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PYROLYSIS OF DIMETHYLETHANOLAMINE OXIDE MONOHYDRATE

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The pyrolysis of dimethylethanolamine oxide was selected as a means of generating acetaldehyde at moderate temperatures from a nonvolatile and relatively nonreactive precursor. The decomposition of trialkylamine oxides to olefin and dialkylhydroxylamine (Cope reaction) is known to proceed in good yield via a cyclic intramolecular transition state (1). The pyrolysis of some N,N-dimethyl-2-hydroxy-cycloalkylamine oxides has been reported (2). These give allylic alcohol and ketone (via enol), in a ratio ranging from 5:1 to 20:1, where stereochemical factors permit competitive elimination. Since only elimination toward the hydroxyl group is possible in dimethylethanolamine oxide, one would predict that the vinyl alcohol – acetaldehyde tautomeric system would be the principal product unless the rate of elimination were so slow that deoxygenation (3) or oxazoline formation (2) became significant. An explosion occurred during the initial preparative-scale pyrolysis. Experiments were then directed toward determination of the products and kinetics of the reaction to ascertain the cause of the violent reaction, and to see whether decomposition could be effected via a controlled reaction.

EXPERIMENTAL

Preparation of Amine Oxides

A mixture of 75 ml of isopropyl alcohol and 75 ml of 50% hydrogen peroxide was placed in a flask thermostatted at 50°. With vigorous stirring, 1.0 mole of amine was added dropwise. The homogeneous mixture was maintained at 50° for several hours; then stirring was resumed and volatile material was removed under reduced pressure. The products were analyzed for amine and amine oxide by nonaqueous acidimetric titration (3). The reaction times and analyses are shown in Table I.

TABLE I

Synthesis of amine oxides

Amine	Reaction time (h)	Product analysis (%)		
		Amine	Amine oxide*	Active oxygen
$Me_2NCH_2CH_2OH$	5	0	103	0.62
$Me_2NCH_2CH_2OAc$	20	2	104	0
$Me_2NCMe_2CH_2OH$	22	70†	30†	0

*As monohydrate.
†Relative mole percent.

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Pyrolysis of Dimethylethanolamine Oxide Monohydrate

A 25 g sample was placed in a vacuum distillation apparatus, with the receiving flask cooled by dry ice – acetone. Heating with a microburner was continued until the temperature reached 110°. The temperature rose rapidly to about 180°; then the flask exploded.

A 0.5 g sample was placed in a flask fitted with a stopcock and a rubber seal. The flask was evacuated, a 10 ml hypodermic syringe (lightly greased) was inserted through the seal, and then the sample was heated with a microburner until the syringe was filled. The contents were immediately injected into the gas chromatograph (6 ft silicone oil column at 80°). Three peaks, identified as water, acetaldehyde, and dimethylhydroxylamine (by retention times), were obtained. These identities were confirmed by mass spectrometry of the eluted samples after degradation in a Perkin–Elmer pyrolysis unit at 200°. Because the water peak showed extensive tailing, a rigorous quantitative determination was not attempted. From peak areas, a molar ratio of water to acetaldehyde to dimethylhydroxylamine of about 2:1:1 was estimated.

The rate of reaction was determined at 127.5° in the manner described previously (3, 4). A rate constant of $(2.8 \pm 0.2) \times 10^{-5}\ s^{-1}$ was obtained.

A 3 μl sample was pyrolyzed in a duPont model 900 differential thermal analysis (DTA) apparatus (5) at a heating rate of 20°/min. The DTA curve is shown in Fig. 1.

