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IDENTIFICATION OF METHYL DIETHANOLAMINE DEGRADATION PRODUCTS BY GAS CHROMATOGRAPHY AND GAS CHROMATOGRAPHY–MASS SPECTROMETRY

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SUMMARY

Partially degraded, aqueous methyl diethanolamine solutions were analyzed by a gas chromatograph equipped with a Tenax column and flame ionization detector; nitrogen was used as the carrier gas. To aid in product identification, the gas chromatograph was coupled to a mass spectrometer operating either in electron impact or chemical ionization mode. The most important degradation products were found to be: methanol, ethylene oxide, trimethylamine, ethylene glycol, 2-(dimethylamino)ethanol, 1,4-dimethylpiperazine, N-(hydroxyethyl)methylpiperazine, triethanolamine; and N,N-bis(hydroxyethyl)piperazine.

INTRODUCTION

Aqueous solutions of methyl diethanolamine (MDEA) are gaining industrial acceptance as solvents for the selective removal of hydrogen sulphide from light hydrocarbon gases containing carbon dioxide (Kohl and Riesenfeld[1]). MDEA's selectivity for hydrogen sulphide is attributed to its inability to form carbamates with carbon dioxide. In addition, the lack of carbamate formation also suggests that CO_2 is unlikely to degrade MDEA, *i.e.* convert it into compounds from which MDEA cannot be regenerated under normal processing conditions. Blanc and Elgue[2] have stated that "No one has been able to show any degradation products in (MDEA) solutions having been used for several years in industrial units". However, Yu *et al.*[3] have suggested that MDEA may also form carbamate ions with carbon dioxide and Chakma and Meisen[4] found in preliminary experiments that MDEA degrades at elevated temperatures and carbon dioxide partial pressures. The formation of degradation compounds is undesirable because they represent a loss of valuable MDEA, may interfere with acid gas aborption and may cause operating problems such as corrosion, fouling and foaming.

The basic objective of the present work was to identify the principal MDEA degradation compounds. Based on preliminary experiments and by using the gas chromatographic technique previously developed by Kennard and Meisen[5] for indus-

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trial diethanolamine (DEA) solutions, it was found that partially degraded MDEA solutions contained several compounds with similar retention times in the gas chromatographic (GC) column. GC coupled with various forms of mass spectrometry (MS) were therefore used in product identification.

EXPERIMENTAL

Degradation of MDEA solutions

Partially degraded MDEA solutions were obtained in a manner similar to that utilized by Kennard and Meisen[6] for DEA. Aqueous solutions of known concentrations were prepared by mixing distilled water with 99+% pure MDEA (supplied by Aldrich, Milwaukee, WI, U.S.A.). The purity of the MDEA was confirmed by GC. A 600-ml stainless-steel autoclave (Model 4560, Parr Instrument, Moline, IL, U.S.A.), was purged with carbon dioxide before heating it to the desired temperature. A known volume of MDEA solution (typically 250 ml) was then transferred into the autocalve and the solution placed under a blanket of carbon dioxide. The autoclave was constantly stirred and the solution temperature was kept at the desired value by means of a controller (Model 4831EB, Parr Instrument). Solution samples (typically 5 ml) were withdrawn from the autoclave at appropriate intervals and their contents analyzed as described below.

Gas chromatographic technique

The GC technique developed by Kennard and Meisen[5] for DEA was modified for the analysis of degraded MDEA solutions. The final, optimal operating conditions are summarized in Table I. The elution times of the important degradation compounds were generally less than about 30 min (see Table II). After each run

