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AFRPL-TR-69-109

**(U) THERMAL DECOMPOSITION
STUDIES OF A NEW
PERCHLORATE OXIDIZER**

AD 503916

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AFRPL-TR-69-109

(U) THERMAL DECOMPOSITION STUDIES OF
A NEW PERCHLORATE OXIDIZER

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Berge B. Goshgarian

Francisco Q. Roberto

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FOREWORD

(C) This is a phase report of work done at the Air Force Rocket Propulsion Laboratory to determine the results of thermal decomposition on methylenedioxyamine diperchlorate (DOAP). This work was accomplished under Project 314804ACP during the period July through October 1968 by Capt Raymond E. Foscante and Mr. Berge B. Goshgarian. Dr. Francisco Q. Roberto served as overall Program Manager for DOAP synthesis and evaluation.

(U) This report has been reviewed and approved.

NORMAN J. VANDERHYDE
Chief, Solid Propellant Branch
Propellant Division
Air Force Rocket Propulsion Laboratory

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ABSTRACT

(C) The initial step in the thermal decomposition of methylenedioxyamine diperchlorate occurs at 60°C with the loss of a perchloric acid group to form the monoacid salt as an intermediate. As the temperature increases, the latter undergoes a concerted cyclization - cleavage reaction to form formamide and hydroxylammonium perchlorate.

(U) Mass spectrometry was used to formulate a working hypothesis for the decomposition. The existence of each of the postulated intermediates in the reaction was verified by independent experiments.

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SECTION I

INTRODUCTION

(C) Methylenedioxyamine diperchlorate (DOAP) is a new material synthesized and characterized within recent months at AFRPL (1). As part of its evaluation as a potential solid propellant oxidizer, studies were initiated to determine the mechanism by which this compound undergoes thermal decomposition. Knowledge of this mechanism was sought to provide a sound basis for predictions and conclusions concerning the stability of DOAP in various thermal and chemical environments. To this end, the thermal behavior of the oxidizer was studied over a broad temperature range to detect endothermic and exothermic transformations, to establish the initial step in the decomposition reaction, and to identify, and, where possible, to isolate intermediate species. Various analytical and experimental techniques were employed, including mass spectrometry, differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), infrared spectroscopy, and X-ray and elemental analysis.

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SECTION II

MASS SPECTROMETRIC DECOMPOSITION STUDIES

(C) Studies of recrystallized DOAP (see Section VIII) were used as the basis for mechanistic conclusions concerning the decomposition behavior of the material. The data obtained for key ion species over the temperature range of 60 to 95°C (0.5°C/min heating rate) for recrystallized DOAP are listed in Table I. These data have been corrected for pressure and the time required to collect a constant quantity of ions on the mass spectrometer photoplate at a given temperature.

(C) The mass spectrum of the decomposition species from DOAP can be grouped according to three main parent species: formamide, hydroxylamine, and perchloric acid. There is also a minor contribution to the spectrum by impurities and species resulting from reaction of the contaminants with perchloric acid.

(U) The effect of these impurities is to reduce the temperature at which decomposition begins. The reaction occurring between the organic impurities and perchloric acid in the solid or on its surface will be exothermic and thereby add thermal energy to the system. This self-heating effect enhances the decomposition rate of impure samples as compared to recrystallized DOAP.

(C) The presence of formamide as an intermediate in the decomposition of methylenedioxyamine diperchlorate was demonstrated by high-resolution mass spectrometry and by comparison with the cracking pattern for a known sample of formamide (Table II). Figure 1 shows a plot of the ion intensities for key species from the cracking pattern of formamide as obtained from DOAP. From Figure 1 it can be seen that the formamide-forming reaction reaches its peak at 85°C (2.3×10^{-5} torr) and is essentially complete by 90°C.

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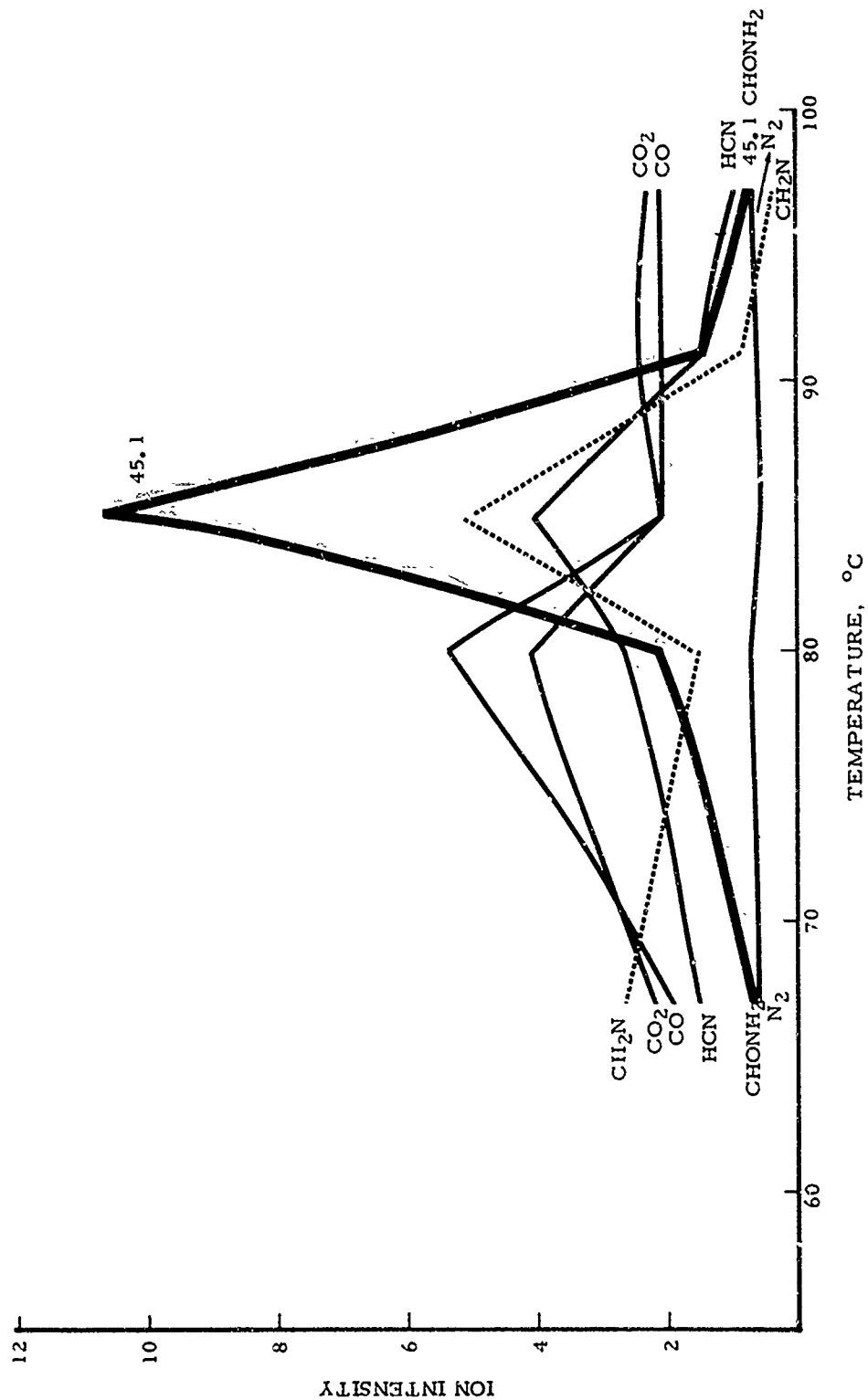


Figure 1. Plot of Ion Intensity versus Temperature for Formamide and Related Species from DOAP Decomposition.

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TABLE I. MASS SPECTRUM OF THERMAL
DECOMPOSITION PRODUCTS FROM DOAP

		Relative Intensity				
AMU	ION	4×10^{-7} mm 67°C	9×10^{-7} mm 80°C	2×10^{-5} 85°C	2.5×10^{-6} mm 91°C	3.4×10^{-6} mm 97°C
27	HCN	1.7	2.6	4.0	1.4	0.85
28	CO	2.2	4.0	2.1	2.1	2.0
28.1	N ₂	0.6	0.7	0.5	0.6	0.6
28.2	CH ₂ N	2.6	1.5	5.0	0.8	0.4
29	CHO	0.5	1.5	1.9	0.7	0.6
30	NO	0.9	3.4	4.2	1.8	5.6
30.1	CH ₂ O	0.2	0.9	0.9	0.5	0.3
31.1	CH ₃ O	0.2	0.2	0.3	0.04	0.03
32	O ₂	0.5	1.4	1.2	1.4	2.7
33	NH ₂ OH	-	0.1	0.08	0.15	0.4
36	HCl	2.1	5.4	2.3	3.1	3.9
44	CO ₂	1.9	5.3	2.1	2.4	2.3
44.1	N ₂ O	0.02	0.4	0.2	0.4	1.0
45.1	CH ₂ ONH	0.7	2.1	10.6	1.4	0.6
46	NO ₂	0.03	0.1	0.15	0.14	0.22
51	ClO	0.4	1.7	3.6	1.7	2.6
58	C ₂ H ₄ NO	0.2	0.1	0.4	-	-
63	COCl	-	0.09	-	-	-
67	ClO ₂	0.45	2.3	6.5	2.1	3.3
83	ClO ₃	0.2	0.26	4.4	0.6	1.0
100	HClO ₄	0.1	0.12	2.6	0.4	0.5

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TABLE II. COMPARATIVE MASS SPECTRA OF FORMAMIDE, DO, AND SELECTED DECOMPOSITION SPECIES FROM DOAP

Ion Specie	Relative Intensity DOA	Relative Intensity DOAP	Relative Intensity Formamide (1)
CH ₂	1.9	4.2	
NH ₂	52.5	8.2	
CH ₂ N	70.0	44.3	
CH ₂ O	22.4	5.6	
NH ₂ OH	105.0	2.7	
CHON	6.0	16.0	16.0
CHONH	45.1	20.7	22.0
CHONH ₂	12.3	100.0	100.0
CH ₂ ONH ₂	100.0	1.6	
HCN	22.5	55.0	

- (1) Only peaks at m/e 43.0, 44.2, and 45.1 can be correlated since there is a contribution of ion fragments from other compounds in DOAP spectrum.

