

# Identification of products resulting from carbonyl sulphide-induced degradation of diethanolamine<sup>☆</sup>

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## ABSTRACT

The degradation of aqueous diethanolamine (DEA) solutions due to carbonyl sulphide (COS) was studied by contacting the solutions (10–40 wt. %) in a well stirred, 600-ml stainless-steel autoclave with COS–nitrogen mixtures at temperatures ranging from 120 to 180°C. Combined gas chromatography-mass spectrometry, melting point determinations and elemental and infrared analyses were used to identify most of the major reaction products, *viz.*, monoethanolamine, ethylaminoethanol, ethyldiethanolamine, hydroxyethylacetamide, hydroxyethylpiperazine, ethanethioic acid S-hydroxyethylaminomethyl ester, bis(hydroxyethyl)ethylenediamine, bis(hydroxyethyl)piperazine, hydroxyethylloxazolidone, hydroxyethylimidazolidone, tris(hydroxyethyl)ethylenediamine, bis(hydroxyethyl)imidazolidone, acetaldehyde, acetone, butanone, acetic acid, ethanol, diethyl disulphide, dithiane and pyridines. In addition, a solid product containing sulphur was formed. The practical implications of the studies for gas plant operators are discussed.

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## INTRODUCTION

Acidic constituents (such as carbon dioxide, hydrogen sulphide, carbonyl sulphide and carbon disulphide) are frequently removed from natural, refinery and synthesis gases by counter-current contact with aqueous solutions of diethanolamine (DEA) in absorbers operating at elevated pressures and low temperatures. The amine solutions are subsequently regenerated by steam stripping at elevated temperatures and reduced pressures before recycling them to the absorbers.

In spite of its resistance to chemical breakdown, plant and laboratory experience indicate that, on prolonged use, DEA can undergo irreversible reactions. This phenomenon, which is called “degradation”, not only leads to a loss of valuable amine, but may also contribute to operational problems such as equipment corrosion and fouling [1–4].

Previous studies [1,5–10] have provided apprecia-

ble insight into DEA degradation due to carbon dioxide (CO<sub>2</sub>). The degradation is believed to occur primarily via DEA carbamate, which may be formed by the direct reaction of CO<sub>2</sub> with DEA. As hydrogen sulphide (H<sub>2</sub>S) is incapable of forming carbamate-type compounds, it is generally agreed that H<sub>2</sub>S does not cause the degradation of DEA, or in general, amines. The results reported by Choy [6] and Kim and Satori [7] suggest that H<sub>2</sub>S in the presence of CO<sub>2</sub> hinders DEA degradation.

Compared with CO<sub>2</sub>-induced degradation, little work has been reported on the degradation of DEA by carbonyl sulphide (COS). Orbach and Selleck [11] contacted pure COS with 20% (w/w) monoethanolamine (MEA) and 35% (w/w) DEA solutions in a bench-scale pilot plant simulating a typical, continuous absorption–regeneration process. The absorber and regenerator were operated at 40 and 104°C, respectively. Periodic analysis of the amine solutions using Kjeldahl analysis and acid titration revealed that, whereas MEA was substantially degraded, no loss of alkalinity occurred in the DEA solution over an 8-h period. Although the formation of a neutral product was reported, the

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amount was "too small to isolate and identify". Believing that this product was formed from small amounts of MEA in the initial DEA solution, they concluded that COS does not degrade DEA.

Pearce *et al.* [12] contacted, in a batch-mode, pure COS with 20 wt.% DEA solutions at temperatures ranging from 40 to 120°C. The solutions were subsequently analysed by infrared and mass spectrometry. Minor amounts of ethanol and oxazolidone were detected. However, they were insignificant compared with those formed when MEA was subjected to COS under similar operating conditions. Pearce *et al.* [12] also contacted COS with DEA continuously using a approach analogous to that of Orbach and Selleck [11]. The concentrations of the DEA solutions at the start and end of the experiments were determined by wet chemical analysis and found to be essentially the same. This again led to the conclusion that COS does not degrade DEA. A further conclusion was that COS underwent significant hydrolysis, as revealed by the presence of CO<sub>2</sub> and H<sub>2</sub>S in the regenerator off-gas and the DEA solution leaving the absorber.

