

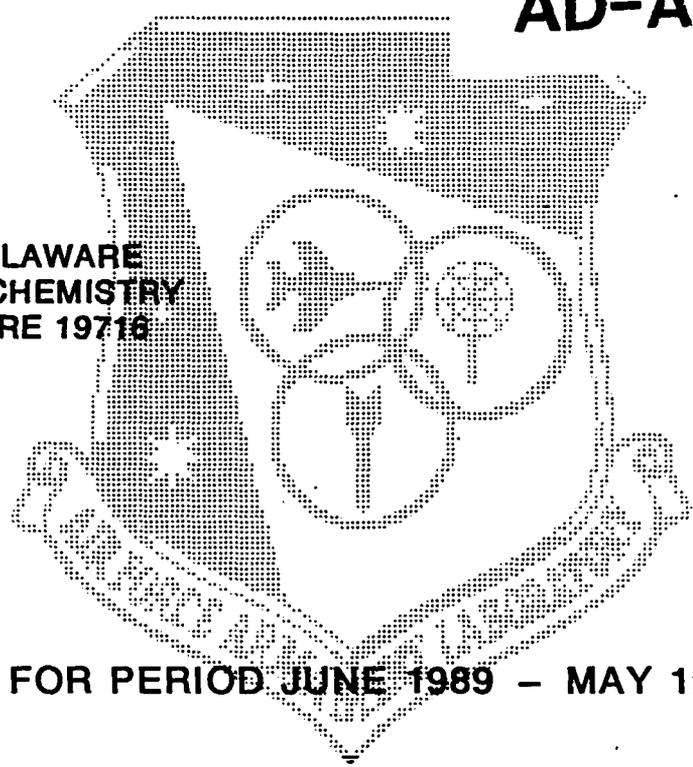
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Characterization of the Thermal Degradation of Selected Energetic Materials and Mixtures by Rapid-Scan Fourier Transform Infrared (RSFTIR) Spectroscopy

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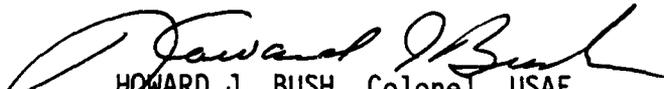
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FOR THE COMMANDER


HOWARD J. BUSH, Colonel, USAF
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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, 1989 through May, 1990.

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SECTION II

EXPERIMENTAL

Samples of CUBAN and CUBDAN were supplied by Dr. R.L. Willer of the Thiokol Corporation, Elkton, MD. A sample of PUDD was prepared by the addition of 6M HNO₃ to the free amine which was supplied by Dr. Alan Marchand of the University of North Texas.

The IR spectroscopy studies described in this 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 2. Typically, 1-2 mg of the 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. H₂O, HNCO and any IR inactive products were not quantified.

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

SECTION III

FAST THERMOLYSIS STUDIES OF CUBAN, CUBDAN, AND PUDD

CUBAN, CUBDAN AND PUDD were rapidly decomposed at a variety of heating rates in the 70-150°C/sec range and pressures of Ar in the 1-1000 psi range. The infrared active gas products were quantified in near real-time simultaneously with the temperature trace of the condensed phase. Representative results for each compound are described here.

1. CUBYLAMMONIUM NITRATE (CUBAN)

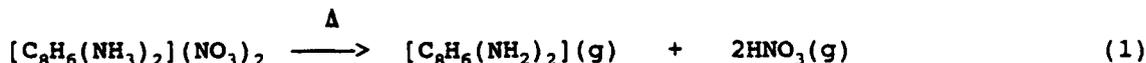
The fast thermolysis results of CUBAN heated at a rate of 90°C/sec under 15 psi Ar are shown in Figure 1. No melting endotherm was detected either by DSC or in the thermal trace of Figure 1. During rapid heating, the decomposition exotherm appeared at 150-175°C depending on the pressure. By DSC the exotherm began at about 140°C. The decomposition gases first appeared at the exotherm. It is interesting to note that in an Ar atmosphere several of the hydrocarbon products (C_2H_2 , C_2H_4) contain multiple bonds so that the full strain energy of the cage is not released in the initial decomposition step. No large organic molecules, such as cyclooctatetraene, are formed. In fact, no unassigned absorbances were present in the IR spectrum of the decomposition gases.

The pressure dependence of the relative concentrations of the initially detected gas products is shown in Figure 2. These data were obtained by decomposing similar-sized samples at a rapid, but relatively similar, heating rate under different static pressures of Ar. Below 7.5 psi Ar, $HNO_3(g)$ is generated by proton transfer followed by desorption. All primary alkylammonium nitrate salts rapidly thermolyzed to date liberate HNO_3 as the first detectable gas decomposition product, Reference 3. In fact, the gas phase basicity of the parent amine qualitatively correlates with the tendency to liberate HNO_3 under rapid thermolysis conditions, Reference 3. This pattern can be used to estimate the gas phase basicity of the cubylamines (*vide infra*). Cubylamine also volatilizes during thermolysis. The $HNO_3(g)$ rapidly recombines with the vaporized cubylamine to form an aerosol of CUBAN. Figure 3 shows the IR spectrum of the aerosol of CUBAN formed in this way compared to the spectrum of a thin film of authentic CUBAN supported between two NaCl plates. The close match of these spectra proves that CUBAN sublimes at low pressure when heated.

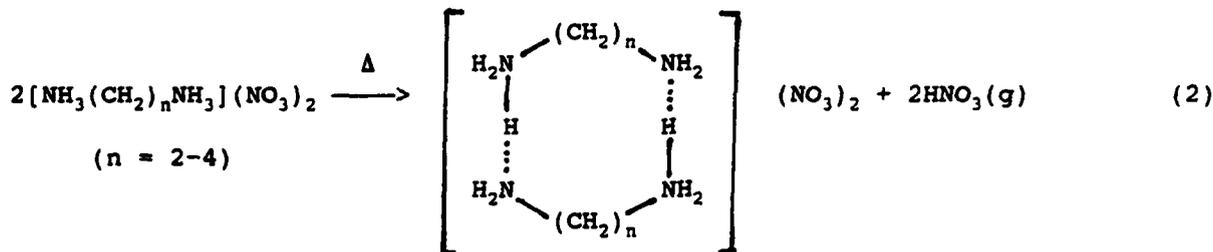
2. CUBANE-1,4-DIAMMONIUM DINITRATE (CUBDAN)

Figure 4 shows the thermal decomposition of CUBDAN when heated at an initial rate of about 60°/sec under 7.5 psi Ar. At about 220°C an exotherm occurs simultaneously with the appearance of gas decomposition products. By DSC the decomposition occurs at 175-200°C. No melting endotherm is found at low (DSC) or high heating rates. Extensive oxidation-reduction chemistry is indicated by the products, but the presence of a significant amount of C₂H₂ shows that the strain energy of cubane is not released in one step under the conditions used. There are no larger hydrocarbon molecules in the gas phase.