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(C) Further insight into the mechanism by which formamide is formed in the decomposition of DOAP was obtained from a comparison of the cracking pattern for the free amine methylenedioxyamine (DO), $\text{CH}_2(\text{ONH}_2)_2$, and the C-H-N-O decomposition products of DOAP. These are shown in Table II. The DO cracking pattern contains a species at m/e 46 ($\text{CH}_2\text{ONH}_2^+$) which is the largest in the spectrum. In the DOAP spectrum the m/e 46 peak is extremely small and is due to the naturally occurring C^{13} isotope of formamide ($\text{C}^{13}\text{HONH}_2^+$) and not $\text{CH}_2\text{ONH}_2^+$. Consequently, the decomposition of DOAP does not occur through dissociation of the salt to the free amine (DO) and perchloric acid. A condensed-phase rearrangement and cleavage is required to give formamide as one of the intermediates.

(U) As the temperature is increased, the peak at m/e 33, identified as NH_2OH^+ , also increases in concentration. Figure 2 gives a plot of the ion intensities/temperature relationship for the cracking fragments of hydroxylamine and its oxidation products from DOAP decomposition. Small amounts of hydroxylamine are being produced during the low-temperature stages of the reaction. An initial maximum concentration of NO is reached at 85°C corresponding to the maximum DOAP decomposition. The NO concentration then decreases until the decomposition of HAP surpasses that for DOAP, at which time the NH_2OH and its oxidation product concentrations increase.

(C) Hydroxylamine is formed by the electron bombardment of methylenedioxyamine; however, since no free amine is detected in the DOAP decomposition pattern under analogous conditions, the hydroxylamine must arise from another source. Similarly, m/e 33 (NH_2OH^+) does not originate from the electron bombardment or fragmentation of formamide. The source of m/e 33 in the DOAP mass spectrum must be another decomposition intermediate more stable than DOAP itself, since the NH_2OH^+ pattern does not contribute appreciably to the overall spectra until relatively high temperatures are reached.

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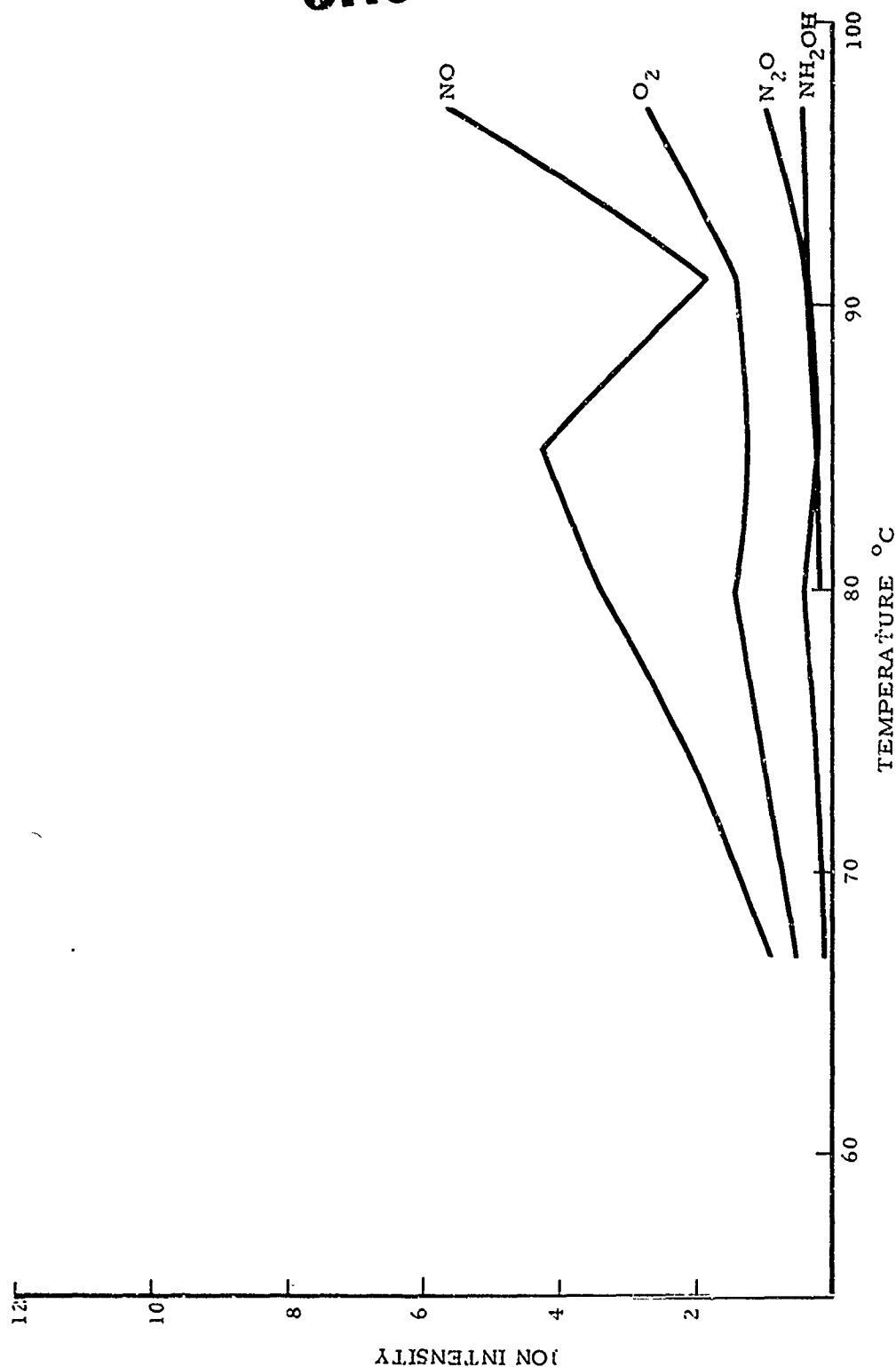


Figure 2. Plot of Ion Intensity versus Temperature for Hydroxylamine and Related Species from DOAP Decomposition.

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(U) Perchloric acid is liberated over the entire temperature range during the decomposition reaction (Figure 3). Removal of one perchloric acid molecule and cleavage of formamide from the remaining mono-acid salt will give hydroxylammonium perchlorate (HAP) as an accompanying intermediate. HAP formation would occur simultaneously with formamide generation; however, the former would remain intact and not contribute substantially to the spectra until an elevated temperature is reached. At this temperature most of the DOAP would have been decomposed, as evidenced from Figures 1 and 2.

(U) The species corresponding to HAP decomposition and fragmentation of its intermediates, i. e., NO , O_2 , NH_2OH , N_2O , and HClO_4 (and its fragments) continue to increase in intensity as the temperature rises (Figures 2 and 3). Those species related to DOAP degradation, i. e., CHONH_2^+ , HCN , and other H-C-N-O fragments, decrease with increasing temperature (Figure 1). The perchloric acid peak intensities observed in the 90° to 100°C range are directly related to the hydroxylamine peak intensities and not to formamide.

(U) In order to substantiate the existence of HAP in the DOAP decomposition pattern, a sample of HAP was heated in the direct inlet of the mass spectrometer, using the identical conditions as in the DOAP runs. Figure 4 presents comparative plots for pressure-temperature data for DOAP and HAP. The curve for HAP parallels that for the DOAP baseline up to the temperature where HAP dissociation is accelerated. It appears from this data that HAP is continually being formed from the DOAP rearrangement and dissociating at the same rate as the known HAP sample. Ion ratios from both the HAP and DOAP data between 92.5° and 95°C are given in Table III. The data correlate well within $\pm 10\%$ experimental error encountered in photoplate data retrieval.

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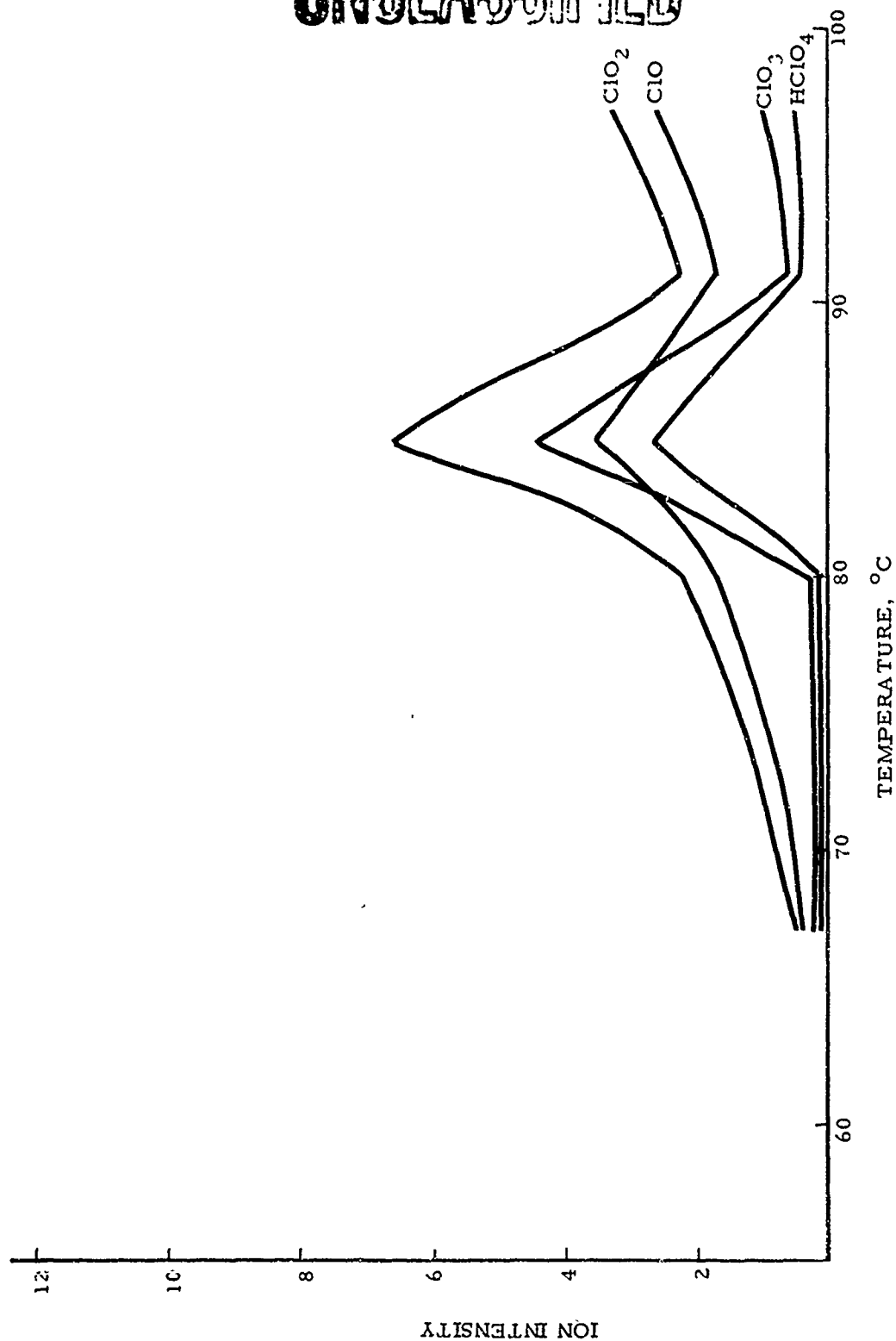


Figure 3. Plot of Ion Intensity versus Temperature for Perchloric Acid and Related Species from DCAP Decomposition.

