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MASS THERMAL ANALYSIS OF HYDROXYLAMINE AND METHOXYAMINE PERCHLORATES

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MASS THERMAL ANALYSIS OF HYDROXYLAMINE AND METHOXYAMINE PERCHLORATES

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FOREWORD

The activation energies for the thermal dissociation of hydroxylamine and methoxyamine perchlorates have not been determined. Little information is available on the comparison of thermal decomposition products of substituted amine perchlorates.

This report describes the application of mass thermal analysis to determine the activation energies for thermal dissociation of hydroxylamine and methoxyamine perchlorates, and to identify oxidation and reaction products. This is a final report of studies conducted at the Air Force Propulsion Laboratory over the period from October 1968 to April 1969, under Project 314804ACP.

The author would like to acknowledge Dr. C. I. Merrill for preparing the methoxyamine perchlorate, and Captain Raymond Foscante for his assistance on data interpretation.

Reviewed and approved for publication

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AESTRACT

Mass thermal analysis was used to study the thermal decomposition of hydroxylamine and methoxyamine perchlorates. The first step in the thermal decomposition of these salts is the proton transfer from the substituted ammonium ion to the perchlorate anion to form the free substituted amine and perchloric acid. Activation energies were determined to be 20.7 ± 2 kcal/mole (65° to 77°C) for the dissociation of hydroxylamine perchlorate, and 30 ± 2 kcal/mole (53° to 77°C) for the dissociation of methoxyamine perchlorate.

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SECTION I

INTRODUCTION

The use of a mass spectrometer to identify the gaseous species formed during controlled thermal degradation of a solid has been termed mass thermal analysis (MTA). This technique may be used in conjunction with differential thermal analysis (1, 2) and thermal decomposition analysis (3, 4) to provide insight into both the physical and chemical processes involved in phase changes, weight loss, and decomposition resulting from the thermal environment of a particular system.

The ion intensities of the gases liberated from the heated samples, and the temperature at which the gases are liberated can be plotted by the Arrhenius method to obtain activation energies for the processing occurring.

MTA technique was chosen for the studies to determine the activation energies necessary for dissociation of hydroxylamine and methoxyamine perchlorates, and to identify the dissociation and oxidation reactions occurring during thermal decomposition.

SECTION II

EXPERIMENTAL PROCEDURE

A self-contained solids sample probe fabricated in the laboratory for these studies is shown in Figure 1. The probe head is made by wrapping 5 inches of No. 28 gage nichrome resistance heater wire around a 30 mm long x 3 mm OD alumina tube. Two copper lead wires, cemented into the alumina probe and used as electrical feed-throughs for the heater, provided mechanical strength for the probe head.

Sample holders were made by fusing the centers of 25 mm x 2 mm OD glass melting point tubes and fitting them tightly into the heater wire-wrapped alumina tube. A chromal-alumel thermocouple extending from the probe rod fitted tightly against the bottom of the sample holder to provide accurate measurement of the sample temperature.

The probe was inserted horizontally through a vacuum seal to within 10 mm of the ion source of a Consolidated Electrodynamics Corporation Model 21-110A mass spectrograph, and the source was evacuated to less than 2×10^{-7} torr.

The heating rate of the sample was controlled by a Hewlett-Packard temperature programmer, and was limited to 0.5°C/minute. This permitted the pumping rate to maintain the total source pressure in the low 10^{-6} torr range during maximum gas evolution.

Spectra were collected on Ilford Q-2 photoplates using a constant exposure value of 7×10^{-12} coulombs. Obtaining this exposure value required from 2 minutes at the beginning of dissociation to less than 1 second during maximum dissociation and reaction. A constant exposure value was used to integrate and identify small quantities of dissociated products during initial stages of thermal dissociation.