Figure 5 shows that below 7.5 psi Ar the predominant decomposition process is deneutralization to form HNO₃ and cubane-1,4-diamine followed by desorption of the neutral molecules (reaction (1)). As shown by the spectra



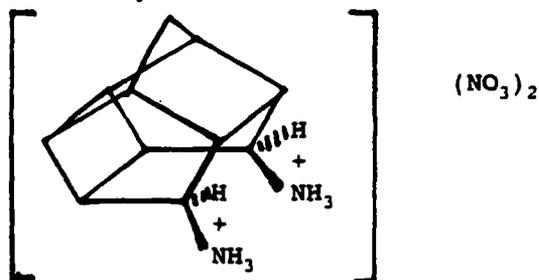
compared in Figure 6, recombination of the products reaction Equation (1) forms CUBDAN aerosol. CUBDAN is one of only two alkyldiammonium dinitrate salt that we have studied which deprotonates at both ammonium sites and thus sublimes. The other is piperazinium dinitrate. All of the other alkyldiammonium dinitrate salts appear to deprotonate at one site, but retain salt properties in the condensed phase (e.g. reaction Equation (2)), Reference 4.



The salt product of reaction Equation (2) then decomposes to small molecule products without releasing the parent amine to the gas phase. Perhaps the cubane backbone prevents CUBDAN from forming the same type of hydrogen bonded framework and, thus, facilitates its sublimation. Another factor may be that neither CUBAN nor CUBDAN melts before decomposition. Most other alkylammonium nitrate salts that we have studied melt before decomposition and thus decompose from the liquid state. Structures, such as that in reaction Equation (2), might be expected to form most easily in the fluid state.

Neutral cubylamines are relatively reactive owing to migration of the lone pair into the C-C bonds and cleavage of the cage. Hence, it may be difficult to measure the gas phase basicity of the cubylamines directly. However, our previous study of primary alkylammonium nitrate salts, Reference 3, coupled with the present study permits an estimate to be made. Figure 7 plots the gas phase basicity of the parent amine versus the initially detected gas products from rapid thermolysis of its nitrate salt. The tendency to liberate $\text{HNO}_3(\text{g})$ decreases as the amine basicity increases. The more basic amines may produce HNO_3 in the condensed phase, but the HNO_3 engages in oxidation-reduction with the alkylamine before it desorbs. Therefore, only redox products are detected. The rapid thermolysis of CUBAN and CUBDAN represented in Figures 2 and 5 most closely resembles diethylammonium nitrate, Reference 3, in terms of the tendency to eliminate $\text{HNO}_3(\text{g})$. This would suggest a gas phase basicity of about 215 kcal/mole for cubylamine and cubane-1,4-diamine. We were surprised by this result given the fact that other primary alkylamines, such as methylamine and butylamine, fall in the 204-209 kcal/mole range, Reference 5. The higher estimated basicity for the cubylamines is counter intuitive because the C-N bond might be expected to have a high percent s character, and thus, withdraw electron density from the amine. A true measurement of the gas phase basicity will be necessary before confidence can be placed in this apparent gas phase basicity value for the cubylamines.

3. PENTA[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]UNDECANE 4-EXO-8-ENDO DIAMMONIUM DINITRATE (PUDD)



The rapid thermal decomposition of PUDD under 15 psi of static Ar and at a heating rate of 100°C/sec is shown in Figure 8. This decomposition spectrum is representative of all pressures studied (15-1000 psi). Subtle differences observed as a function of pressures will be noted. The sample heats until a large endotherm is detected at 135°C. This corresponds to the simultaneous melt/decomposition observed by other techniques (Table 1). The initial

decomposition products (CO_2 , NO , CO , NH_3 , H_2O , NO_2 , PUDD_(aerosol) and an unknown) are detected in this temperature region. Nitrate salts sublimation is observed only at 15 psi. H_2O , PUDD and the unknown are not quantified. The research program ended before confident identification of the unknown could be made. Qualitatively, the IR intensity of the nitrate salt aerosol is very small. These products are detected prior to an exotherm at 220°C. The relative percent composition of the thermally stable decomposition products (NO and CO) increases at the exotherm, while the NO_2 concentration becomes negligible. The exotherm is detected at all pressures. The pressurization of PUDD above 15 psi has no significant effect on the product evolution sequence and distribution. However, the exotherm temperature is pressure dependent (Table 2). As the applied pressure is increased to 1000 psi the melt/decomposition temperature becomes indistinguishable from the exotherm temperature. This behavior resembles that of several of the nitrate salt mixtures studied previously, Reference 6.

The unknown detected during thermolysis shows a C-H asymmetric and symmetric stretching (2800 cm^{-1} region) and C=O stretch (1766 cm^{-1}). Therefore, the formation of a carbonyl occurs during oxidation of the cage. Backbone oxidation by HNO_3 produces all the decomposition products mentioned above. No $\text{HNO}_3(\text{g})$ is detected at any pressure studied. This is in contrast to the rapid thermolysis of other dinitrate salts studied in this program.

Some common temperature relationships are observed during rapid and slow decomposition. Similarities have been shown to exist during dinitrate salt thermolysis independent of the heating rate, Reference 7. This is not necessarily the case for all energetic materials, Reference 8. The temperature for initial product evolution at rapid heating rates matches the onset of decomposition by DSC. When slow heating rates are employed (1-5°/min), a heating rate dependence is observed. PUDD decomposition at 1°C/min shows a single decomposition event (endothermic) upon heating, however, at 5°C/min decomposition begins with endothermic chemistry then transforms into exothermic decomposition at 175°C. This sequence observed at 5°/min is also observed during rapid heating (Figure 8). Pressurization causes endothermic decomposition to transit to exothermic decomposition in nitrate salt thermolysis. This transition is explained by the compression of the size of the reaction zone which induces a self-acceleratory decomposition reaction.

The same pattern is found at all pressures studied. Therefore, endothermic decomposition of PUDD occurs in advance of self-acceleratory decomposition irrespective of the applied pressure.

SECTION IV

CONCLUSIONS

1. Proton transfer leading to $\text{HNO}_3(\text{g})$ is the trigger linkage that initiates thermal decomposition of CUBAN and CUBDAN.
2. CUBDAN is a rare example of an alkyldiammonium dinitrate salt that is able to sublime.
3. The gas phase proton affinity of the cubylamines is estimated to be about 215 kcal/mole.
4. The amount of energy that is presumed to be available from CUBAN and CUBDAN may be lowered somewhat by the fact that hydrocarbon fragments of the cage (C_2H_2 and C_2H_4) are released under conditions where the oxygen content is insufficient to give carbon oxides.
5. $\text{HNO}_3(\text{g})$ is not detected upon fast thermolysis of PUDD indicating that HNO_3 is retained in the condensed phase and engages in redox reactions.