TABLE I

SPECIFICATION OF THE GAS CHROMATOGRAPHIC SYSTEM

Gas chromatograph	
Manufacturer	Hewlett-Packard
Model	5830A
Detector	H_2 flame ionization
Chromatographic column	
Material	Stainless steel
Dimensions	1/8 in. O.D., 9 ft. long
Packing	Tenax GC, 60–80 mesh
Operating conditions	
Carrier gas	Nitrogen at 25 ml/min
Injection port temperature	300°C
Detector port temperature	300°C
Column temperature	Isothermal at 100°C for 0.5 min, then raised at 8°C/min to 300°C.
Syringe	
Manufacturer	Hamilton, Reno, NV, U.S.A.
Model	701, 0.01 ml with fixed needle and Chaney adeptor
Injected sample size	0.001 ml

TABLE II

RETENTION TIMES OF VARIOUS COMPOUNDS IN GC COLUMN

Compound name	*Abbreviation*	*Retention time (min)*
Ethylene oxide	EO	1.3–1.4
Trimethylamine	TMA	1.9–2.0
Ethylene glycol	EG	7.2–7.3
N,N-Dimethylaminoethanol	DMAE	8.4–8.6
2-Methylaminoethanol	MAE	8.5–8.6
Dimethylpiperazine	DMP	11.5–11.6
Methyl diethanolamine	MDEA	14.7–14.8
Diethanolamine	DEA	14.8–14.9
Hydroxyethylmethylpiperazine	HMP	16.5–16.7
Triethanolamine	TEA	20.1–20.3
N,N-bis(hydroxyethyl)piperazine	BHEP	21.4–21.6
3-(Hydroxyethyl)-2-oxazolidone	HEOD	22.2–22.4
N,N,N-Tris(hydroxyethyl)ethylenediamine	THEED	25.5–25.7
N,N,N,N-Tetra-(hydroxyethyl)ethylenediamine	TEHEED	27.8–28.0

lasting approximately 40 min, the column was cooled from 300 to 100°C over a 10-min period.

GC–MS techniques

To facilitate the identification of degradation compounds, a microprocessor based gas chromatograph–mass spectrometer (Model 5985B, Hewlett-Packard, Palo Alto, CA, U.S.A.) was used. This instrument could be operated in electron impact (EI) and chemical ionization (CI) mode. In the latter case, methane was chosen as the reagent gas[7]. The computer was equipped with the EPA/NIH mass spectral data base[8] which enabled ready comparison of experimental and reference spectra.

Hydroxyl group number determination

Many of the compounds in degraded MDEA solutions contain hydroxyl groups. The silylation techniques described by Hsu and Kim[7] and Hsu[9] were used to determine the number of hydroxyl groups as further confirmation of a compound's identity.

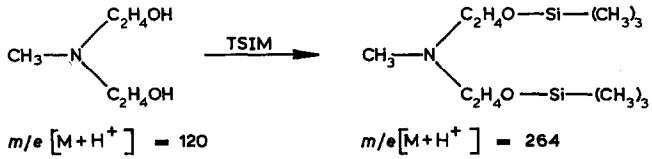
Since water may interfere with the silylation technique, it was first removed by saturating the samples with potassium carbonate and extracting them with isopropyl alcohol. The alcohol was later eliminated again by vaporization.

Two silylation reagents were examined. The first consisted of hexamethyldisilazane (HMDS), trimethylchlorosilane (TMCS) and anhydrous pyridine as suggested by Hsu and Kim[7]. Mixtures of 1 ml HMDS, 0.5 ml TMCS and 2 ml pyridine were added to 5 ml of dehydrated samples in 10-ml screw-cap vials. The vials were shaken vigorously for about 5 min and then allowed to stand for at least 10 min to ensure complete silylation. It was observed that, in some cases, silylation of amino groups occurred as well.

The second reagent was N-trimethylsilyl imidazole (TSIM). A 5-ml volume of TSIM were added to 5-ml samples in 20-ml screw-cap vials and reacted following the

procedure described above. TSIM was found to silylate the hydroxyl groups only while leaving the amino groups unaffected. Consequently, TSIM was primarily used for selective hydroxyl silylation in this study.