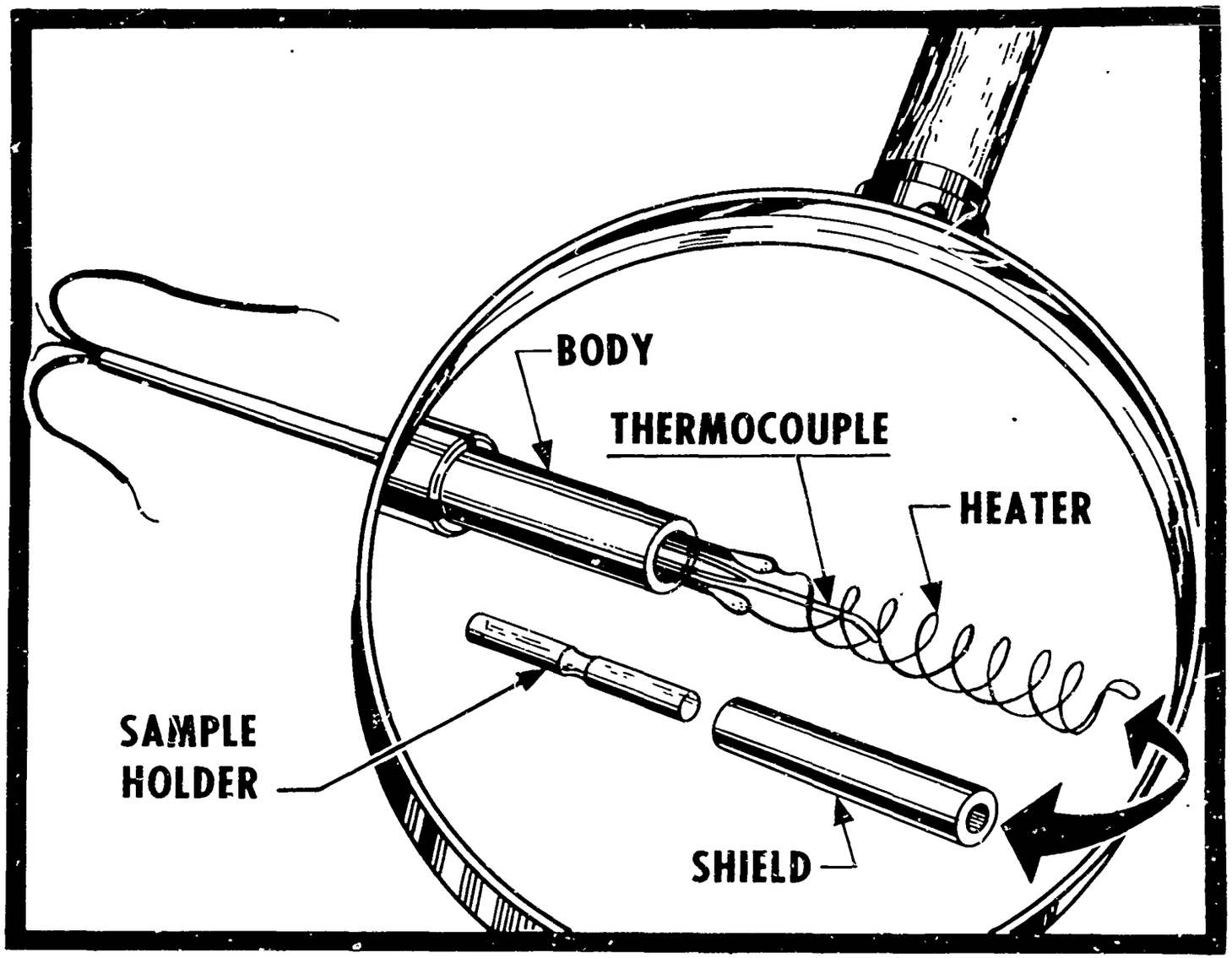

Figure 1. Sample Probe

Densities of the ion lines on the photoplates were obtained from a microphotometer trace and were reduced by computer. Line width and mass position corrections were made; however, no relative sensitivity corrections were made.

Reduced ion line density data were divided by the time required to obtain 7×10^{-12} coulombs exposure at a specific temperature, to yield an ion intensity-time relationship. The logarithm of the ion intensity was plotted versus the inverse absolute temperature and the resultant slope value was inserted in the Arrhenius equation to obtain activation energies.

SECTION III

RESULTS AND DISCUSSION

A. HYDROXYLAMINE PERCHLORATE

An Arrhenius plot of the hydroxylamine (NH_2OH) and chlorate (ClO_3) ion intensities resulting from controlled thermal dissociation of hydroxylamine perchlorate (NH_3OHClO_4) and perchloric acid ($HOClO_3$) is shown in Figure 2. A change in slope of the ion intensity lines is evident at 64°C; this may be the result of a crystalline phase transition for hydroxylamine perchlorate which has been reported (5) to occur between 57° and 62°C. An activation energy of 57.7 ± 2 kcal/mole was calculated for the transition from the slope of the line below 64°C.

