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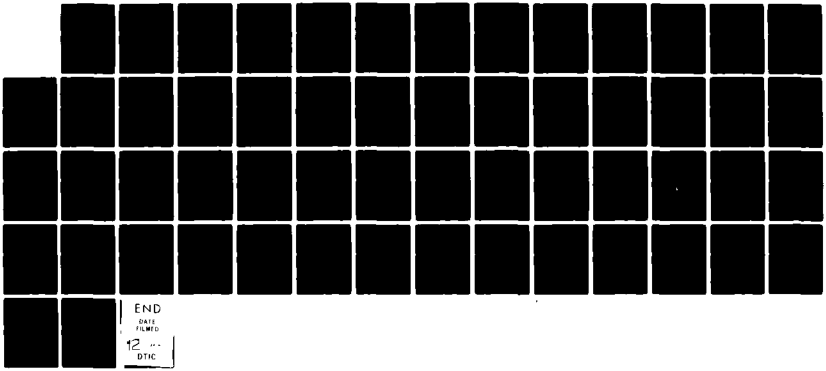

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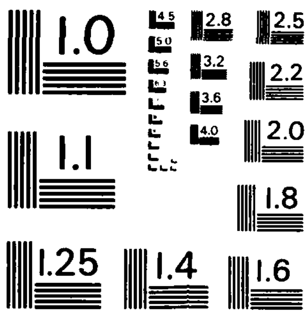
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MASS SPECTROMETRIC THERMAL DECOMPOSITION STUDIES ON SEVERAL AZIDO AND NITRATO POLYMERS, THERMAL PLASTICIZERS AND NOVEL NITRAMINES

Milton Farber, S. P. Harris and R. D. Srivastava

ANNUAL SUMMARY REPORT

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glycidyl azide polymer (GAP)
bis ethoxy methyl oxetane (BEMO)
bis fluoro methyl oxetane (BFMO)
thermal decomposittion
activation energies
mass spectrometry
copolymers

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Effusion mass spectrometric investigation of BAMO, AMMO, AZOX and GAP yielded primary decomposition of N_2 release at approximately 120 C and E_a values of 170 - 180 kJ mol^{-1} (43 - 43 kcal mol^{-1}). The 50-50% copolymer of BAMO-BNMO decomposes initially through the nitrato constituent at approximately 100 C followed by the azide decomposition. The thermal degradation mechanism for BEMO appears to be a stepwise breaking of the ethoxy-methyl bonds followed by the stripping of the methylene groups. BFMO is stable to temperatures greater than 200 C

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) with initial decomposition products of HF, with considerable depolymerization occurring. The major decomposition product of the NSWC novel nitramine, $C_6H_8N_8O_{12}$, is the eight-membered nitramine ring less two NO_2 molecules, molecular weight 292. The decomposition product is stable in the gas phase at 300 C.

A-1

I. INTRODUCTION

Thermal decomposition studies were performed by effusion-mass spectrometry on a number of propellant materials, including azido polymers, nitrato polymers, thermal plasticizers and novel nitramines.

The azido polymers included formulations of BAMO, AMMO and AZOX synthesized by Dr. G. E. Manser of Morton Thiokol Wasatch Division, and GAP, prepared by Dr. M. B. Frankel of the Rocketdyne Division of Rockwell International. The nitrato compounds included BNMO supplied by Dr. Manser and TMETN prepared by Dr. Russell Reed of the Naval Ordnance Test Station, China Lake. Samples of two thermal plasticizers, BEMO and BFMO, also were supplied by Dr. Manser. A novel nitramine was furnished by Dr. Horst Adolph of the White Oak Naval Surface Weapons Center.

Reaction kinetics and mechanisms were proposed from the mass spectra obtained for the degradation products and are discussed in the following sections of this report.

II. MASS SPECTROMETER STUDIES

A. Thermal Decomposition of Azido Polymers

A paper entitled "Mass Spectrometric Kinetic Studies on Several Azido Polymers" coauthored by Milton Farber, S. P. Harris, and R. D. Srivastava will appear in "Combustion and Flame" in the near future. A preprint of the paper is presented in Appendix A.

B. Thermal Decomposition of Nitrato Compounds

1. Thermal Decomposition of the 50-50% BAMO-BNMO Copolymer

The 50-50% BAMO-BNMO copolymer was purified for approximately 60 hours in vacuum at 60 C. This removed all traces of the solvent methylene chloride (less than one part in 10^6 as seen with the mass spectrometer). The purified copolymer appears to be stable to nearly 100 C, as can be seen from Fig. 1, which shows small concentrations of NO_2 at that temperature. Upon heating the copolymer to 150 C the BAMO constituent begins to decompose, with the release of 44 amu fragments, presumably C_2H_4O and CO_2. At 170 C the decomposition of BAMO has increased to where the 44 amu concentration is greater than that of the NO_2 from the BNMO constituent.

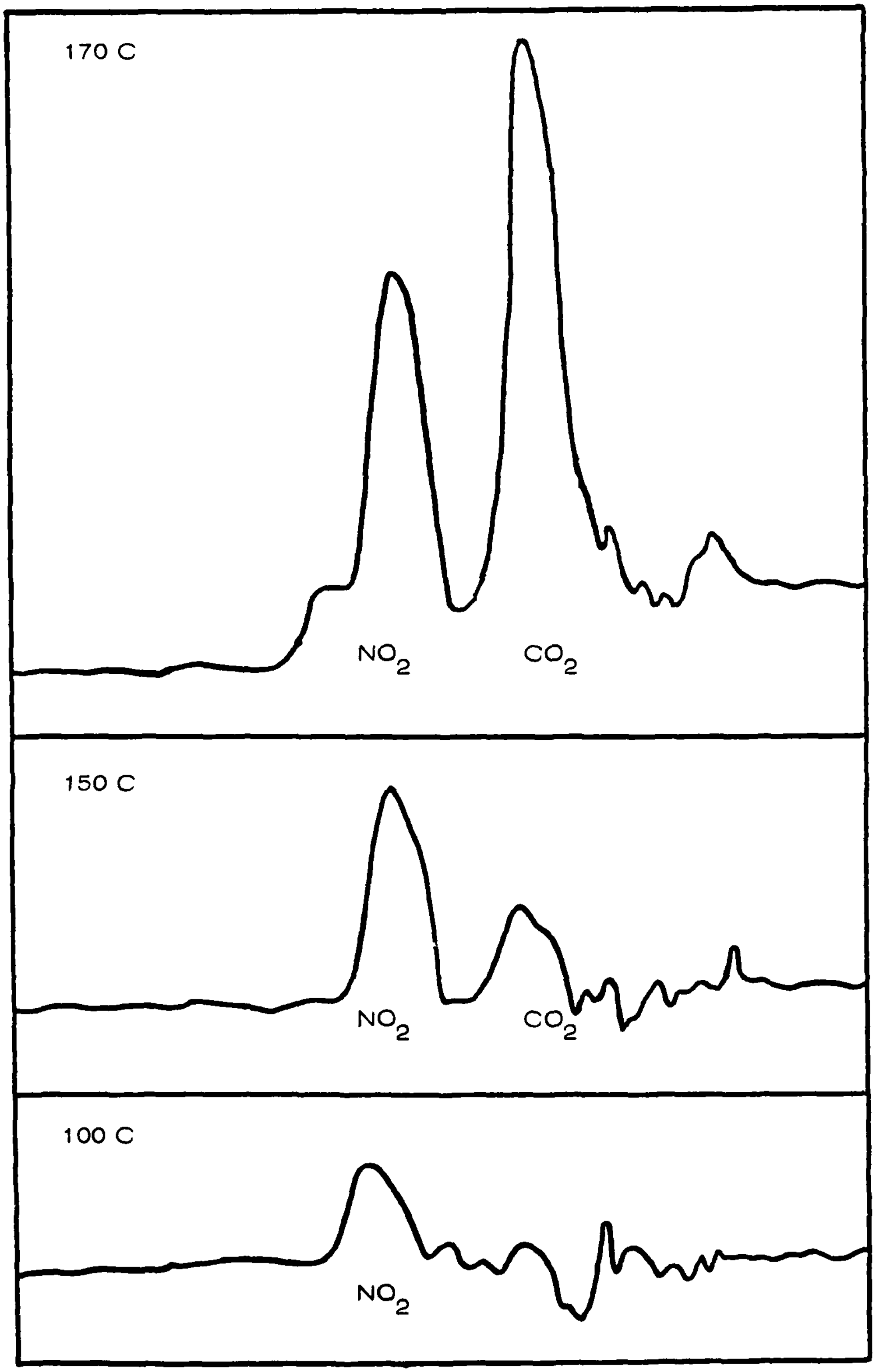


Fig. 1. Relative NO_2 and CO_2 comparison as a function of temperature for decomposition of 50–50% BAMO-BNMO

Figure 2 compares the rate of decomposition of the two polymers which make up the copolymer at three temperatures. This figure clearly shows the dramatic change in decomposition rates of the various species in the 14 to 50 amu range as the temperature is increased from 140 to 200 C.

2. Unstabilized TMETN

In order to compare the thermal decomposition characteristics of the BAMO-BNMO copolymer, studies were made on a nitrated plasticizer, trimethyl ethane trinitrate (TMETN), unstabilized. However, such a comparison should be considered as very qualitative since these are two entirely different classes of compounds; i.e., a monomer against a polymer, although both contain ONO_2 groups. Figure 3 shows the mass peaks resulting from the heating of TMETN in vacuum arriving at the mass spectrometer at a fairly low temperature, 50 C. The mass fragments are similar to those of BNMO, although they are observed at lower temperatures.

C. Degradation of Thermal Plasticizers

1. Thermal Decomposition of BEMO

A combined three-laboratory research program was undertaken to investigate bis (ethoxy methyl) oxetane, BEMO. Synthesis and TGA analyses were performed at Morton Thiokol Wasatch Division by Dr. G. E. Manser's group. Thermal degradation and mechanistic studies were conducted by Professor L. H. Sperling's group at Lehigh University, and the mass spectrometric thermal decomposition investigations were performed at Space Sciences, Inc. A joint paper is being prepared for publication in an appropriate polymer journal.

A melting point for BEMO of 80 $\pm$ 2 C was determined in vacuum. This polymer is stable to approximately 200 C. However, at 150 C very small concentrations of decomposition products are seen. Figure 4 shows mass spectra at three isothermal temperatures, 100, 150 and 200 C. As can be seen, at 150 C there are three definite regions of decomposition products, 56, 70, and 84 amu. At 200 C decomposition is slightly more pronounced but appears to be in the same spectral region.

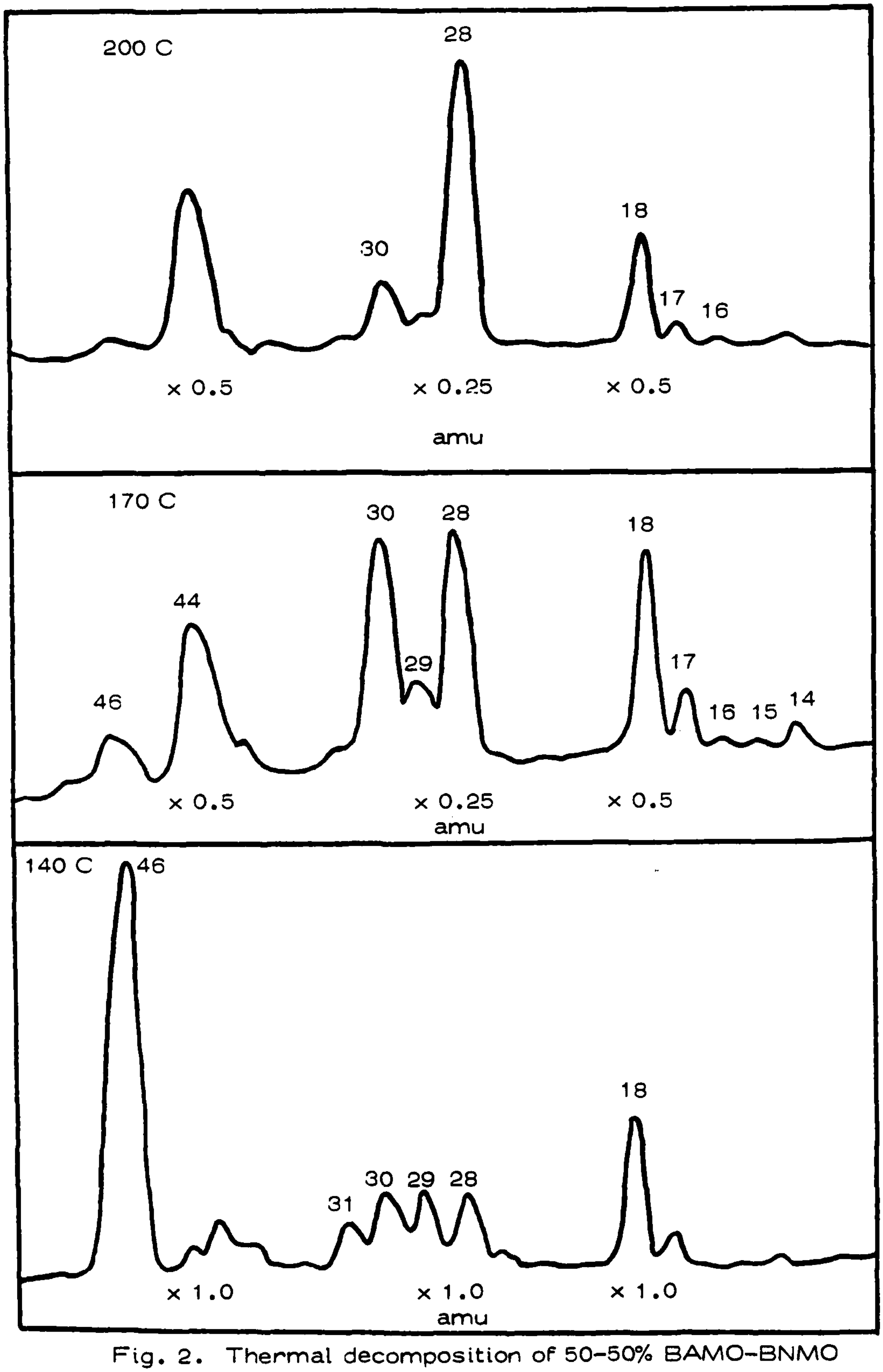


Fig. 2. Thermal decomposition of 50-50% BAMO-BNMO as a function of three temperatures in three amu ranges