Notwithstanding the conclusions of the earlier studies, there are three reasons to believe that COS may degrade DEA: (i) COS may be hydrolysed to H<sub>2</sub>S and CO<sub>2</sub>, with the latter causing CO<sub>2</sub>-induced degradation; (ii) previously used reaction times were too short, as amine degradation is a slow process; and (iii) past analytical techniques were inadequate.

In connection with the first reason, Chakma's study [10] on the CO<sub>2</sub>-methyldiethanolamine (MDEA) system revealed that degradation is possible via amine protonation and carbamate formation. As COS is hydrolysed in aqueous systems to yield H<sub>2</sub>S and CO<sub>2</sub>, significant concentrations of H<sup>+</sup> and CO<sub>2</sub> can result, which lead to DEA degradation.

Second, Sharma [13] reported that the COS-DEA reaction to form thiocarbamate is more than two orders of magnitude slower than the CO<sub>2</sub>-DEA reaction which produces DEA carbamate. As CO<sub>2</sub>-induced degradation of DEA occurs primarily via the carbamate, it is likely that the COS-induced degradation of DEA via the thiocarbamates is correspondingly slower. The CO<sub>2</sub>-induced degradation of DEA in itself is not a fast process. For instance, Kennard [9] found that at 120°C with a CO<sub>2</sub> partial

pressure of 4.1 mPa and an initial DEA concentration of 30% (w/w), it took almost 20 h to obtain a 5% reduction in the amine concentration. During this period, only one degradation compound was detected at a concentration of about 1% (w/w). When CO<sub>2</sub>-DEA degradation experiments were conducted over more than 8 days, significant accumulations of degradation compounds were noted at 120°C [7,9]. As Orbach and Selleck [11] conducted their DEA degradation experiments over 8 h, it is not surprising that significant amounts of degradation compounds could not be detected (the duration of the experimental runs performed by Pearce *et al.* [12] was not clearly indicated).

Third, the analytical techniques used previously may not have been sufficiently sensitive to detect the compounds arising from the degradation reactions. Gas chromatography (GC) and GC-mass spectrometry (GC-MS) using columns packed with Tenax GC [14] provide a more reliable and sensitive analysis of fresh and degraded alkanolamine solutions [7,15-19].

As the information in the literature on the COS-induced degradation of DEA is inconclusive and as such degradation is an important industrial problem, the present fundamental study was initiated.

## EXPERIMENTAL

The degradation experiments were conducted by using a 600-ml stainless-steel reactor [8] which was partially filled with the amine solution of the desired concentration. The solution temperature was continuously measured by a J-type thermocouple and controlled within  $\pm 0.5^\circ\text{C}$  of the set point. The solution could be stirred at speeds up to 600 rpm and the system pressure was measured with a Bourdon pressure gauge graduated in 5 p.s.i. subdivisions. Liquid samples could be taken from the reactor by means of a stainless-steel sampling coil fitted with inlet and outlet valves. Pressure-lok syringes (supplied by Supelco, Oakville, Canada) were used for sampling the gas phase.

The following materials were used: DEA of 99+ % purity was purchased from Aldrich (Milwaukee, WI, USA), COS from Matheson (Edmonton, Canada) with a purity of COS 97.7, CO<sub>2</sub> 1.4, CS<sub>2</sub> 0.19, H<sub>2</sub>S 0.01, O<sub>2</sub> 0.1 and CO and/or N<sub>2</sub> 0.6 mol% and N<sub>2</sub> of 99+ % purity from Medigas (Vancouver, Canada).

