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Characterization of the Thermal Degradation of Selected Energetic Materials and Mixtures by Rapid-Scan Fourier Transform Infrared (RSFTIR) Spectroscopy

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The rapid thermal decomposition characteristics of ammonium nitrate (AN), 1,2-ethanediammonium dinitrate (EDD), EDD/AN (50/50), and EDD/AN/KN(46/46/8), where KN is potassium nitrate, have been characterized by infrared spectroscopy. The thermolysis of the mixtures strongly resemble the sum of the thermolysis characteristics of the individual components. However, there are differences in the amount of NH_3 and HNO_3 which relate to the stability of the mixtures.

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PREFACE

This program was conducted by personnel at the Department of Chemistry, University of Delaware, Newark, Delaware 19716, under contract F08635-87-C-0130 with the Air Force Armament Laboratory, Eglin AFB, FL 32542-5434. Dr. Robert L. McKenney Jr, MNE, managed the program for the Air Force Armament Laboratory. The program was conducted during the period June, 1988 through June, 1989.

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SECTION I

INTRODUCTION

There has been considerable interest in ethylenediammonium dinitrate (EDD) as a component of mixtures with other nitrate salts and various organic molecules for use in melt castable explosives. Most of this work is described in the international patent literature. A review of the German activity in this field in World Wars I and II ~~was~~ complied by Dobratz in 1983, Reference 1. It has long been known that EDD mixtures with ammonium nitrate (AN) are more thermally stable than EDD alone, Reference 2, and ~~that~~ they have better performance than AN alone, Reference 3. The eutectic mixture has a lower melting point than either component making it suitable for melt casting. However, EDD/AN mixtures suffer from volume changes with temperature because of the phase transitions of AN. The addition of potassium nitrate (KN) stabilizes the AN and counters the expansion of AN at 32°C caused by one of the solid-solid phase transitions, Reference 1.

This Interim Report describes the fast thermal decomposition processes of AN, EDD and two heterogeneous mixtures: EDD/AN (50/50) and EDD/AN/KN (46/46/8), called EAK. The techniques employed are rapid scan Fourier Transform Infrared (FTIR) Spectroscopy/Temperature Profiling as the main technique and differential scanning calorimetry (DSC) to support the temperature profiling data obtained at the high heating rates. Keywords: Thermolysis, Pyrolysis, Thermal Stability. (AW)

SECTION II

EXPERIMENTAL

The IR spectroscopy studies described in this Interim Report were conducted on a Nicolet 60SX FTIR spectrometer with an MCT-B detector. The sampling technique used is Temperature Profiling/FTIR Spectroscopy which was developed in our laboratory and has been described elsewhere, Reference 4. Typically, 1-2 mg of sample was thinly spread on a nichrome ribbon filament. The Ar atmosphere in the cell was set at the desired pressure. The filament was fired, and, while the temperature of the condensed phase was being measured simultaneously, spectroscopy of the gas products was conducted. The products were quantified by using their absolute intensities. H_2O, HNCO and any IR inactive products were not quantified.

DSC measurements were made on a DuPont 9000 Analyzer with a Model 910 DSC head. The heating rate was 5°C/min.

Samples of the mixtures were prepared by mixing the appropriate quantities of each material by weight with a mortar and pestal and then drying them in vacuum for 24 hours. In other cases, the samples were melted together to optimize homogeniety. No significant difference in the thermolysis pattern was observed for samples made in these two different ways.

SECTION III

FAST THERMOLYSIS STUDIES OF AN AND EDD

An extensive amount of work has been performed on the thermal decomposition of AN (References 5-7) which will not be reviewed here. Most of this past research has involved slow heating studies or time delayed analysis and is not directly relevant to the methods applied in our research. However, many of the past conclusions about AN under slow heating conditions are supported by our findings at high heating rates.

Fast thermolysis studies of pure AN and EDD were conducted as a basis for examining the mixtures. About fifty separate experiments for each salt were performed using controlled initial heating rates in the 70-200°C/sec range and for about five different pressures from 1 to 1000 psi Ar. The effect of sample size was tested on 1 mg and 2.5-3 mg samples. The infrared active gas products evolved by high rate thermolysis were quantified in real time by using rapid scan infrared spectroscopy and procedures described in Reference 4. Simultaneous with this gas product analysis, the temperature profile of the condensed phase was measured. Representative results for AN and EDD are provided in this report.

1. AMMONIUM NITRATE (AN)

By superimposing the quantified gas products for AN on the thermal trace of the filament (Figure 1), some of the complex details of the fast decomposition of AN come to light. The sample initially heats at 130°C/sec. Endothermic melting occurs at 170°C which is about the melting point AN measured by DSC. At about 180°C the first products are detected. These are $HNO_3(g)$ and $NH_3(g)$ which form from proton transfer followed by desorption. Shortly thereafter, AN begins to be detected in the gas phase from the recombination of $HNO_3(g)$ and $NH_3(g)$. Reaction equation (1) summarizes this well known process, References 8 and 9. AN(g) is largely an aerosol.

$$NH_4NO_3(s) \longrightarrow (HNO_3 + NH_3)\ \text{absorbed} \longrightarrow$$
$$HNO_3(g) + NH_3(g) \longrightarrow NH_4NO_3(g) \qquad (1)$$

The sample continues to heat until about 310°C where a combination of significant sublimation and endothermic degradation reactions occur leading to the products of reaction equation (2).

$$4NH_4NO_3 \longrightarrow 2NH_3 + 3NO_2 + NO + N_2 + 5H_2O \qquad (2)$$

NH_3, unlike HNO_3, persists in the gas phase while the relative concentration of NO_2 from HNO_3 decomposition grows. NO is detected later in the reaction and is probably associated with the decomposition of NO_2 at the hot filament.