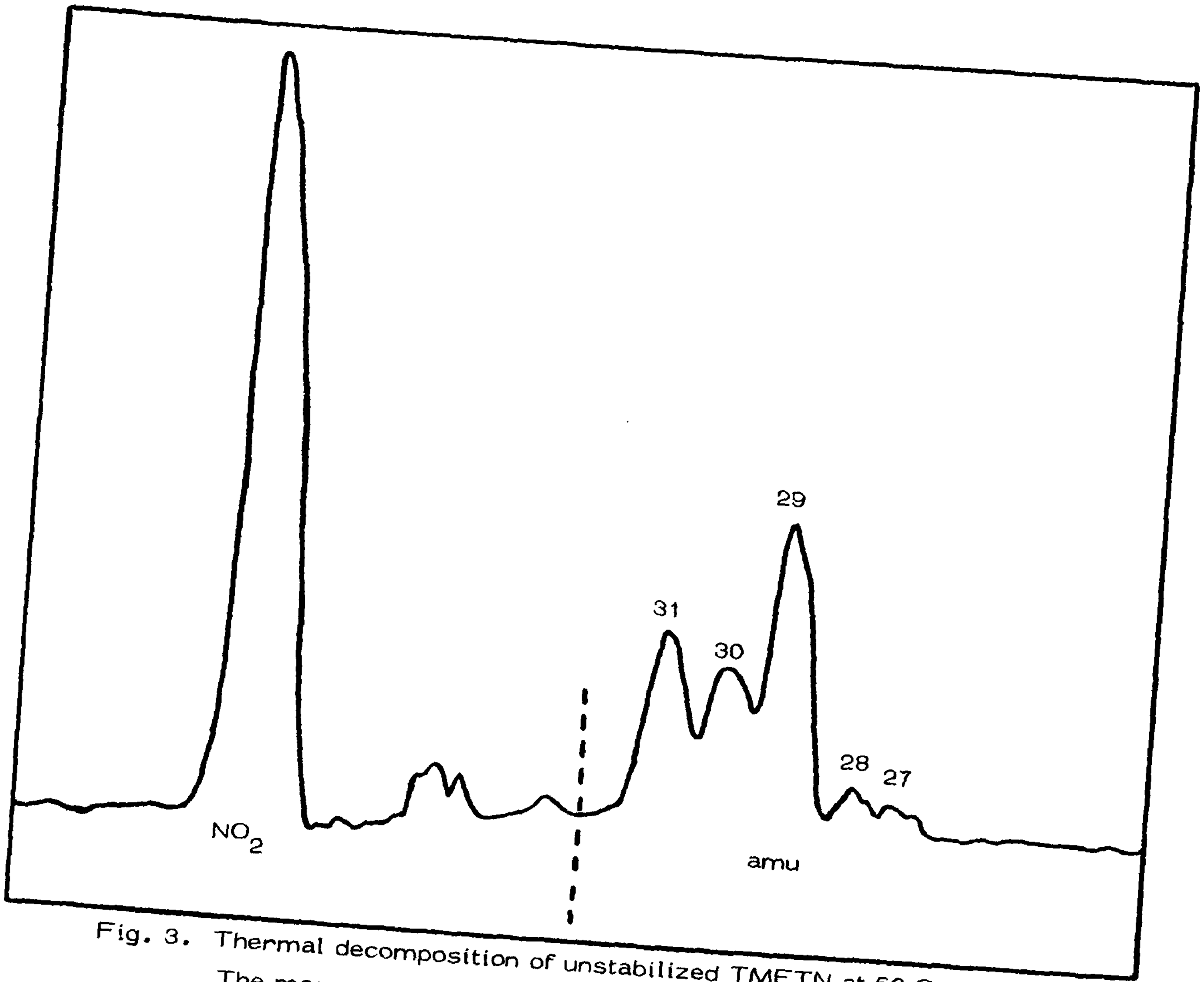


Fig. 3. Thermal decomposition of unstabilized TMETN at 50 C.
The mass spectra are relative only within the dashed lines.

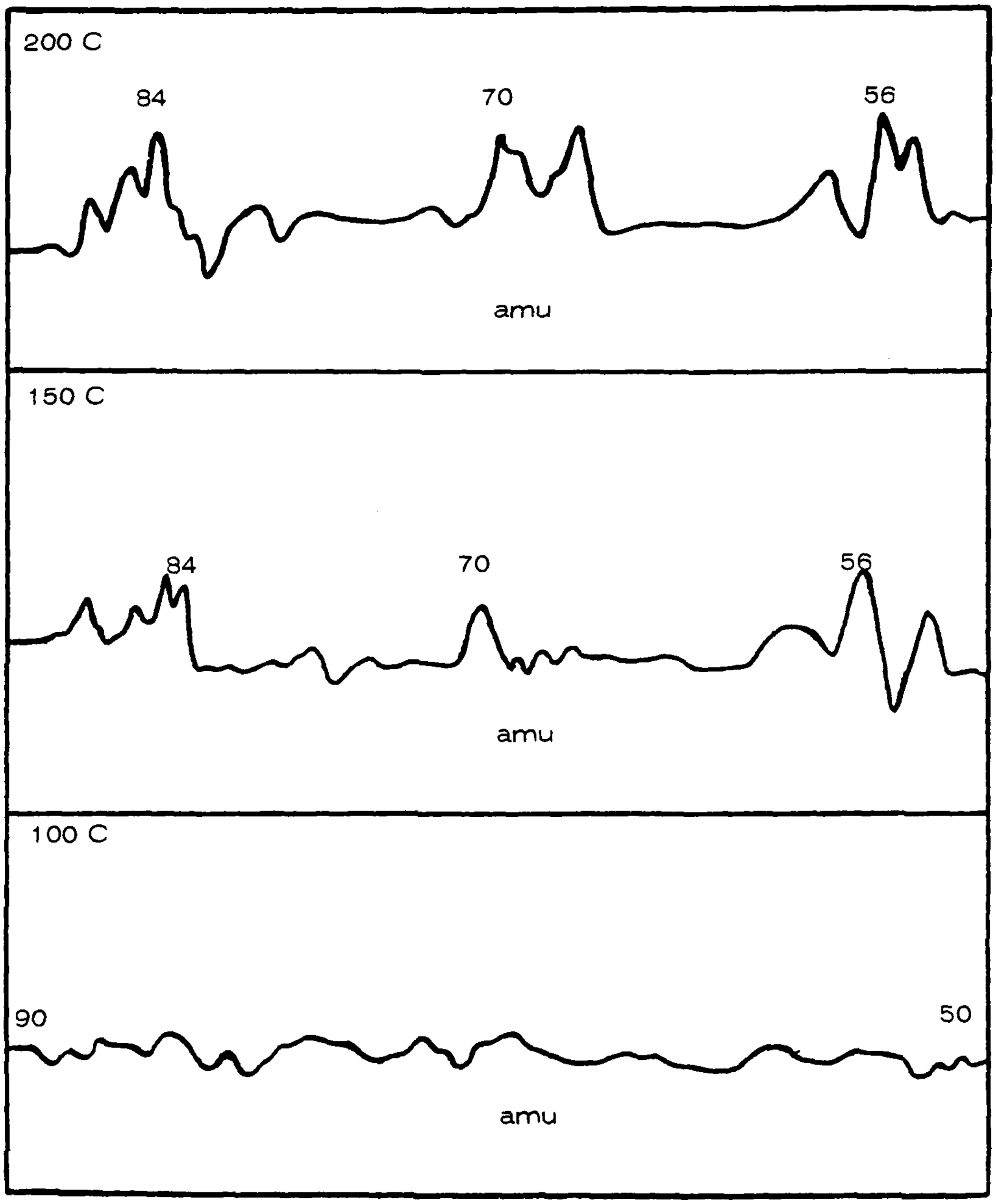


Fig. 4. Thermal decomposition of BEMO at three isothermal temperatures: 100, 150 and 200 C. The mass spectra are in the range 50 - 90 amu.

Above 200 C several prominent high amu peaks appear, indicating that both decomposition and depolymerization are occurring simultaneously. Figure 5 shows the increase in concentration as a function of temperature of several decomposition products. It can be seen that these mass peaks at amu values of 98, 102 and 112 increase rapidly with temperature. An activation energy, E_a, of 60 $\pm$ 10 kcal/mol is calculated within this temperature range (see Fig. 6). This was accomplished by plotting the log of the relative intensities of the 98 atomic mass peaks against the reciprocal of the absolute temperature.

At 230 C the depolymerization of BEMO definitely occurs (Fig. 7), with both higher and lower amu fragments of depolymerization and decomposition. As thermal energy is adsorbed in the polymer the ethoxy methyl groups attached to the central carbon begin to decompose, releasing a number of low molecular weight fragments. The decomposition at this temperature produces many small amu fragments in the range of 13 to 18 amu, including CH, CH_2, CH_3, OH and H_2O (Fig. 8). Numerous fragments are also produced in the 26 to 32 amu range (also shown in Fig. 8). Decomposition products in the 40 to 45 amu range can be seen in the third segment of this figure. The spectra are continuous only within the dashed lines. Figure 9 shows a 100 mass unit scan of BEMO at 260 C. While decomposition is occurring the backbone of the polymer also depolymerizes with multiples of the three-carbon backbone released as vapor species. The relatively low concentration of the monomer probably indicates that although depolymerization of the polymer is occurring, a considerable amount of decomposition is also taking place and that the higher amu species (below and above the monomer) are depolymerized fragments of the backbone where the bonding structure to the ethoxy methyl groups has been destroyed.

The mass spectrometric studies indicated that complex mechanisms were involved. The D.S.C. experiments on BEMO by R. B. Jones of Lehigh University produced thermograms (Fig. 10) showing four finger-like peaks which were attributed to the complex decomposition processes. An Arrhenium plot of the lnk vs. $1/T_D$ yielded an activation energy of 52.4 kcal/mol.

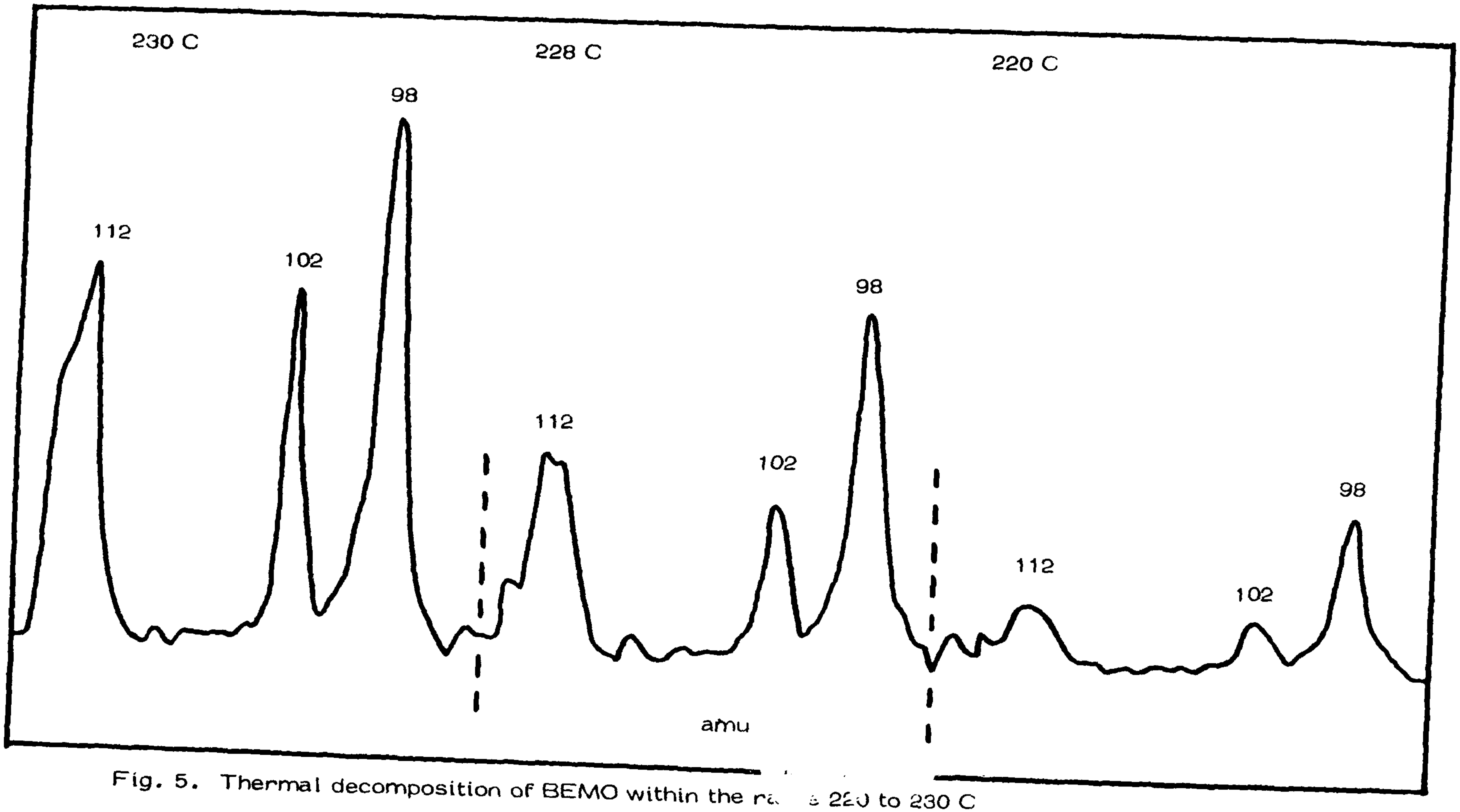


Fig. 5. Thermal decomposition of BEMO within the ra[illegible]e 220 to 230 C

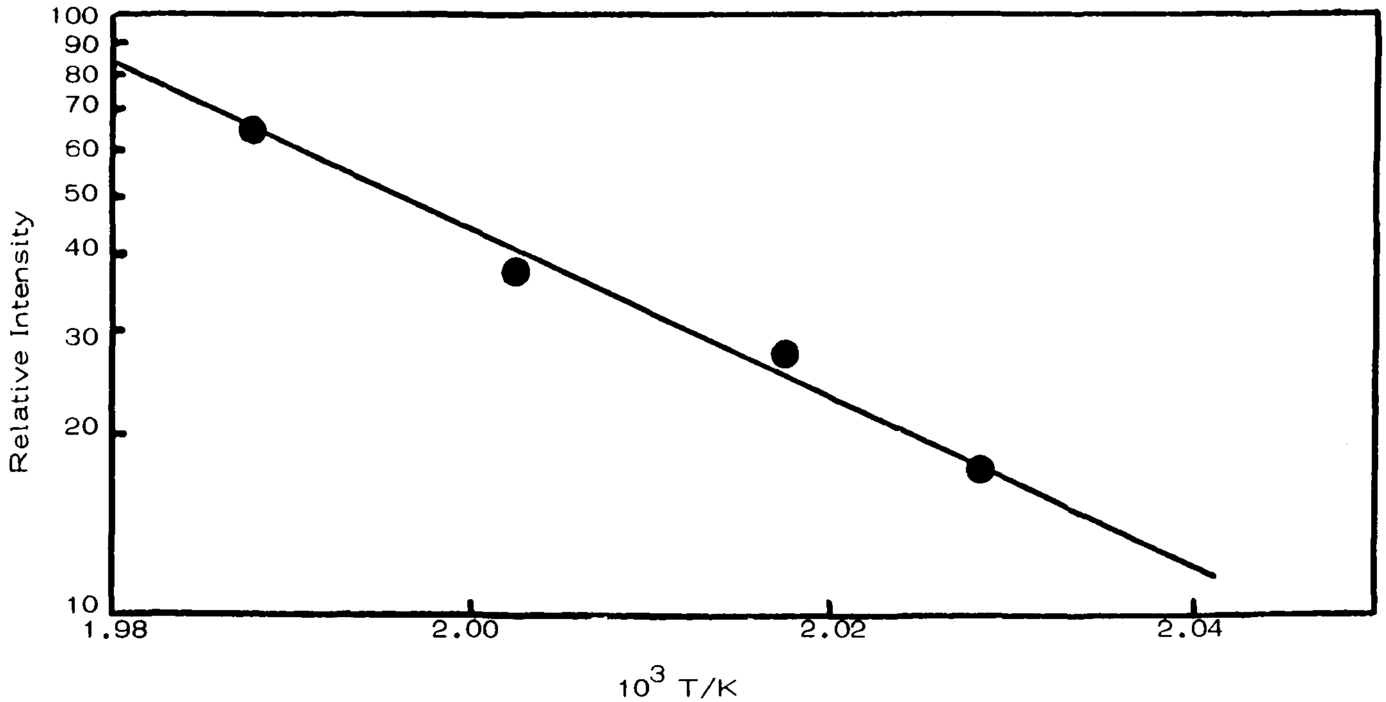


Fig. 6. Plot of the intensity of the 98 amu peak against the reciprocal of the absolute temperature (220 - 230 C), yielding an E_a of 60 $\pm$ 10 kcal/mol