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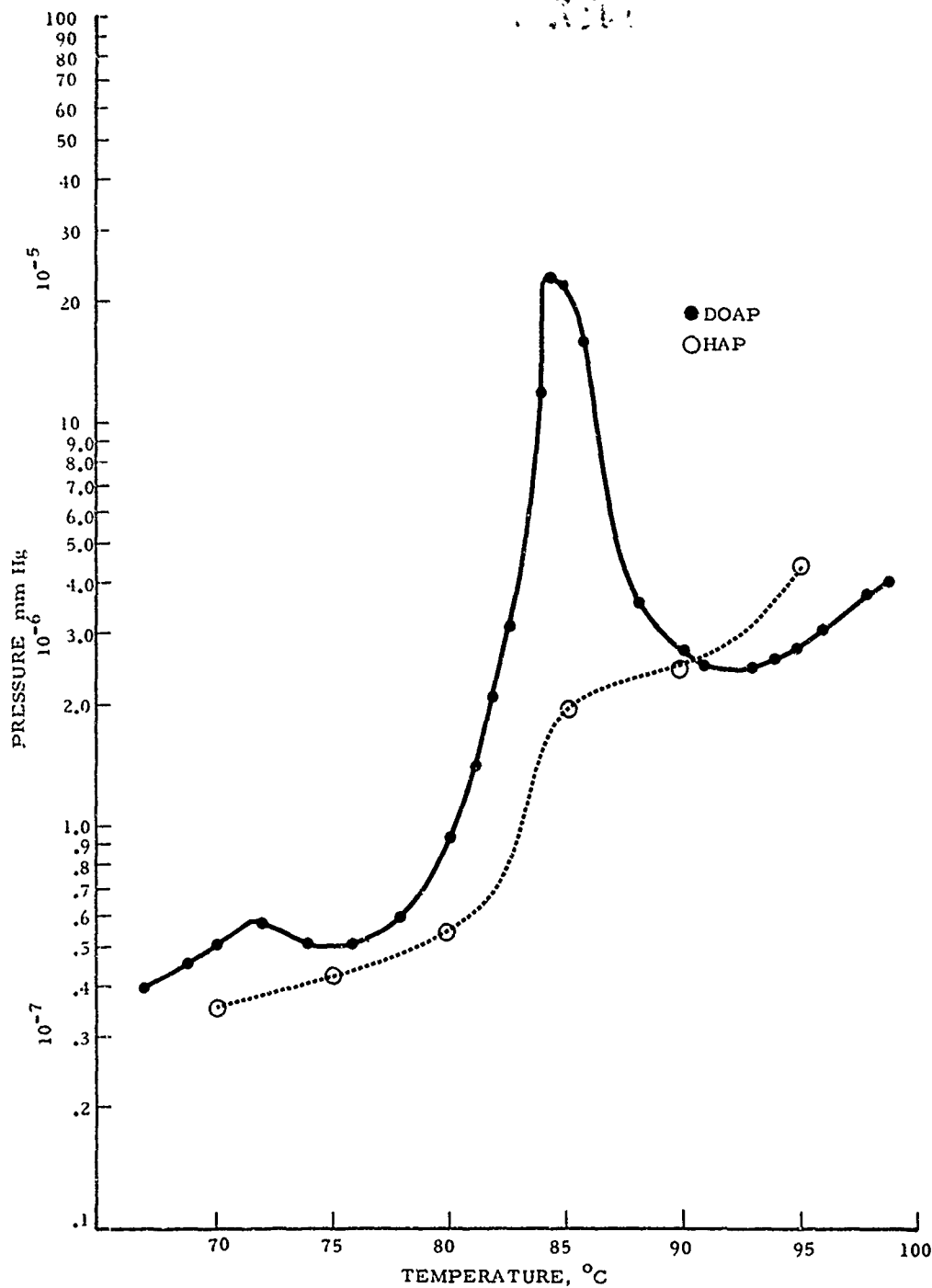


Figure 4. Comparative Plot of Pressure versus Temperature for Decomposition of DOAP and HAP.

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(C) Based on the mass spectral data a preliminary working hypothesis can be formed. The decomposition of methylenedioxyamine diperchlorate appears to be initiated by the loss of one perchloric acid group to form the monopерchlorate salt. Since no parent species other than m/e 45 (formamide), 100 (perchloric acid), and 33 (hydroxylamine) are observed in the cracking pattern, a condensed-phase concerted rearrangement-cleavage reaction must be postulated as leading to two major intermediates, formamide and hydroxylammonium perchlorate.

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TABLE III. MASS SPECTRAL ION RATIOS FOR HAP AND DOAP

HAP		DOAP	
Ion	Ratio	Ion	Ratio
N ₂	1.5	N ₂	1.2
NO	12.0	NO	11.8
O ₂	5.2	O ₂	6.9
NH ₂ OH	1.0	NH ₂ OH	1.0
N ₂ O	3.4	N ₂ O	2.4
ClO ₂	10.3	ClO ₂	9.3
ClO ₃	1.7	ClO ₃	3.0
NO ₂	0.8	NO ₂	0.7

Pressure 2.5×10^{-6} mm

Pressure 3×10^{-6} mm

Temperature 92.5 – 95°C

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SECTION III

VERIFICATION OF INTERMEDIATES

(C) Perchloric acid liberation and decomposition in general were noted to begin at 65°C in the mass spectral decomposition studies. Rapid-heating-rate experiments at atmospheric pressure, such as DTA, TGA, DSC, show decomposition occurring at 140°C after the sample has melted. These data, taken under different heating-rate conditions, imply an induction period prior to bulk decomposition. Several other experiments were run to clarify this point and to verify the existence of the postulated intermediates in the decomposition. Samples of DOAP were placed in an evacuated glass tube and heated in a constant-temperature bath at 60°C. In less than 2 days the samples liquified. No gaseous decomposition products (or pressure rises) were detected above the samples when the tubes were opened into a vacuum rack. Infrared analysis of the residue gave absorbances for perchlorate and amide groups. The characteristic absorbances for DOAP (Figure 5) were missing, indicating decomposition of the starting material at a temperature far below that determined by such conventional methods as DTA.

(C) The weight loss from DOAP was monitored at 60, 70, and 85°C. Samples (in this case unrecrystallized DOAP) were placed in a continuously evacuated oven/(<100 microns) and weighed periodically. At 85°C, both samples liquified after 16 hours and resolidified when the temperature was reduced below 80°C. The average weight loss from the sample for the duration of the experiment was 39%. DTA of the treated sample gave a thermogram (Figure 6) which very closely matches that for HAP (Figure 7). The melting endotherm for DOAP is missing in the thermogram for the thermally treated sample and only a minimal amount of starting material is present, as indicated by the slight exotherm at 150°C. The DTA thermogram for a pure sample of DOAP is shown in Figure 5. Melting occurs at 115°C followed by exothermic decomposition of the melt over a range from 140 to 160°C (peak at 150°C). A white solid forms after decomposition at

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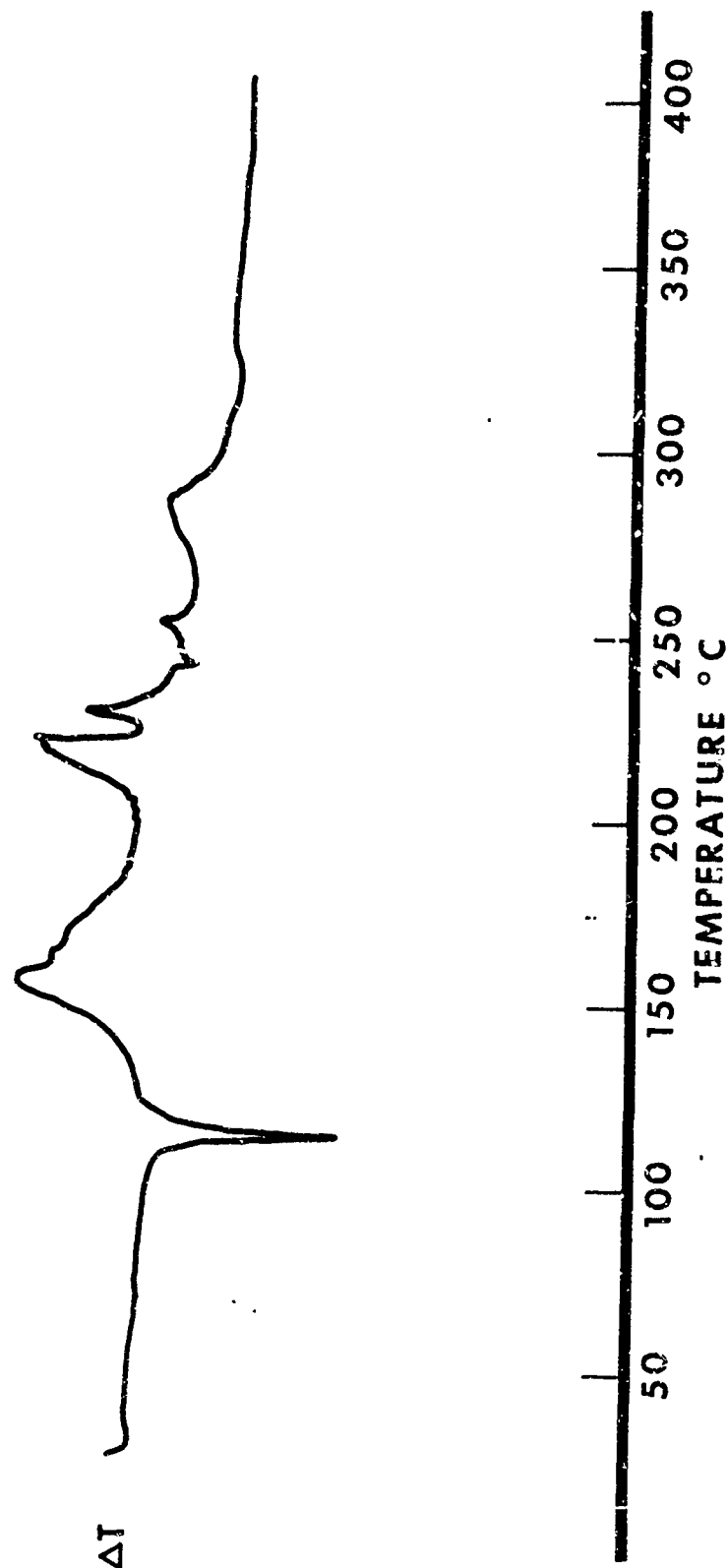