THE
APPENDIX

ABSTRACTS OF PAPER PUBLISHED FROM THIS PROGRAM

1. FAST THERMOLYSIS OF AMMONIUM NITRATE, ETHYLENEDIAMMONIUM DINITRATE AND HYDRAZINIUM NITRATE AND THE RELATIONSHIP TO THE BURNING RATE, REFERENCE 6.

High-heating-rate ($\leq 100^\circ\text{C/s}$) thermolysis studies at various pressures (1-1000 psi) are described for NH_4NO_3 (AN), $[\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3](\text{NO}_3)_2$ (EDDN), $[\text{NH}_2\text{NH}_2](\text{NO}_3)$ (HN), 50/50 AN/EDDN, and 67/33 HAN/HN (HAN = hydroxylammonium nitrate) by using the rapid-scan FTIR/thermal profiling technique. For all of the solid materials, melting is detected in advance of decomposition. HNO_3 is the first gas decomposition product detected, and undoubtedly is formed by endothermic proton transfer. Pressures above atmospheric are required to produce exothermic events, probably because the gas decomposition products are able to build around the condensed phase to the critical concentration needed for ignition. HN_3 is a significant decomposition product of HN and mixtures containing HN, which may contribute to the high impact sensitivity of the material. For all of the nitrate salts and mixtures investigated, AN is found to be a recombination product during thermal decomposition. This fact may contribute to the similarity of the burning rates of aluminized propellants made from these materials.

2. FAST THERMOLYSIS PATTERNS OF POLY(METHYL), POLY(ETHYL), AND PRIMARY ALKYLAMMONIUM MONONITRATE SALTS, REFERENCE 3.

Fast thermolysis ($\geq 100^\circ\text{C/sec}$)/FTIR spectroscopy of alkylammonium mono-nitrate salts is described in terms of the gas products and the temperature and time correlations of their evolution. The salts studied are $[(\text{CH}_3)_n\text{NH}_{4-n}]\text{NO}_3$, $n = 1-3$; $[(\text{CH}_3\text{CH}_2)_n\text{NH}_{4-n}]\text{NO}_3$, $n = 1-4$; and $[\text{CH}_3(\text{CH}_2)_n\text{NH}_2]\text{NO}_3$, $n = 0-3$. In addition to the patterns among the small molecule thermolysis products, the tendency to form nitrosamines, amides, and alkylnitrates is presented. The release of HNO_3 qualitatively correlates with the basicity of the parent amine. The tertiary ammonium nitrate salts did not release $\text{HNO}_3(\text{g})$. The release of $\text{NH}_3(\text{g})$ appears only to occur when the residue can stabilize itself. Otherwise, the parent alkylamine is released. The formation of nitrosamines upon fast thermolysis of di- and trialkylammonium nitrate salts makes these materials a potential health risk in formulations. There is no evidence that the nitrate salts convert to nitrosamines through a nitramine intermediate.

3. FAST THERMOLYSIS PATTERNS OF ALKANEDIAMMONIUM DINITRATE SALTS
[H₃N(CH₂)_nNH₃](NO₃)₂, n = 1-4, 6, REFERENCE 4.

Rapid-scan FTIR/temperature profiling studies of the fast thermal decomposition of alkanediammonium dinitrate salts [H₃N(CH₂)_nNH₃](NO₃)₂, n = 1-4, 6 are described. All of the salts liberate HNO₃ and NH₃ early in the first stage. When n = 1-3, small molecule products from redox reactions occur in the second stage of decomposition. When n = 4,6, the second stage involves cycloelimination to form pyrrolidine (n = 4) and α-ethylpyrrolidine (n = 6). The temperature of the onset of thermal decomposition is lower when n = 1 than when n is larger. Intra- and intermolecular hydrogen bonding are proposed to play a significant role in these decomposition patterns.

4. FAST THERMOLYSIS OF CYCLIC AND ACYCLIC ETHANEDIAMMONIUM DINITRATE SALTS AND THEIR OXONIUM NITRATE DOUBLE SALTS, REFERENCE 9.

Fast thermolysis/FTIR spectroscopy of [H₃NCH₂CH₂NH₃](NO₃)₂ (EDD), [H₂N(CH₂CH₂)₂NH₂](NO₃)₂ (PIPDN), and [HN(CH₂CH₂)₃NH](NO₃)₂ (DABCOD) and new oxonium nitrate (H₃O⁺NO₃⁻) double salts of PIPDN and DABCOD is described. EDD initially yields HNO₃ and then small molecule decomposition products from redox reactions when heated at ≥100°C sec⁻¹. PIPDN initially yields HNO₃, but then generates a significant amount of N,N'-dinitrosopiperazine along with small molecule fragments. DABCOD produces no HNO₃(g), but instead gives CH₂O, N-N'-dinitrosopiperazine and small molecule products. These patterns are entirely consistent with the behavior observed for primary, secondary, and tertiary ammonium mononitrate salts in our previous work. The presence of nitrosamines strongly increases the health hazard of the materials upon heating. No nitramines were detected as thermolysis products. Thermolysis of the oxonium nitrate double salts liberates HNO₃ and H₂O at a relatively low temperature (~60°C). Above this temperature, the thermolysis proceeds in the same way as that of pure PIPDN and DABCOD. The crystal structure of PIPDN is described.

5. FAST THERMAL DECOMPOSITION OF FIVE N-METHYL SUBSTITUTED ETHANEDIAMMONIUM DINITRATE SALTS, REFERENCE 10.

The fast thermolysis of N-methyl substituted ethanediammonium dinitrate salts is described by temperature profiling/FTIR spectroscopy. The salts described are [CH₃NH₂CH₂CH₂NH₃](NO₃)₂ (MEDD), [CH₃NH₂CH₂CH₂NH₂CH₃](NO₃)₂ (SDMEDD), [(CH₃)₂NHCH₂CH₂NH₃](NO₃)₂ (UDMEDD), [(CH₃)₂NHCH₂CH₂NH₂CH₃](NO₃)₂ (TRMEDD), and [(CH₃)₂NHCH₂CH₂NH(CH₃)₂](NO₃)₂ (TMEDD). MEDD, UDMEDD, SDMEDD and TRMEDD more

closely resemble the behavior of alkylammonium mononitrate salts than primary alkanediammonium dinitrates in terms of the temperature at which HNO_3 is released. However, TMEDD resembles the dinitrates. Both C-C and C-N bond fission occur based on the nature of the alkylamine products that are liberated.