At 500 psi Ar, many of the same events take place but are compressed more in time. As shown in Figure 2, melting still takes place at 170°C. AN(g) is detected at the time melting occurs. The sample then gradually heats with sublimation of AN being detected until about 230°C. At about this temperature N_2O is detected. At about 310°C the endotherm which occurs at 15 psi Ar is replaced by an exotherm at this higher pressure indicating that a self-acceleratory reaction takes place. The reaction leads predominately to N_2O and H_2O.

As is true of many other energetic materials, Reference 10, pressures above atmospheric are required to achieve ignition or explosion of hot AN. This observation is in keeping with the fact that confinement of the gas decomposition products around AN is needed to create ignition, Reference 5.

2. ETHYLENEDIAMMONIUM DINITRATE (EDD)

The IR active gas products from EDD heated at 70°C/sec under 15 psi Ar are shown in Figure 3. The thermal trace for this process is more informative when it is presented as a difference trace (the reference trace minus the sample trace) because of the subtleties that are difficult to see in the sample thermal trace alone. This difference trace is shown superimposed on Figure 3. The difference trace reveals considerable detail about the decomposition mechanism of EDD.

Melting takes place at 180°C which is about equal to the melting point of EDD measured by DSC. Melting is complete by 200°C. This is not an isothermal event because, at fast heating rates, the solid and melt are in equilibrium at one temperature. The melt heats to 270°C at which temperature the first gas products are detected. $HNO_3(g)$ from proton transfer initially dominates as shown by reaction equation (3).

$$[H_3NCH_2CH_2NH_3](NO_3)_2 \longrightarrow [H_3NCH_2CH_2NH_2](NO_3) + HNO_3(g) \qquad (3)$$

However, C-N bond fission and, possibly, H· migration also occur leading to $NH_3(g)$. Reaction equation (3) and the C-N bond fission step must be net endothermic because an endotherm is clearly present in the difference trace while these reactions are occurring. The recombination of $NH_3(g)$ and $HNO_3(g)$ leads to a small amount of $NH_4NO_3(g)$ which is an aerosol that is detected, but not quantified. At 330°C an exotherm occurs that appears to involve oxidation of the backbone. CO_2, HCN and NO rise in concentration, while $HNO_3(g)$, which is a major oxidizer, sharply drops in concentration.

At 500 psi Ar (Figure 4) melting is still detected at 180°C. $HNO_3(g)$ is detected at 260°C. Exothermic ignition occurs at 280°C which causes a sharp drop in $HNO_3(g)$, the oxidizer, and a sharp rise in NO, CO, CO_2, HNCO, H_2O and HCN. An ignition exotherm of EDD can be induced by as little as 40 psi Ar pressure at these heating rates. The magnitude of exotherm involving ignition is accentuated as the pressure becomes higher.

SECTION IV

FAST THERMOLYSIS STUDIES OF MIXTURES

1. EDD/AN (50/50)

About 40 complete studies of this mixture were conducted at various heating rates from 70-200°C/sec and pressures from 2 to 500 psi Ar using rapid scan infrared spectroscopy. Figure 5 gives the gas products quantified when the mixture is heated at 95°C/sec under 15 psi Ar superimposed on the temperature profile for the condensed phase. Superimposing these two figures shows that a melting endotherm occurs at about 110°C, which is well below that of pure AN (170°C) and EDD (180°C), but closely matches the melting endotherm for the mixture measured by DSC of 109°C. The melt then heats liberating $HNO_3(g)$ at 210°C and then $NH_3(g)$ at about 230°C. The initial decomposition closely resembles that for this mixture measured by others (Reference 2, 11) to be 200-210°C. $HNO_3(g)$ and $NH_3(g)$ continue to dominate until about 310°C where an exothermic event takes place. An exotherm was previously noted at 300°C in Reference 11. At this temperature NO_2, CO_2, N_2O, H_2O and HNCO increase snarply in concentration and some $NH_4NO_3(g)$ appears. A notable difference between the decomposition of this mixture and the pure compounds is that NH_4NO_3 sublimation is strongly suppressed in the mixture.

The products and thermal profiles of EDD/AN mixtures above the melting point resemble those of the pure components. However, AN decomposition in the form of $NH_3(g)$ and $HNO_3(g)$ dominates in the 210-260°C range. Endothermic chemistry characteristic of EDD then occurs at 260°C producing more or less the same initial products as NH_4NO_3. At 310°C endothermic chemistry occurs in which EDD backbone products are liberated. About 11 percent of the products should be CO_2 provided that no undetected carbon-containing species are produced. Figure 5 shows that the amount of CO_2 is about 10 percent.

Increasing the pressure to 40 psi and then to 200 psi Ar causes approximately the same decomposition pattern and temperature of events, but the exotherm at 300°C is accentuated. In effect, diffusion of the reactive gas products away from the condensed phase is retarded at higher pressure which narrows the reaction zone. The exothermic reactions become self-accelerating creating at least partial ignition. HNO_3 appears to be the oxidizer. NO, CO_2 and H_2O are the predominant products detected by IR spectroscopy.