All compounds used for the calibration of the gas chromatograph were purchased from Aldrich, except hydroxyethylloxazolidone (HEOD), hydroxyethylimidazolidone (HEI), tris(hydroxyethyl)ethylene diamine (THEED) and bis(hydroxyethyl)imidazolidone (BHEI), which were not commercially available. HEOD was synthesized as described by Drechsel [20]. The final HEOD purity exceeded 97% as shown by GC analysis. The procedure described by Kennard [9] was used to synthesize THEED and gave a mixture containing about 48 mole% THEED, 47 mole% DEA and 5 mole% bis(hydroxyethyl)piperazine (BHEP). HEI was synthesized according to the procedure of Moller and Osberghaus [21]. The final product purity exceeded 97%. BHEI was formed by reaction of bis(hydroxyethyl)ethylenediamine (BHEED) with urea at 225°C for 4 h. This technique is an adaptation of the procedure for synthesizing HEI. The crude product mixture was purified by column chromatography using 70–230-mesh silica gel and water as solvent. A final product purity of 95+ % was obtained.

#### *Procedure for COS-induced DEA degradation*

Typically, 250 ml of an aqueous DEA solution with the desired concentration were placed in the reactor, the stirrer was turned on and air was purged from the reactor by passing nitrogen through it for about 15 min. The reactor was then sealed and brought to the desired temperature; once a steady state had been achieved, COS was introduced through a stainless-steel tube connected to a pressurized COS cylinder fitted with a pressure regulator. The regulator was set so that its outlet pressure equalled the desired reactor pressure. The tube was left open and connected throughout the experiments to ensure a constant pressure in the reactor. The degradation experiments were conducted under the following operating conditions: DEA concentration, 10–40 wt.% (ca. 1–4 M); temperature, 120–180°C; and COS partial pressure, 0.3–1.17 MPa.

#### *Chromatographic separation of reaction mixture*

Liquid samples (typically 2 ml) were forced from the reactor at predetermined intervals into a stainless-steel sampling coil and quickly cooled to room temperature. Their constituents were then separated and determined using a Hewlett-Packard Model 5830A gas chromatograph equipped with an inte-

grator terminal. The operating conditions were similar to those used by Kennard and Meisen [16] and Chakma and Meisen [19]: column, Tenax GC (60–80 mesh) packed in a 9 ft. × 1/8 in. I.D. stainless-steel column (supplied by Supelco); detector, hydrogen flame ionization, maintained at 300°C; temperature programme, isothermal at 150°C for 0.5 min, then increased to 300°C at 8°C/min; carrier gas, nitrogen at 23 ml/min; sample size, 0.001 ml.

#### *Identification of degradation products*

In order to identify the products of the degradation reactions, four successive methods were used.

*GC.* This technique (the details of which are described above) provides the retention times of the unknown compounds and, with the aid of relevant calibration data, the concentrations of the identified compounds.

*GC-MS.* A Hewlett-Packard Model 5985B GC-MS system was used and could be operated in both the electron impact (EI) and chemical ionization (CI) modes. The latter displays a prominent (usually the most abundant) protonated molecular ion  $[M + 1]^+$ , from which the molecular weight of the unknown is inferred, whereas the former provides information on the fragmentation patterns, which are then compared with literature spectra [9,18,22,23].

*GC-MS of silylated derivatives.* To gain further insight into the structure of the degradation products, the degradation compounds were treated with trimethylsilylimidazole (TSIM) following a procedure similar to that employed by Chakma and Meisen [19] in order to replace active hydrogen atoms with trimethylsilyl groups. A 5-ml volume of a degraded solution was placed in a glass vial and saturated with potassium carbonate to dehydrate the sample. Isopropanol was then added to extract the degradation compounds from the mixture. The extract was transferred to another vial where the alcohol was removed by evaporation, leaving a viscous oil. An excess of TSIM was added to the oil and the mixture was thoroughly shaken and left for at least 1 h at room temperature to ensure complete derivatization. The derivatized sample was then analysed by GC-MS. GC was performed as described above, but a fused-silica megabore column (50% phenylmethylsilicone, 10 m × 0.53 mm I.D.) was used to separate the mixture because Tenax GC proved to