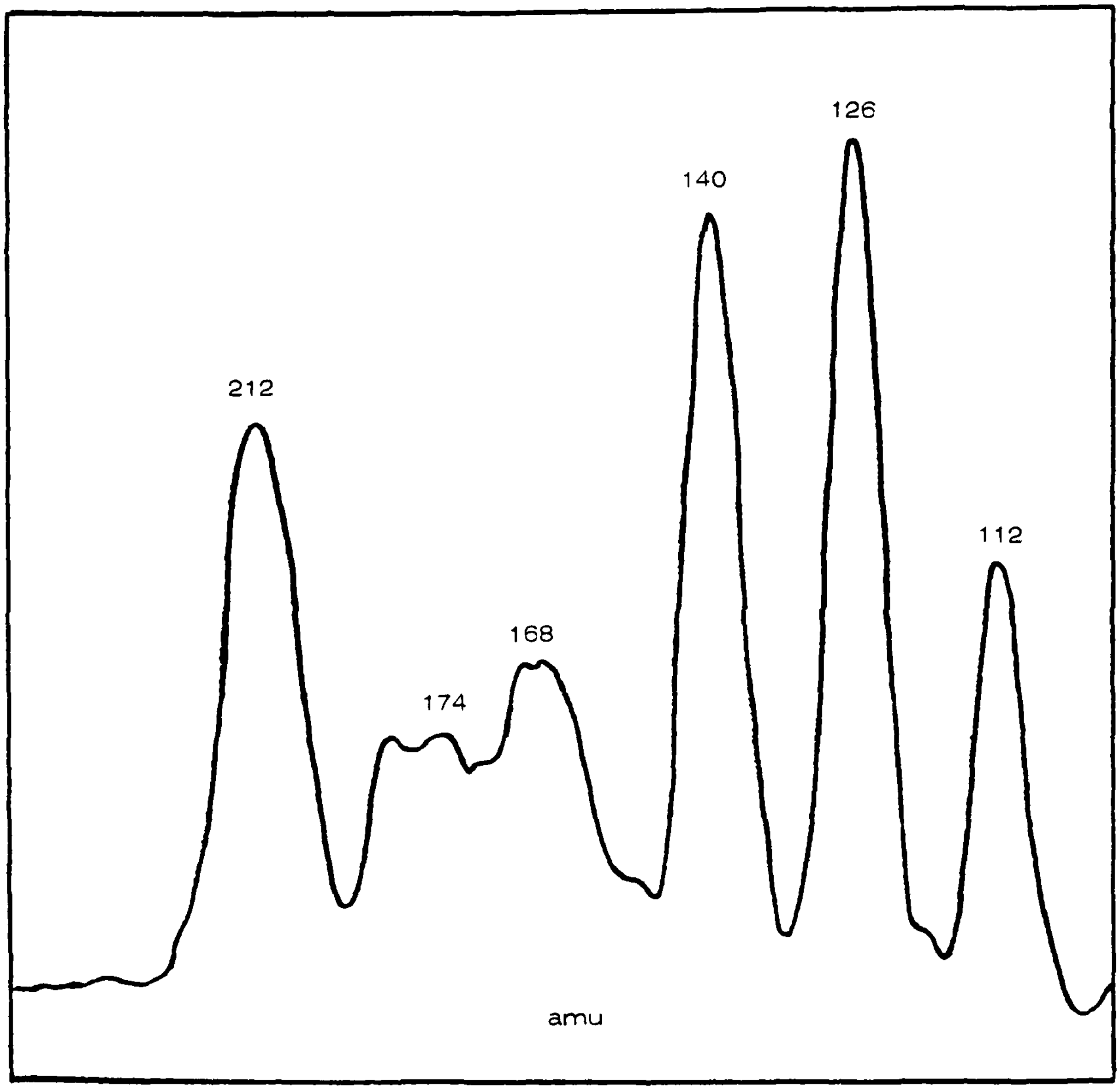


Fig. 7. Decomposition and depolymerization products of BEMO at 230 C

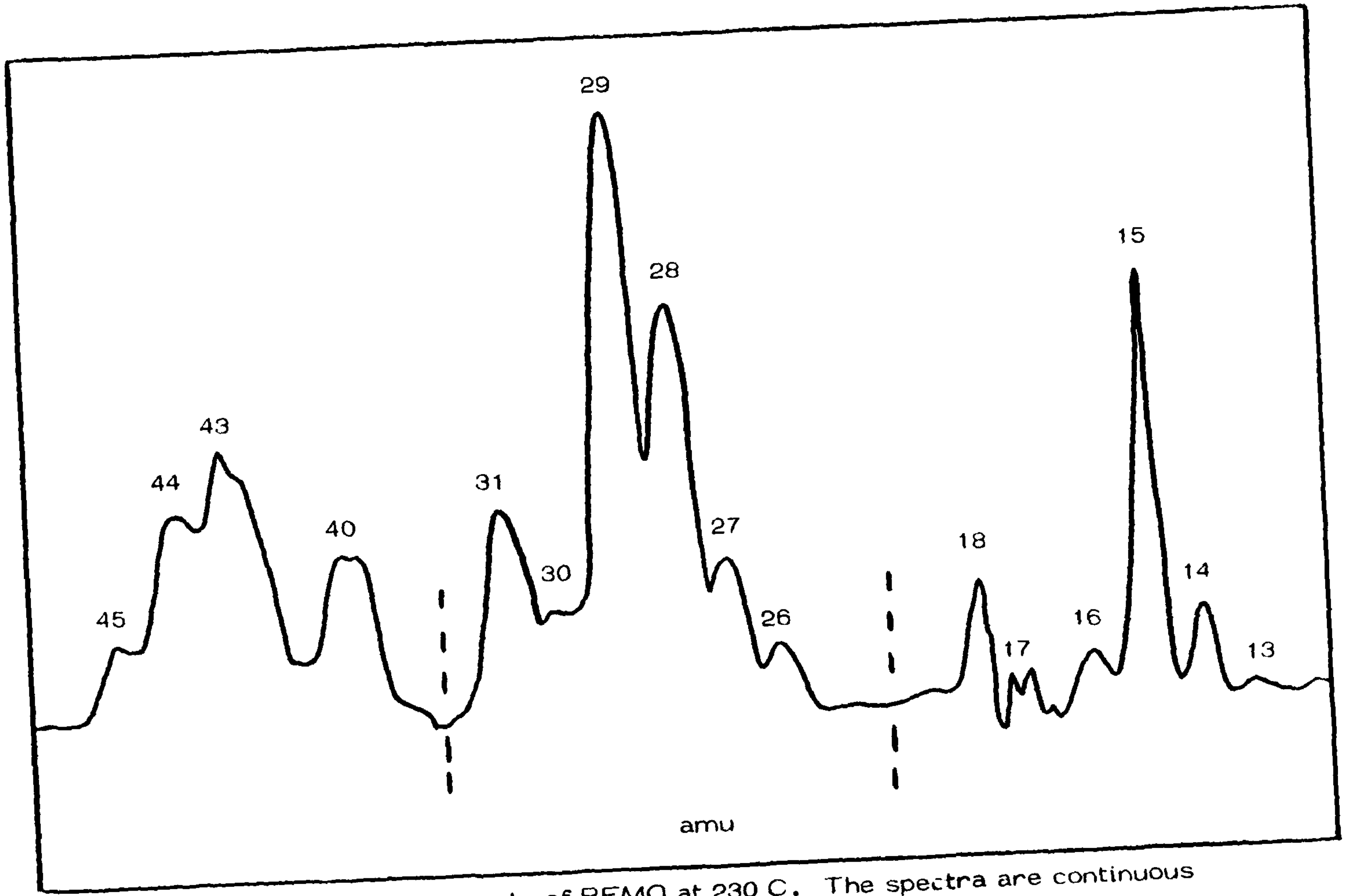


Fig. 8. Decomposition fragments of BEMO at 230 C. The spectra are continuous only within the dashed lines.

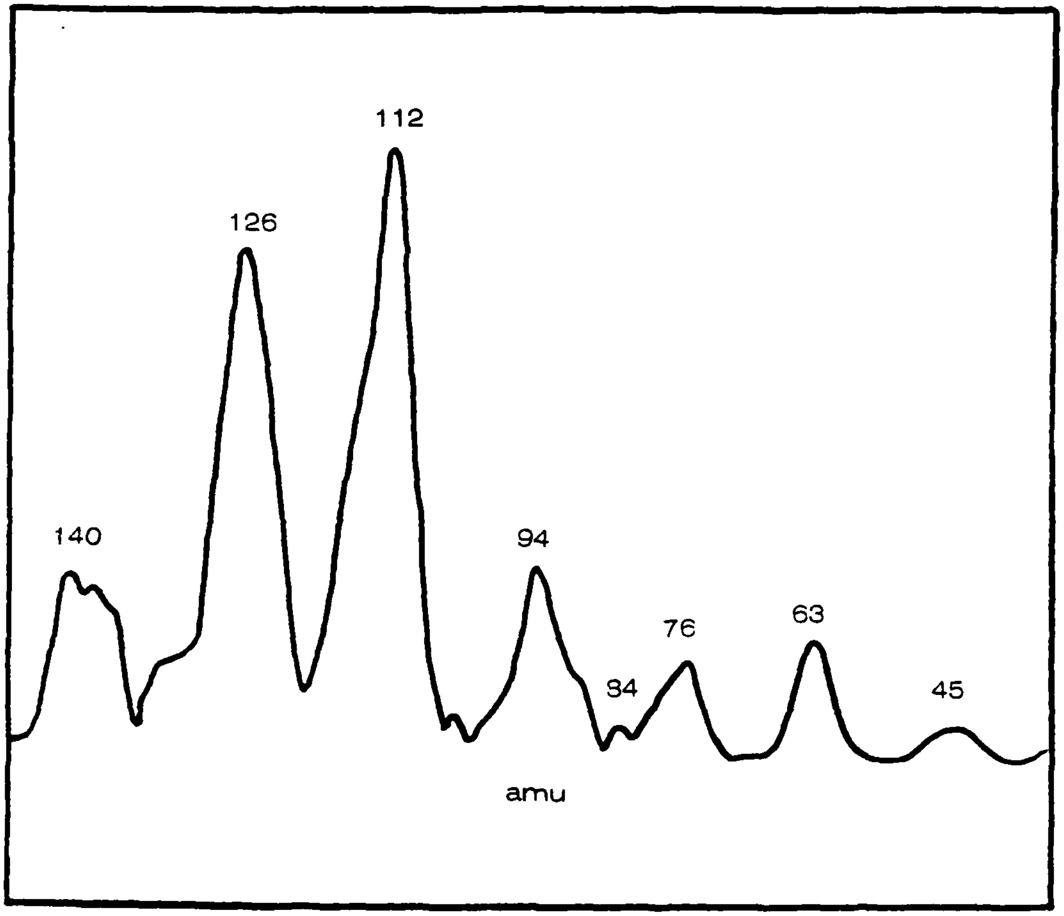


Fig. 9. 100 mass unit scan of BEMO at 260 C

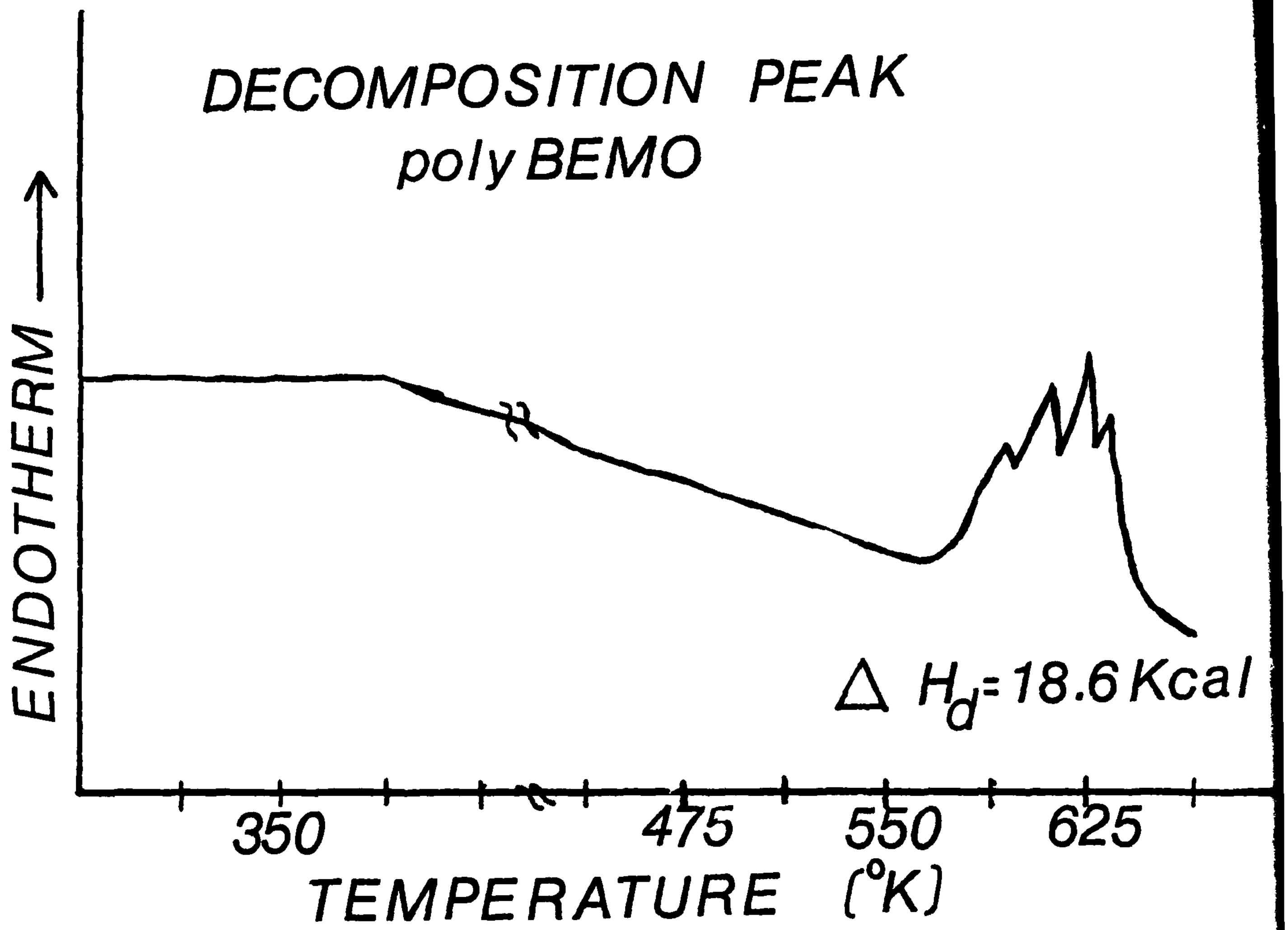
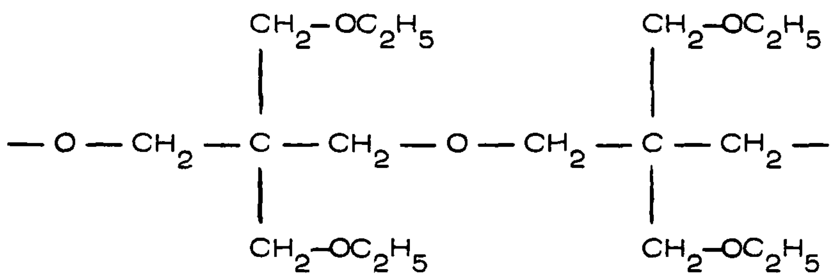


Fig. 10. D.S.C. thermogram of BEMO

From the mass spectra Jones has proposed a mechanism for the decomposition, suggesting that the major route of degradation is through the cleavage of the C–O bond both in the appendages and in the backbone of the chain. This is consistent with the fact that a quaternary carbon-carbon (C–C) bond is stronger than a carbon-oxygen (C–O) bond by about 5 kcal/mol.