Figure 5. DTA Thermogram for DQAP

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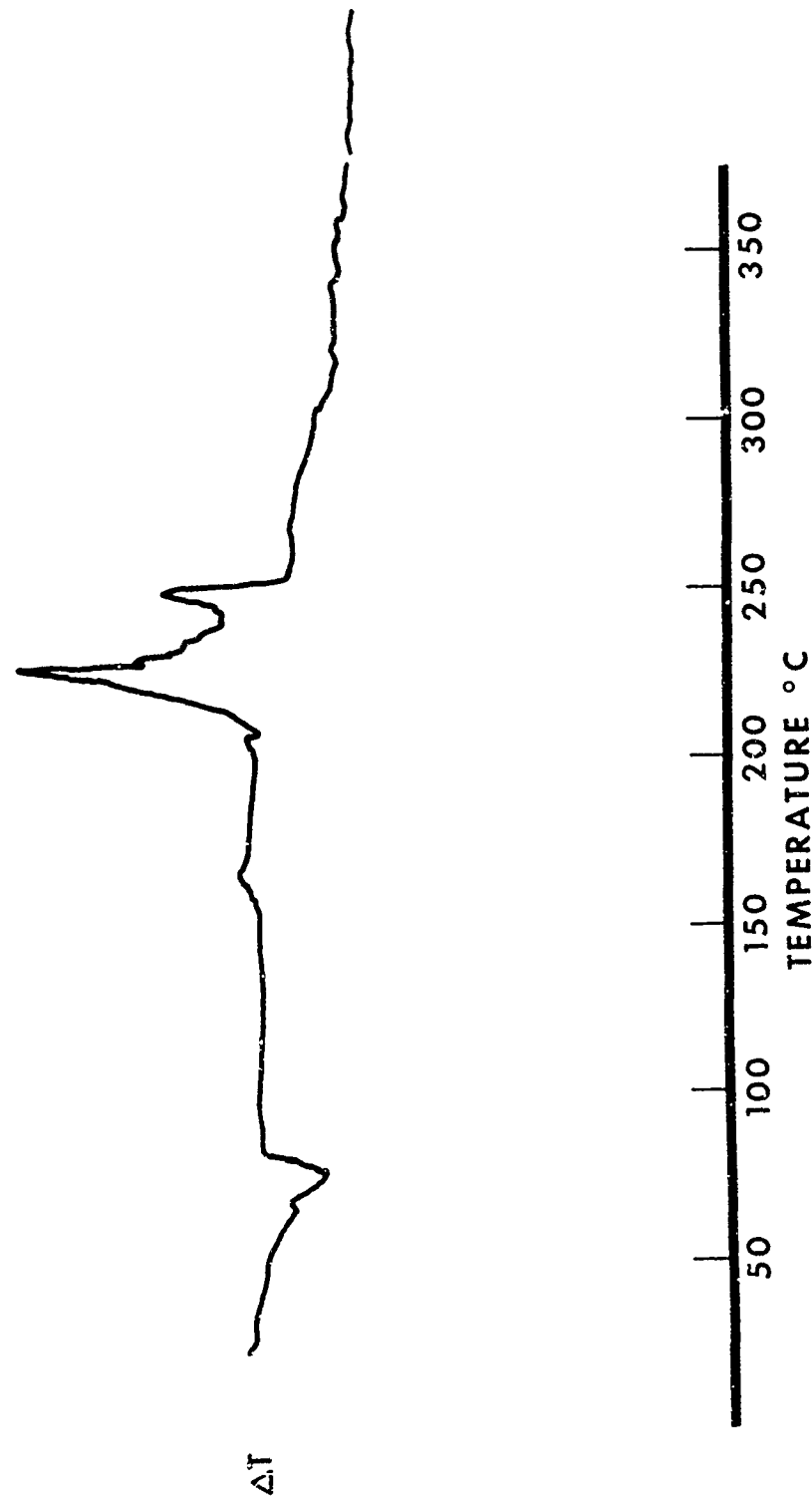


Figure 6. DTA Thermogram for 80°C Vacuum-Treated DOAP

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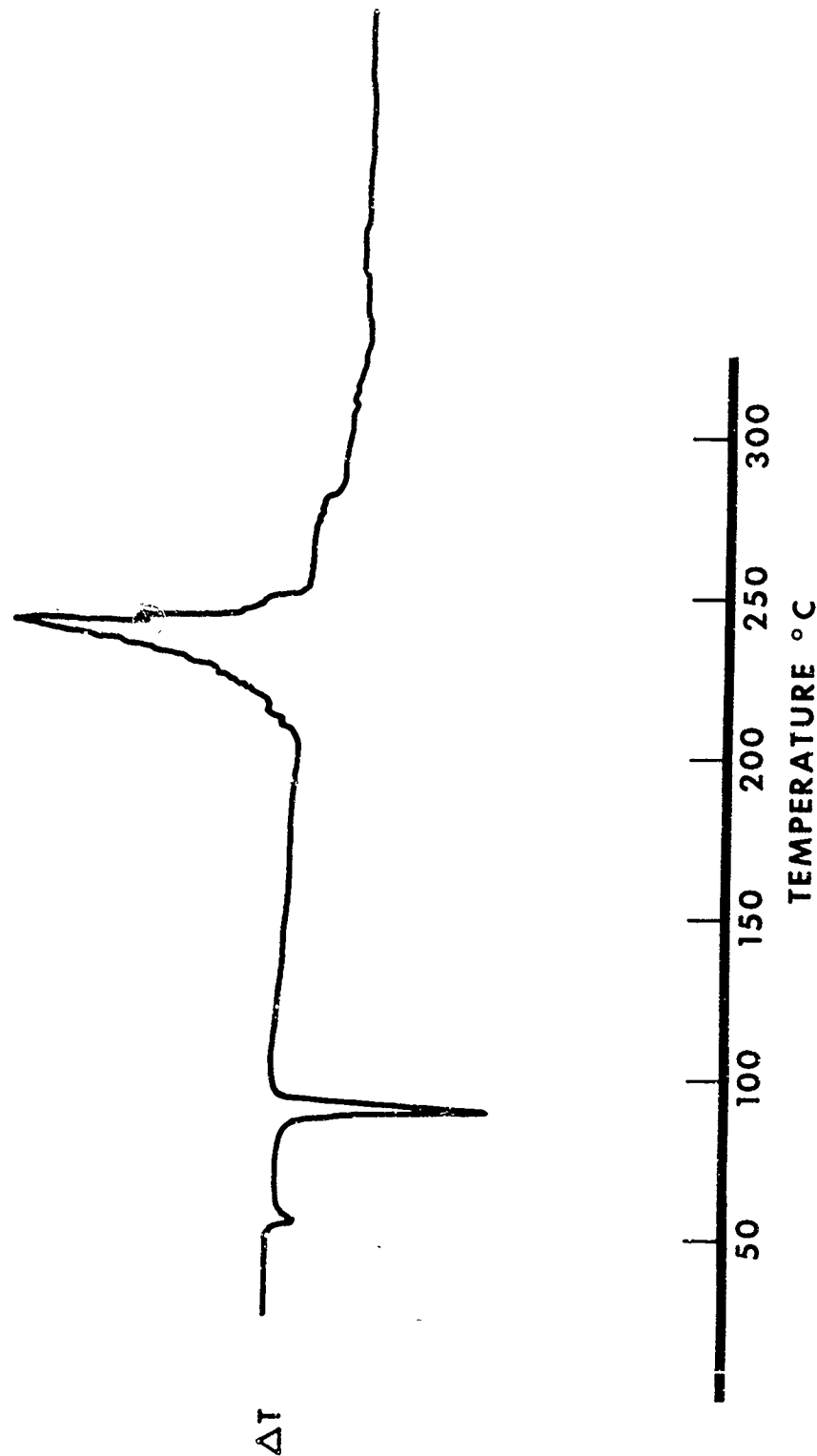


Figure 7. DTA Thermogram for Hydroxylammonium Perchlorate

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~180°C (visually observed in DSC experiments). The second exotherm, occurring at 260°C corresponds to the HAP exotherm, thereby supporting the premise that the latter compound is formed as a stable decomposition product.

(C) The presence of other decomposition species (formamide) in the erstwhile DOAP sample act as contaminants, thereby lowering the melting point of the HAP formed.

(C) Elemental analyses of the 80°C vacuum-treated samples are given in Table IV. The average elemental ratios in the samples are $C_1H_{20}N_{5.2}$. Since all the formamide and perchloric acid formed during the vacuum thermal treatment would be removed by vaporization, only HAP and undecomposed DOAP remain. Based on this assumption and the average weight loss of 39%, a HAP-DOAP ratio of 3 to 1 results from treatment under these temperature, time, and pressure conditions.