be unsuitable. As TSIM attacks primarily hydroxyl groups, the CI mass spectra could be used to determine the molecular masses of the silylated compounds and hence the number of hydroxyl groups per molecule. The silylating trimethylsilicon ion (TMS) has a molecular mass of 73 and replaces the hydrogen in OH groups. Thus silylation of a compound increases its molecular mass by  $72n$ , where  $n$  is the number of hydroxyl groups in the compound.

*GC of degraded mixtures spiked with suspected compounds.* Once GC-MS analysis had provided information on the possible identities of the degradation compounds, pure forms of these compounds were purchased or synthesized when commercially unavailable. The pure compounds were added to the degraded solutions and the spiked solution samples were then analysed by GC using the conditions given above. The resulting peak areas and retention times were compared with those for the unspiked sample. An increase in the area of a particular peak due to spiking, together with GC-MS analysis, can provide conclusive proof of the identity of an unknown compound.

## RESULTS AND DISCUSSION

Before proceeding with the main experimental program, it was necessary to conduct some preliminary experiments aimed at evaluating the effects of certain operating variables on the degradation reactions.

Elevated temperatures were used in this study to speed up the degradation reactions. The result obtained under such conditions will only have industrial relevance if the alkanolamines are not thermally degraded and the reaction products are similar to those obtained at the lower temperatures commonly used in industry. Thermal degradation experiments, conducted by heating aqueous solutions of DEA under a blanket of nitrogen, revealed no significant change in solution composition within 220, 60 and 48 h at temperatures of 150, 165 and 180°C, respectively [24]. Under these conditions, thermal degradation was negligible, and these findings agreed with the results of Kennard and Meisen [8]. As most of the high-temperature degradation runs were conducted within 48 h, the influence of thermal degradation on the results can be dismissed.

Typical chromatograms of aqueous DEA solu-

tions degraded in the presence of COS are shown in Fig. 1. The qualitative similarity of the traces is obvious. This suggests that the basic reaction mechanism is not affected by temperature. As industrial DEA regenerators operate at reboiler temperatures of up to 140°C, the products obtained in this study should also be formed under industrial conditions.

Two runs were performed with and without a Pyrex liner in the reactor. The results indicated very similar products and hence the liner had a negligible effect on the reaction mechanism.

### Degradation compounds

Fig. 2 shows the chromatograms of samples from a typical run conducted with a 40% (w/w) DEA solution at a COS partial pressure of 0.34 MPa and a temperature of 180°C. The gradual formation of reaction products is obvious. In addition, it was noted that the samples became more pungent and viscous as the degradation progressed. Some particulate matter was also found in the samples.

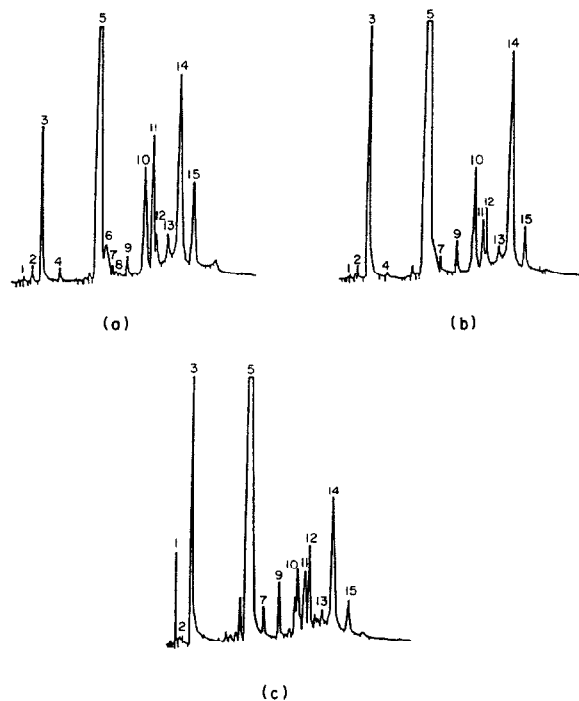


Fig. 1. Chromatograms of partially degraded DEA solutions of 4 M initial concentration. (a) 180°C, 0.34 MPa COS, time 30 h; (b) 150°C, 0.34 MPa COS, time 50 h; (c) 120°C, 0.68 MPa COS, time 215 h. For peaks, see Table I.