Apparently the C–O bond in the side chain breaks first. A possible explanation for this occurrence can be seen from an examination of the dimer:

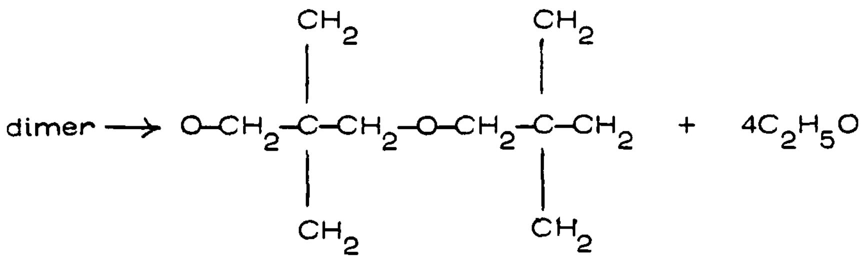


The carbon-oxygen bonds of the backbone are equal in strength due to the symmetric nature of the structure. In the side chain the quaternary carbon-carbon bond is stronger than the C–O bond of the ethoxy methyl group.

Thus it appears that the main mode of cleavage is the C–O bond which is slightly weaker than the quaternary C–C bond. The C–O bond in the appendage breaks before the C–O bond in the main chain since the C–O bonds in the backbone are equal in strength due to the symmetry, while C–O bonds in the appendage are weakened due to the quaternary C–C bond.

Although the kinetics and mechanisms of BEMO are quite complicated, the clearly defined mass peaks (Fig. 7) suggest a step-wise degradation mechanism as follows:

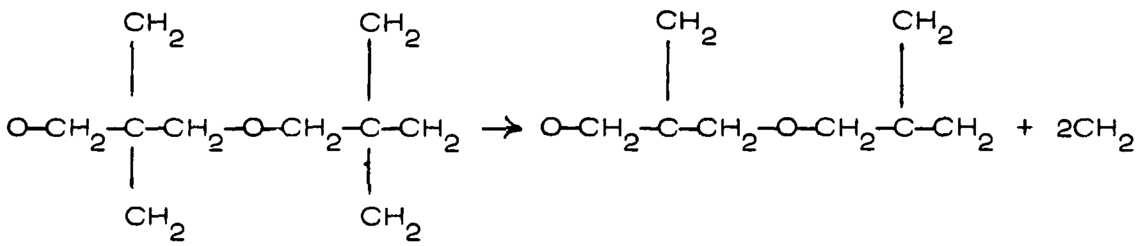
The dimer decomposes from its original 348 amu value to



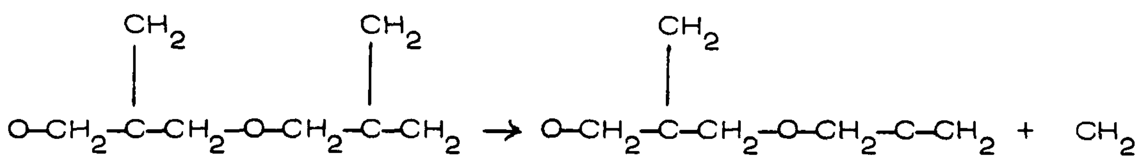
168 amu 45 amu

by losing the four ethoxy groups.

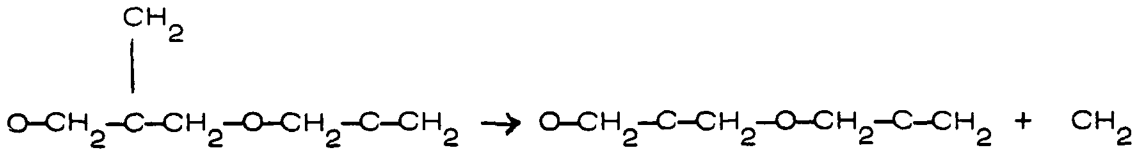
The remaining structure continues to lose methylene groups, CH_2, as



168 amu 140 amu 14 amu

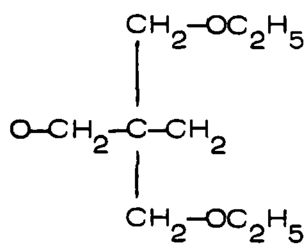


140 amu 126 amu 14 amu



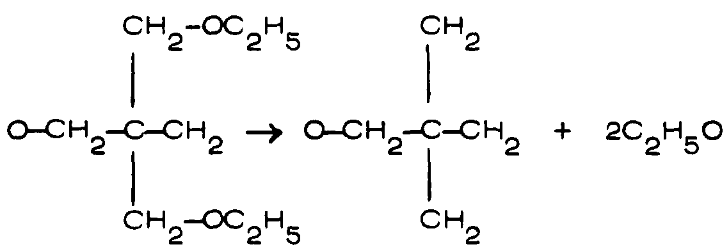
126 amu 112 amu 14 amu

Likewise, the mass spectra of Fig. 4 support the monomeric component



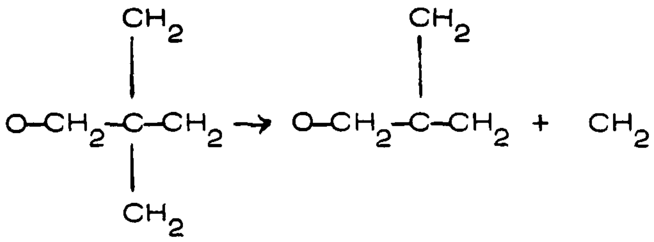
174 amu

decomposition by also losing the two ethoxy groups:

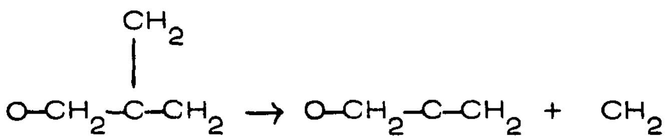


174 amu 84 amu 45 amu

This is followed by the release of CH_2 groups as



84 amu 70 amu 14 amu



70 amu 56 amu 14 amu

Reactions of the fragments within the effusion cell produce other products as shown in Fig. 8.

2. Thermal Decomposition of BFMO

Thermal decomposition experiments were commenced on bis (fluoro methyl) oxetane, BFMO. The polymer was found to have a melting point of 105 $\pm$ 2 C. The polymer was found to be quite stable to 200 C. At 225 C HF at amu 20 was observed as a decomposition product. Other decomposition products observed at this temperature included 42, 44, 45, 47, 54, 56 and 60 (Fig. 11).

At temperatures above 250 C depolymerization occurs. Intensity peaks ranging from 75 to 244 amu can be seen in Fig. 12. The

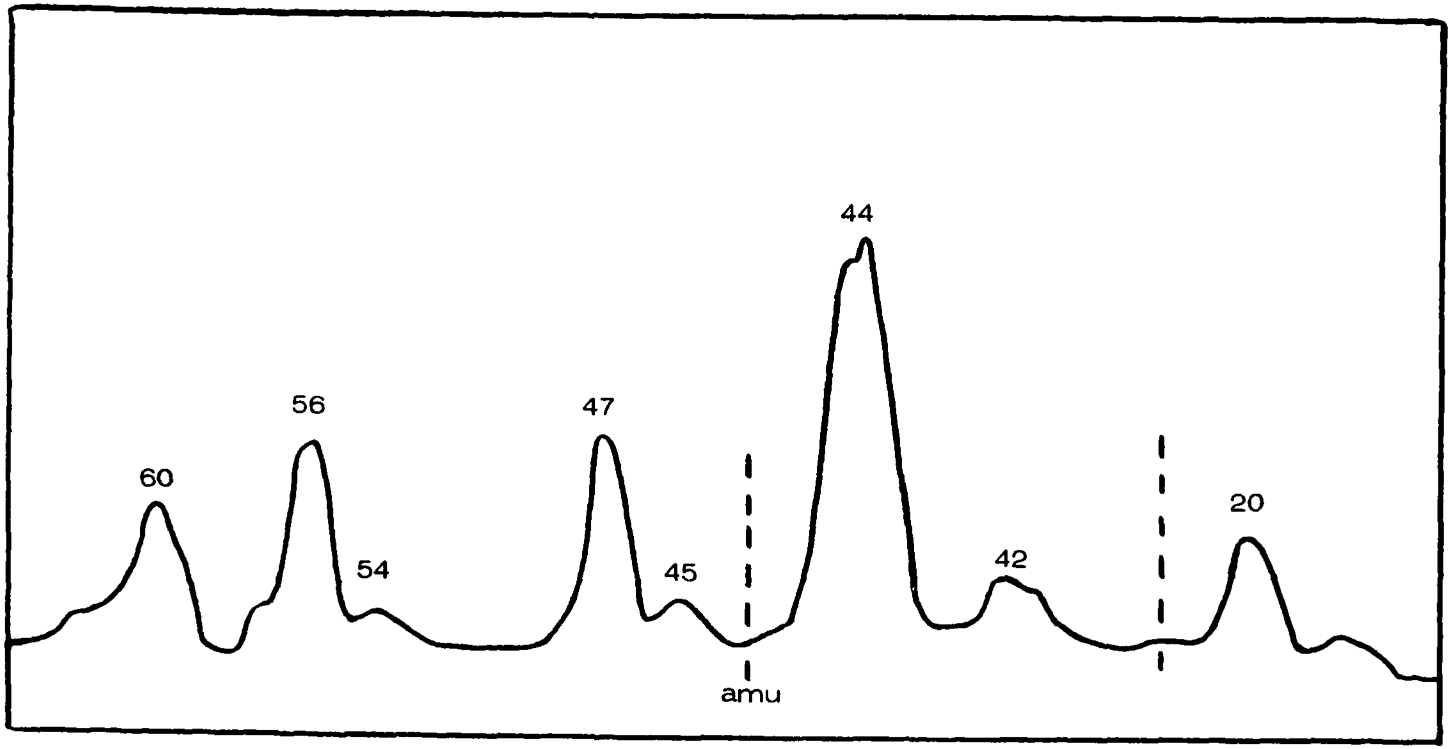


Fig. 11. Decomposition products of BFMO at 225 C in the amu range 20 - 60. Intensities are relative only within the dashed lines.

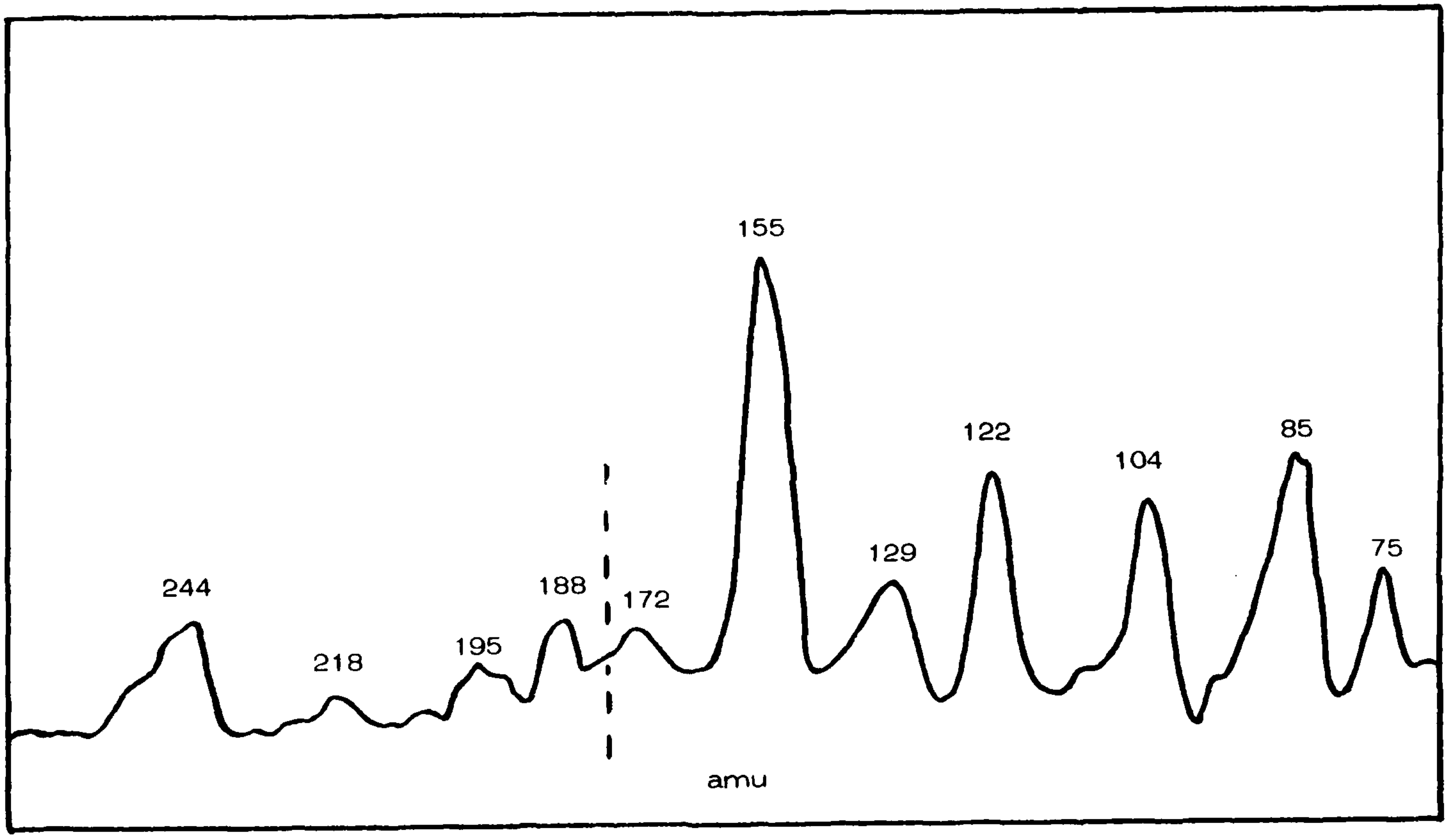


Fig. 12. Depolymerization of BFMO at 255 C. Intensities are relative only within the dashed lines.

molecular weight for the monomer is 122 and 244 for the dimer. Peaks for both of these are shown in Fig. 12, although their concentrations are not relative.

D. Thermal Decomposition of New Nitramines

1. 2,6,tetranitro-4,8,dinitro-4,8,diazo cyclooctane

The investigation of the cyclooctane ring compound obtained from the White Oak Naval Surface Weapons Center was continued. After initial release of two NO_2 groups at approximately 150 C a stable gaseous cyclooctane ring compound appears at amu 292, with a probable configuration of single NO_2 groups on the 2,6 C and 4,8 N ring atoms. This configuration appears in the gaseous phase at approximately 300 C (Fig. 13).