Selective silylation results in the addition of silyl groups to hydroxyl groups in the sample. This increases the mass-to-charge ratio of the pseudomolecular ions in proportion to the number of hydroxyl groups present. Thus by comparing the mass-to-charge ratios of the pseudomolecular ions of CI spectra before and after silylation, the number of hydroxyl groups in a compound can be calculated. For example, when MDEA is silylated with TSIM, the active hydrogens are replaced by the trimethyl silyl group –Si (CH_3) or TMS:



The formula mass of the TSIM group is 73 a.m.u. and it replaces one active hydrogen atom. Therefore, the addition of each TSIM group increases the mass-to-charge ratio of the pseudomolecular ion by 72. In general, the number of hydroxyl groups can simply be calculated from the difference in the mass-to-charge ratios of the pseudomolecular ions before and after silylation, *i.e.*

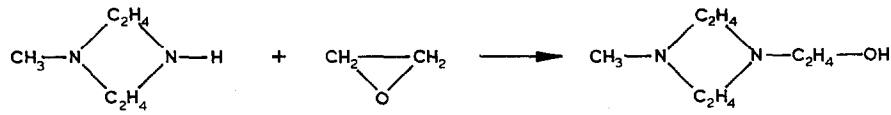
Number of OH groups = $\{m/e[M + H^+]_{silylated} - m/e[M + H^+]_{unsilylated}\}/72$.

Synthesis of select MDEA degradation compounds

In order to identify the MDEA degradation compounds conclusively and to determine their concentrations, the suspected compounds were purchased, whenever possible, in pure form. However, HMP, HEOD and THEED were unavailable in sufficiently pure form and had to be synthesized.

HMP synthesis

HMP was formed by placing approximately 20 ml of 1-methylpiperazine (MP) into a glass beaker and bubbling ethylene oxide (EO) through the mixture at ambient conditions. The following reaction occurred:

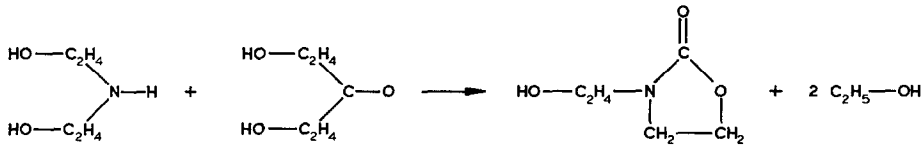


Bubbling was continued until MP was no longer detectable. A product purity of over 97% HMP was obtained.

HEOD synthesis

Kennard[10] attempted various method of HEOD synthesis, but was unsuccesful in obtaining sufficient purity for GC calibration. A procedure similar to that of Kim and Sartori[11] and Drechsel[12] was therefore adopted for this study.

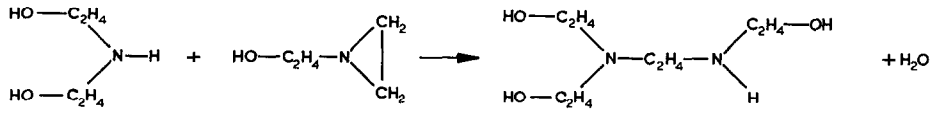
A 210-g amount of DEA, 260 g of diethylcarbonate and 2 g of sodium methoxide were placed into the autoclave described before. The temperature was gradually raised to 130°C while continuously stirring the solution and keeping the pressure at 1 atm. The following reaction occurred:



After approximately 2 h, the ethanol formation ceased. The autoclave was then cooled to room temperature by passing water through its internal cooling coil. The reaction product was found to be a mixture of ethanol and HEOD with a purity (as determined by GC analysis) in excess of 90%. The HEOD was further purified to over 95% by adding SGL activated carbon (Calgon, Pittsburg, PA, U.S.A.) to the sample.