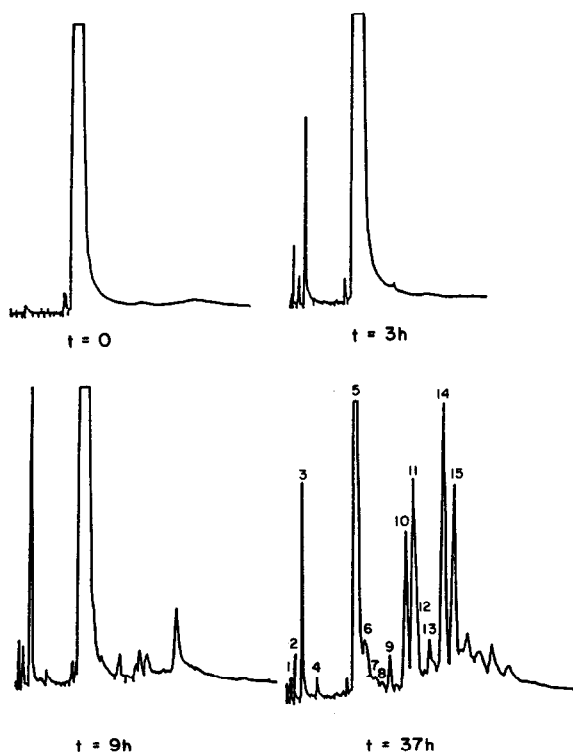


Fig. 2. Chromatograms showing the gradual formation of degradation products in a COS-DEA system (4 M DEA, 180°C, 0.34 MPa).  $t$  = time.

By following the techniques described above, the compounds responsible for the peaks labelled in Figs. 1 and 2 were identified and are listed in Table I. Figs. 3 and 4 show the various spectra for DEA and BHEI. For the compounds that are not available commercially (*e.g.*, BHEI), the library EI mass spectra refer to the spectra of the compound synthesized in the laboratory. The detailed spectra for the other compounds were provided by Dawodu [24].

A consistent pattern in the fragmentation of these hydroxylamino compounds is the loss of hydroxymethyl radicals ( $m/e$  31) from the parent compounds to produce, in general, the most abundant ions. Ions of mass 30 for MEA, 58 for ethylaminoethanol (EAE), 74 for DEA, 72 for hydroxyethylacetamide (HEA), 102 for ethyldiethanolamine (EDEA), 143 for BHEP and BHEI, 100 for HEOD and 99 for HEI and hydroxyethylpiperazine (HEP) were generated in this manner. For BHEED and