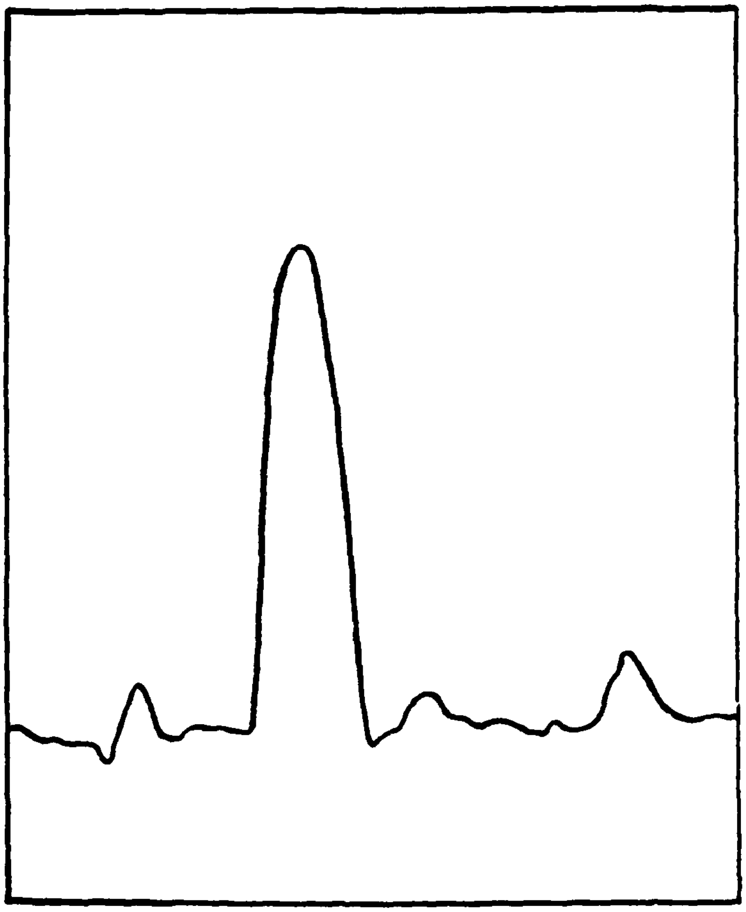


Fig. 13. High temperature stable gaseous species at 280 C resulting from the thermal decomposition of 2,6 tetranitro-4,8 dinitro-4,8 diazo cyclooctane

APPENDIX A

MASS SPECTROMETRIC KINETIC STUDIES ON SEVERAL AZIDO POLYMERS

In process of publication:
"Combustion and Flame"

MASS SPECTROMETRIC KINETIC STUDIES ON SEVERAL AZIDO POLYMERS

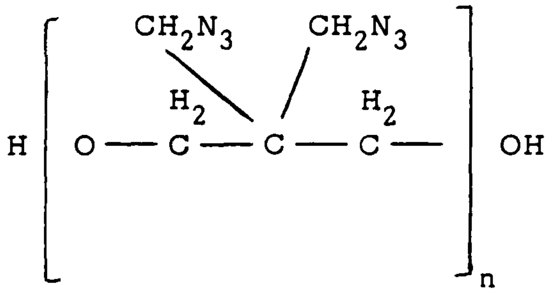
Milton Farber, S. P. Harris and R. D. Srivastava
Space Sciences, Inc., Monrovia, California

A mass spectrometric study of the thermal decomposition was made on four azido polymers which are possible new candidates for propellant formulations: bis azido methyl oxetane (BAMO), azido methyl methyl oxetane (AMMO), azido oxetane (AZOX), and glycidyl azide polymer (GAP). All the polymers begin to decompose at approximately 120 C, with the primary decomposition mechanism being the rupture of the azide bond to release molecular nitrogen. Activation energies obtained were 42.7 kcal/mole for BAMO, 43.6 kcal/mole for AMMO, 40.1 kcal/mole for AZOX, and 42.2 kcal/mole for GAP. The polymeric E_a values were close to those of a number of azido monomers having E_a values of 39 to 40 kcal/mole. Secondary decomposition at higher temperatures (above 200 C) involved rupture of the carbon backbone into smaller fragments. Irradiation at 366 nm (3.29 eV) ruptured the azide bonding with considerable cross-linking, transforming the polymer from a viscous liquid into a rubbery material.

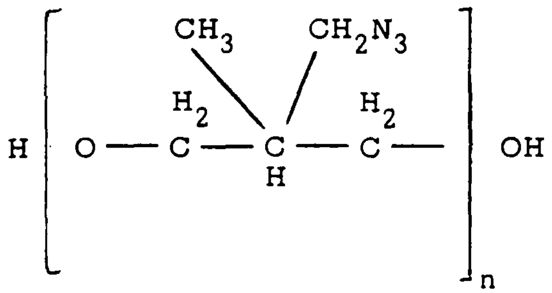
INTRODUCTION

In the search for new energetic binder materials a great deal of interest has centered recently on one group of azido compounds in particular. These current prime candidates for propellant formulations include four polymeric materials, three of which have a repeating three-carbon backbone and one of which has a repeating two-carbon backbone, with one or two azide groups attached directly or indirectly. Their molecular weights range from 2000 to 5000 molecular mass units. These polymeric compounds are:

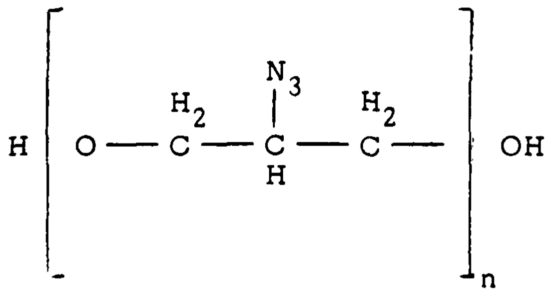
bis azido methyl oxetane (BAMO),



azido methyl methyl oxetane (AMMO),

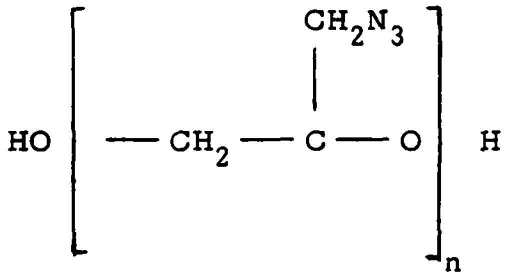


azido oxetane (AZOX),



and

glycidyl azide polymer (GAP)



The thermal decomposition study of these four polymers was undertaken with the aid of effusion-mass spectrometry to determine primary and secondary decomposition mechanisms, activation energies and products of decomposition. Their stability to UV radiation under ambient conditions was also investigated.

A search of the open literature revealed no prior publications involving the four polymers covered in this paper.

EXPERIMENTAL APPARATUS AND PROCEDURES

Details of the dual vacuum chamber-quadrupole mass spectrometer system used in these experiments have been presented previously (1), as well as a schematic depiction of the apparatus (2). The polymer samples, weighing 5 to 50 mg, were placed in a small pyrex capsule within an alumina effusion cell 25 mm long with an inside diameter of 6.8 mm; an elongated orifice 0.75 mm in diameter by 5.5 mm long was employed for beam collimation (see Fig. 1). The temperature was measured with the thermocouple in contact with the sample and was accurate to $\pm$ 2°C at the absolute temperature and within $\pm$ 0.5°C as a differential temperature. The cell was positioned within 5 cm of the ionization chamber of the mass spectrometer, allowing species leaving the solid or liquid surface to be measured within approximately 10 μsec after their exit from the cell. These times are calculated from species velocities effusing from the effusion cell and will vary with cell temperature and pressure. The alumina cell was heated by a resistance furnace and temperature measurements were made by means of thermocouples imbedded in the cell body. The method for determining ion intensities, mass spectrometer resolution, as well as the measurement of the isotopic abundance ratios, has been presented previously (3). All quadrupole experimental mass discrimination effects were taken into account and the necessary corrections to ion intensity relationships were made when quantitative partial pressures were desired. Only the chopped, or shutterable, portion of the intensities was recorded, since the mass spectrometer was equipped with a beam modulator and a phase sensitive amplifier. The experimental procedure has been described previously (1,3-7). ^{127}I and $^{254}I_2$ as well as the standard gases N_2, O_2, NO_2, NO, H_2, and NH_3 were employed for the amu calibration. Partial pressures were obtained from the calibrated data by means of the relationship

$$p_i = \frac{I_i (\sigma \gamma)_a}{I_a (\sigma \gamma)_i} p_a,$$

where a is the calibrated species, i is the unknown species, and σ and γ are, respectively, ionization cross sections and electron multiplier corrections.

It was necessary to ascertain with a high degree of confidence that the measured ion intensities were those from the parent species and not from the fragments of the larger molecules. In order to ensure the survival of ions from the parent species the mass spectrometer was operated at low ionization voltages (i.e., 1 to 2 volts above appearance potentials (1,3-9) when establishing a species identification. For example, the ionization potential of CO is 14 eV whereas the IP for N_2 is 15.6 eV. Thus the concentration of species at amu 28 at an electron impact energy of < 15.5 volts would be entirely due to CO.

Melting points were obtained only for BAMO since the other three polymers are viscous liquids at ambient temperatures. Decomposition rates to determine activation energies were obtained at constant electron impact ionization voltages of 20 eV and at a heating rate of one degree per minute.

The experiments involving UV radiation employed 254 nm and 366 nm wavelengths, corresponding to 4.88 eV and 3.39 eV, respectively. These energies correspond to 112 kcal/mole and 78 kcal/mole, respectively. The deposition energy 2.5 cm from the lamp is 7200 μwatts/cm^2 and 10,000 μwatts/cm^2 for the short and long wave lamps. The samples weighed 25 mg and were spread over a 1 sq cm area.

RESULTS AND DISCUSSION

Weight Loss and Effusion Mass Spectrometer Experiments

Thermal decomposition of bis azido methyl oxetane (BAMO)

Isothermal experiments were performed at 10^{-7} torr from 80 to 250 C on BAMO polymer with a molecular weight of approximately 3000.

Weight loss experiments on 25 mg samples of BAMO were performed for periods of 3 hours each at temperatures of 82, 100, 118, 130, 135, and 202 C. These data are presented in Table 1. No apparent decomposition occurred at 80, 100, or 120 C, although at 120 C the sample turned from white to a slightly off-white, or cream, color. Effusion cell pressures were determined by the Knudsen equation,

$$P_{mm} = 17.4 \frac{G}{KA}\sqrt{\frac{T}{M}}$$

where G = weight loss in g sec^{-1}
K = Clausian factor
A = orifice area in sq cm
T = temperature in degrees K
M = molecular weight

Slight decomposition began at 130 C, with a rate of decomposition at 200 C almost 20 times that at 130 C. A 25 mg sample maintained at 200 C for 3 hours lost 80% of its initial mass, leaving behind a carbonaceous tar residue. The melting point of the BAMO polymer was found to be 75 C.

Employing the sample container shown in Fig. 1, effusion-mass spectrometer experiments were performed on 25 mg BAMO samples. These spectra were obtained at an ionization voltage of 20 eV. The release of molecular nitrogen is observed as low as 130 C; a much higher rate of N_2 evolution occurs at temperatures above 160 C, as can be seen in Fig. 2, which depicts the N_2 concentration as a function of temperature. At any given temperature the decomposition rate is essentially constant, whether in a heating or cooling cycle.

An activation energy study of the primary decomposition path, the release of N_2 from the azide groups, was also completed. The heating rate for the temperature dependence investigation was 1^{o} per minute. A plot of the N_2 intensity versus the reciprocal of the absolute temperature yielded an E_a for the BAMO polymer of 178.7 kJ mol^{-1} (42.7 kcal/mole) (see Table 2). This study shows that the primary mechanism for BAMO decomposition is the release of N_2 from the rupture of the azido bond. The three-carbon backbone of the polymer appears to remain intact initially since other gaseous species are not observed until the sample is heated to higher temperatures, approximately 160 C.

In addition to molecular N_2, the mass spectrometer showed a peak at 27 amu corresponding to HCN as well as peaks of amu 2, 14, 15, 16, 17, and 18 attributable to H_2, CH_2, CH_3, O (fragment of O_2), OH and H_2O, respectively. A representative spectrum of this secondary decomposition at 200 C is shown in Fig. 3. The intensities in Fig. 3 are only relative within the dashed lines. The products in the 40 to 48 amu range are presumably due to effusion cell reactions. The formation of NO_2, for example, may require cell reactions of the following type:

$$CH_2 = N\cdot + OH \longrightarrow CH_3\cdot + NO$$

and

$$NO + O \longrightarrow NO_2.$$

High temperature (200 C) decomposition products of BAMO include mass peaks at 40, 42, 43 and 44 amu. Within the effusion cell, where numerous collisions between gaseous species and the cell walls and also with the condensed polymeric materials can occur, the probability is high that some of the products observed mass spectroscopically are produced within the effusion cell itself and are not original decomposition products from the condensed phase. The three-membered carbon backbone of BAMO is definitely disintegrating at 200 C, as can be seen in Fig. 3, with the production of HCN at amu 27 and CH_2O and CH_2OH at amu values of 30 and 31. The relative concentrations of these species, however, are low compared with the combined N_2 + CO evolution.

Thermal decomposition of azido methyl methyl oxetane (AMMO)

The thermal decomposition of a relatively new azide polymer, azido methyl methyl oxetane (AMMO) was also investigated. This polymer is similar to BAMO except that it has one azido methyl group on the center carbon of the three-carbon backbone, whereas BAMO has two.

AMMO was found to have a somewhat higher stability than the other azide polymers. A study of N_2 evolution, which is the onset of thermal decomposition, shows that it continues until the destruction of the azide group is completed when no further release of molecular N_2 is observed. An activation energy of 182.4 kJ mol^{-1} (43.6 kcal/mole) was calculated from these data (Table 2).

The thermal decomposition of AMMO was measured from 120 to 300 C. Its stability can be seen in Fig. 4, which shows very little backbone decomposition at 210 C. At 290 C a 30 amu peak corresponding to CH_2O indicates backbone decomposition (Fig. 5). The relative OH and H_2O concentrations increase significantly at 290 C. Also some methyl radicals at amu 15 were observed.

A qualitative indication of the relative thermal stability of BAMO and AMMO at 235 C can be seen in Fig. 6.a. Considerably more H_2O is apparent from BAMO decomposition (Part B, Fig. 6.a.), indicating the release of greater quantities of OH, which recombine within the effusion cell to form water. Also, the relative amount of CH_3 radicals is larger from BAMO decomposition than from that of AMMO. As the temperature increased from 215 to 235 C (Fig. 6.b.) the thermal decomposition rate of BAMO increased rapidly, creating a fairly high cell pressure causing OH recombination to form H_2O. This did not occur with AMMO; even at temperatures as high as 290 C the OH/H_2O ratio of AMMO appeared fairly constant.

Thermal decomposition of azido oxetane (AZOX)

An azido polymer, AZOX, in which the azide group is directly attached to the backbone central carbon was studied. As in the previous azido polymers, molecular N_2 was the first thermal decomposition product occurring at approximately 120 C. By plotting the log of the N_2 intensity against the reciprocal of the absolute temperature an activation energy of 167.8 kJ mol^{-1} (40.1 kcal/mole) was obtained (Table 2). As the temperature is raised above 200 C the three-membered carbon backbone of AZOX begins to disintegrate more rapidly with the ion spectra showing the species CH_2, CH_3, OH, and H_2O in the low mass range. The higher amu range shows peaks attributed to CO, CH_2OH, C_2OH, and CO_2 at 230 C (Fig. 7). A small ion intensity may be attributed to HN_3 at amu 43; however, it is more likely due to C_2H_3O.

Thermal decomposition of glycidyl azide polymer (GAP)

The three polymers, BAMO, AMMO and AZOX had their azide groups attached directly or indirectly to the central carbon of the three-membered polymeric oxetane backbone. A fourth azido polymer investigated was the glycidyl azide polymer, with a repeating two-carbon backbone.

As in the case of the other azido polymers, the GAP appears to be fairly stable to 120 C, when molecular N_2 is released. The results of the decomposition study of this polymer as a function of temperature were employed to obtain an activation energy for the primary decomposition mechanism, the release of N_2. For a 20-degree rise in temperature the rate of N_2 evolution increased by approximately a factor of 10. In the amu range 24 to 32 the major ion intensity constituent is molecular N_2. This appears to be the same pattern as found in the thermal decomposition of BAMO. A plot of the log N_2 against 1/T, as shown in Fig. 8, yielded an activation energy of 176.6 kJ mol^{-1} (42.2 kcal/mole). However, at temperatures above 170 C a slight intensity of amu 27, HCN, was observed, approximately 1% to 2% of the N_2 intensity. It is likely that secondary decomposition begins at a slightly lower temperature for GAP than for BAMO. An example of the decomposition products in the 14 - 48 amu range at 200 C can be seen in Fig. 9. We understand that work has been performed to obtain thermal decomposition kinetics of GAP (10) and that the measured activation agrees with the value reported here.

Azido Monomers

Although not directly involved in energetic binder formulations, it was felt that the thermal decomposition of a representative azido monomer should be obtained. The AZOX monomer was chosen for this study, with its vapor released directly into the heated effusion cell.

Figure 10 shows the mass spectra of the thermal decomposition from 160 to 195 C. In this 35-degree range the N_2 intensity increased by a factor of 20. These graphs are composites of the individual peak heights and are continuous within the dashed lines as a function of temperature. In this temperature range for the AZOX monomer an activation energy of 40 kcal/mole was obtained. This apparently is typical of azide monomers, as shown in a recent publication by Isayev, et al (11). Several monomers were investigated, with reported E_a values of approximately 39 kcal/mole (Table 2) for aliphatic azides including β-triazoethanol, 1,3,diazide propanol, 1,3,diazide propylene ester of acetic acid, and 1,3,diazide propylene acid.