(C) Another DOAP sample was subjected to similar treatment at 60°C for 600 hours. These data are plotted in Figure 8. There is a weight loss for the first 2 hours amounting to 2% per hour. After 24 hours, the sample has lost 5.5% of its initial weight. The weight loss rate continued to decrease to the end of the run, where the total change after 600 hours was 20%. This represents an average rate of 0.03%/hour at 60°C and of 100 microns. DTA of this sample showed no difference between the starting material (DOAP) and the sample after vacuum thermal treatment (Figure 9).

(C) The remainder of the sample was reheated at 70°C under vacuum (100 micron) until 50% by weight of the remaining sample has been lost. The DTA thermogram for this sample is shown in Figure (10). Once again, the starting material (DOAP) was almost completely converted to HAP. This sample did not melt or liquify, since the melting point of HAP was not reached. Elemental analysis of this material, assuming only HAP and

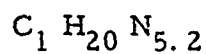
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TABLE IV. ELEMENTAL ANALYSIS OF 80°C VACUUM-TREATED DOAP

Element	Theoretical	Original Sample	Vac Heat Treated 82° C 100 _m	Vac Heat Treated 85° C 100 _m	Avg Treated
C	4.3%	4.5%	1.7%	1.6%	1.65%
H	2.9%	2.8%	2.8%	2.7%	2.75%
N	10.1%	10.0%	10.1%	10.0%	10.05%

Elemental Ratio



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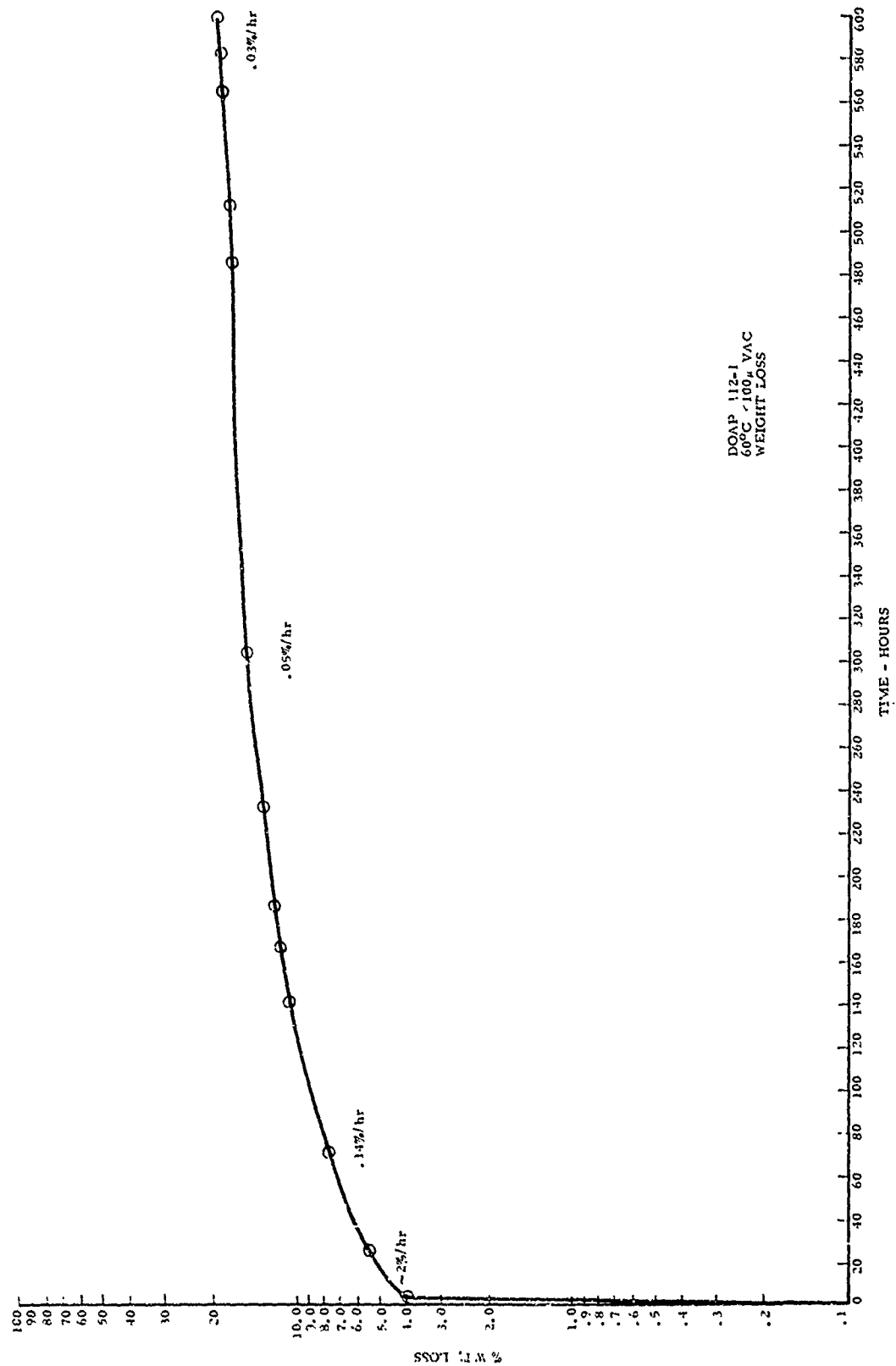


Figure 8. Plot of Weight Loss versus Time
for 60°C and Vacuum-Treated DOAP

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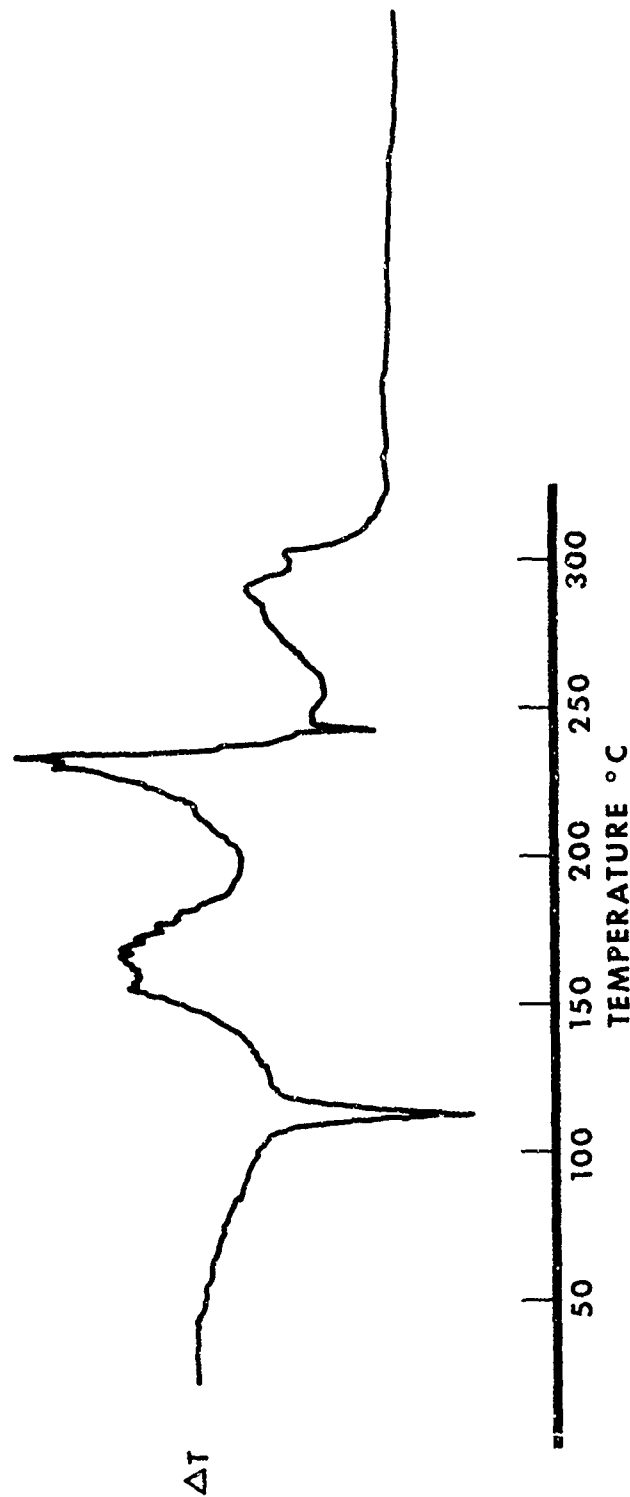