2. EDD/AN/KN (46/46/8)

This mixture was studied at 1 to 40 psi Ar and at heating rates from 75-120°C/sec. As shown in Figure 7, melting occurs at about 110°C which compares to a value of 107°C by DSC. At about 200°C, the first gas products are detected which resembles the results for pure AN and EDD/AN. A second endotherm is detected resembling that of pure EDD. Finally, a third endotherm appears at about 325°C resembling that of pure AN. Thus, the mixture decomposition process bears a strong resemblance to the decomposition of the pure components.

A curious difference between EDD/AN/KN and the EDD/AN mixture is that $NH_3(g)$ is usually detected in advance of HNO_3 in the former while the reverse is true of the latter. Since NH_3 is a known inhibitor to the decomposition of AN, References 12 and 13, the excess NH_3 during fast heating may limit the buildup of HNO_3 and, therefore, stabilize this mixture relative to the EDD/AN mixture. In other words, KN changes the characteristics of the decomposition of AN and EDD with respect to the formation of NH_3.

SECTION V

CONCLUSIONS

1. AN

The following are the principal conclusions to be drawn about the fast thermal decomposition of AN: In all fast heating experiments up to the 200°C/s limit used for this compound, melting is detected at about 170°C. Melting always occurs in advance of detection of the first gas decomposition product (HNO_3). The HNO_3 results from endothermic N-H bond heterolysis. AN(g) is always detected at or above the melting point. The time increment separating the melting point and the detection of AN(g) depends on the applied Ar pressure. Above 200 psi Ar, these two elements are not separable by our method. The endotherm present at 310°C when the Ar pressure is less than 200 psi is replaced by an exotherm when the pressure is above 200 psi. This is probably because the HNO_3 is forced to remain in contact with the condensed phase for a longer period of time.

2. EDD

As with AN, melting of EDD is detected at about the known melting point when fast heating conditions are employed. The first detected gas decomposition products result from endothermic reactions. As the pressure is raised, the temperature range in which endothermic chemistry is detected becomes the temperature range at which exothermic chemistry occurs. However, by conducting the experiment under a pressure (such as 15 psi Ar) at which the classes of gas products can be distinguished, some of the sequential decomposition steps are apparent. The initial reaction appears to be proton transfer (NH bond heterolysis) to liberate $HNO_3(g)$. Some endothermic CN bond fission and H· transfer then take place, leading to $NH_3(g)$. The desorbed HNO_3 and NH_3 recombine to form $NH_4NO_3(g)$. Exothermic reactions involving the backbone then occur between adsorbed HNO_3 and the residue, leading to CO_2, NO, HCN, N_2O, HNCO, and possibly, IR-inactive products.

3. EDD/AN

The thermochemical events of this mixture resemble the sum of the pure components except that the melting point is suppressed to about 110°C. AN decomposition dominates initially, producing $HNO_3(g)$. However, the sublimation of AN is suppressed in the mixture implying that NH_3 is not released. This buildup of NH_3 in the condensed phase would have a stabilizing influence on the mixture, References 12 and 13, as is known to be the case in other work, Reference 2. Raising the pressure causes the highest temperature endotherm to become an exotherm.

4. EDD/AN/KN

The major thermochemical events of this mixture resemble the sum of the thermochemical event of the individual components. However, the addition of KN to the EDD/AN mixture appears to alter the decomposition of AN and EDD to some extent as evidenced by the fact that $NH_3(g)$ is released in advance of HNO_3, while the reverse is true of AN and EDD/AN mixtures. The excess NH_3 may prevent the buildup of HNO_3. The lower amount of HNO_3 reduces the rate and extent of heat release which has a stabilizing effect on this mixture.