Effects of UV Radiation

The azido polymers were subjected to UV radiation as described in the Experimental Section. After several preliminary experiments at 254 nm tests were discontinued due to considerable adsorption by air (12). Short wave UV irradiation studies would thus best be accomplished in a vacuum enclosure. A typical result, qualitative only, is shown in Fig. 11 for AMMO. Employing 360 nm light the samples were irradiated at distances of 2.5 cm (10,000 μwatts/cm^2), 7.5 cm (1,120 μwatts/cm^2), and 15 cm (380 μwatts/cm^2) for periods up to five hours. The radiation intensity, for example, at a distance of 2.5 cm from the sample surface provided 36 J/cm^2 for each hour of exposure. At this wave length the radiation energy is 3.39 eV (78 kcal/mole) which is sufficient to rupture the azide bond and release molecular N_2. Considerable bubbling appears in the sample, indicating gaseous release. Cross linking apparently takes place, producing rubbery solids from the initial viscous liquids. The irradiated samples (homopolymers and copolymers) were maintained for a number of weeks under ordinary atmospheric conditions as well as under vacuum. No further reactions were observed.

CONCLUSIONS

All the azido polymers, including their monomers, homopolymers, and copolymers, were found to have activation energies from 165 to 182 kJ mol^{-1} (40 to 43 kcal/mole). These results, based on the number of azide materials investigated, should be conclusive evidence that the polymers, copolymers, or monomers decompose primarily by the fracturing of the azide bond. Polymerization apparently has little or no effect on the thermal decomposition of the azide compounds.

The primary mechanism for thermal decomposition of the azido polymer is the fracturing of the azide, $-\mathrm{N}{\not-}\mathrm{N}_2$, with the release of molecular N_2. The kinetics are comparable for all the materials. Once the azide structure is destroyed, in all probability there occurs electron shifting of the unpaired electron from the azide group. Internal electron resonance occurs, which reduces the stability of the remaining organic structure.

Upon continued heating enough thermal energy is adsorbed so that the molecular structure of the polymer undergoes further rupturing of the aliphatic organic bonds with the release of various low molecular weight molecules and radicals. As found in this investigation, the backbone of the AZOX polymer ruptures at lower temperatures than do the BAMO and AMMO polymers. Since the AZOX backbone is immediately affected when the azide group ruptures, its stability is impaired. Thus less thermal energy is required for its decomposition than for the polymers in which the azide group is attached to the methyl group arms. The slightly higher stability of AMMO to BAMO is due to the fact that only one azide group is attached to the arms whereas BAMO has two.

ACKNOWLEDGMENT

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REFERENCES

1. Farber, M., Frisch, M. A. and Ko, H. C., Trans. Faraday Soc. 65, 3202 (1969).
2. Farber, M. and Srivastava, R. D., Combust. Flame 42, 165 (1981).
3. Farber, M. and Srivastava, R. D., Combust. Flame 20, 33 (1973).
4. Farber, M., Srivastava, R. D. and Uy, O. M., J. Chem. Soc. Faraday Trans. I 68, 249 (1972).
5. Farber, M. and Srivastava, R. D., J. Chem. Soc. Faraday Trans. I 70, 1581 (1974).
6. Farber, M. and Srivastava, R. D., J. Chem. Soc. Faraday Trans. I 73, 1692 (1977).
7. Farber, M. and Srivastava, R. D., Chem. Phys. Letts. 51, 307 (1977).
8. Farber, M., Srivastava, R. D. and Moyer, J. M., J. Chem. Therm. 14, 1103 (1982).
9. Farber, M. and Srivastava, R. D., J. Chem. Phys. 74, 2160 (1981).
10. Goshgarian, B., AFRPL, Edwards, California, private communication.
11. Isayev, B. M., Kanashin, S. P., Kozhukh, M. S. and Tokarev, N. P. "Investigation of the Combustion of Certain Organic Azides," Khimicheskaya fizika protessov goreniya i vzryva. Kinetika khimicheskikh reaktsiy. Cernogovka, 1980, 97-101. (Series Note: Vsesoyuznyy simpozium po goreniyu i vzryvu, 6-th Alma-Ata, 23-26 Sept. 1980. Materialy.)
12. Herzberg, G., "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," D. van Nostrand, New York 1950.
13. Manser, G. E., "Synthesis of Energetic Polymers," Final Report, Contract N00014-79-C-0525, SRI International, Sept. 1982; Manser, G. E., U. S. Patent No. 4,393,199, July 1983.
14. Frankel, M. B., "Energetic Azide Compounds," Annual Report, Contract N00014-79-C-0043, Rockwell International Rocketdyne Division, March 1980.

Table 1

Thermal Decomposition of BAMO

Temp. (^{o}C)	Experiment Duration (hours)	Initial Sample Weight (gms)	Final Sample Weight (gms)	Rate of Decomposition (g/sec)	Appearance
82	3	0.0226	0.0226	0	No color change; sample melted
100	3	0.0226	0.0226	0	No color change; sample melted
118	3	0.0226	0.0226	0	Slightly off-white
130	3	0.0248	0.0235	1.2×10^{-7}	Cream colored
135	3	0.0347	0.0309	3.5×10^{-7}	Cream colored
202	3	0.0252	0.0045	19.1×10^{-7}	Brownish-black char

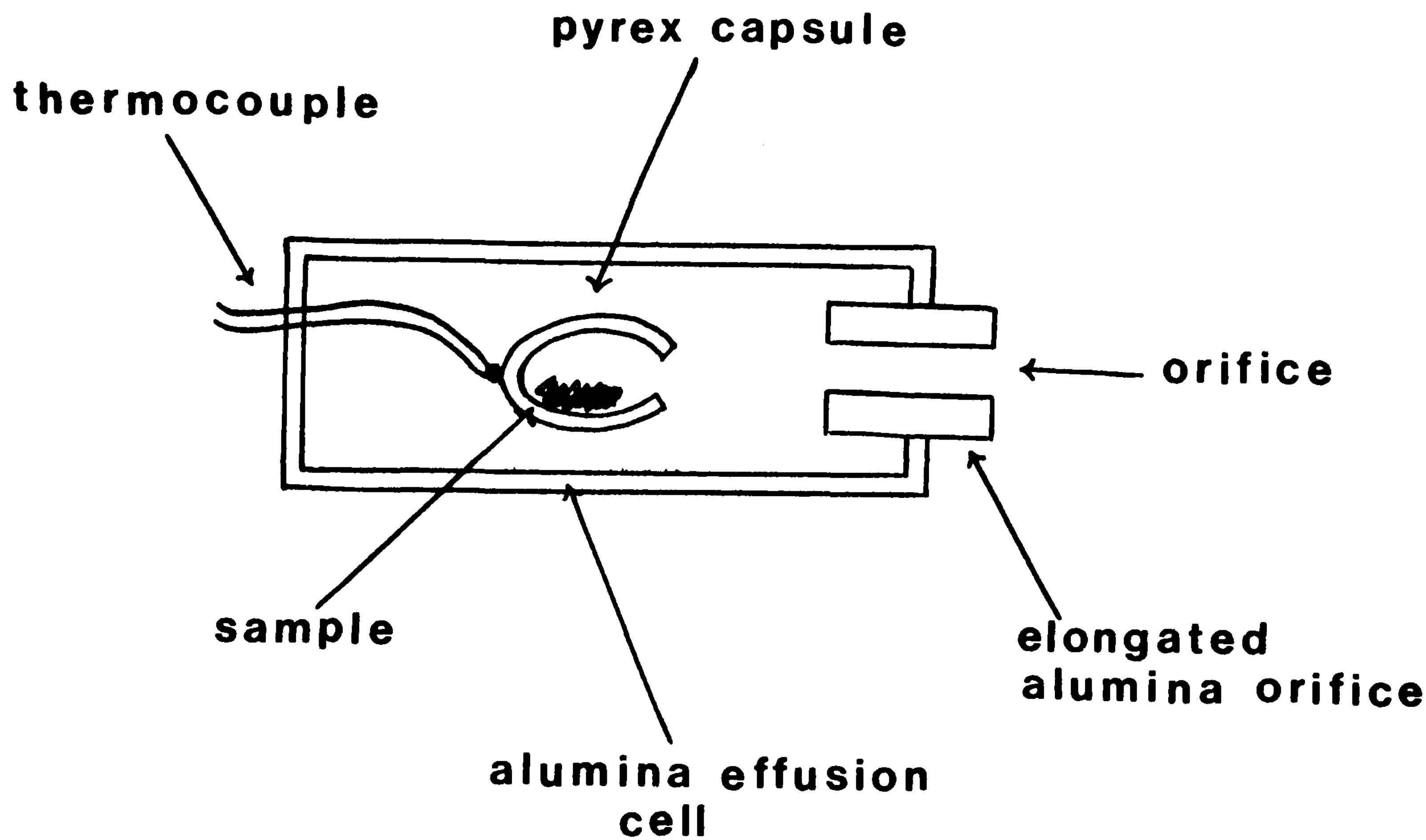

Fig. 1. Sample capsule within effusion cell with elongated orifice

Table 2

Activation Energies for Azido Polymers and Monomers

		E_a kcal mol^{-1}	E_a kJ mol^{-1}	
	Azido Polymers			
BAMO	bis azido methyl oxetane	42.7	178.7	
AMMO	azido methyl methyl oxetane	43.6	182.4	
AZOX	azido oxetane	40.1	167.8	
GAP	glycidyl azide polymer	42.2	176.6	
	Azido Monomers			
AZOX		40.0	167.4	
β-triazoethanol		37.8	158.2	(Ref. 11)
1,3,diazide propanol		38.2	159.8	(Ref. 11)
1,3,diazide propylene ester of acetic acid		38.8	162.3	(Ref. 11)
1,3,diazide propylene acid		38.8	162.3	(Ref. 11)

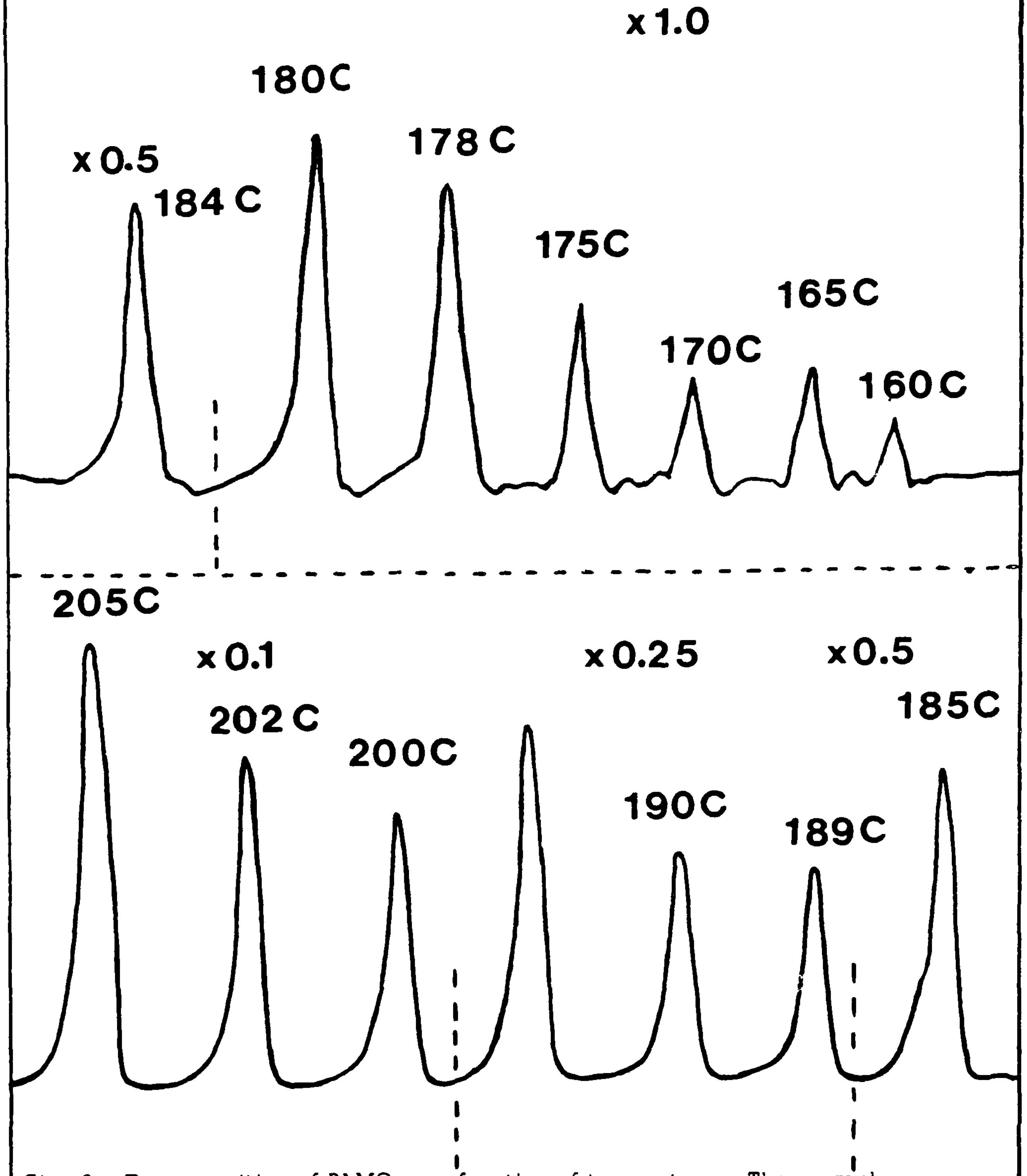

Fig. 2. Decomposition of BAMO as a function of temperature. These graphs are a composite of the individual peak intensities and are continuous as a function of temperature within the dashed lines. The multiplication factor is the amount of intensity reduction within each dotted section. Ionization energy = 20 eV.