Figure 9. DTA Thermogram for 60°C Vacuum-Treated DOAP

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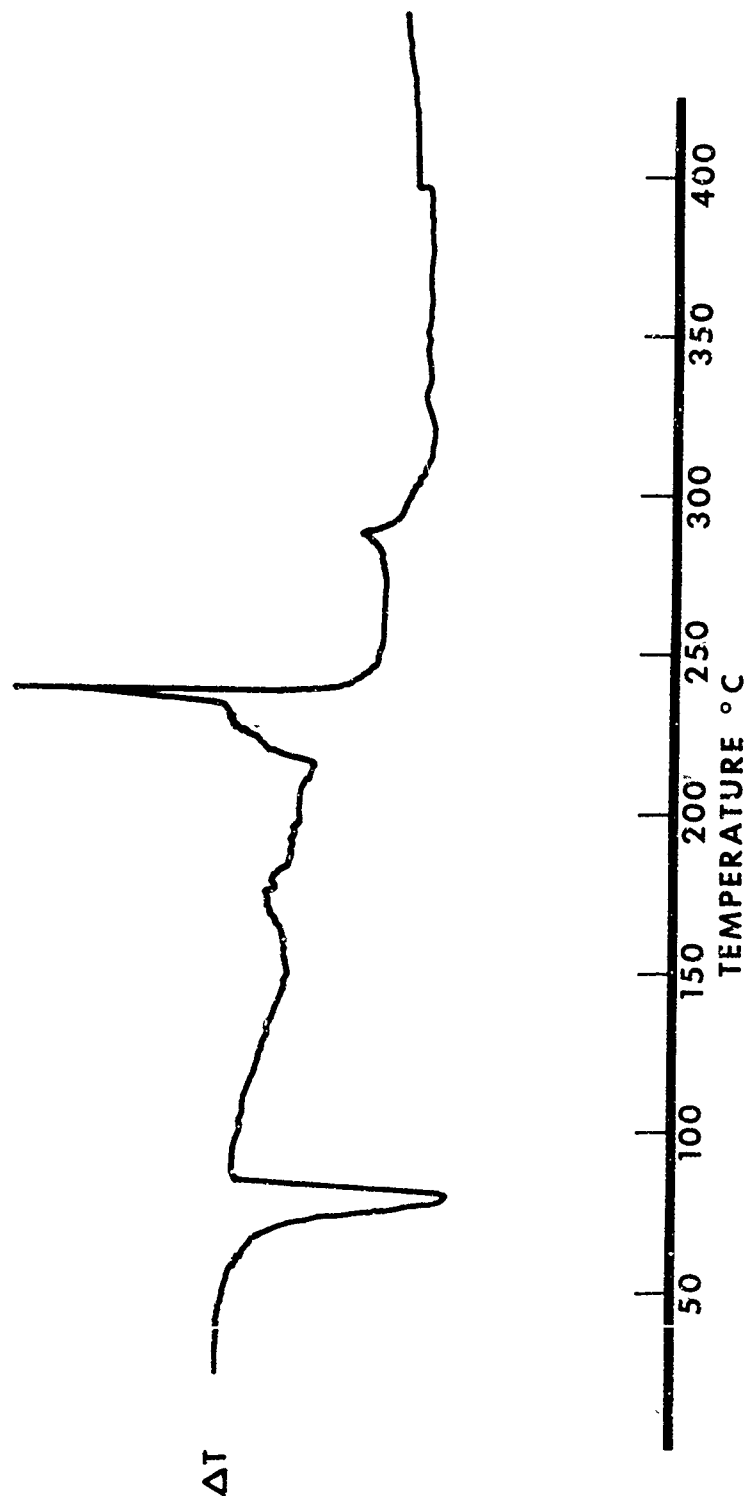


Figure 10. Thermogram for 70°C Vacuum-Treated DOAP

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DOAP to be its components, gave a ratio of 6.8 to 1 (HAP/DOAP) based on an elemental ratio of $C_{1H_{35.2}N_{8.8}}$.

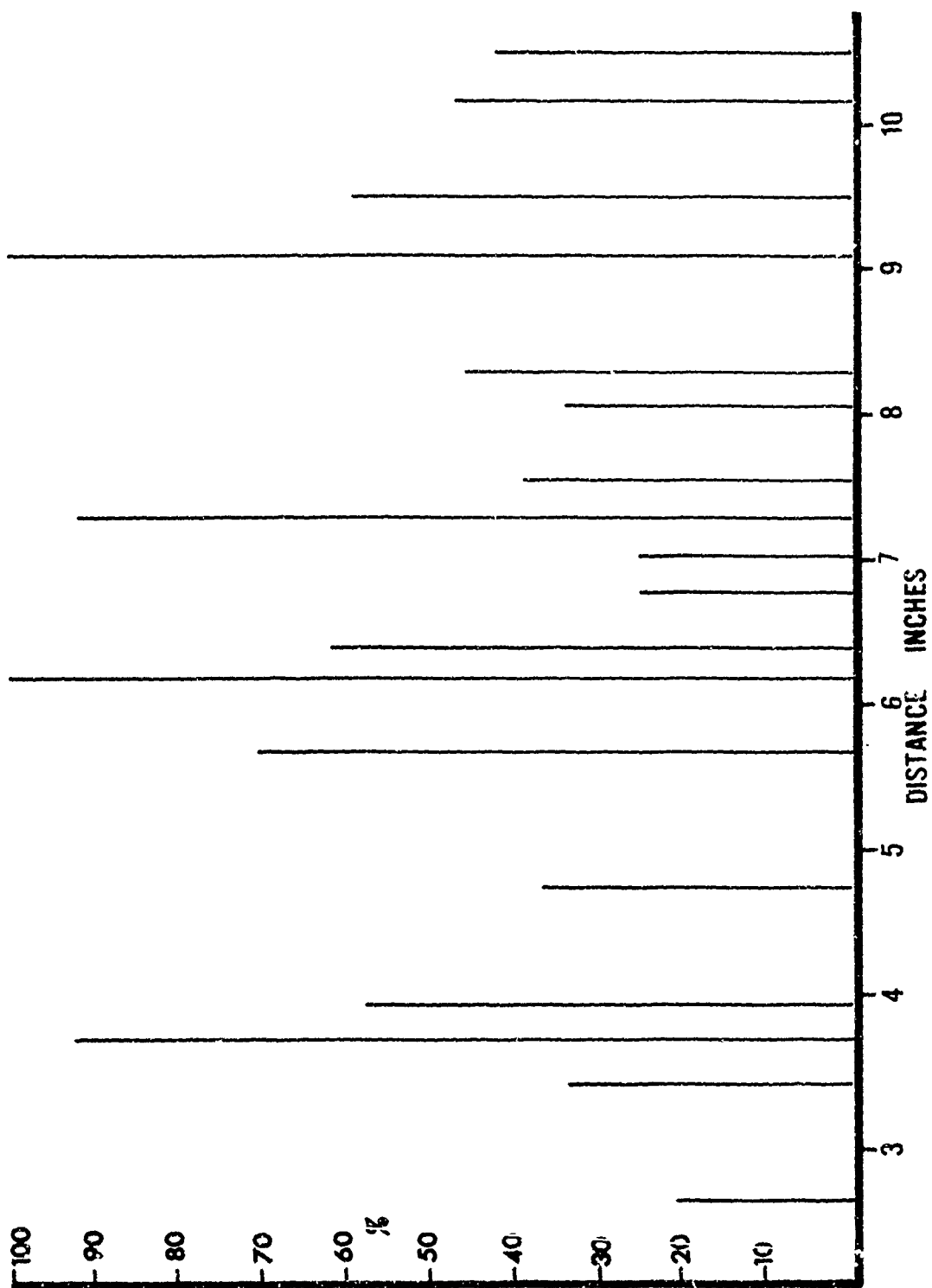
(C) X-ray analysis of the 70°C vacuum-treated sample confirms the observation that the solid remaining after DOAP decomposition is HAP. Recorded density values for the X-ray diffraction patterns for HAP, DOAP, and thermal vacuum-treated (TVT) DOAP are given in Figures 11, 12, and 13. Every line corresponding to HAP is present in the TVT-DOAP sample pattern, with the exception of one line noted in the TVT-DOAP pattern at 5.28 inches.* The lines for DOAP at 5.54, 5.91, and 6.32 inches are masked in the TVT-DOAP pattern by the intense HAP lines at 5.6, 6.1, and 6.3 inches.

(C) Based on these data, it is concluded that the majority of the 70°C vacuum-treated DOAP sample was converted to HAP; approximately 12% of the original DOAP survived. Melting of the bulk sample is apparently not required for decomposition and rearrangement. A solid-phase or surface reaction is implied.

*All measurements are made from a starting point on the recorder curves common to all three X-ray films.

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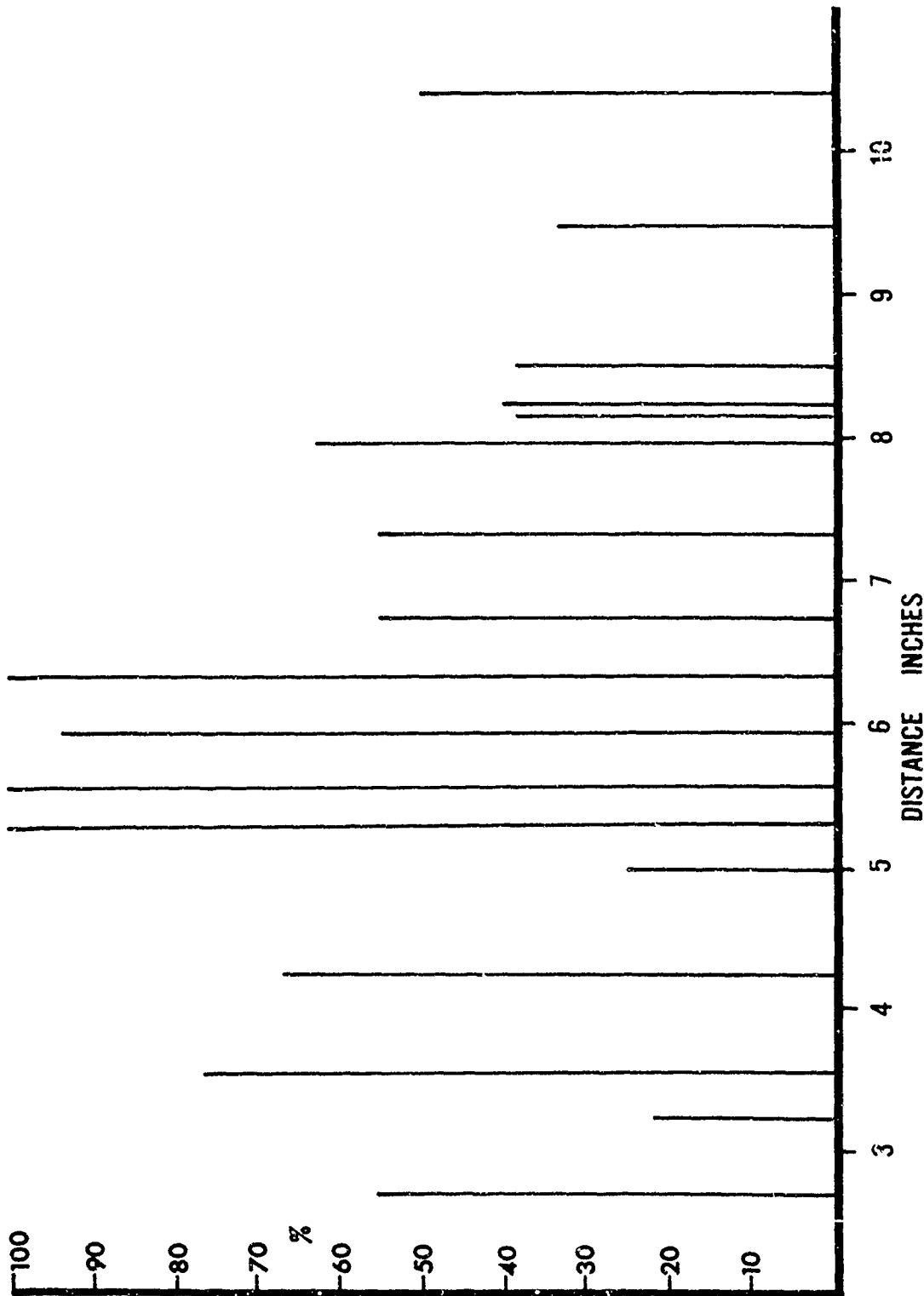