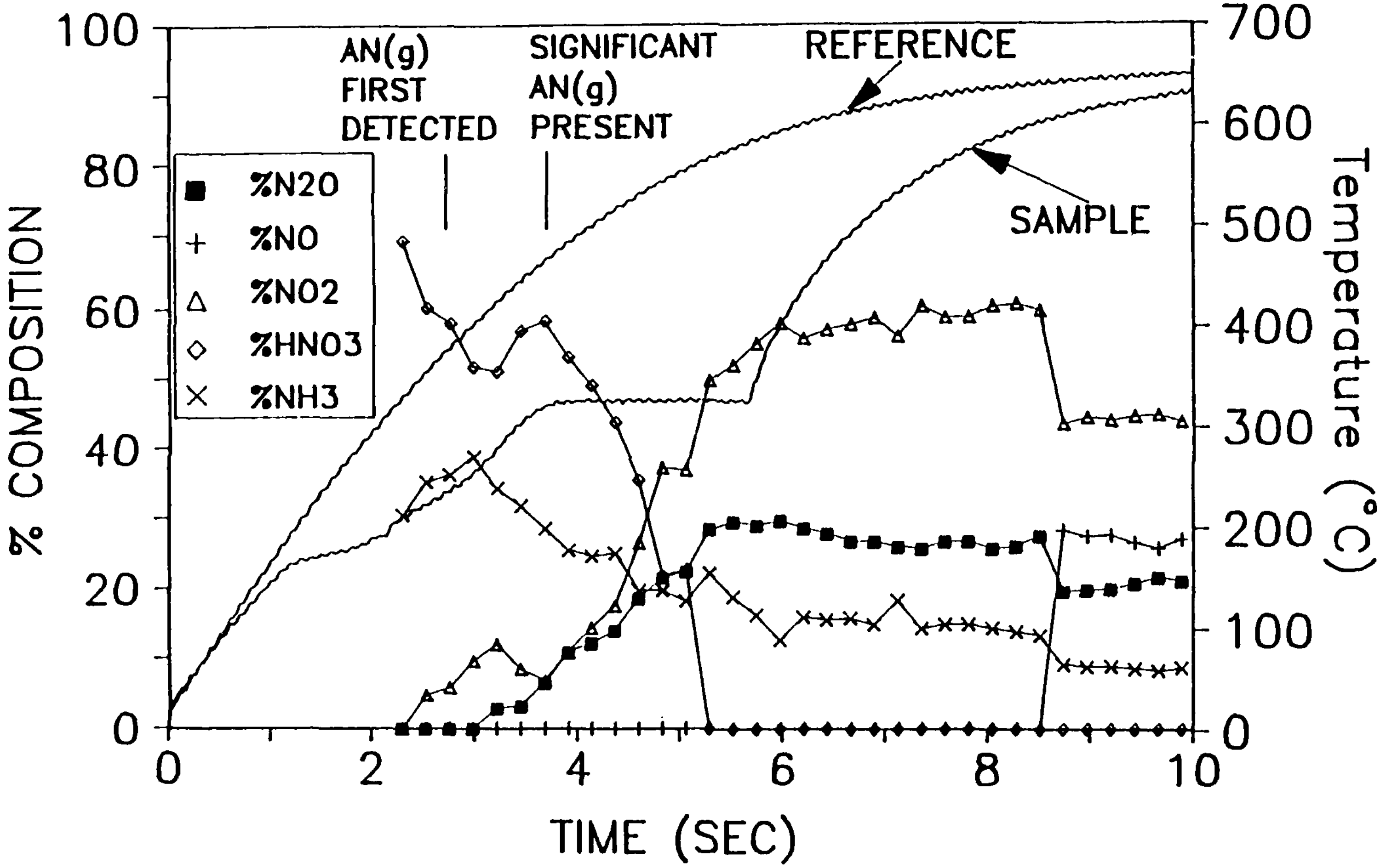

Figure 1. Fast Thermolysis of AN 15 psi Ar

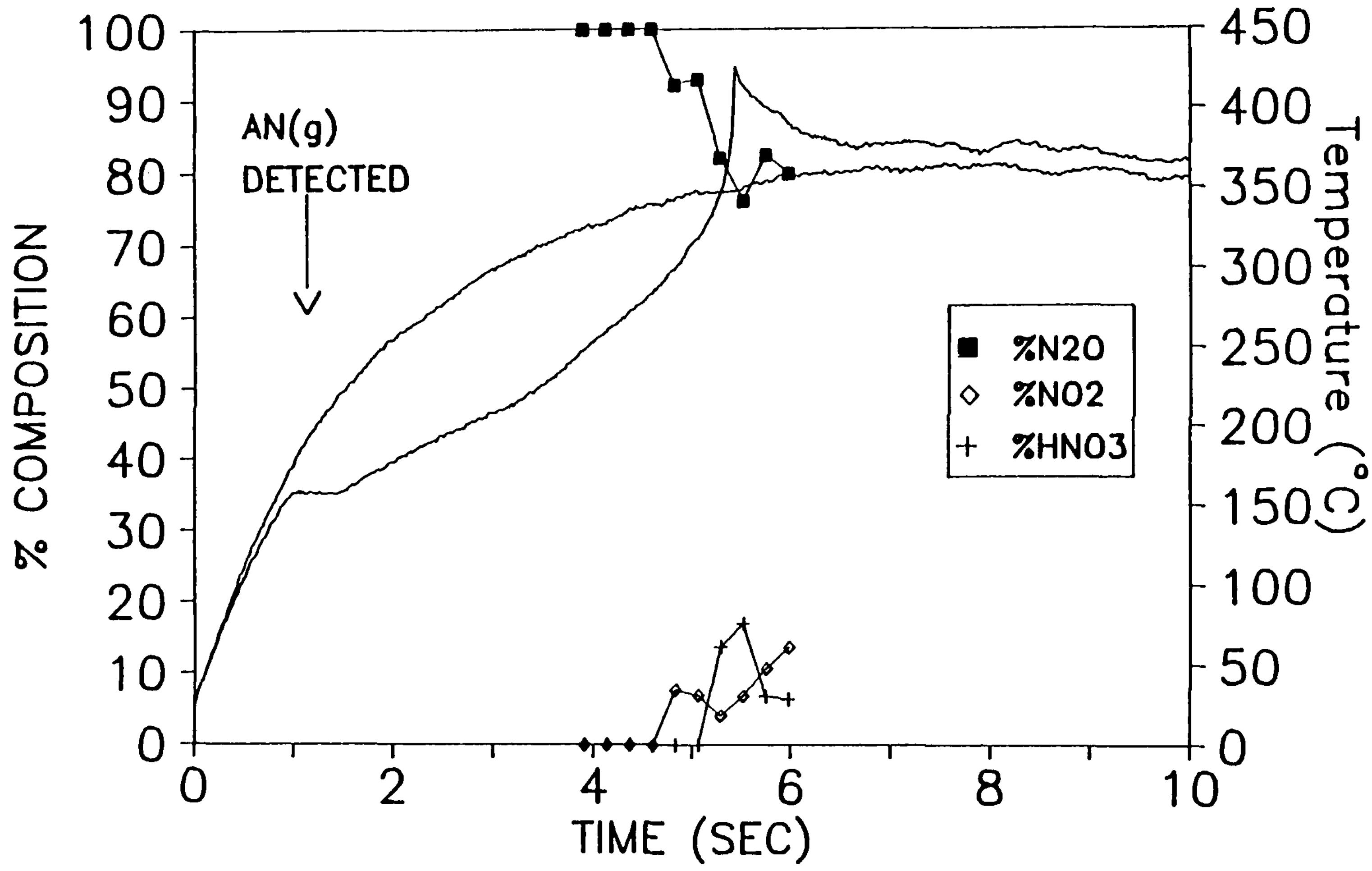

Figure 2. Fast Thermolysis of AN at 500 psi Ar

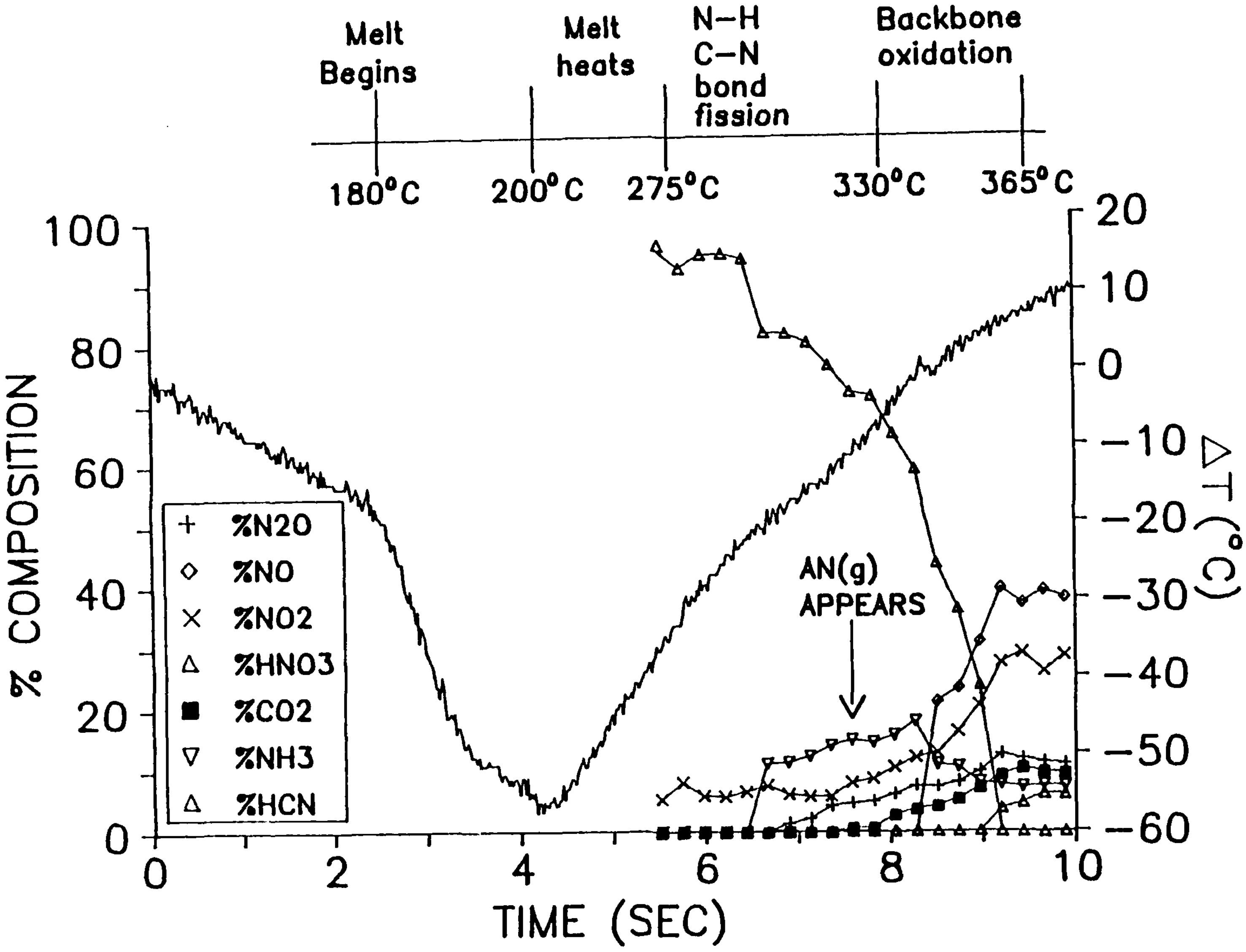

Figure 3. Fast Thermolysis of EDD at 15 psi Ar

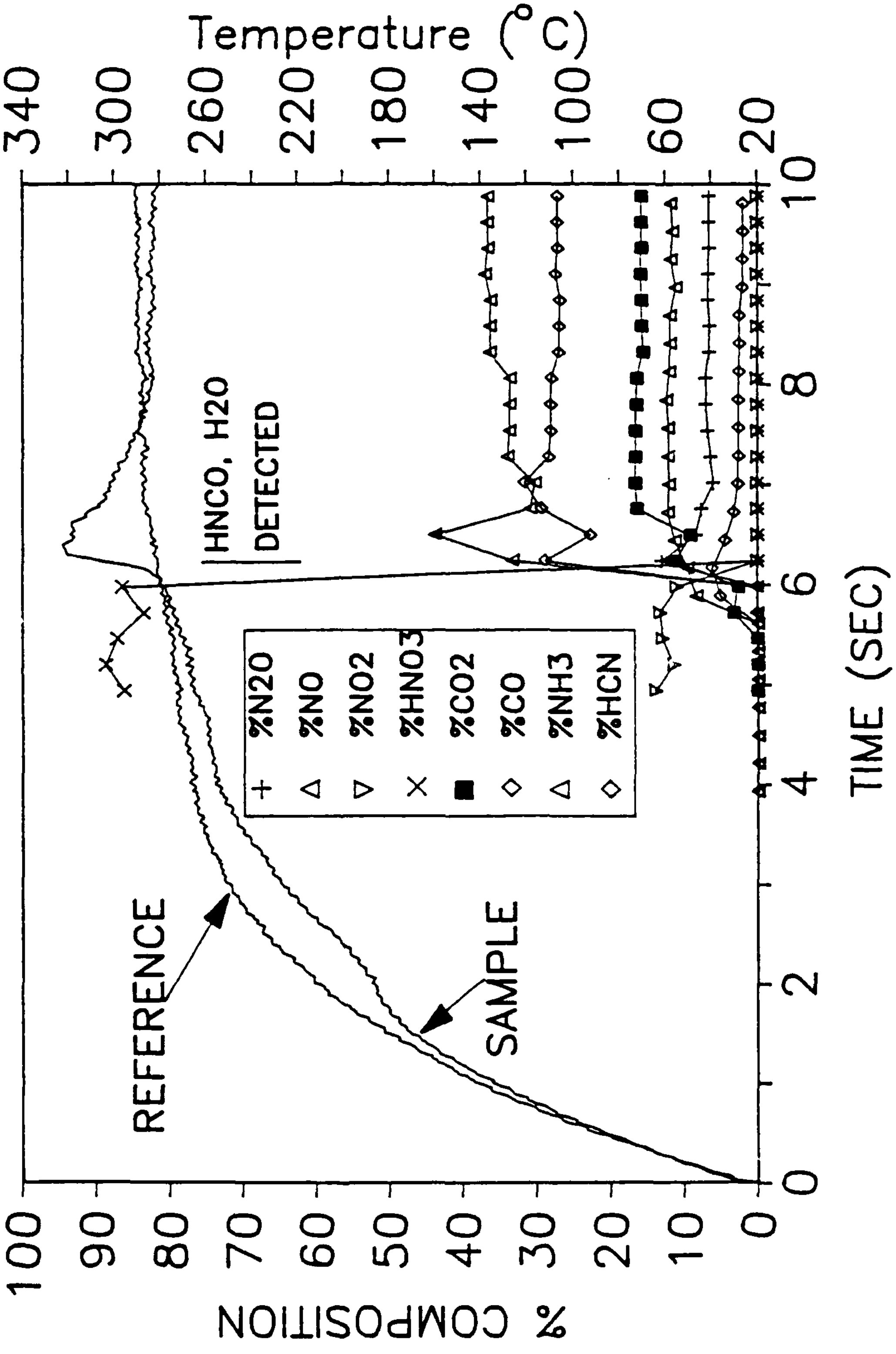

Figure 4. Fast Thermolysis of EDD at 500 psi Ar