6. FAST THERMOLYSIS OF CUBYLAMMONIUM NITRATE AND CUBANE-1,4-DIAMMONIUM DINITRATE, REFERENCE 11.

The rapid thermal decomposition ($dT/dt \geq 70^\circ\text{C}/\text{sec}$) of cubylammonium nitrate (CUBAN) and cubane-1,4-diammonium dinitrate is described in terms of the temperature profile and gas products as a function of pressure (1-200 psi Ar). In this environment, the full strain energy of cubane is not released simultaneously with the redox reactions that involve the ammonium nitrate site because C_2H_4 and/or C_2H_2 are evolved. No large hydrocarbons form during rapid thermolysis, although both salts sublime to some extent below 7 psi Ar. CUBDAN is the only alkyldiammonium dinitrate salt that we have found to sublime during fast thermolysis. An estimated gas phase basicity of about 215 kcal/mole for the cubylamines is obtained from the tendency to release $\text{HNO}_3(\text{g})$. This value is surprising in light of the basicity values for other primary amines.

7. RAPID THERMAL DECOMPOSITION OF THE PROPYL-1,3-DIAMMONIUM SALTS OF NO_3^- AND ClO_4^- , AND THE CRYSTAL STRUCTURE OF THE ClO_4^- SALT, REFERENCE 12.

The temperature dependence of the IR spectra of the condensed phase ($dT/dt = 5^\circ\text{C min}^{-1}$) and the fast thermolysis ($dT/dt \geq 100^\circ\text{C sec}^{-1}$) of propyl-1,3-diammonium dinitrate (PDD) and diperchlorate (PDP) are compared. Rapid-scan FTIR/temperature profiling shows that PDP explodes on heating while PDD decomposes with much less energy. $\text{HNO}_3(\text{g})$ is formed by deneutralization in the initial decomposition of PDD, but $\text{HClO}_4(\text{g})$ is not detected from PDP. PDP is unique among the compounds that we have studied in that a solid-solid phase transition can be detected during rapid heating. The initial phase of PDP was characterized by x-ray crystallography.

TABLE 1. MELTING AND DECOMPOSITION EXOTHERM TEMPERATURES (°C) FOR PUDD AT VARIOUS HEATING RATES

Event	100°C/sec	5°C/ min	
		DSC	Capillary tube
Melt	135	138	138-42
Exotherm	140-225 ^a	175	-

^a Depends on the pressure

TABLE 2. PRESSURE DEPENDENCE OF MELTING AND EXOTHERM TEMPERATURES FOR PUDD

Pressure, psi Ar	Melting Temperature, °C	Exotherm Temperature, °C
15	135	225
40	135	200
200	135	180
500	140	165
1000	148	150