Figure 12. X-Ray Diffraction Pattern for Methyleneoxyamine Diperchlorate (DOAP)

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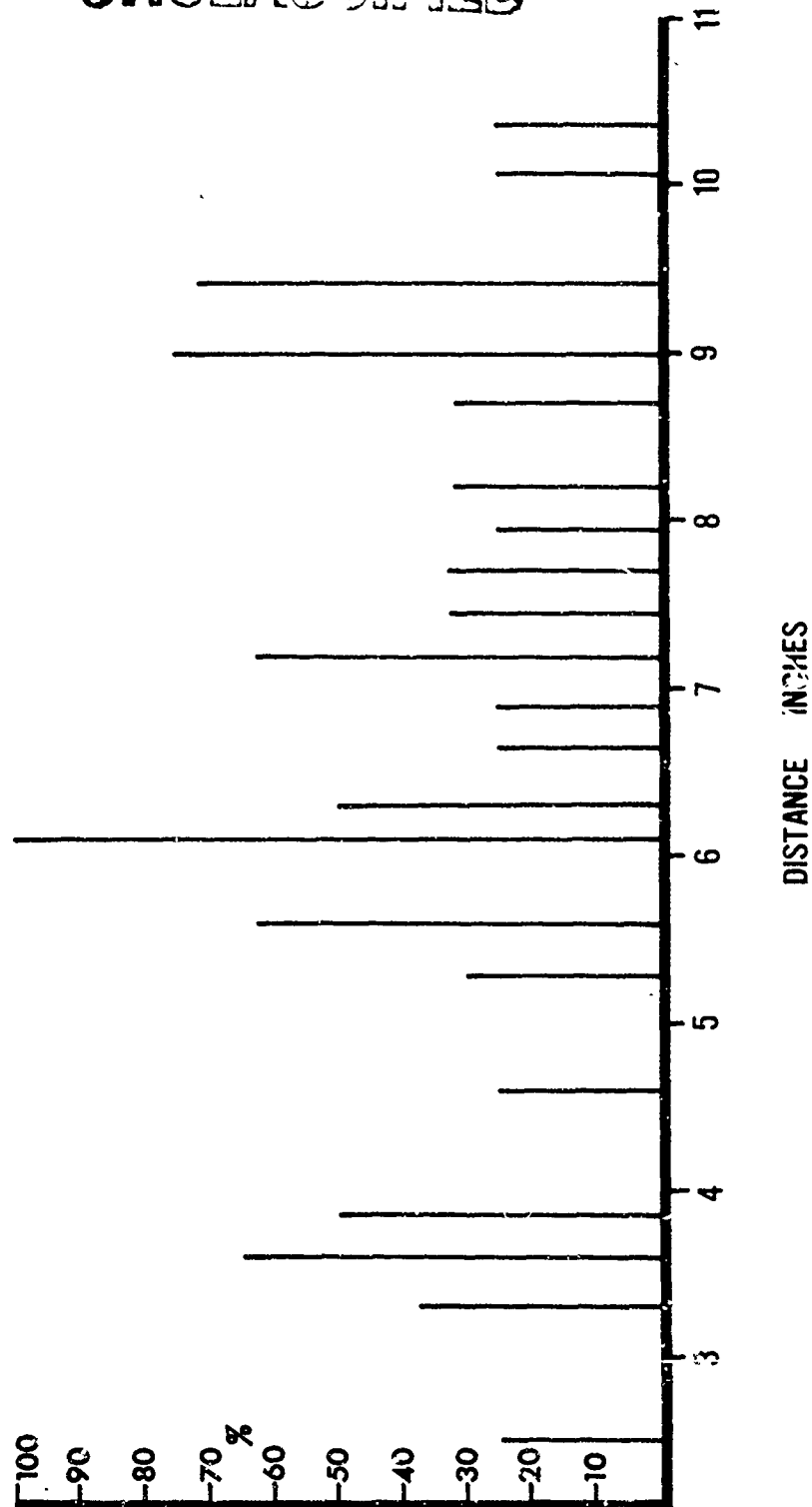


Figure 13. X-Ray Diffraction Pattern for 70°C Vacuum-Treated DOAP

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SECTION IV

DECOMPOSITION OF METHYLENEDIOXYAMINE MONOPERCHLORATE

(C) In order to verify the proposed mechanism for thermal rearrangement/decomposition of DOAP, a sample of methylenedioxamine monoperchlorate, $\text{H}_2\text{NOCH}_2\text{ONH}_2 \cdot \text{HClO}_4$ (DOAMP), was prepared (2) and decomposed in the mass spectrometer under the same experimental conditions used in the DOAP study. The ion source pressure during programmed heating of the monoperchlorate reached maxima at two temperatures, 85 to 86°C and 90°C. A third temperature-pressure rise began at 92°C and continued to the termination of the experiment at 97°C.

(U) The initial pressure rise was accompanied by a cooling of the sample (endothermic reaction). The second pressure increase occurred simultaneously with sample self-heating (exothermic reaction). Table V shows the key ion intensities appearing during the initial stages of each pressure rise.

(U) The initial pressure rise may be attributed to the liberation of occluded starting material, mostly the free amine (DO). Such a reaction is endothermic (boiling). The mass spectrum observed in this region is identical to the cracking pattern for DO (Table V). An excess of the free amine was used in the preparation of the mono-acid salt; hence, occlusion of residual starting material in the solid is a reasonable explanation for the effects noted in the temperature range.

(U) The second pressure rise is attributable to the formation and liberation of formamide from the salt. The majority of the spectrum at this temperature correlates with the cracking pattern for formamide.

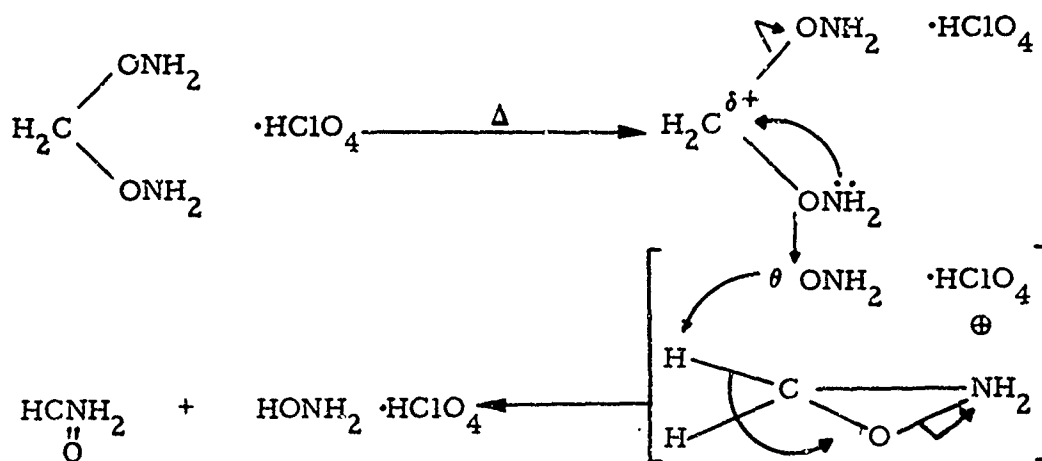
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(C) Initial liberation of perchloric acid does not occur until after the maximum concentration of formamide (and its fragments) is achieved. Perchloric acid liberation also parallels the pressure rise and the observed exothermicity effects. Subsequently the hydroxylamine species, as well as NO, O₂, N₂O, NO₂, and perchlorate fragments all increased in concentration. The mass spectrum in this temperature range can be attributed to the thermal decomposition of HAP (Table V).

(U) These data support the segmental aspects of the mechanism proposed for DOAP decomposition. After initial loss of perchloric acid from the di-acid salt (DOAP), the monoperochlorate remains as a stable intermediate. Degradation of the latter gives formamide, which is not accompanied by perchloric acid formation, and hydroxylammonium perchlorate as the temperature is increased.

(C) The mechanism for methylenedioxyamine monoperochlorate decomposition can be formalized as follows:



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TABLE V
COMPARATIVE MASS SPECTRA FOR DO AMP DECOMPOSITION AND
SELECTED SPECIES FROM DO6, FORMAMIDE, HAP

Ion Specie	84°C 3.5×10^{-6} mm	DOA Pattern	88°C 1×10^{-5} mm	Formamide Pattern	88.5°C 1.5×10^{-5} mm	92°C 6.5×10^{-6} mm	HAP Pattern
H ₂ CN	12.5	22.5	34.5		21.4	55.2	
CO	17.4		12.5		14.2	240.6	
N ₂	13.5		5.6		4.0	115.1	150.0
CH ₂ N	19.3	70.0	36.0		40.0	6.4	
CHO	38.3		13.9		7.6	61.9	
CH ₂ NH	1.5		--		0.6	--	
NO	29.4		18.4		15.4	1246.0	1200.0
CH ₂ O	24.7	22.4	8.5		3.2	23.0	
NHO	7.1	10.2	1.8		0.6	238.6	
CH ₃ O	14.5		17.6		2.3	--	
O ₂	0.3		0.2		4.6	882.0	520.0
NH ₂ OH	30.7	105.0	9.4		13.4	100.0	100.0
CON	0.8	0.8	1.7		2.4	16.5	
CHON	4.1	6.0	11.6	16.0	11.0	69.7	
CO ₂	10.8	21.3	4.7		12.2	467.0	
N ₂ O	12.5		2.0		0.3	104.5	340.0
CH ₂ ON	16.5	45.1	20.6	22.0	16.6	14.3	
CH ₂ ONH	12.6	12.3	100.0	100.0	100.0	10.1	
NO ₂	--		--		0.4	79.3	80.0
CH ₂ ONH ₂	100.0	100.0	6.0		2.2	--	
ClO	--		--		14.9	478.0	590.0
C ₂ H ₄ NO	15.2		39.4		3.5	--	
ClO ₂					26.5	812.0	1030.0
ClO ₃					25.3	109.0	170.0
HClO ₄					16.8	57.1	80.0

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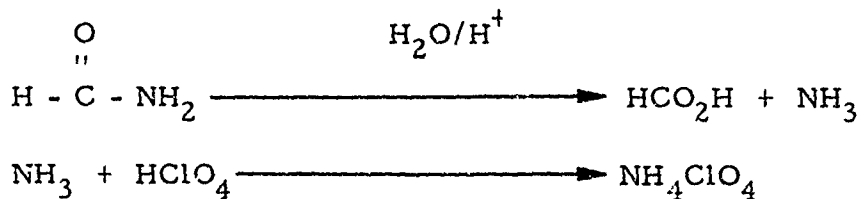
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SECTION V

SIDE REACTIONS DURING DECOMPOSITION

(U) The majority of the experiments described above were conducted under conditions in which initial volatile decomposition products such as perchloric acid and formamide were removed from contact with the solid starting material and its residue. Several experiments were run to identify the reactions and products of the decomposition intermediates which would occur in a closed system.