THEED synthesis

THEED was synthesized according to Kennard's unpublished procedure[10]:



A 105-g amount of DEA, 87 g of N-(2-hydroxyethyl)ethylimine (HEM) and 5 g of aluminum chloride were placed inside the previously described autoclave fitted with a pyrex liner. The autoclave was then sealed and pressurized to 0.7 MPa with nitrogen. The contents were constantly stirred and maintained at 120°C for 24 h. Upon rapid cooling, THEED of 80+% purity was obtained. This product was further refined by diluting it with water and then passing it at a flow-rate of 0.5 ml/min through a 0.40m x 20 mm I.D. long glass column filled with 60–200 mesh silica gel and trace amounts of aluminum hydroxide. The product was concentrated by boiling to drive off the water. THEED of 98+% purity was thus obtained.

RESULTS AND DISCUSSION

Fig. 1 shows a typical chromatogram of a 4.28 *M* MDEA solution after it was degraded for 144 h at 180°C under a CO_2 partial pressure of 2.59 MPa. Apart from the MDEA peak (peak 9), various other peaks representing degradation compounds are evident.

Peaks 1–7 were found to be methanol, ethylene oxide (EO), trimethylamine (TMA), N,N-dimethylethanamine, ethylene glycol (EG), 2-(dimethylamino)ethanol (DMAE) and 4-methylmorpholine, respectively, by matching their EI mass spectra with library spectra[8] stored in the GC–MS.

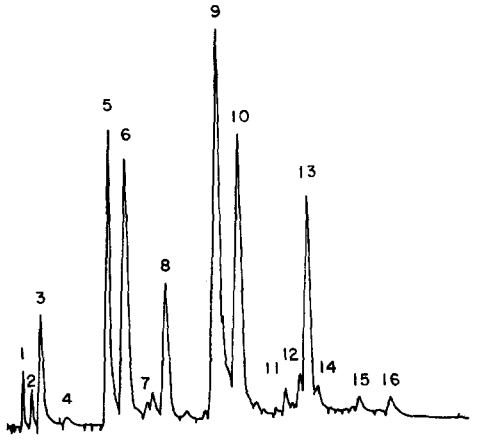


Fig. 1. Chromatogram of a partially degraded MDEA solution of 4.28 *M* initial concentration, degraded at 180°C under a carbon dioxide partial pressure of 2.59 MPa for 144 h.

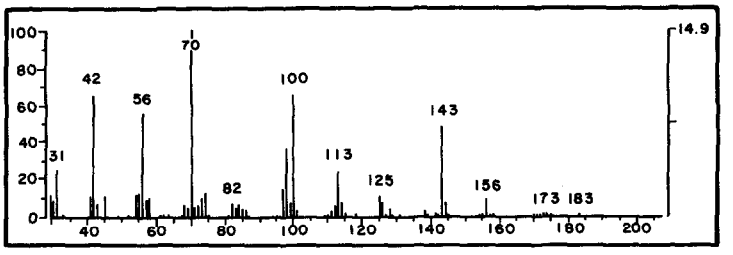


Fig. 2. EI mass spectrum of peak 13 identified as BHEP.

Peak 8 was identified to be 1,4-dimethylpiperazine (DMP) by matching its EI mass spectrum with that given in the *Eight Peak Index of Mass Spectra*[13].

The EI mass spectra of peaks 13, 14 and 15, which are shown in Figs. 2–4, were attributed to N,N-bis-(2-hydroxyethyl)piperazine (BHEP), 3-(hydroxyethyl)-2-oxazolidone (HEOD), and N,N,N-tris-(hydroxyethyl)ethylenediamine (THEED), respectively. The reason for this is that they matched the unpublished spectra obtained by Kennard[10].

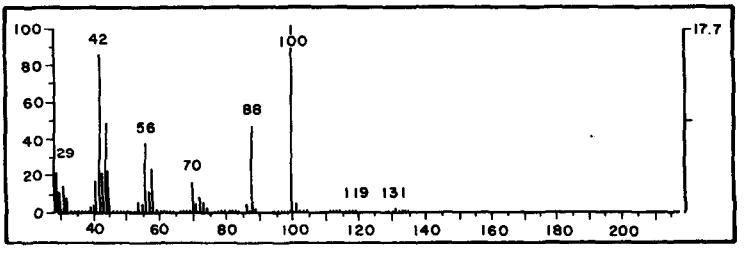


Fig. 3. EI mass spectrum of peak 14 identified as HEOD.