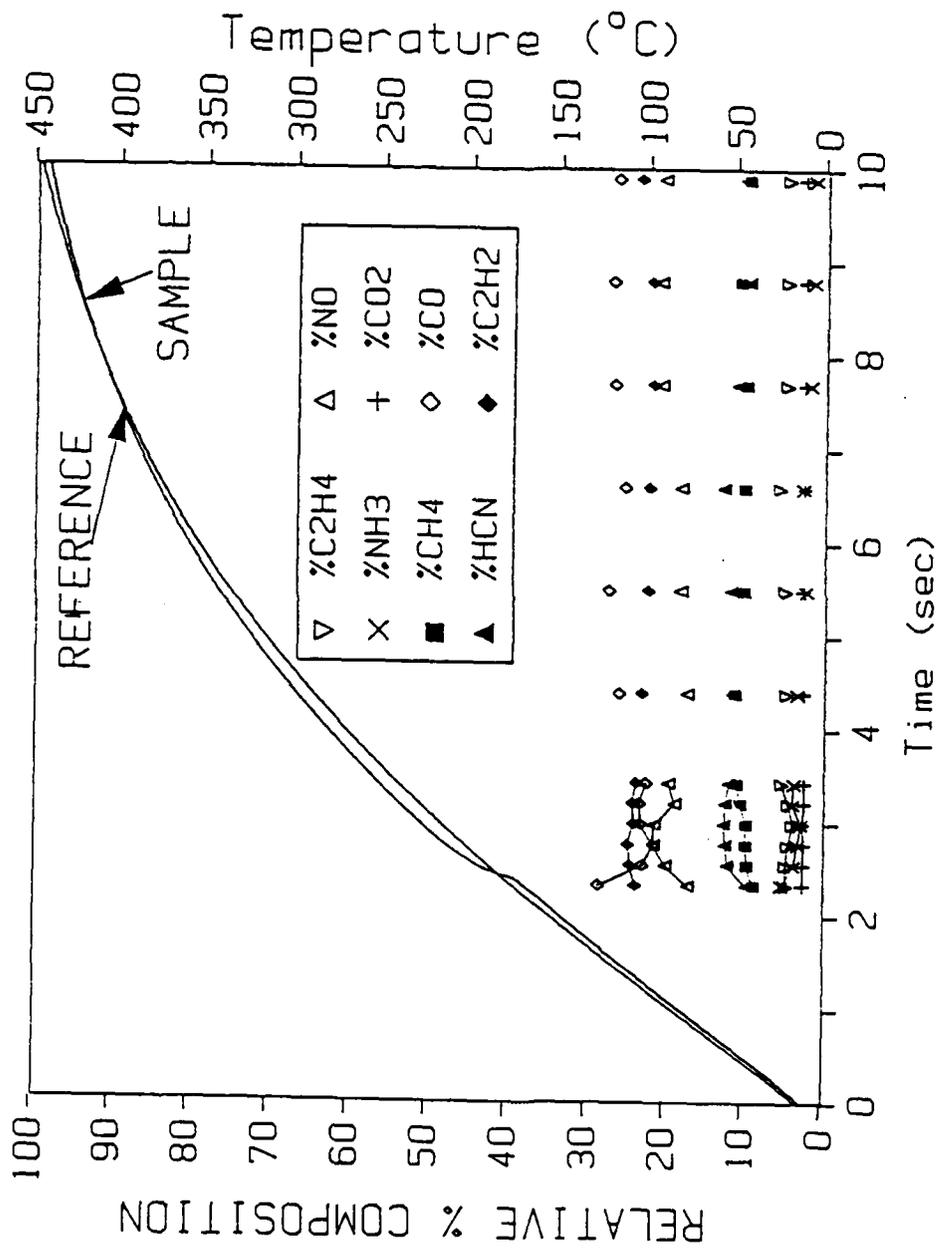


Figure 1. Fast Thermolysis of CUBAN at 15 psi Ar

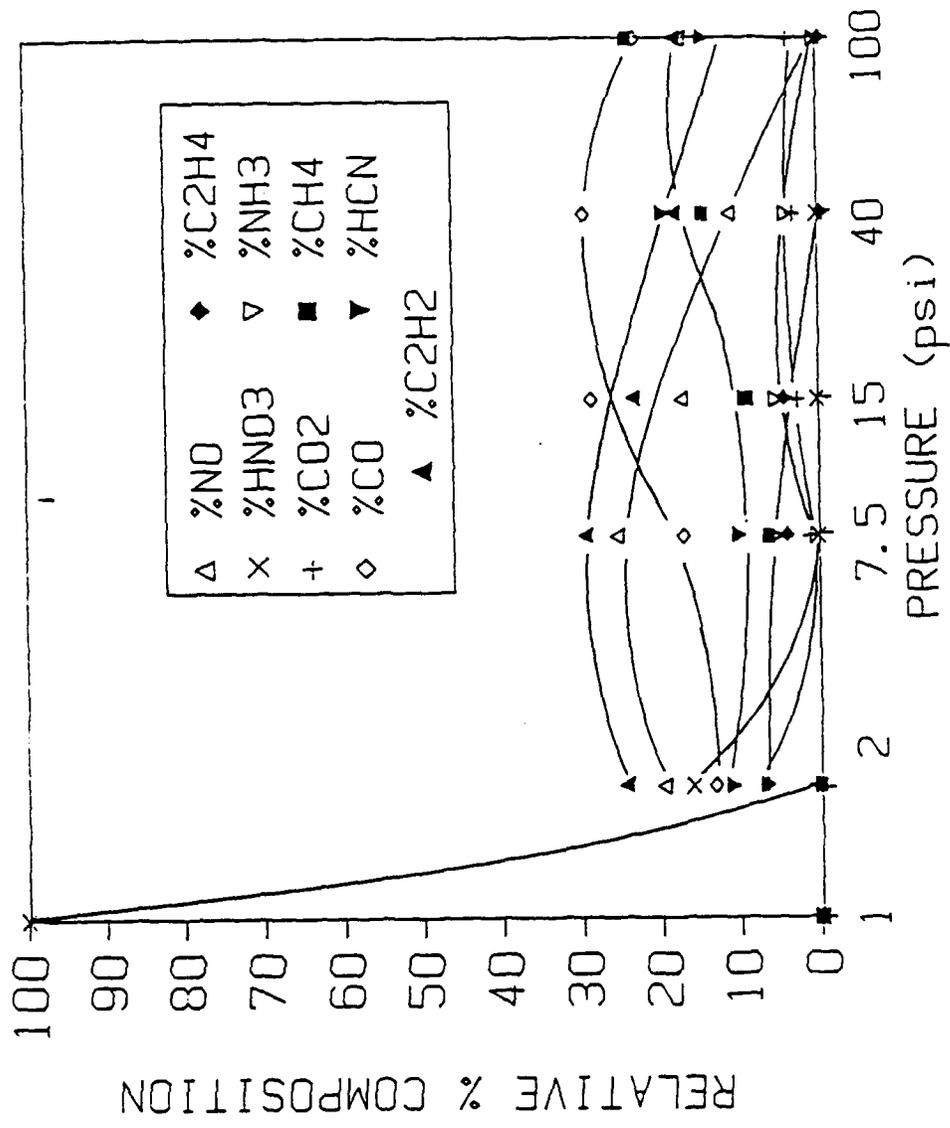


Figure 2. Pressure Dependence of the Initial Products from CUBAN

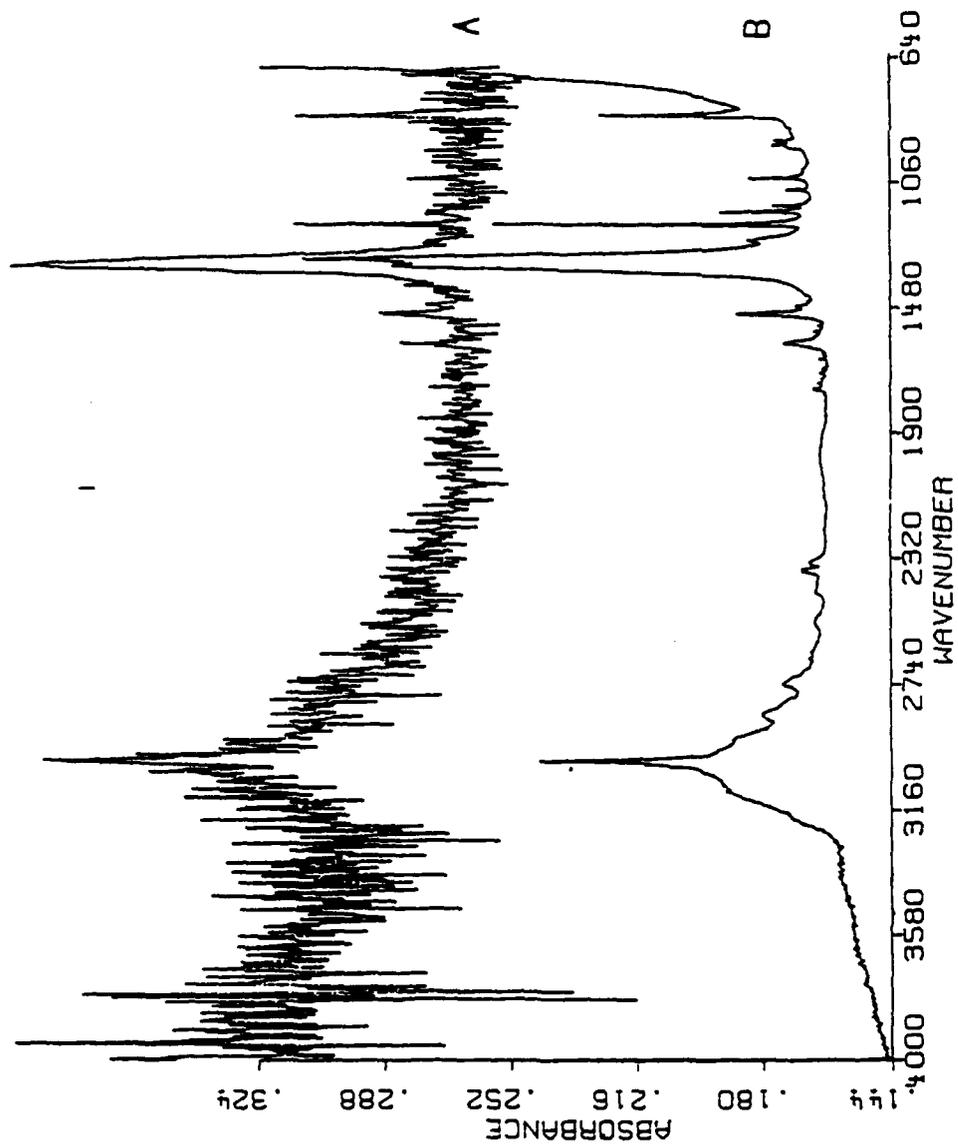


Figure 3. The Gas Products from CUBAN (A) Compared to Solid CUBAN (B)