Once the crystalline phase transition is complete, dissociation of the solid hydroxylamine perchlorate continues smoothly to its melting point at 80°C. Melting was noted by a variation in relative peak intensities from the slope as well as by momentary cooling of the sample temperature, as would be expected for the endothermic melting process.

The activation energy for the dissociation of hydroxylamine perchlorate to hydroxylamine and perchloric acid between 65° and 77°C, calculated from the slope of the hydroxylamine ion intensity line, is 20.7 ± 2 kcal/mole.

The calculated activation energy obtained from the slope of the chlorate ion intensity line, resulting from perchloric acid dissociation was 46.4 ± 2 kcal/mole. This value compares favorably with the value of 45.1 kcal/mole obtained by Levy (6) for the activation energy of the homogeneous thermal decomposition of perchloric acid vapor to HO and ClO_3. The activation energy thus corresponds to the HO-ClO_3 bond strength of 45 kcal.

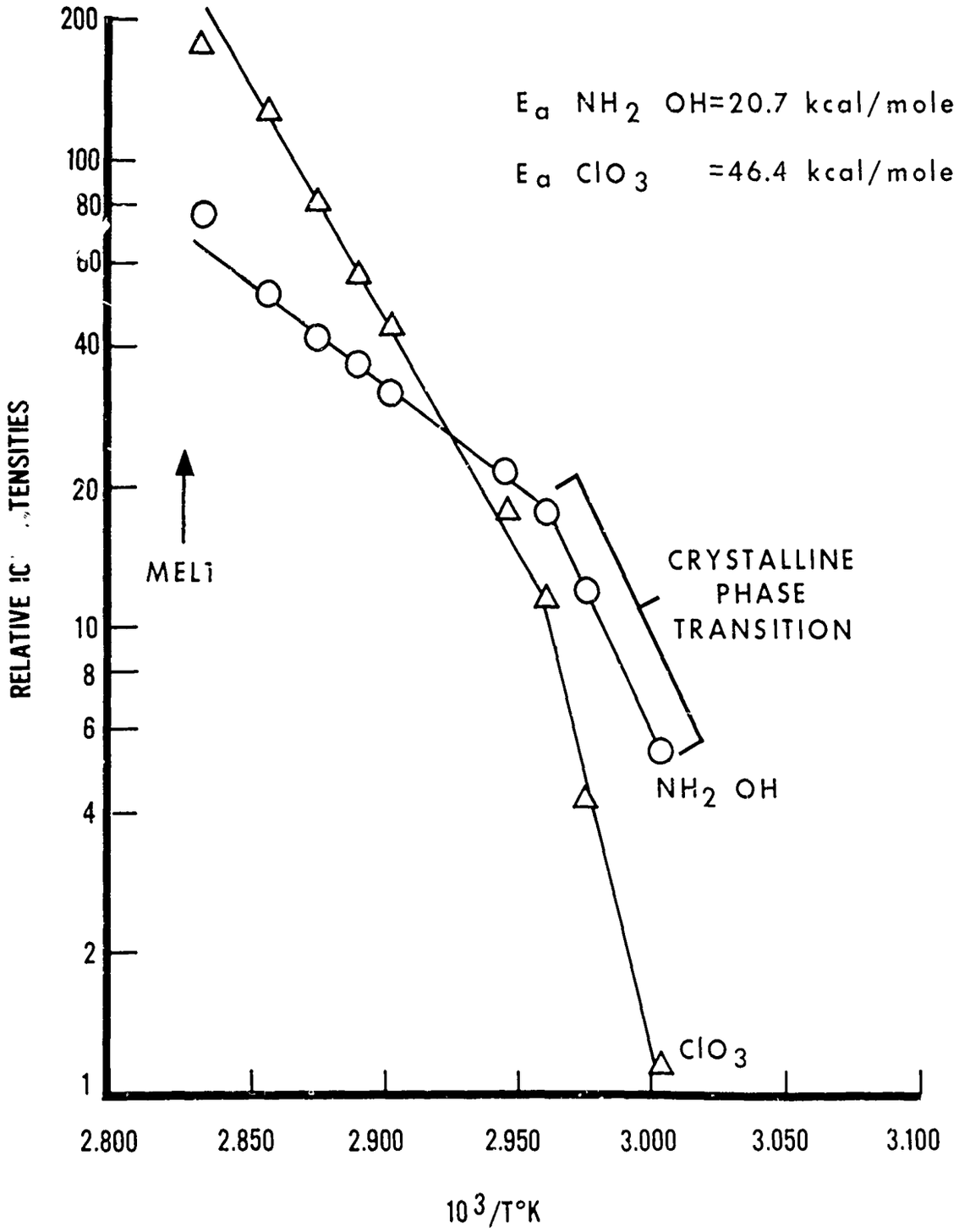

Figure 2. Hydroxylamine Perchlorate Dissociation