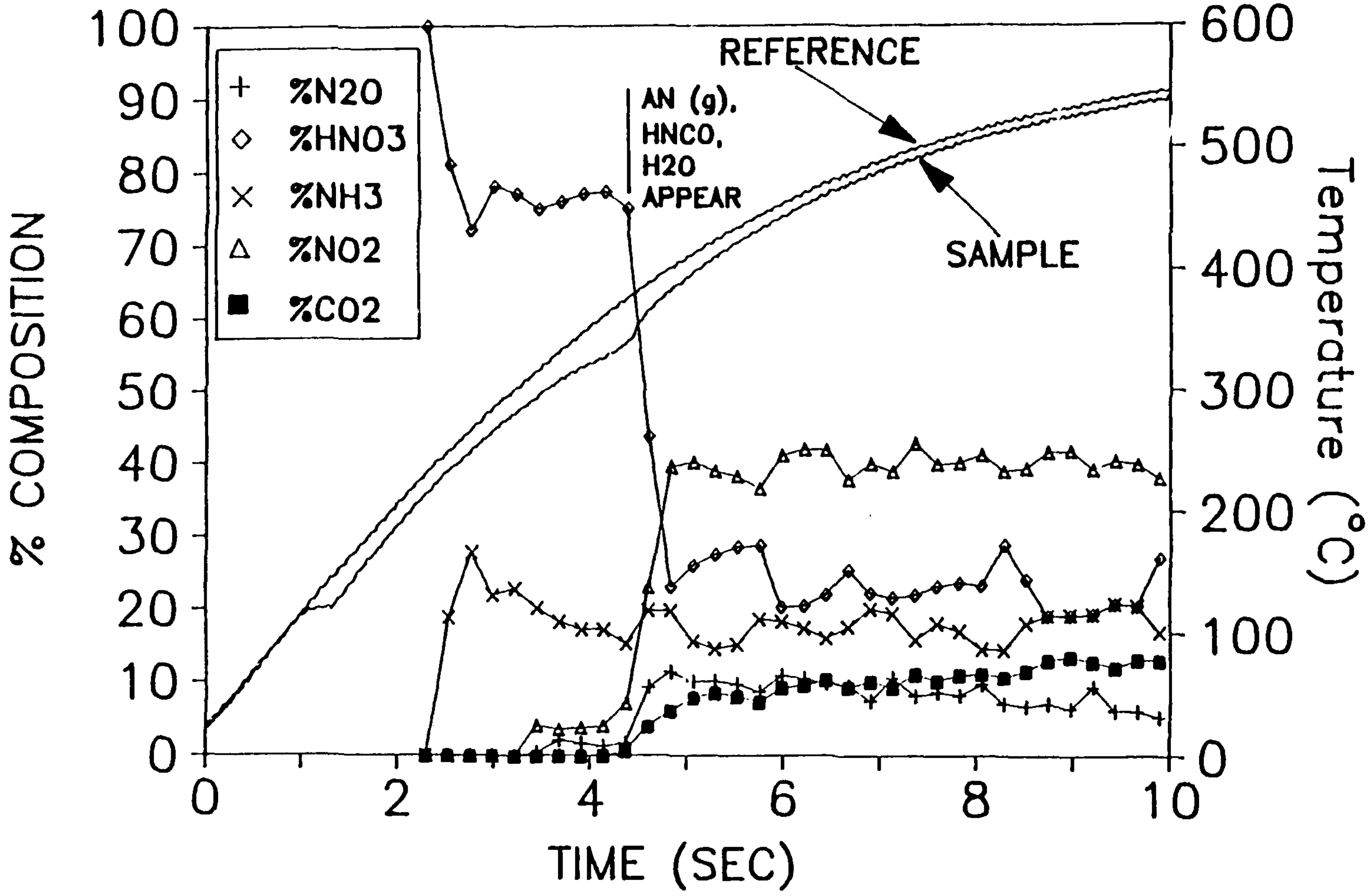

Figure 5. Fast Thermolysis of AN/EDD at 15 psi Ar

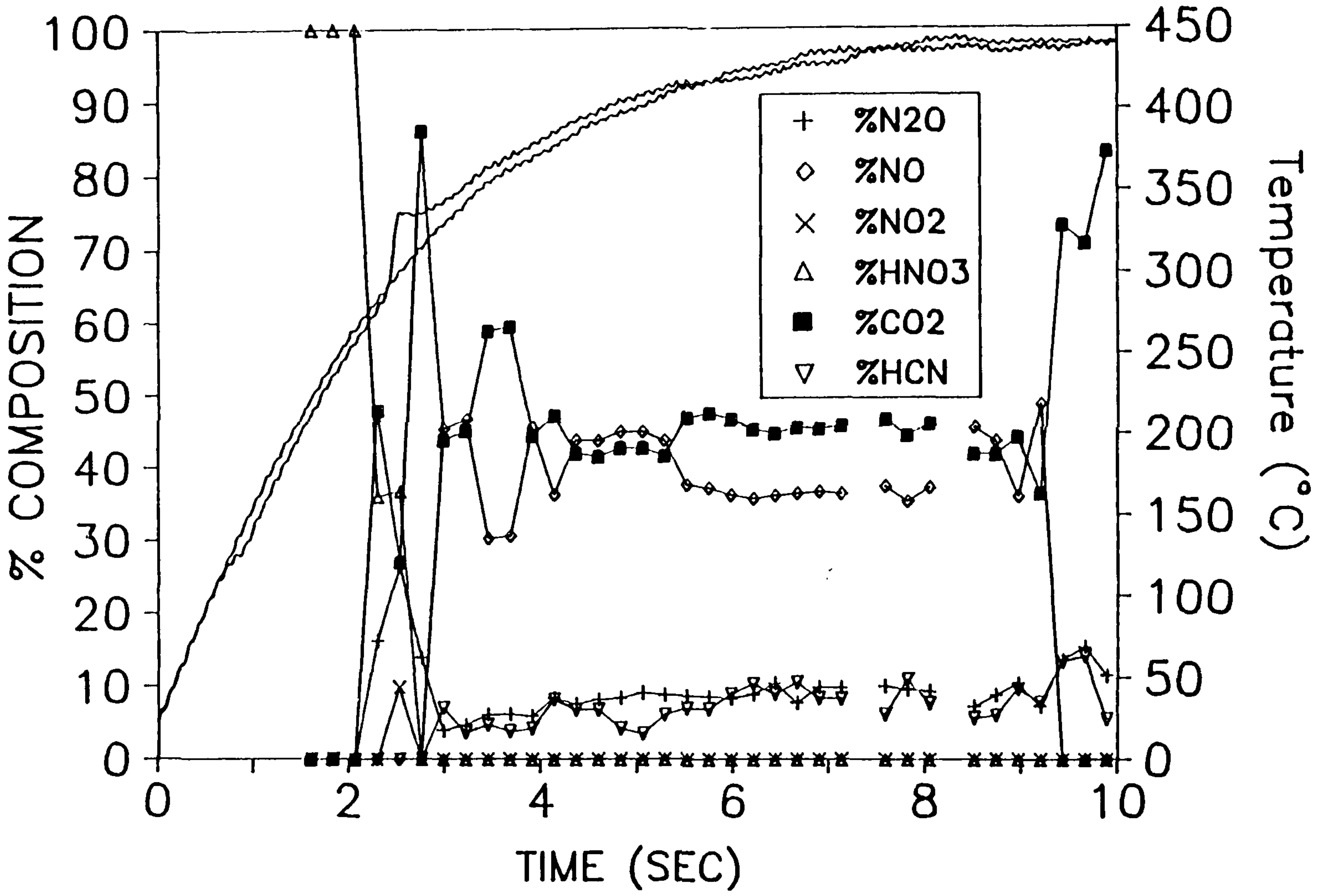

Figure 6. Fast Thermolysis of AN/EDD at 200 psi Ar

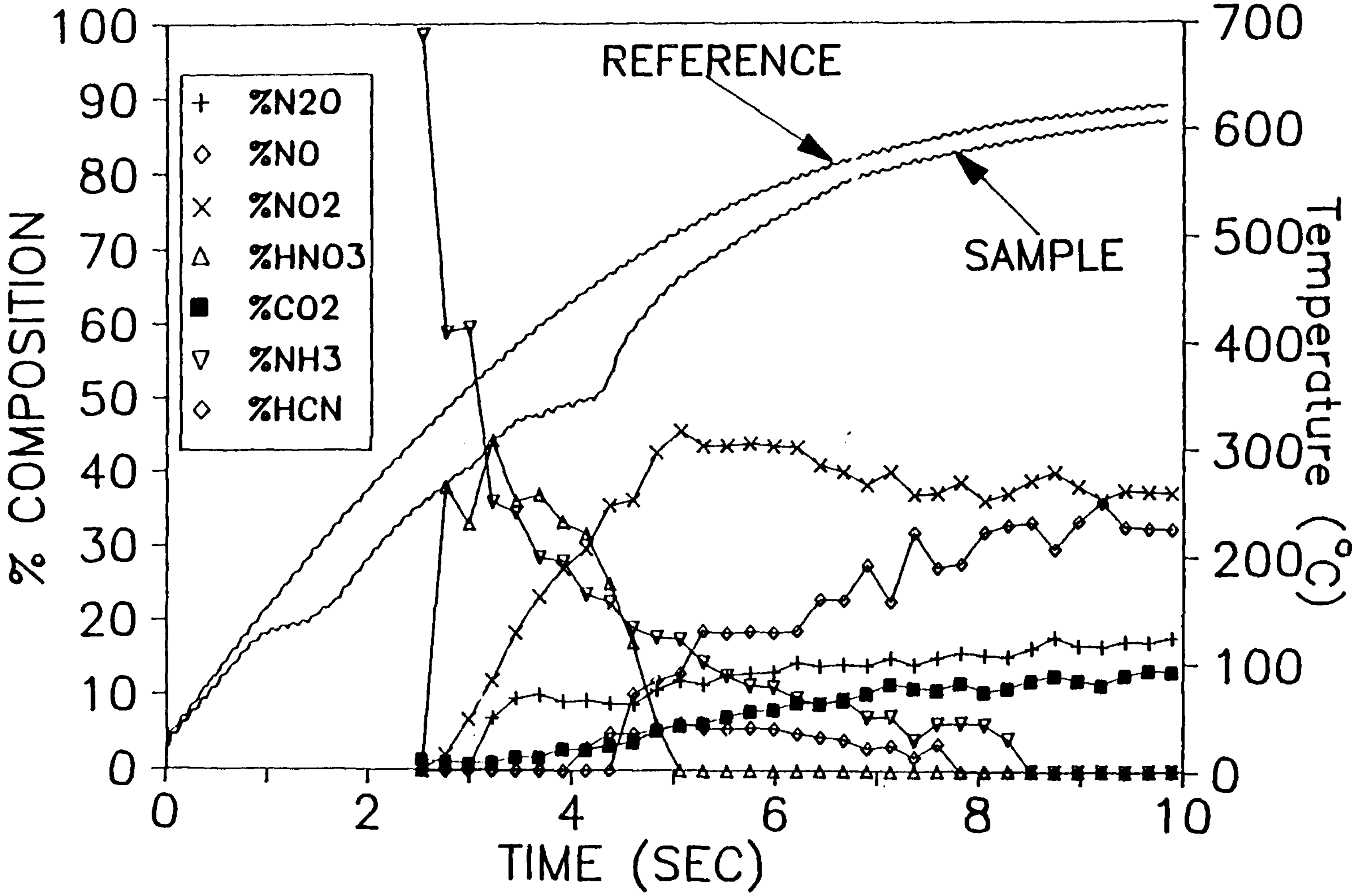

Figure 7. Fast Thermolysis of 46/46/8 AN/EDD/KN at 2 psi Ar

REFERENCES