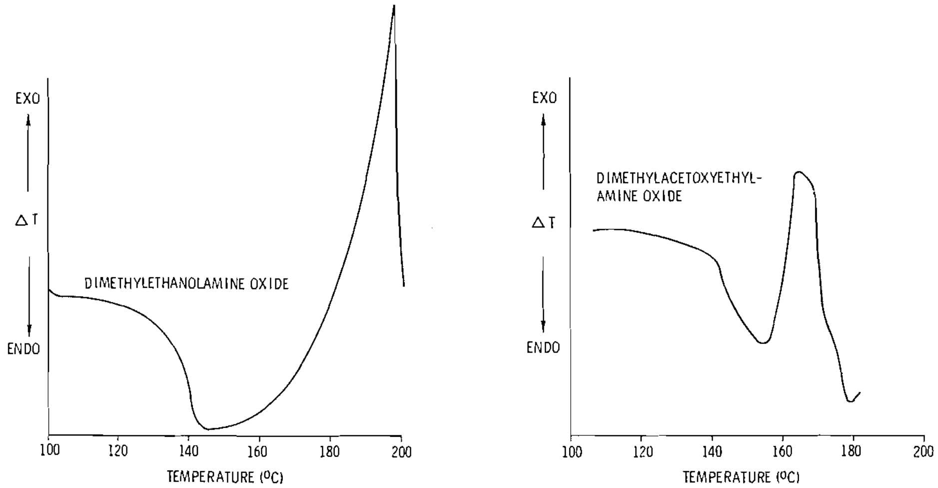

FIG. 1. DTA of dimethylethanolamine oxide and dimethyl-2-acetoxyethylamine oxide.

A 6.78 mg sample was placed in the tungsten crucible of the Knudsen cell inlet of a Bendix time-of-flight mass spectrometer and heated at a rate of 14°/min. Spectra were recorded at 1 min intervals; then the heights of peaks characteristic of each product were plotted versus temperature. The mass spectrometric thermal analysis (MTA) curve is shown in Fig. 2. The activation energies for the formation of each product were derived from the linear portion of semilogarithmic plots of peak height versus reciprocal temperature (water 6.2, acetaldehyde 32, dimethylhydroxylamine 36, and dimethylethanolamine 20 kcal mole^{-1}).

Differential Thermal Analysis of Dimethyl-2-acetoxyethylamine Oxide Monohydrate

A DTA taken on a 3 μl sample at a heating rate of 20°/min is shown in Fig. 1.

Pyrolysis of 2-Dimethyloxamino-2-methyl-1-propanol

A 5.0 g sample was added dropwise to a distilling flask (at 150 ± 5°) which formed part of a microdistillation apparatus. Gas chromatographic analysis (6 ft silicone oil column at 80°) of the distillate showed four components: dimethylhydroxylamine, water, and a 23:1 ratio of methallyl alcohol to isobutyraldehyde.

DISCUSSION

The expected products from the pyrolysis of dimethylethanolamine oxide monohydrate, i.e. water, dimethylhydroxylamine, and acetaldehyde, were observed gas chromatographically. Based on the mass spectra of the products, characteristic peaks of m/e 17 for water, 29 (CHO) for acetaldehyde, and 58 for dimethylhydroxylamine were selected for

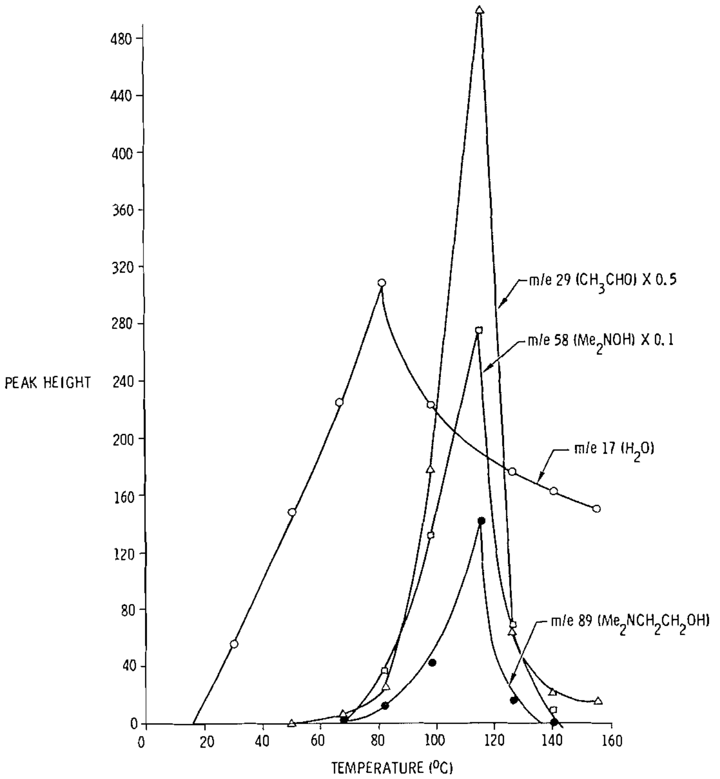

FIG. 2. MTA of dimethylethanolamine oxide.