Figure 3 presents Arrhenius plots for the NH_2O ion and N_2O oxidation product ion. Dissociation of the hydroxylamine and subsequent oxidation by perchloric acid require activation energies falling between 28 and 32 kcal/mole. The difference in activation energy required to dissociate the hydroxylamine perchlorate and that required to dissociate the hydroxylamine is 8 kcal/mole. This is the energy which must be added to the system in order to dissociate the hydroxylamine after the hydroxylamine perchlorate has begun to dissociate. Once the hydroxylamine dissociates, oxidation of the dissociation products by perchloric acid proceeds.

Proposed thermal decomposition reactions for hydroxylamine perchlorate are shown as follows:

	Ea kcal/mode
$NH_3OHClO_4 \longrightarrow NH_2OH + HOClO_3$	20.7
$HO\text{-}ClO_3 \longrightarrow HO + ClO_3$	46.4
$NH_2OH + OH \longrightarrow NH_2O + H_2O$	28.6
$NH_2O + ClO_3(HOClO_3) \longrightarrow$ Oxidation Products	28 to 32

The rate-limiting reaction is the dissociation of the hydroxylamine perchlorate to the free amine and perchloric acid. Once dissociation occurs, further energy is required to dissociate the free amine and to oxidize the dissociation products.

Products identified during the oxidation of dissociated hydroxylamine by perchloric acid include water, oxides of nitrogen, oxygen, and hydrogen chloride, all formed by processes exhibiting activation energies between 28 to 32 kcal/mole.