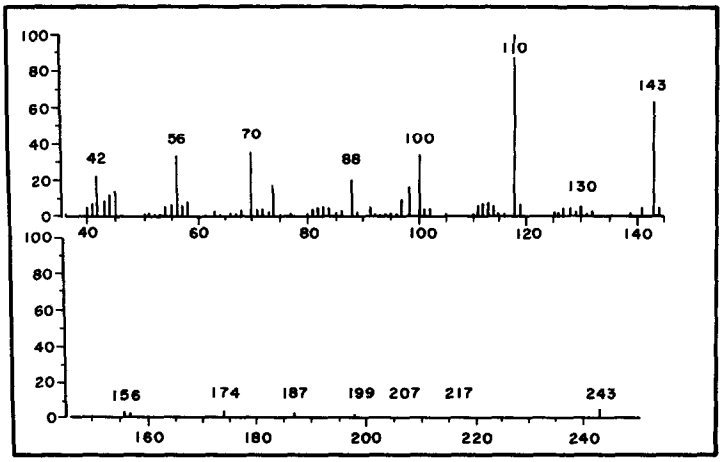


Fig. 4. EI mass spectrum of peak 15 identified as THEED.

The EI mass spectrum of peak 12 is shown in Fig. 5 and, based on the charged ion distribution, was suspected to be either N,N-bis-(hydroxyethyl) glycine (BHG) or triethanolamine (TEA). These compounds were purchased in pure form and their standard EI mass spectra produced. The mass spectrum corresponding to peak 12 is quite similar to the BHG and TEA spectra (see Figs. 6 and 7). Therefore, definite identification was not possible based on the EI mass spectra. However, peak 12 had a retention time in the GC column of 20.1–20.3 min. which compares well with that of TEA. By contrast, BHG had a retention time of 22.1–22.2 min. To provide further evidence that peak 12 is due to TEA, known quantities of TEA were added to a partially degraded MDEA sample. The chromatograms of samples before and after TEA addition resulted in an area increase of peak 12. When a similar experiment was performed with an aqueous BHG solution, a new peak arose. Consequently, it was concluded that peak 12 is due to TEA.

Peak 10, whose EI mass spectrum is given in Fig. 8, corresponds to another major, unknown degradation compound. Although the fragmentation pattern suggested the compound to be some kind of piperazine, no satisfactory match with a library mass spectrum was found. Based on Fig. 8, the molecular peak was thought to contain 126 a.m.u. However, no plausible piperazine compound with a molecular mass of 126 could be formulated.

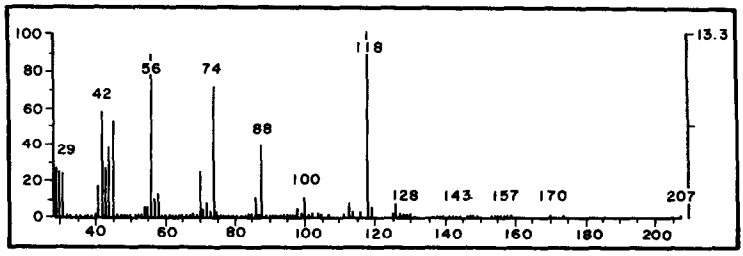


Fig. 5. EI mass spectrum of peak 12.

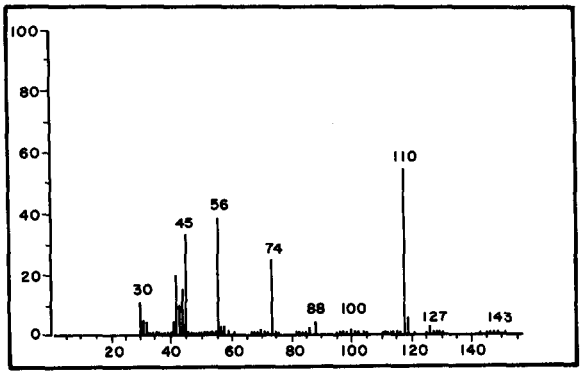


Fig. 6. EI mass spectrum of BHG.