the MTA.[2] The only identifiable peaks observed in the MTA in addition to those from fragmentation of the three principal products were peaks characteristic of an amine with a molecular ion at m/e 89. This must be dimethylethanolamine formed by deoxygenation of the amine oxide. No corresponding increase in the m/e 32 or 34 peaks was observed; hence, deoxygenation does not proceed with liberation of oxygen or hydrogen peroxide.

It is also possible to derive activation parameters from the MTA data. Based on the assumption that, in the rapidly pumped vacuum system of the mass spectrometer, the intensity of the characteristic ion is proportional to the rate of production of a species, a plot of log peak height versus reciprocal temperature should be linear as long as the concentration of the reactant is essentially unchanged. For olefin formation, an activation energy of 34 ± 2 kcal mole^{-1} was observed, based on the average for acetaldehyde and dimethylhydroxylamine; for deoxygenation the value is 20 kcal mole^{-1}, and for dehydration 6.2 kcal mole^{-1}. These values agree well with those of 36.3 and 20.6 kcal mole^{-1} determined for corresponding reactions of dimethyllaurylamine oxide. The activation energy for dehydration is in the range which one would expect for breaking a hydrogen bond.

It is clear from the MTA curve (Fig. 2) that dehydration precedes elimination, as has been postulated previously based on kinetic evidence (6). The DTA (Fig. 1) also shows

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[2] *The m/e 18 peak for water was off scale. The m/e 43 peak was a major dimethylhydroxylamine fragment, and was therefore not characteristic for acetaldehyde. Only a minor molecular ion (61) peak was observed for dimethylhydroxylamine. The spectra of dialkylhydroxylamines will be reported subsequently.*

a two-stage reaction: an endotherm (dehydration) followed by an exotherm (degradation). Dimethylethanolamine oxide decomposition releases several times more energy than decomposition of its acetate ester. This extra energy must be derived from the isomerization of vinyl alcohol to acetaldehyde.

There seems to be a marked effect of pressure on the reaction. The preparative pyrolysis became uncontrollable at about 110°, and the maximum rate in the MTA is observed at 115°. In contrast, the DTA shows degradation occurring at 140–200°, and a slow rate of reaction was measured at 127.5° under atmospheric pressure. The enhanced rate *in vacuo*, which leads to an uncontrollable reaction on a preparative scale, is no doubt due to the greater use of removing water from the hydrate and the resulting rapid decomposition of anhydrous amine oxide, as shown by Sahyun and Cram (6).

Determination of the relative rates of aldehyde and allylic alcohol formation was accomplished by the competitive intramolecular reaction of 2-dimethyloxamino-2-methyl-1-propanol. The 23:1 ratio of methallyl alcohol to isobutyraldehyde shows that elimination of the methylol hydrogen is slower than that of the methyl hydrogen. If one compensates for the number of hydrogens of each type available (6:2), elimination toward a methylol group is about one-eighth as fast as that toward methyl. The corresponding factor for secondary alcohol – methylene competition ranges from 0.1 to 0.4 (2).

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ERRATUM: THE OCCURRENCE OF 2,3-DIBROMOBENZYL ALCOHOL 4,5-DISULFATE, DIPOTASSIUM SALT, IN POLYSIPHONIA LANOSA

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On page 74, lines 4–7 of the Introduction should read "-benzaldehyde has been shown to occur in *Polysiphonia morrowii* (3), and two other compounds (believed to be brominated sulfonated hydroxybenzoic acids) with the empirical formulae $C_7H_2O_9S_2Br_2K_2$