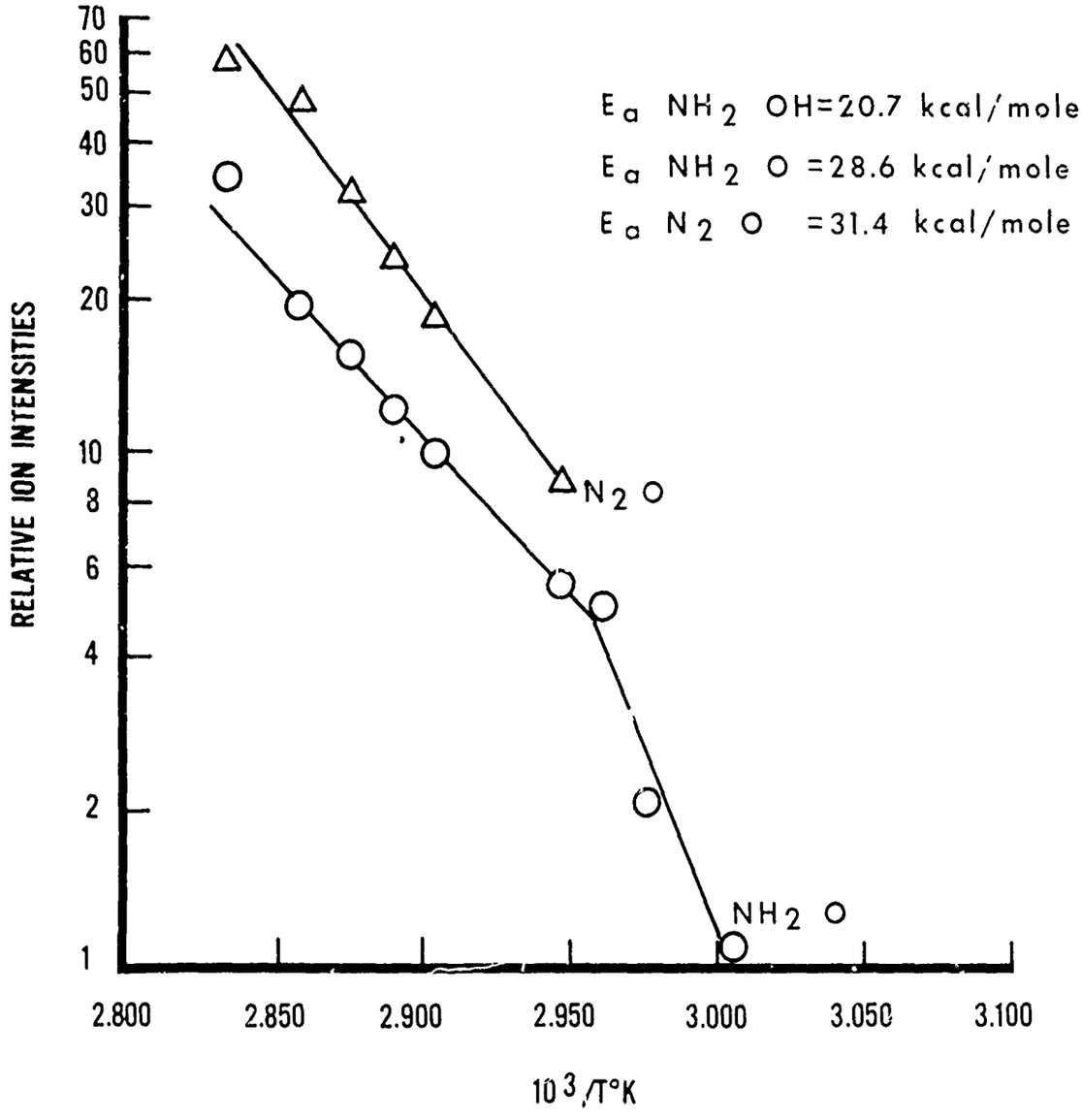

Figure 3. Hydroxylamine Perchlorate Decomposition and Reaction Products

B. METHOXYAMINE PERCHLORATE

An Arrhenius plot of the methoxyamine (CH_3ONH_2) and chlorate (ClO_3) ion intensities resulting from the thermal dissociation of methoxyamine perchlorate ($CH_3ONH_3ClO_4$) and perchloric acid ($HOClO_3$) are shown in Figure 4. No crystalline phase transitions for methoxyamine perchlorate occur in the temperature range studied, consequently, no changes in slope are observed.

The activation energy for the dissociation of methoxyamine perchlorate to methoxyamine and perchloric acid between 53° and 77°C, as calculated from the slope of the methoxyamine ion intensity line, is 30 ± 2 kcal/mole.

The slope of the chlorate ion, representing the dissociation of perchloric acid, yields an activation energy of 44.2 ± 2 kcal/mole. This value is similar to the previous activation energy calculated for the perchloric acid dissociation in the hydroxylamine perchlorate case.

Arrhenius plots for some of the products of methoxyamine and perchloric acid interreactions are shown in Figure 5. The activation energies for these products lie in the range 28 to 32 kcal/mole, as with that calculated for the dissociation of methoxyamine perchlorate. Therefore, once methoxyamine perchlorate dissociates, sufficient energy is available in the system for the dissociation and reaction of the amine with perchloric acid to proceed.

A proposed mechanism for the thermal decomposition of methoxyamine perchlorate is shown in the following:

$CH_3ONH_3ClO_4 \longrightarrow CH_3ONH_2 + HOClO_3$	30 kcal/mole
$HO\text{-}ClO_3 \longrightarrow HO + ClO_3$	44.2 kcal/mole
$CH_3ONH_2 \longrightarrow CH_3O^+ + \cdot NH_2$	A. P. = 19 ± 0.5 ev