(U) Mixing formamide and aqueous perchloric acid at room temperature gave rise to instantaneous precipitate formation. The latter was identified as ammonium perchlorate by infrared and DSC analyses. Infrared analysis of the volatiles from the reaction mixture showed the major product to be formic acid. The formamide was hydrolyzed to the acid and ammonia. The latter then reacted with perchloric acid to give the salt



(C) Hydroxylammonium perchlorate is completely miscible with formamide. After 24 hours at 60°C, appreciable amounts of ammonia and carbon dioxide were detected when the volatiles from the mixture were expanded into a vacuum rack and analyzed by infrared analysis. Some dissociation of HAP to hydroxylamine and perchloric acid will occur under these conditions (60°C, vacuum). Water is formed among other products from the HAP decomposition reaction. Hence, in a closed system, decomposition of DOAP to HAP, formamide and free perchloric acid can give rise to numerous side products, including ammonium perchlorate, formic acid,

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ammonia, carbon dioxide (from oxidation of formamide by perchloric acid or one of its oxidizable decomposition species), water and the decomposition products of hydroxylamine.

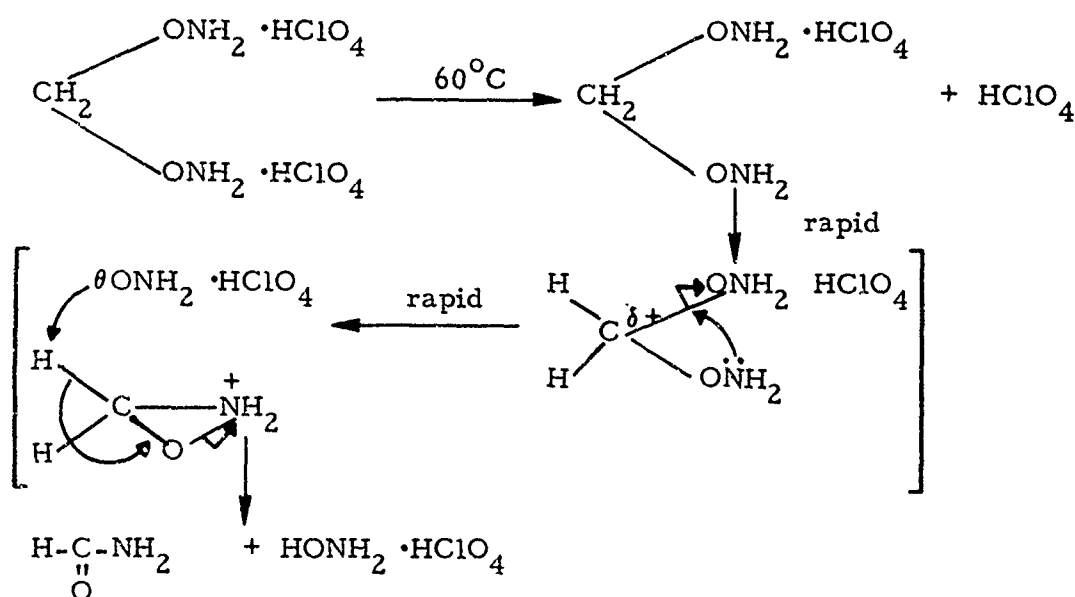
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SECTION VI

MECHANISTIC HYPOTHESIS

(C) Based on the evidence cited, the mechanism proposed for the primary decomposition route of methylenedioxyamine dperchlorate is:



(C) Loss of one perchloric acid group leaves the mono-acid salt in a configuration which is sterically unfavorable. The crystal structure of the dipe. ~chlorate has been destroyed. The mobile free oxyamine group lies adjacent to the oxyammonium perchlorate group, an equally electron-rich group. This electronically repulsive situation contributes to the driving force for the rearrangement. The oxyamine nitrogen is in position relative to the electrophilic methylene carbon to attack the latter and initiate a concerted cyclization-cleavage reaction. Such a mechanism is reasonable in light of the weakness of the C-O bond and the known existence of three-membered heterocycles of analogous structure (3) to the postulated protonated oxazirane transition state. Electronic charge balance leads to

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formation of formamide and hydroxylammonium perchlorate. The driving force, once again, is conversion to more stable products. In essence, the overall driving force for the reaction is the transition from an unstable intermediate (sterically distorted monoperchlorate) to a more stable product.

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COMPARISON WITH OTHER AMINE PERCHLORATES

(C) The decomposition of methylenedioxyamine diperchlorate is reminiscent of the thermal behavior of hydrazinium diperchlorate (HP-2) (References 4 through 7). Both are strong acids; one perchlorate group is lost relatively easily. Both give more stable solid intermediates, though in the case of HP-2 the first step in the decomposition is less complex and cleaner. That is, loss of one perchloric acid group gives only the stable monopерchlorate as product. Loss of perchloric acid from DOAP gives rise to a thermally unstable form of its mono-acid salt which continues to degrade to hydroxylammonium perchlorate, a stable intermediate, plus formamide. The latter is incompatible with its environment under these conditions and will react to give volatile products (NH_3 , CO , CO_2 , HCO_2H) and possibly some AP.

(C) The key difference between the two oxidizers lies in the hazardous nature of their composition products. HP-2 continually degrades to a more hazardous material, i. e., HP-1, while DOAP does not. In terms of perchloric acid liberation, the temperature threshold for this occurrence in the HP-2 decomposition is considerably lower, i. e., 40°C compared to 65°C for DOAP. This implies better compatibility behavior for DOAP than HP-2 under processing and storage conditions.

(C) The temperature threshold for decomposition of DOAP is lower than that for HAP, the latter being a stable product of DOAP degradation. The rate at which perchloric acid is evolved from DOAP is greater than that for HAP.

(C) Compatibility behavior dependent only on these factors (thermal stability and perchloric acid evolution) should be better in the HAP system.

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This would be especially true for those effects attributable only to perchloric acid reactions under long-term aging conditions. i. e., HAP propellants should age better at room temperature than propellants containing DOAP. This is an oversimplification, however, since factors such as hygroscopicity and crystalline phase changes also appear to effect HAP reactivity (4, 5). The endothermic transition undergone by HAP at 55°C is also accompanied by a marked increase in reactivity. DOAP is less hygroscopic than HAP and it does not undergo any phase changes below its melting point. A comparison of the reactivities of these oxidizers is presently underway at AFRPL. Conclusions concerning DOAP and HAP compatibility will have to await the results of this study.

(C) For the sake of completeness, the obvious should be stated: ammonium perchlorate is significantly more stable than DOAP.

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SECTION VIII

EXPERIMENTAL PROCEDURE

(U) DOAP samples of 0.01 mg were packed into 2mm OD glass capillary tube and placed on the end of a direct-inlet mass spectrometer probe. The probe consisted of a nichrome wire heater wrapped around a ceramic 2mm ID tube. The sample-containing capillary tube was placed in the ceramic tube and rested on a thermocouple.

(U) The probe was placed into the ion-source housing of a CEC 21-110 double-focusing mass spectrometer, such that the sample tube exit was within 1/2 inch of the perpendicular electron ionizing beam. The ion source housing was evacuated to 2×10^{-7} torr and warmed to 40°C overnight prior to a run. Heating rates were regulated to 0.5°C/minute with a temperature programmer for 40°C to 100°C. Ions produced from the ionization of gases being liberated from the sample were collected on an ion-sensitive photographic plate.

(U) The ion exposure energy transmitted to the plate was kept constant while the time required for a constant-energy-exposure value varied. Data was collected at each degree sample temperature. Pressure measurements were obtained from the ion-source ionization pressure gage.

(U) A total of 30 spectra were recorded on the plate for each experimental run. After plate development, the data was reduced by measuring the ion line positions, for accurate mass measurements, and density for relative quantitative measurements. No ion sensitivity corrections were made since only relative quantitative and qualitative data were desired.

(U) Weight-loss measurements were made on 0.2 gram samples of DOAP. Samples were weighed to 0.1 mg and placed in a vacuum oven present at the desired temperature. Continuous evacuation was conducted with

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an effective oven vacuum of less than 100 microns. Samples were periodically removed and cooled in an inert atmosphere dessicator prior to weight-loss measurements.

A. SAMPLE PREPARATION

(U) The samples of DOAP employed in this study were purified by recrystallization from ethanol. Elemental and perchlorate analyses indicated this material to be 98% pure DOAP.

B. THERMAL ANALYSIS

(U) The thermal behavior of various materials was studied on a Perkin-Elmer Model 1B Differential Scanning Calorimeter and a Dupont Model 900 Differential Thermal Analyzer.

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13. ABSTRACT

(C) The initial step in the thermal decomposition of methylenedioxyamine diperchlorate occurs at 60°C with the loss of a perchloric acid group to form the monoacid salt as an intermediate. As the temperature increases, the latter undergoes a concerted cyclization - cleavage reaction to form formamide and hydroxylammonium perchlorate.

(U) Mass spectrometry was used to formulate a working hypothesis for the decomposition. The existence of each of the postulated intermediates in the reaction was verified by independent experiments.

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