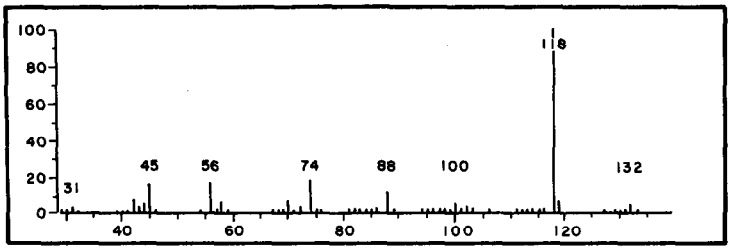


Fig. 7. EI mass spectrum of TEA.

Molecular mass determination by CIMS

The methane CI mass spectra of MDEA, BHEP and HEOD are presented in Figs. 9–11, respectively. It is evident that the peaks of the protonated molecular ions, [M + H]+, are very distinctive in the methane CI spectra compared with the molecular ion peaks in the EI spectra. The methane CI mass spectrum of peak 10 is shown in Fig. 12. Although the molecular ion peak appears to be 126 a.m.u. in the EI spectrum, the methane CI spectrum shows a protonated molecular ion peak of 145 a.m.u. thus indicating a molecular mass of 144 a.m.u. Careful inspection of the EI spectrum also shows a very small peak at 144 a.m.u. which is easily overlooked in favour of the more distinct peak at 126 a.m.u. This clearly indicates that molecular mass determination from EI spectra may sometimes be misleading.

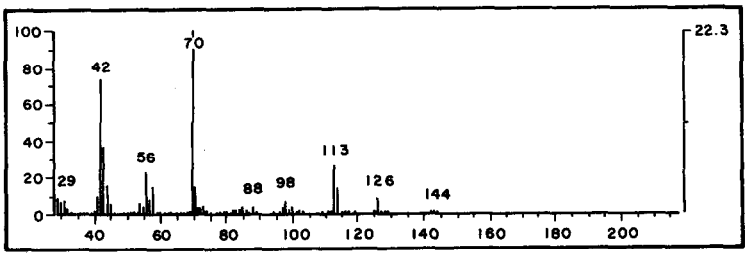


Fig. 8. EI mass spectrum of peak 10.

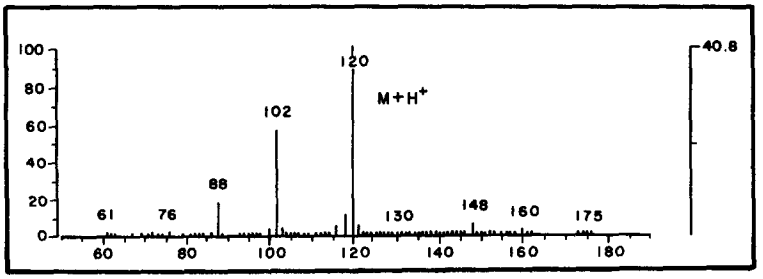


Fig. 9. Methane CI mass spectrum of MDEA.

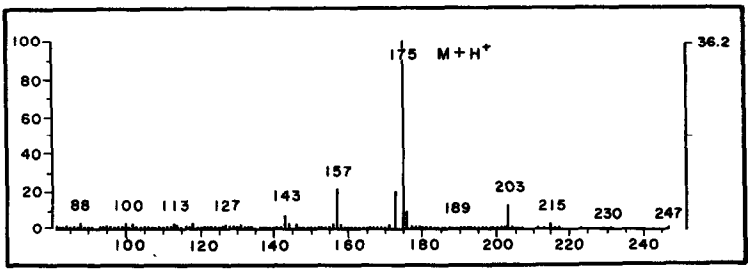


Fig. 10. Methane CI mass spectrum of BHEP.