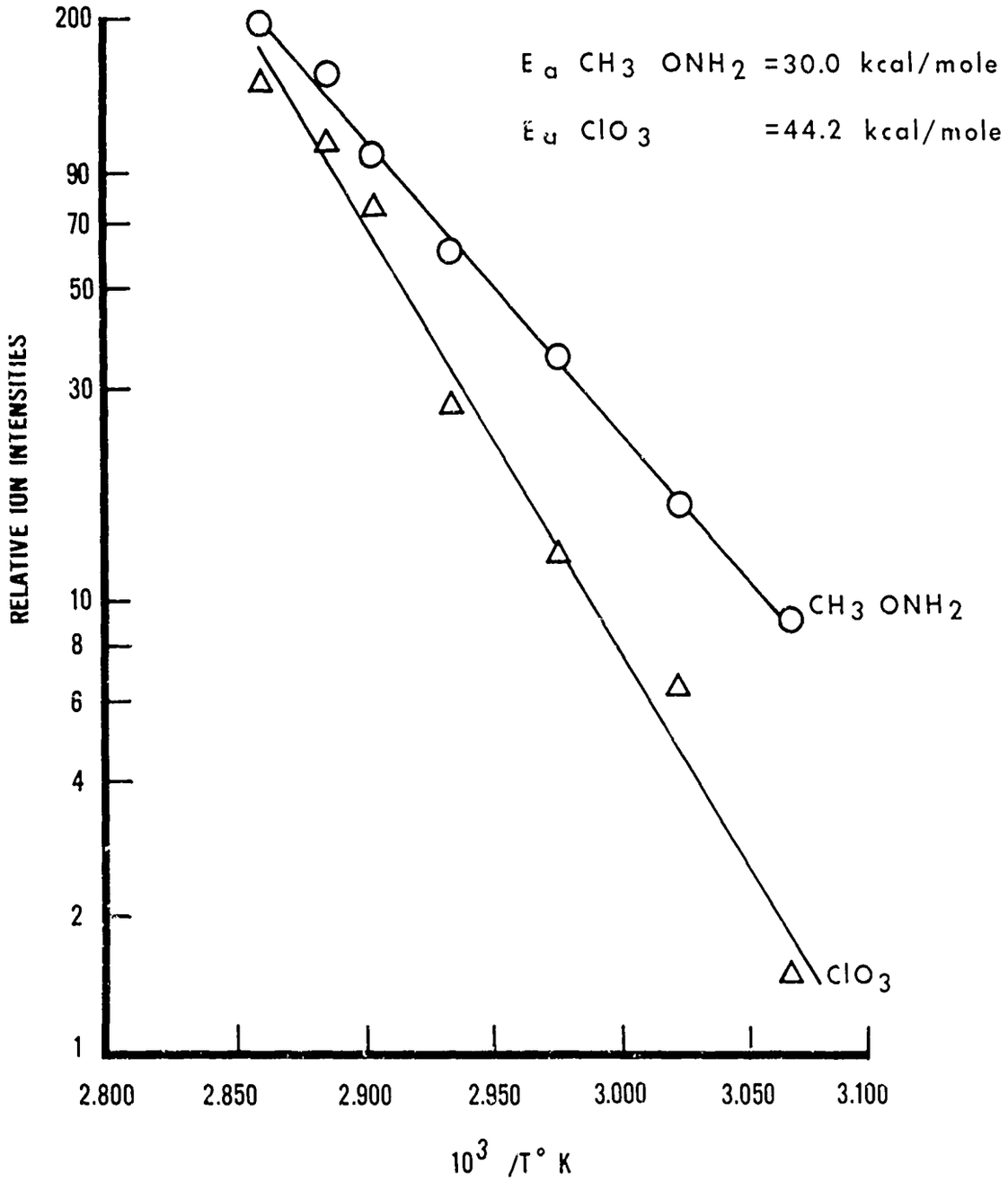

Figure 4. Methoxyamine Perchlorate Dissociation

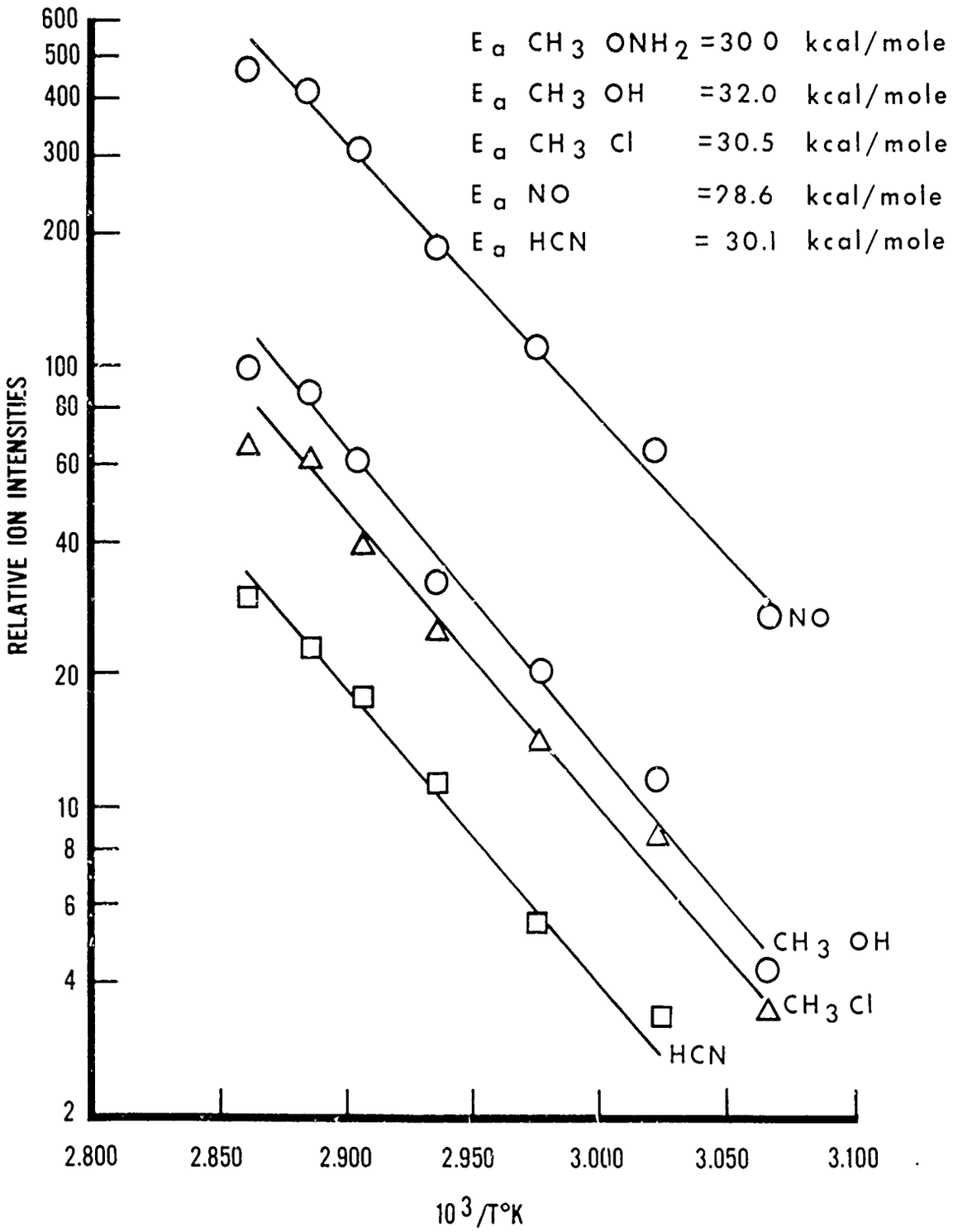

Figure 5. Methoxyamine Decomposition and Reaction Products

$CH_3ONH_2 \longrightarrow CH_3\cdot + {}^{+}ONH_2$ A. P. = 17 ± 0.5 ev

CH_3ONH_2 dissociation products + ClO_3 ($HOClO_3$)

$\longrightarrow$ reaction and oxidation products 28 to 32 kcal/mole

The rate-limiting reaction is the thermal dissociation of the methoxyamine perchlorate. Once this dissociation occurs, the methoxyamine immediately decomposes, forming either CH_3O and NH_2 or CH_3 and NH_2O. Appearance potential data for methoxyamine indicate that the CH_3-O bond is weaker than the O-NH_2 bond. Therefore, preferential fragmentation will be CH_3 and NH_2O, with the methyl radical reacting further to form methylated compounds and oxides of carbon. The NH_2O radical will readily oxidize to nitrogen oxides and water.

Reaction and oxidation products include methyl chloride, methyl alcohol, hydrogen chloride, methyl perchlorate, water, and the oxides of carbon and nitrogen. All products exhibit activation energies between 28 and 32 kcal/mole.

SECTION IV

CONCLUSIONS

The methoxyamine is a stronger base than hydroxylamine since the thermal dissociation of methoxyamine perchlorate requires a greater activation energy than that for the hydroxylamine perchlorate.

The mass thermal analysis method can be used successfully to obtain thermochemical data and to identify reaction processes occurring during the thermal decomposition of amine perchlorate salts.

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