THEED, hydroxymethyl radicals were also lost, but the principal fragmentation resulted from the cleavage of the C-C bond between two nitrogen atoms giving ions with mass 74 for BHEED (N,N'-isomer) and 118 for THEED as the most abundant ions. The loss of water molecules also occurred. For example, ions of mass 74 lost water to give ions with a mass of 56 in the case of DEA. The molecular ion peaks are not prominent in most of the EI mass spectra because of the ease with which the hydroxymethyl groups break from the molecules. The characteristic peaks in the CI mass spectra of the hydroxylamino compounds are produced by the  $[M+H]^+$ ,  $[M+C_2H_5]^+$  and  $[M-CH_3]^+$  ions. For the silyl derivatives, the CI mass spectra show prominent  $[M+H]^+$ ,  $[M+C_2H_5]^+$  and  $[M-CH_3]^+$  ions. The  $[M-CH_3]^+$  ion is characteristic of the silylating agent (TSIM). The previous, tentative identification [25] of peak 9 as bis(hydroxyethyl)aminoethanol (BHEAE) now appears to be invalid. The compound has a molecular mass (MW) of 149 as indicated by its CI mass spectrum (Fig. 5). Its silyl derivative has a molecular mass of 221, which suggests that it contains one hydroxyl group. The EI mass spectrum shows the most abundant ion as having a mass 74. Loss of the characteristic hydroxymethyl radical does not produce a prominent peak, even though the compound appears to have an hydroxyethyl attachment (deduced from the ion of mass 74). This, in addition to the prominent ion of mass 89 in the CI mass spectrum, suggests that the compound is not very stable and fragments on electron bombardment to give ions with a mass of 89 or, more likely, 74. Based on the available information, the most likely structure for this compound, ethanethioic acid S-[(2-hydroxyethyl)amino]methyl ester (ETAHEAME), is  $CH_3C(O)SCH_2NHCH_2CH_2OH$ . This compound is unavailable commercially and it was therefore not possible to compare its retention time under the present GC conditions with that of peak 9.

It also appears that triethanolamine (TEA) was formed as a degradation compound but could not be distinctively separated from BHEED under the analytical conditions used. This supposition arises from the fact that the GC analysis of the silyl derivatives showed a peak before BHEED, having a molecular weight of 365. This would suggest an undervivatized hydroxylamino compound with a molec-

TABLE I  
MAJOR DEGRADATION COMPOUNDS DETECTED IN THE COS-DEA SYSTEM

Peak No.	Retention time (min)	Characteristic EI ions	Molecular weight		<i>n</i> OH <sup>b</sup> , (M* - M)/72	Identity
			M	M* <sup>a</sup>		
1	1.4- 1.5	43, 58	58			Acetone
2	2.2- 2.3	29, 43, 57, 72	72			Butanone
3	3.1- 3.3	30, 42, 61	61	133	1	MEA
4	5.2- 5.3	30, 56, 74 42, 58, 89	89	161	1	EAE
5	9.2-10.0	45, 56, 74	105	249	2	DEA
6	10.9- 11.1	30, 56, 74, 102 45, 58, 88, 133	133	277	2	EDEA
7	11.5-11.6	30, 60, 73 43, 72, 85	103	175	1	HEA
8	12.0-12.1	42, 70, 112 56, 88, 130	130	202	1	HEP
9	13.4-13.5	56, 74, 118 61, 89, 149	149	221	1	ETAHEAME
10	15.2-15.5	44, 74, 100, 56, 88, 118, 127	148	292	2	BHEED
11	16.2-16.6	42, 70, 100, 125 56, 88, 113, 143 156, 174	174	318	2	BHEP
12	16.7-16.9	42, 74, 100 56, 88, 131	131	203	1	HEOD
13	18.2-18.4	42, 70, 99 56, 85, 130	130	202	1	HEI
14	19.7-19.8	42, 70, 100, 130 56, 88, 118, 143 174	192	408	3	THEED
15	21.0-21.3	42, 70, 114, 143 56, 99, 130, 174	174	318	2	BHEI

<sup>a</sup> M\* is the molecular weight of the derivatized compound.

<sup>b</sup> *n* OH refers to the number of hydroxyl groups in each compound.