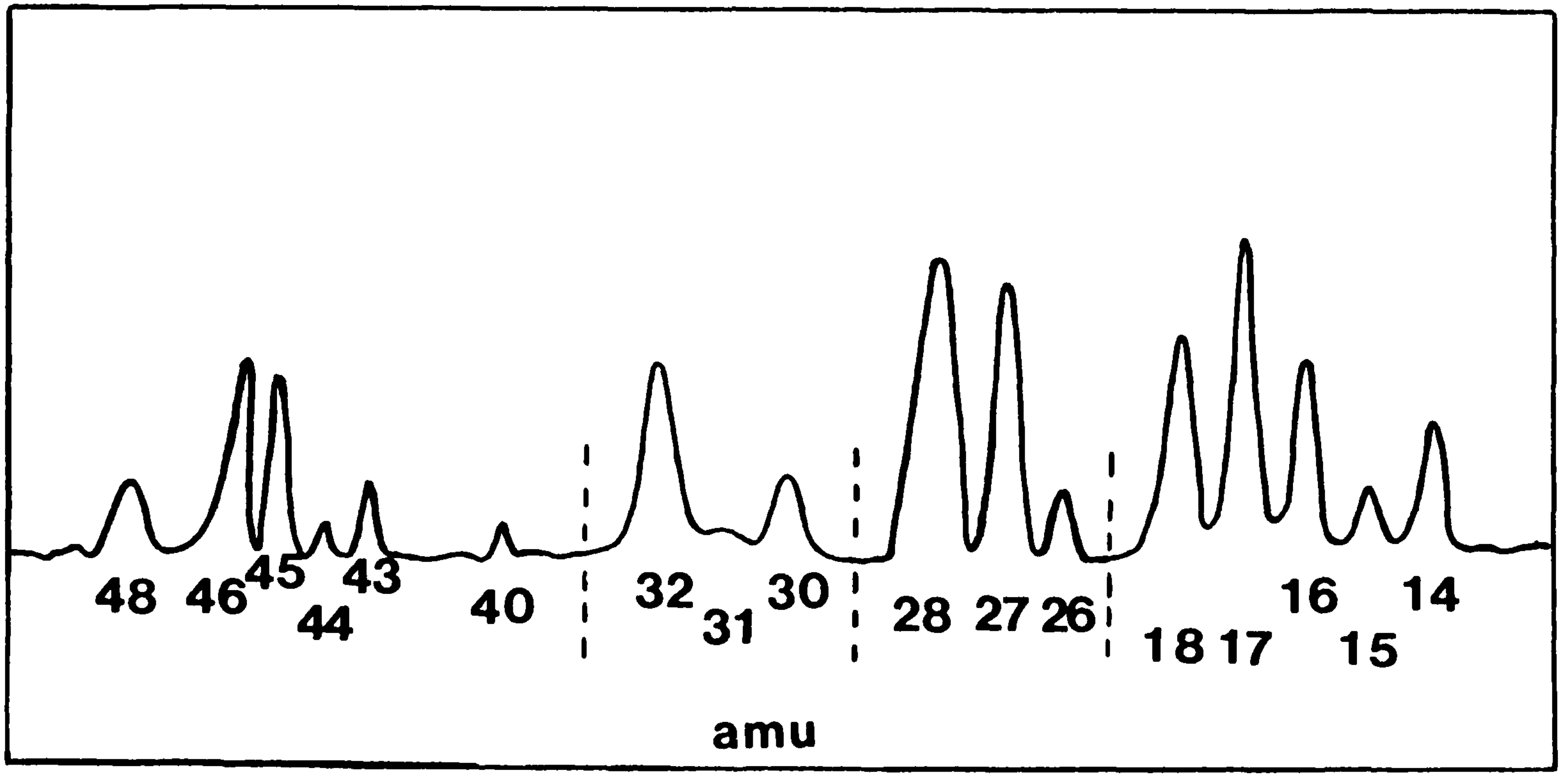

Fig. 3. Products from the thermal decomposition of BAMO at 200 C. Peak heights are only relative within the designated sections.

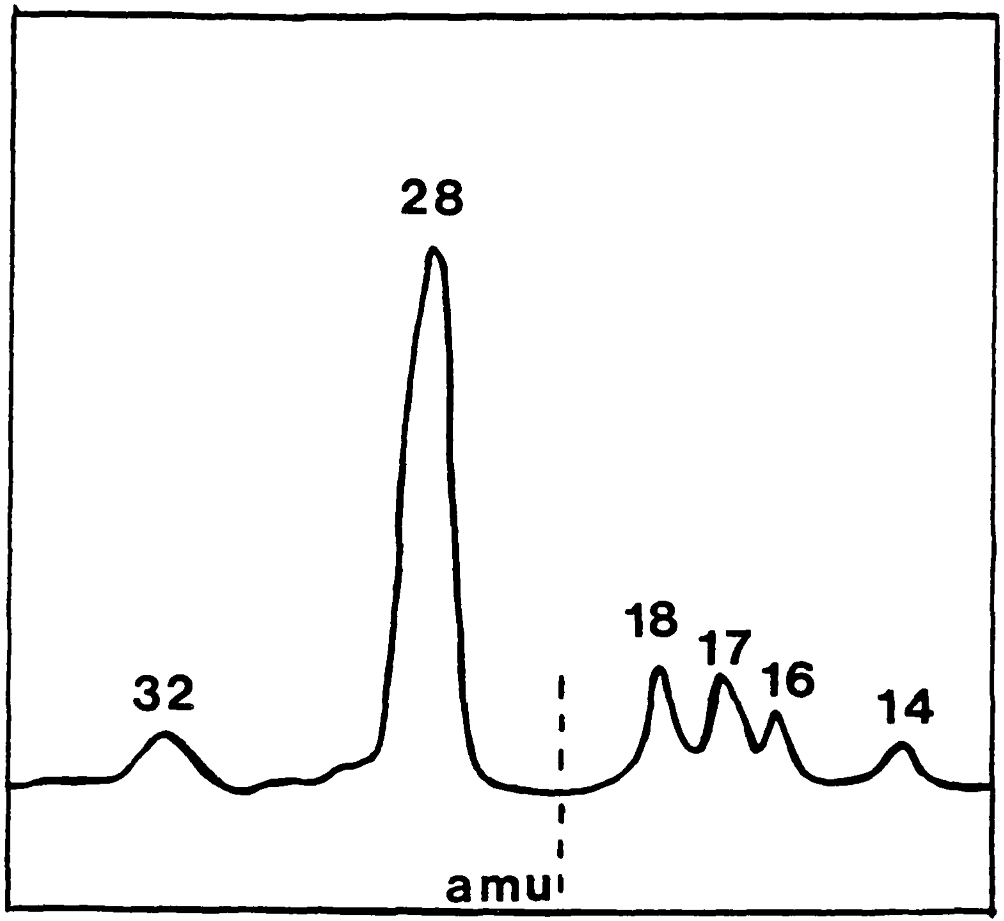

Fig. 4. Thermal decomposition of AMMO at 210 C. The azide group is decomposing, with the release of N_2. Some end group decomposition is also taking place; OH and H_2O peaks are observed at amu 17 and 18.

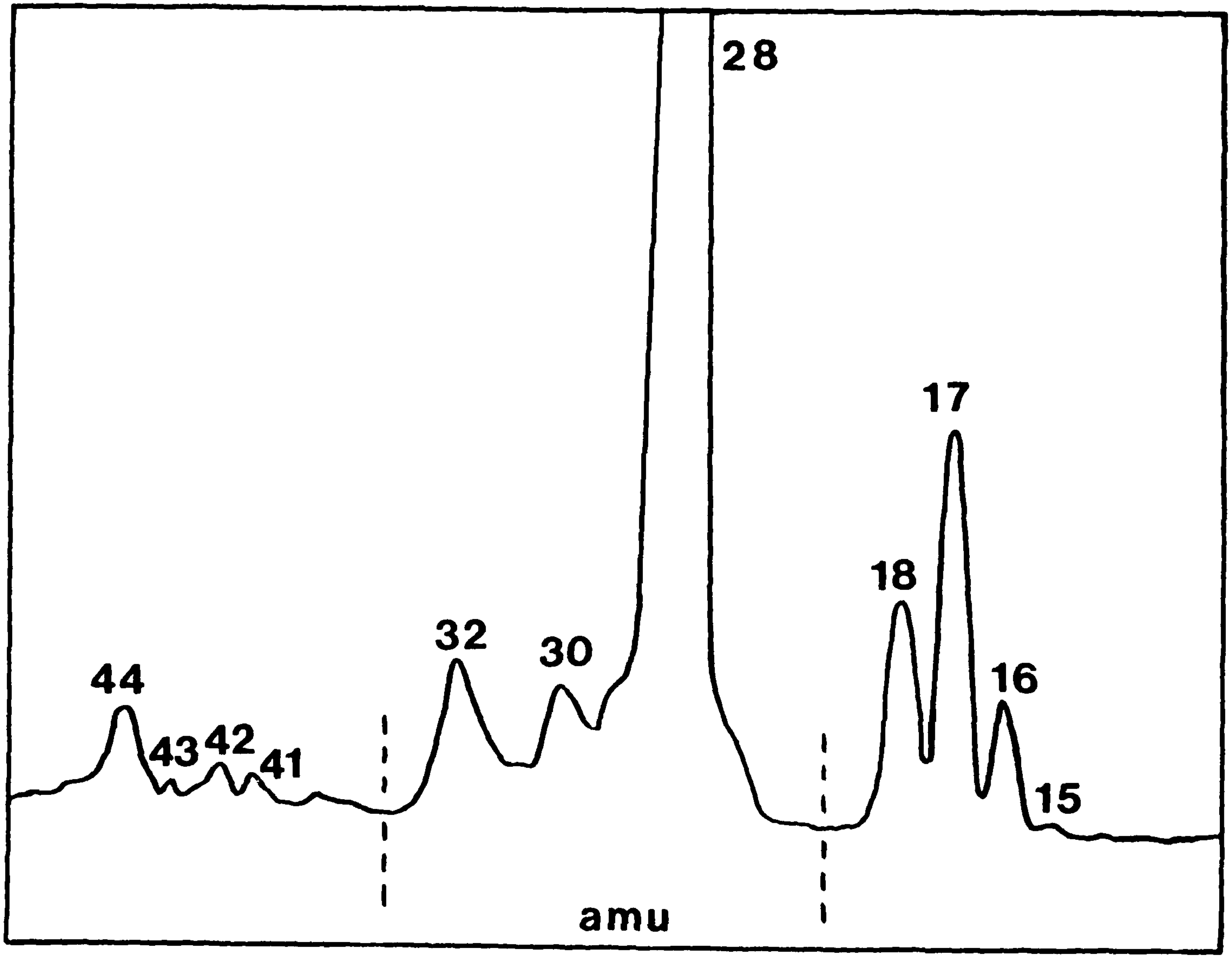

Fig. 5. AMMO products at 290 C in three amu ranges showing disintegration of the backbone

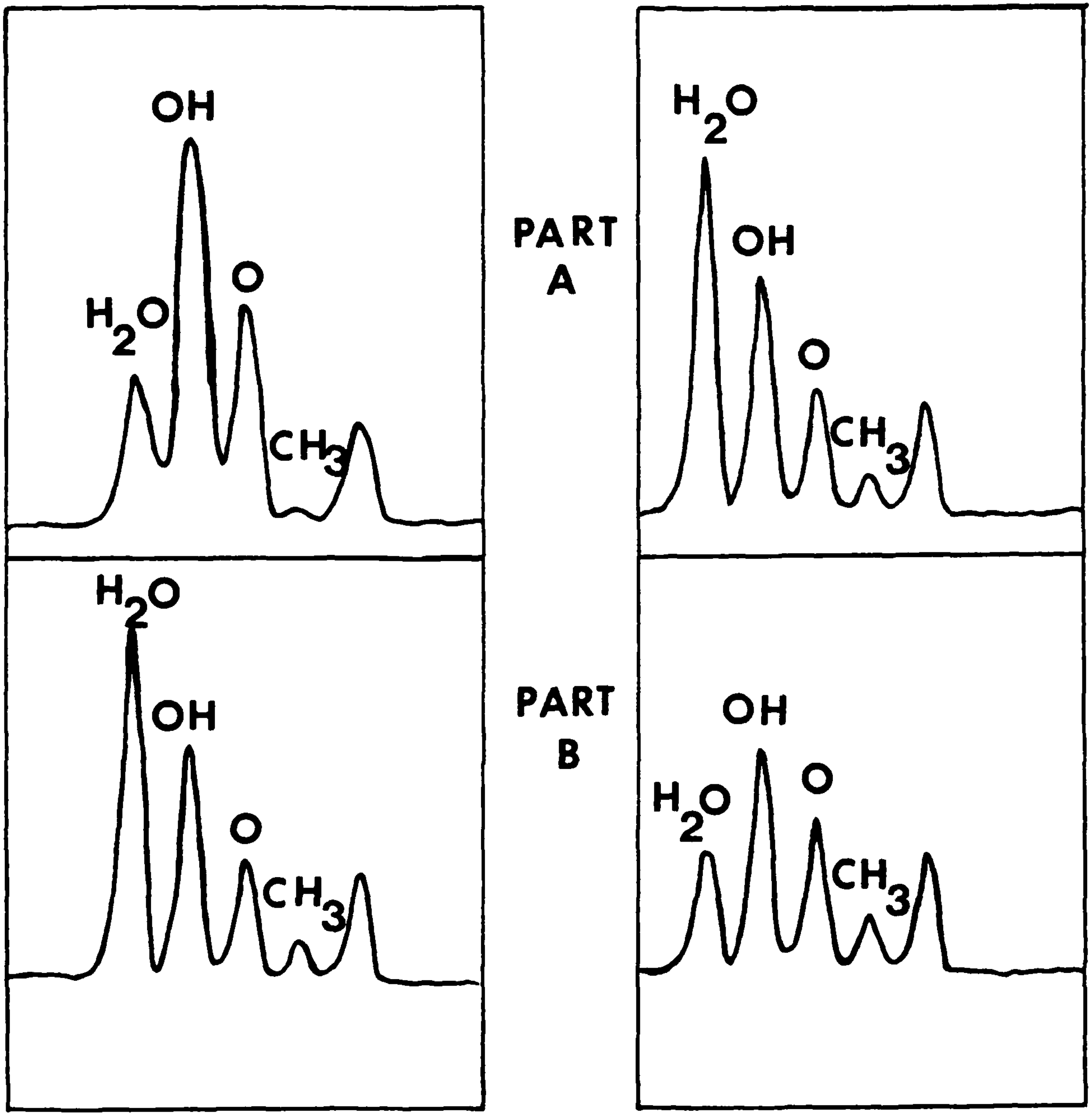

Fig. 6.a. Thermal decomposition comparison of AMMO (Part A) and BAMO (Part B) showing relative peaks of OH, H_2O and CH_3

Fig. 6.b. Thermal decomposition comparison of BAMO at 235 C (Part A) and 215 C (Part B) showing the reversal of the relative concentration of OH and H_2O at 215 and 235 C

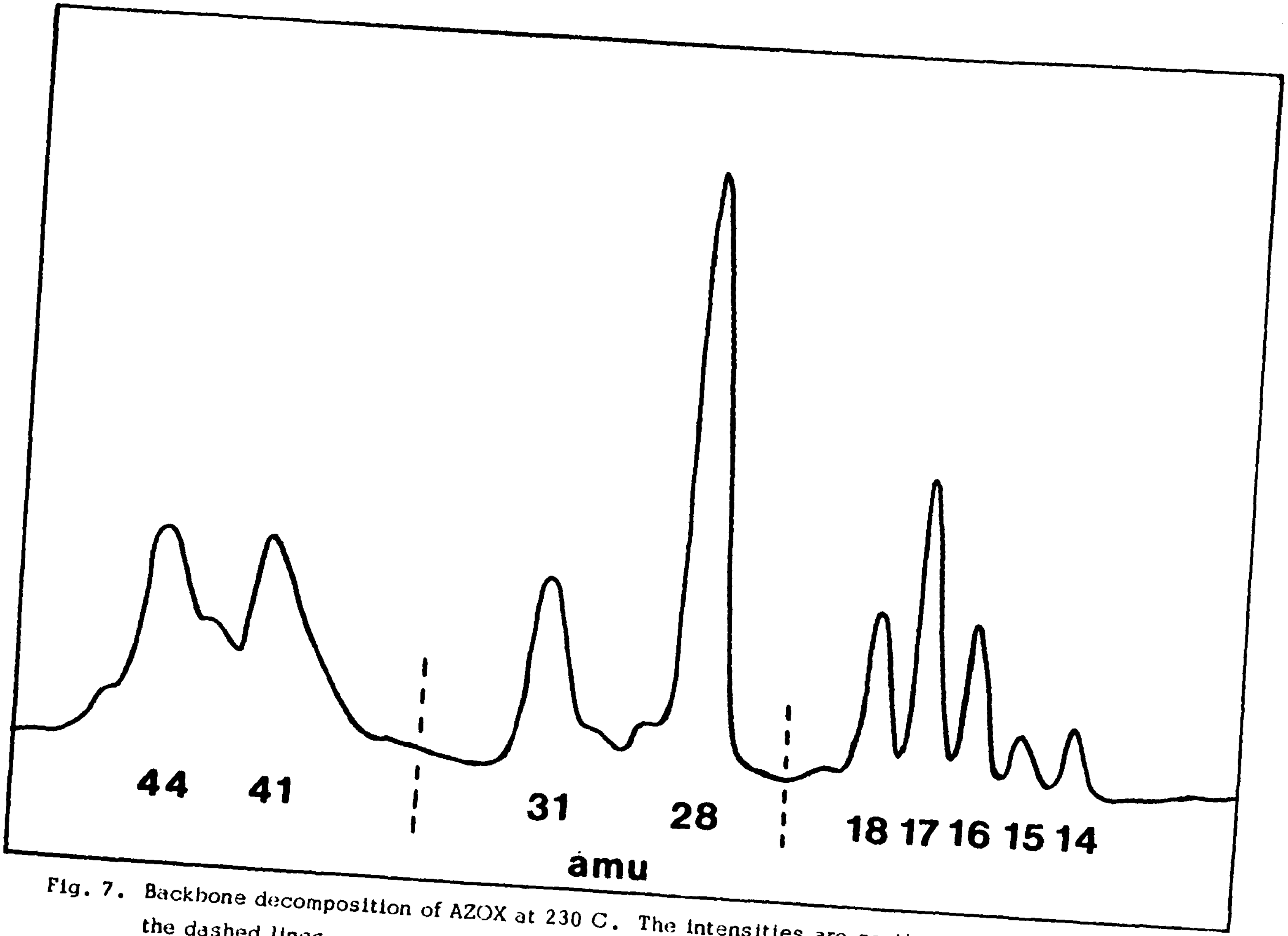

Fig. 7. Backbone decomposition of AZOX at 230 C. The intensities are continuous only within the dashed lines.