1. B.M. Dobratz, Report Number LA-9732H, UC-45, Los Alamos National Laboratory, Los Alamos, NM, 1983.
2. L. Medard, Mem. Poudres, **34**, 147 (1952).
3. A. LaRoux, Mem. Poudres, **32**, 121 (1950).
4. J.T. Cronin and T.B. Brill, Applied Spectroscopy, **41**, 1147 (1987).
5. B.T. Federoff, "Encyclopedia of Explosives and Related Items", Vol 1, A311-379 (1960).
6. A. Biskupski and A. Kolaczkowski, Chem. Stoscow, **27**, 179 (1983).
7. J.H. Koper, O.G. Jansen, and P.J. van den Berg, Explosivestoffe, **8**, 181 (1970).
8. W.A. Rosser, S.H. Inami, and H. Wise, Journal of Physical Chemistry, **67**, 1753 (1963).
9. G. Feick, Journal of the American Chemical Society, **76**, 5858 (1954).
10. Y. Oyumi and T.B. Brill, Combustion and Flame, **68**, 209 (1987).
11. M.J. Urizar, Los Alamos National Laboratory, unpublished results, 1982.
12. A. Kolaczkowski, A. Biskupski and J. Schroeder, Journal of Chemical Technology and Biotechnology, **31**, 327 (1981).
13. A. Kolaczkowski and A. Biskupski, Przem. Chemistry, **59**, 621 (1980).