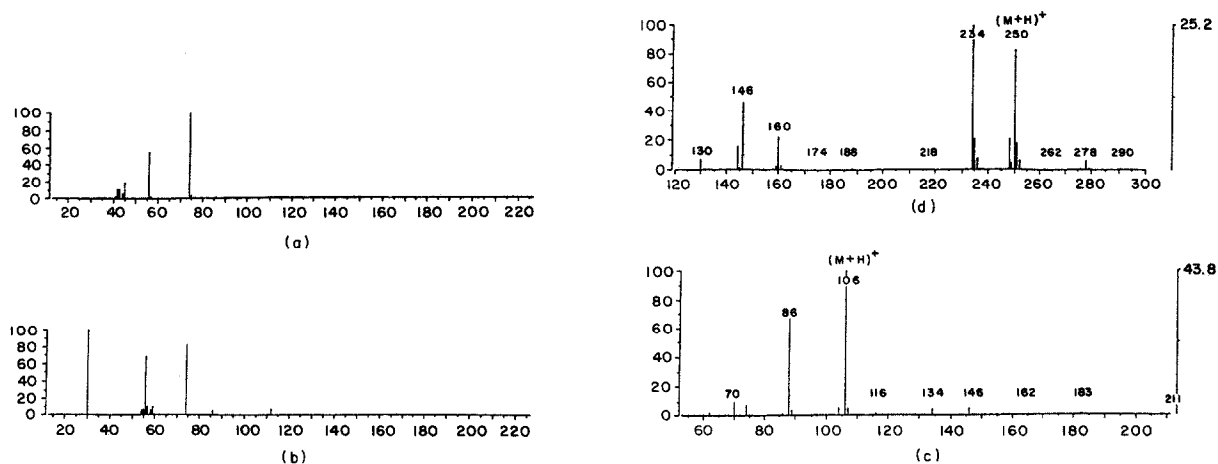


Fig. 3. Mass spectra of DEA. (a) EI spectrum; (b) EI library spectrum; (c) CI spectrum; (d) CI spectrum of silyl derivative.

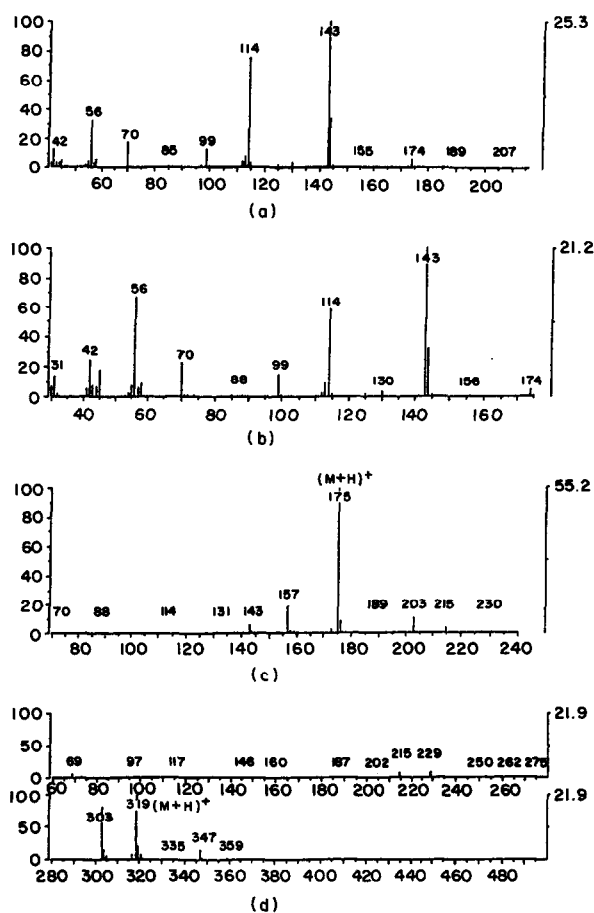


Fig. 4. Mass spectra of BHEI. (a) EI spectrum; (b) EI library spectrum; (c) CI spectrum; (d) CI spectrum of silyl derivative.

ular weight of 149 and three hydroxyl groups. Triethanolamine fits this structure.

The degradation compounds may be conveniently grouped into two categories: low-boiling degradation compounds which elute before DEA and high-boiling degradation compounds which elute after DEA. Other low-boiling degradation compounds include methanol, ethanol, acetaldehyde, acetic acid, methylpyridine, diethyl disulphide, ethyl methyl pyridine and 1,2-dithiane.