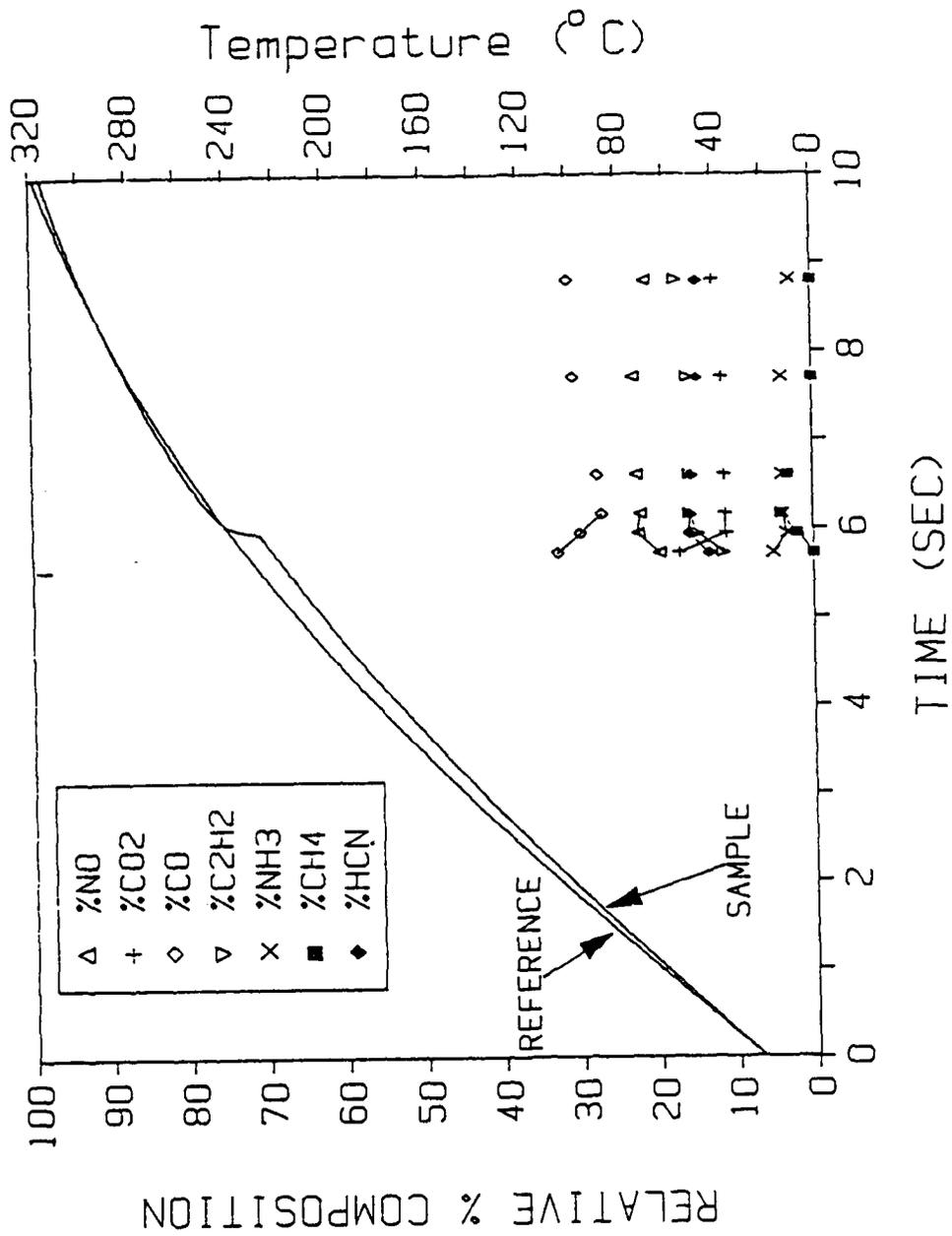


Figure 4. Fast Thermolysis of CUBDAN at 7.5 psi Ar

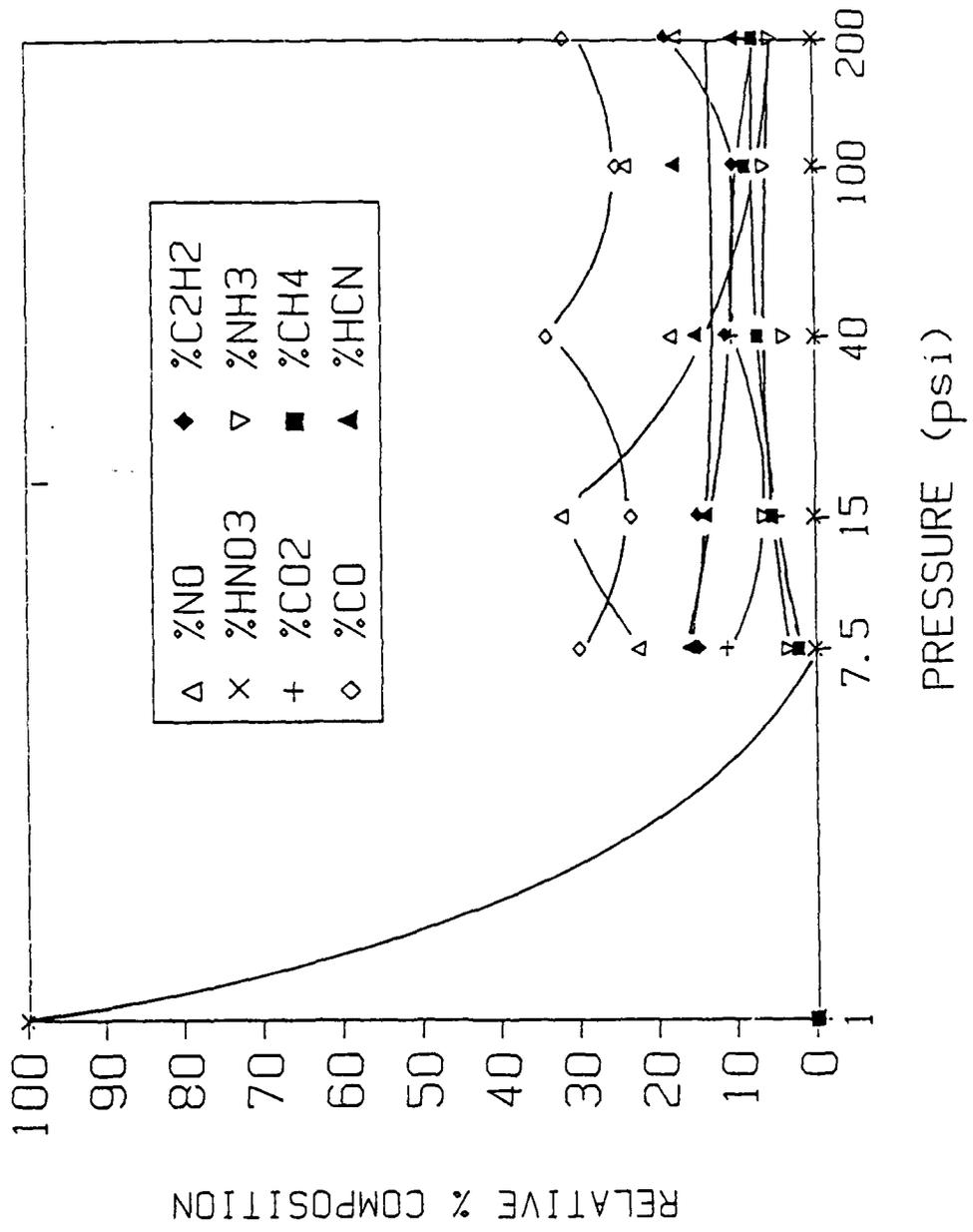