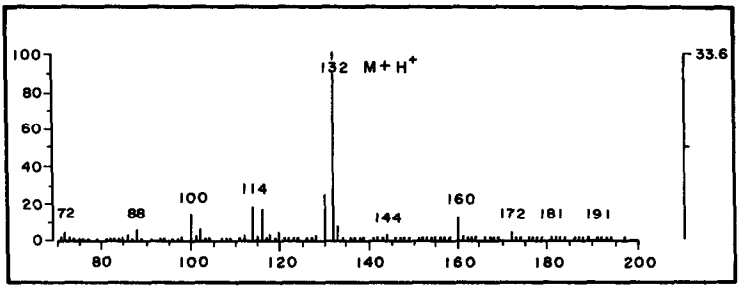


Fig. 11. Methane CI mass spectrum of HEOD.

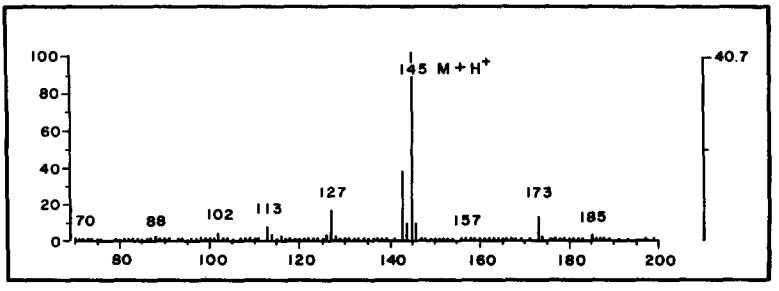


Fig. 12. Methane CI mass spectrum of peak 10.

TABLE III

RESULTS OF HYDROXYL GROUP CALCULATIONS

Compound	*[M + H⁺] unsilylated (a.m.u.)*	*[M + H⁺] silylated (a.m.u.)*	*Number of -OH groups*
MDEA	120	264	2
TEA	150	366	3
BHEP	175	319	2
Peak 10	145	217	1

Hydroxyl group determination

The methane CI spectra of MDEA, BHEP, TEA and peak 10 after silylation were obtained and the results of the hydroxyl group calculation are summarized in Table III. The validity of the silylation method is demonstrated by the accurate hydroxyl group determination for MDEA, TEA and BHEP. Peak 10 has a molecular mass of 144 and contains one–OH group. Based on this information and its fragmentation pattern, which suggested the presence of a piperazine ring, the compound was identified as 1-(2-hydroxyethyl)-4-methyl piperazine (HMP). As a further check, HMP was synthesized as described before. Its retention time in the GC column and its mass spectrum were compared with those of peak 10. A good match was found and HMP was thus confirmed as being responsible for peak 10. The mass spectrum of synthesized HMP is shown in Fig. 13.

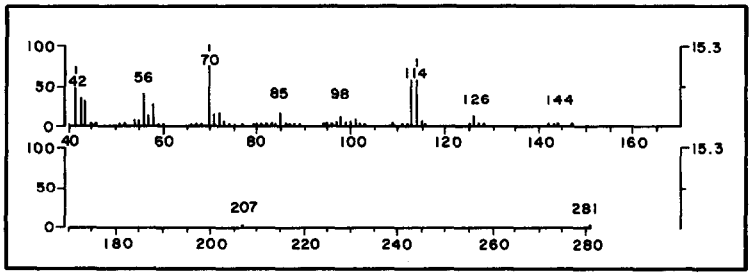


Fig. 13. EI mass spectrum of HMP synthesized in the laboratory.

CONCLUSIONS

The major MDEA degradation products, which result from its exposure to carbon dioxide at elevated temperatures and pressures, have been identified by GC coupled with EI- and CI-MS.

ACKNOWLEDGEMENTS

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