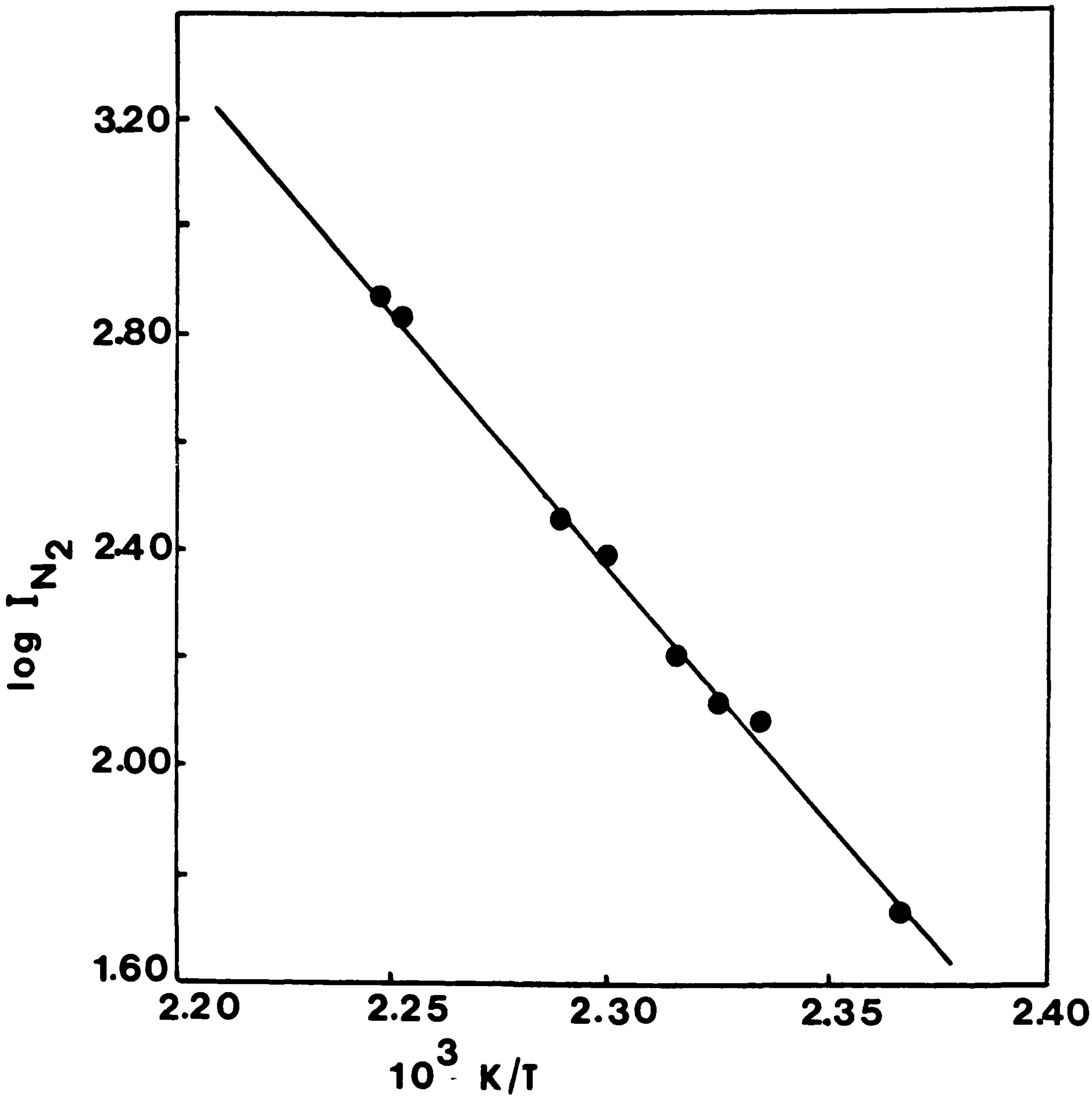

Fig. 8. Log of the relative intensity of N_2 from the thermal decomposition of GAP plotted as a function of the reciprocal of the absolute temperature. Activation energy = 176.6 kJ mol^{-1} (42.2 kcal/mole)

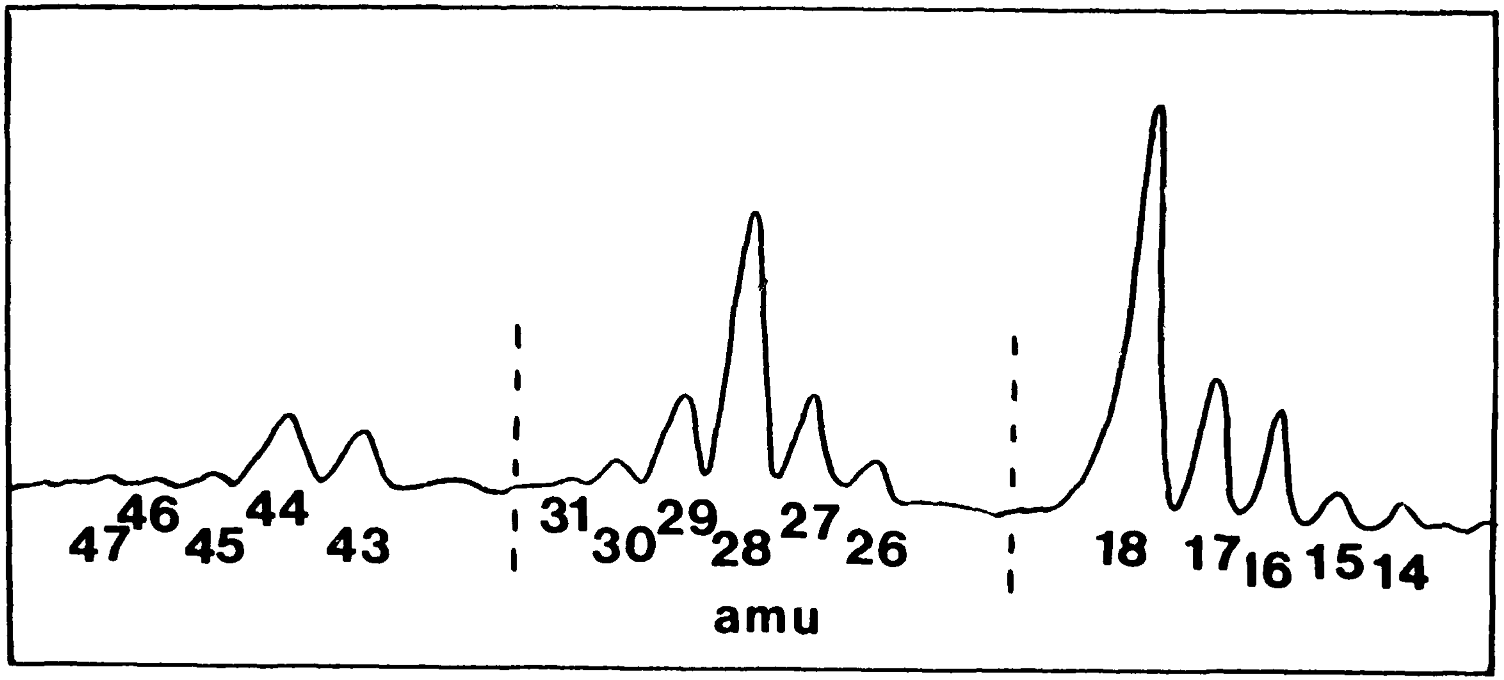

Fig. 9. Secondary decomposition products of GAP observed at 200 C. The intensities are continuous only within the dashed lines.

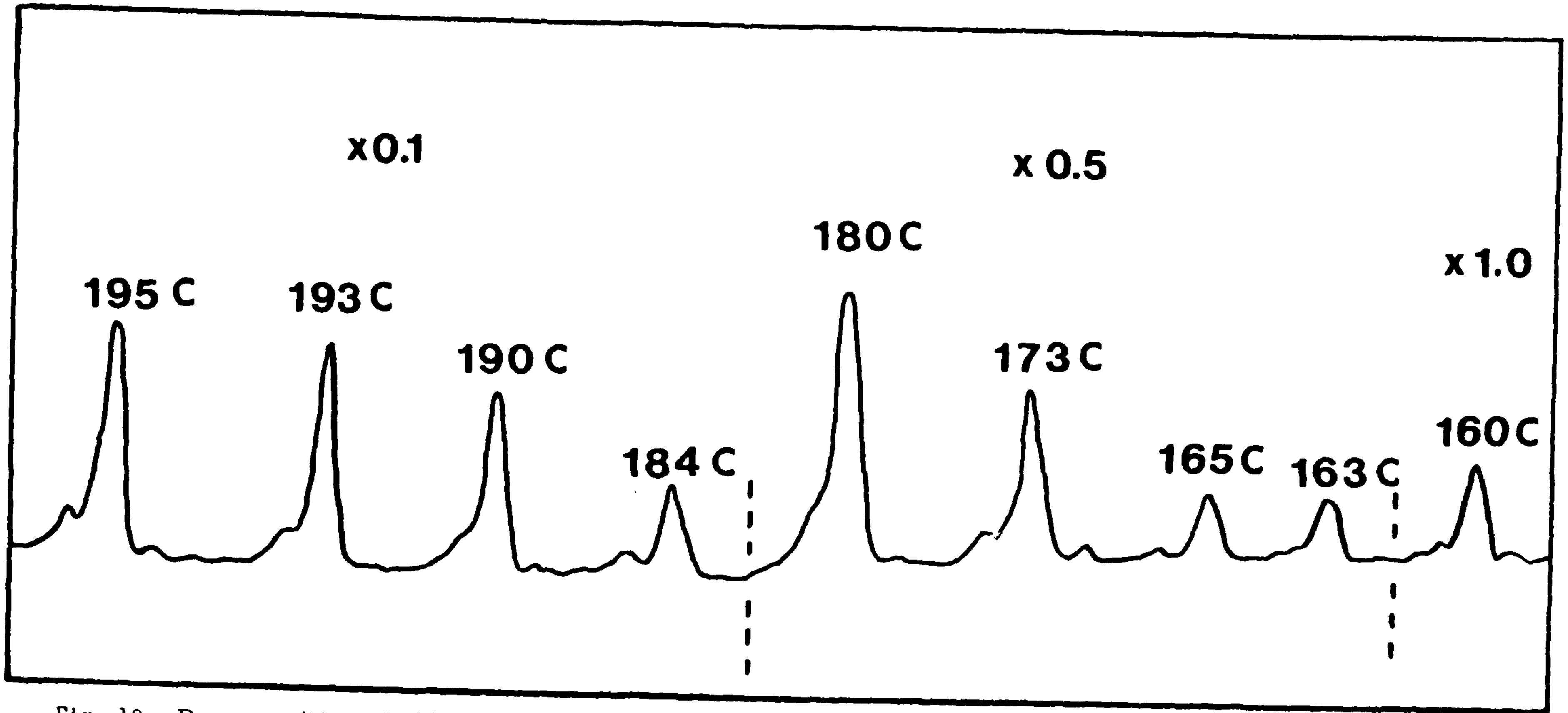

Fig. 10. Decomposition of AZOX monomer as a function of temperature with relative intensities of N_2. This is a composite of the individual peak heights and are continuous within the dashed lines as a function of temperature. Amu range = 24 to 32. The central peaks are molecular nitrogen, with smaller peaks on each side of HCN at 27 amu and HCO at 29 amu. The multiplication factor is the amount of intensity reduction within each dotted section.

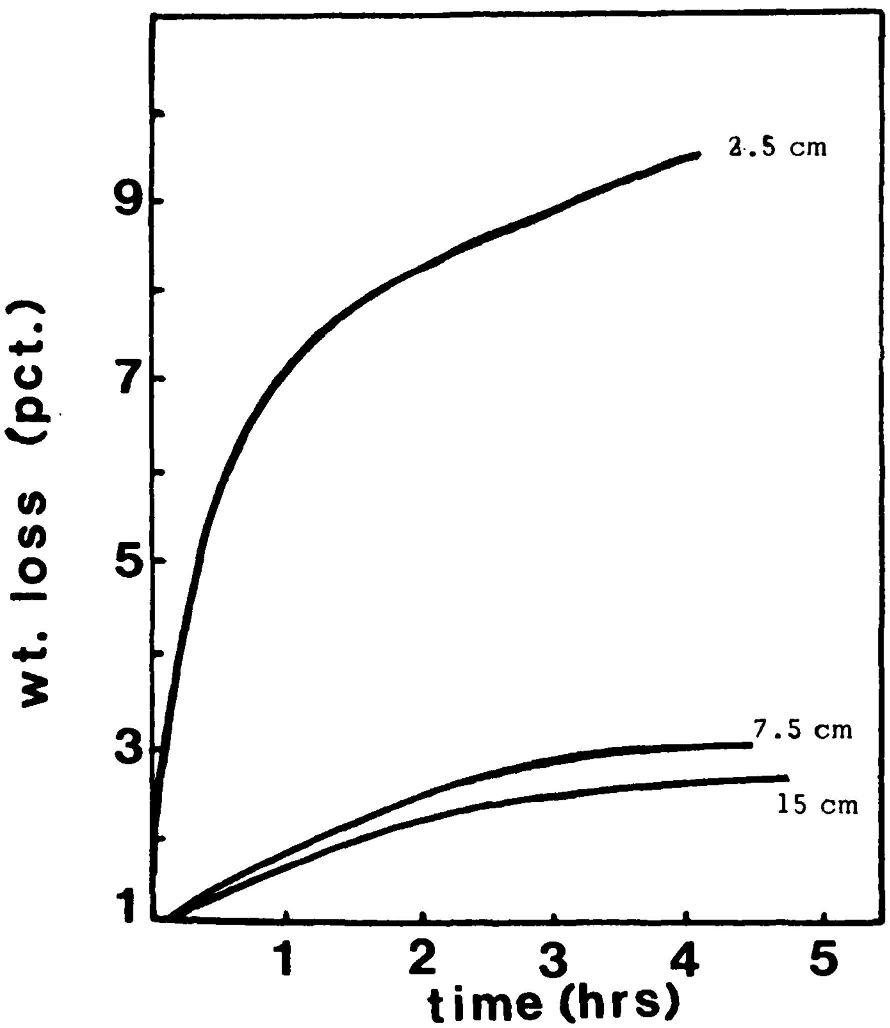

Fig. 11. Weight loss of AMMO homopolymer as a function of long wave (360 nm) ultraviolet radiation at distances of 2.5 cm (10,000 μwatts/cm^2), 7.5 cm (1,120 μwatts/cm^2), and 15 cm (380 μwatts/cm^2) from the sample surface. The intensity of the radiation is 3.39 eV (78 kcal/mole)

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