Figure 5. Pressure Dependence of the Initial Products from CUBDAN

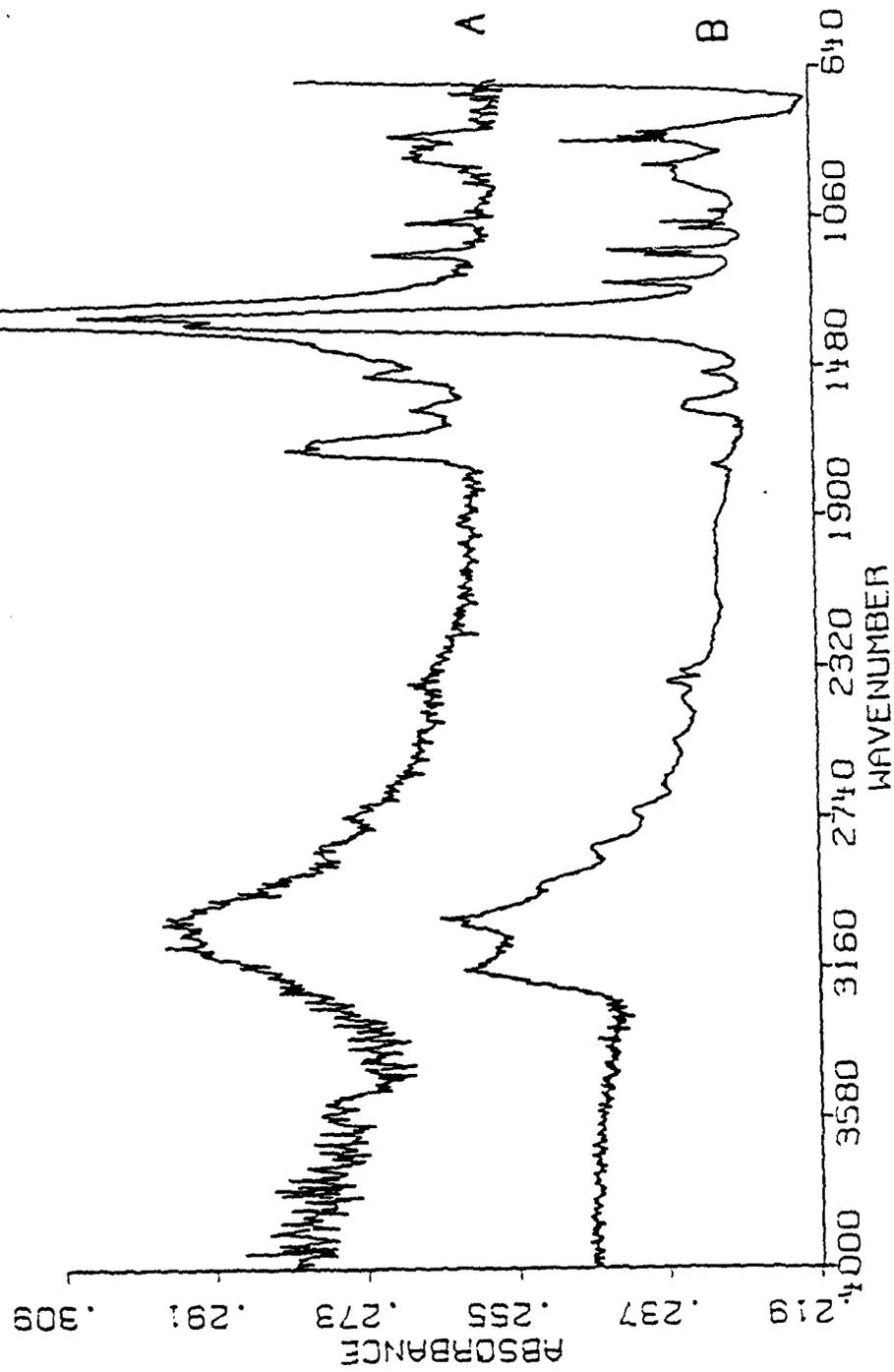


Figure 6. The Gas Products from CUBDAN (A) Compared to Solid CUBDAN (B)

