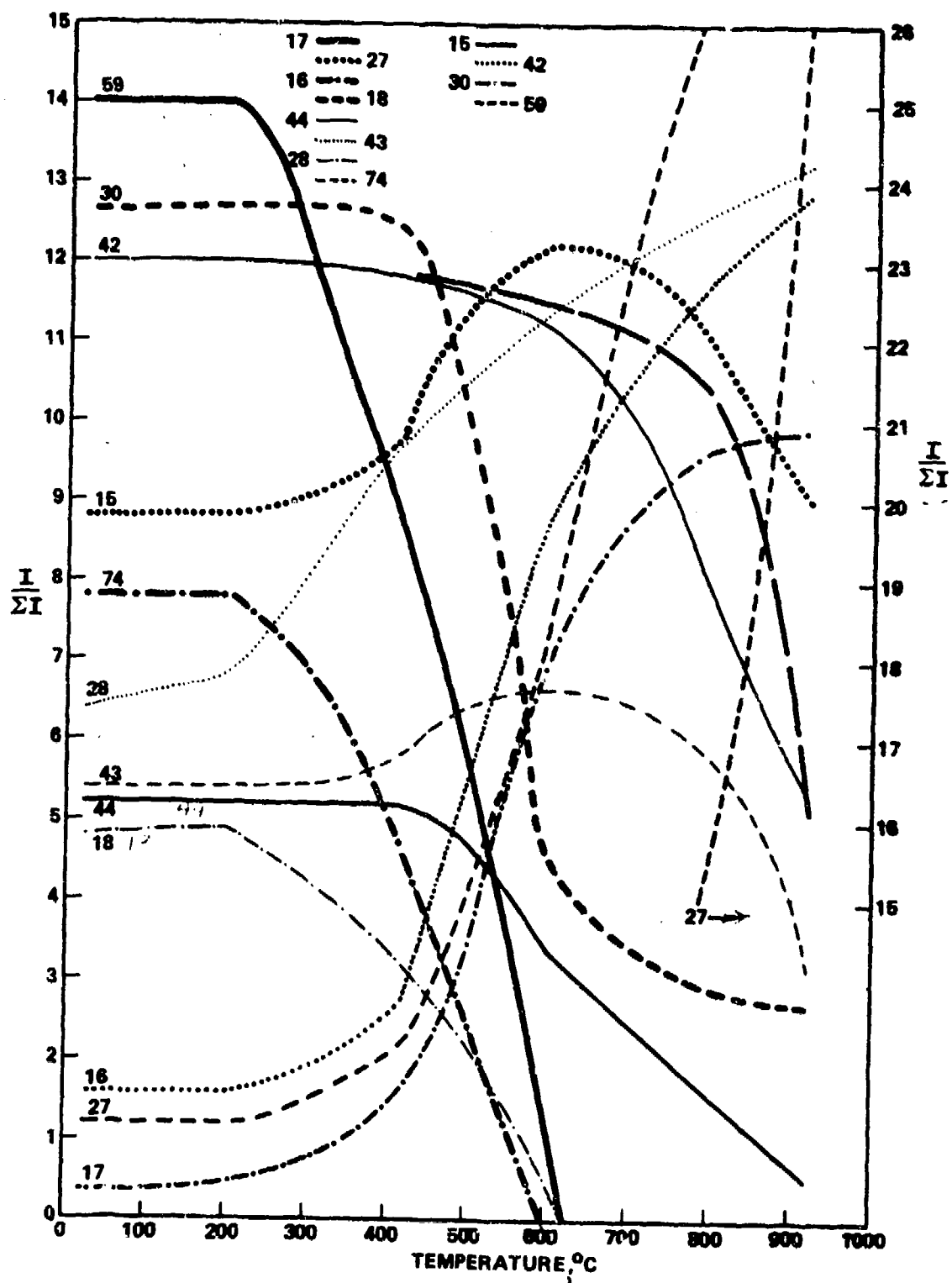
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Figure 7. Mass Spectrum of TMH

Figure 8. Thermal Decomposition of TMH

REFERENCES

1. Martignoni, P., Nappier, H. A., Duncan, W. A., Murfree, J. A., Jr., and Wharton, W. W.; The Thermal and Catalytic Decomposition of Ammonia and Hydrazine; U.S. Army Missile Command; Redstone Arsenal, Alabama; Report No. RK-TR-70-2.

2. Martignoni, P., Nappier, H. A., Duncan, W. A., Murfree, J. A., Jr., Phillips, J., and Wharton, W. W.; Thermal and Catalytic Decomposition of Methoxyl Amine; U.S. Army Missile Command; Redstone Arsenal, Alabama; Report No. RK-TR-70-14.

3. Rockenfeller, J. D., Private communication.

4. Class, J. E., Aston, J. G., and Oakwood, T. S.; J. Am. Chem. Soc.; 75; p. 2937 (1953).

5. Dibeler, V. H., Franklin, J. L., and Reese, R. M.; J. Am. Chem. Soc.; 81, p. 68 (1959).

6. Eberstein, I. J., and Glassman, I., Ninth Symposium (International) on Combustion, pp. 365-374 (1965).

7. Gray, P., and Spencer, M., Combustion and Flames, 6, p. 473 (1961).

8. Fisher, I P., and Henderson, E., Trans. Faraday Soc., 63, p. 1342 (1967).

9. Cordes, H. F., J. Phys. Chem., 65, p. 1473 (1961).