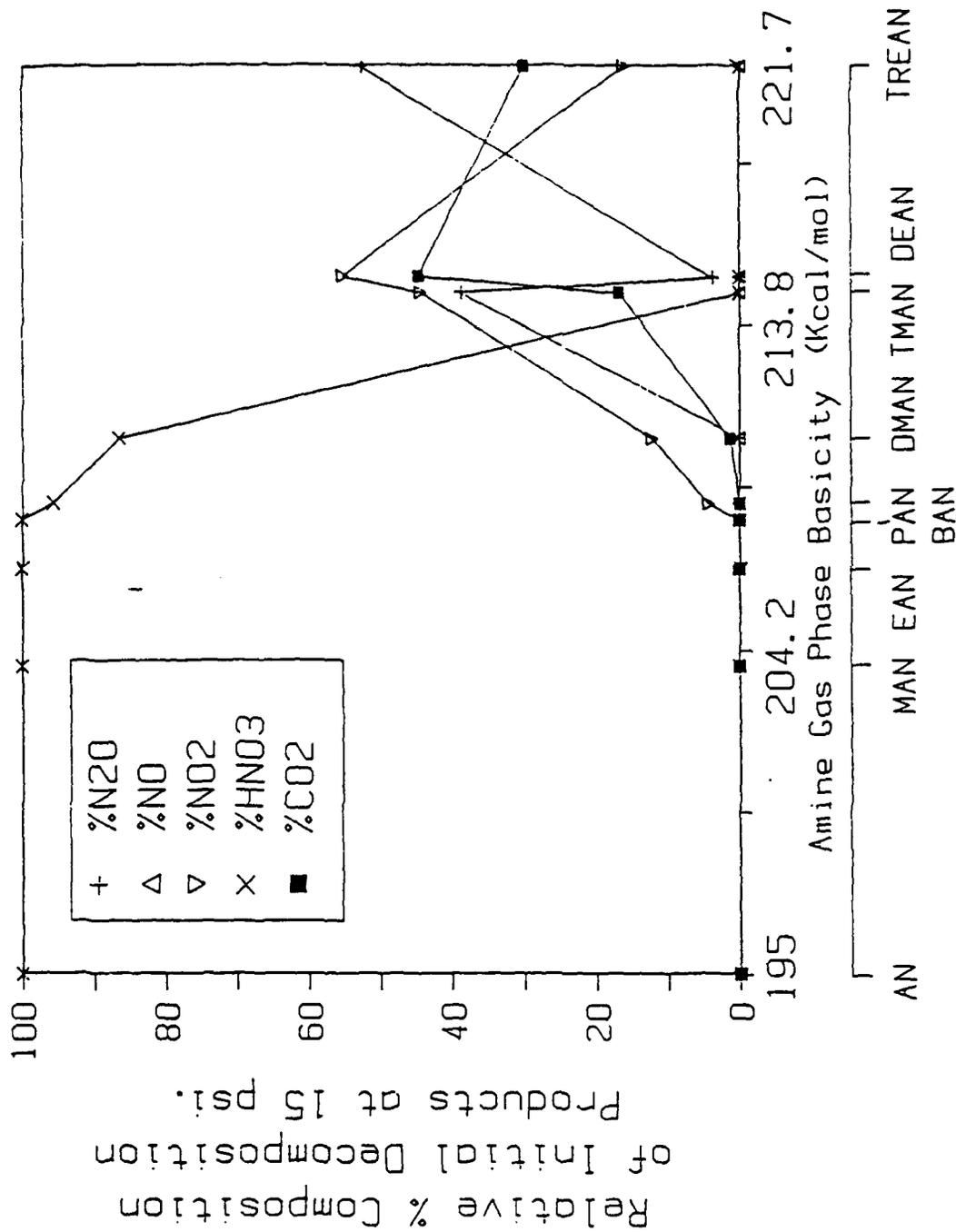


Figure 7. A Plot of the Initially Detected Gas Products at 15 psi Versus the Gas Phase Basicity of the Parent Amine

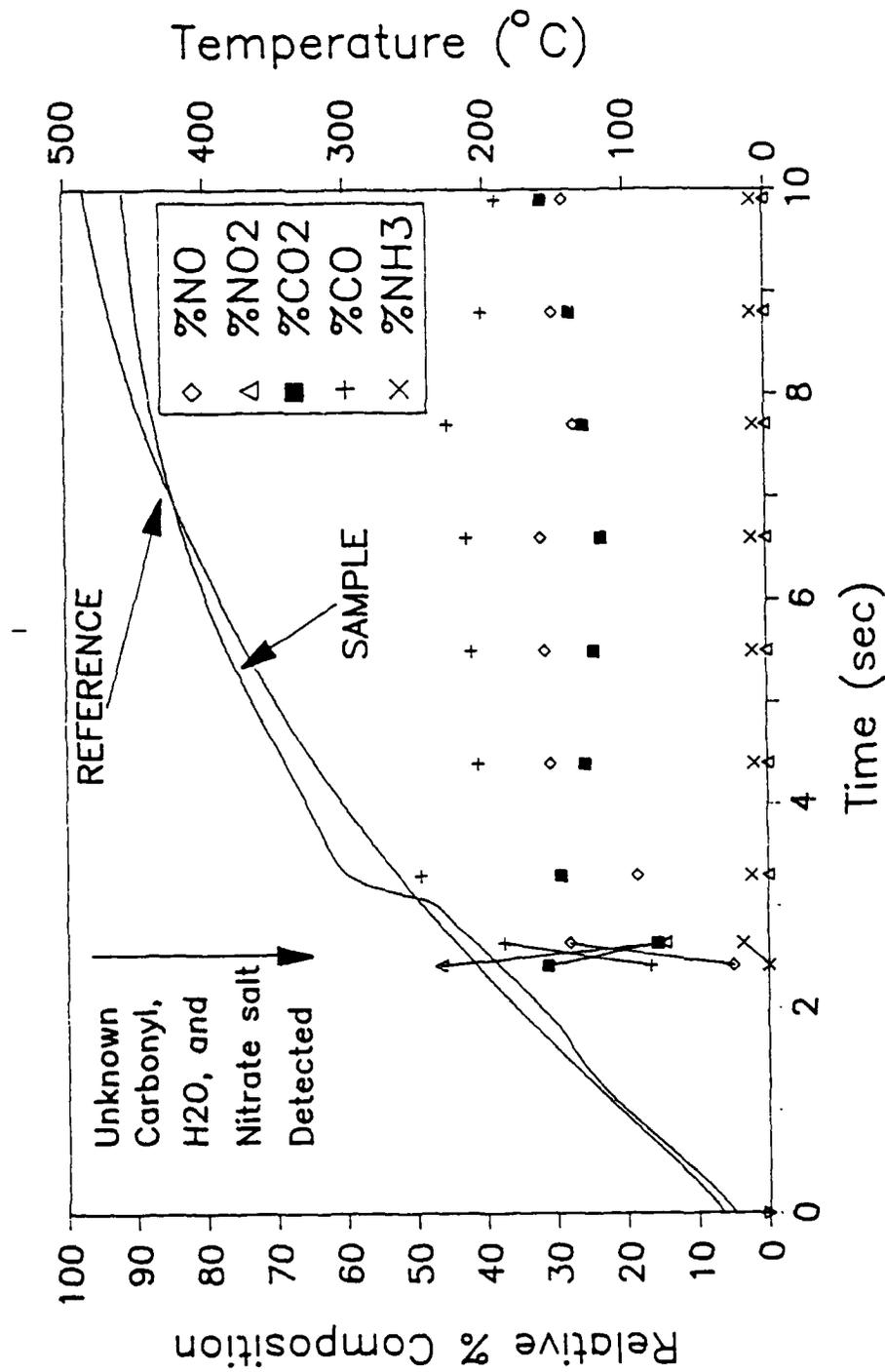


Figure 8. Fast Thermolysis of PUDD at 15 psi Ar

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