Analysis of the gas phase also revealed the presence of ethanol, acetone, butanone, higher molecular weight ketones and some of the other low-boiling degradation compounds found in the liquid phase.

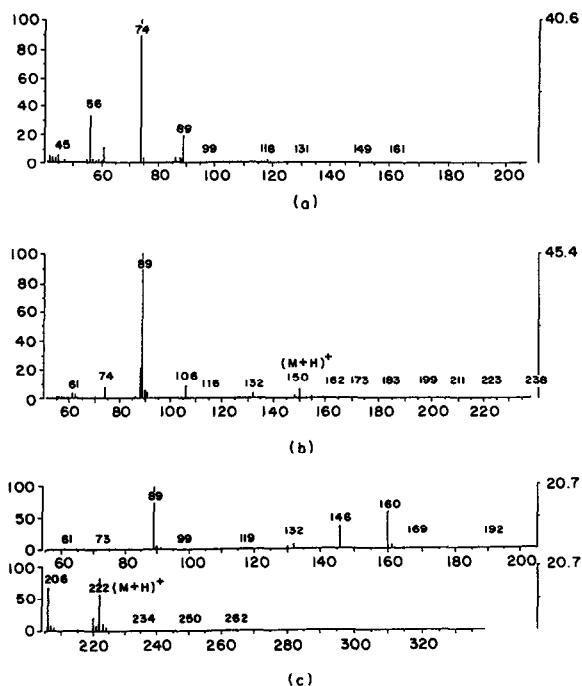


Fig. 5. Mass spectra of peak 9 identified as ETAHEAME. (a) EI spectrum; (b) CI spectrum; (c) CI spectrum of silyl derivative.

In addition to the water-soluble degradation compounds, an insoluble, sticky, light-brown solid product was formed. The product was insoluble in water, ethanol, methanol, toluene, diethyl ether, acetone and carbon disulphide (even at their boiling points). However, boiling dimethylformamide dissolved the product with precipitation occurring as soon as the solution was cooled. The insoluble nature of the solid suggests that it is a polymeric material.

The melting point of the solid was determined using a Kofler hot-stage microscope. A small chip of the solid product was placed on a slide on the hot bench and the temperature was raised at 4°C/min. At the melting temperature, the sample became fluid and the phase change was clearly visible. Four determinations were made for each sample and the average temperatures were recorded. The solid was found to melt in the range 124–138°C with most of it melting above 135°C. The broad melting range is an indication that the solid is impure.

The elemental composition of the solid was determined by the Canadian Microanalytical Laborato-

TABLE II  
ELEMENTAL COMPOSITION OF SOLIDS GENERATED  
IN THE COS-DEA SYSTEM

Element	Composition			
	150°C		180°C	
	% (w/w)	Mole%	% (w/w)	Mole%
C	41.95	28.31	44.11	29.07
H	7.08	57.34	7.26	57.41
N	1.76	1.02	2.94	1.66
O	2.87	1.45	3.94	1.95
S	46.92	11.88	40.14	9.92
Total	100.58	100.00	98.39	100.00

ry (New Westminster, Canada) and the results are given in Table II. The composition of the solid depends on the operating conditions of the degradation runs. The percentage of sulphur decreased with increasing temperature whereas the reverse occurred for the other elements. This trend could be due to the fact that, except for sulphur, all other elements are contained in the amine whose initial concentration increases with increasing operating temperature (due to increased evaporation of water). In the same vein, increasing temperature limits the solubility of COS, and consequently the amount of sulphur available for reactions in the liquid phase. The differences in the elemental compositions could also be related to the purity of the solid produced under the various operating conditions. The degradation was more pronounced as the temperature increased, resulting in higher concentrations of the degradation products. As most of the products do not contain sulphur, the solid recovered from the run conducted at 180°C would contain more sulphur-free impurities (and thus have a lower sulphur content) than the solid recovered at lower temperatures. The ratios of the elements could be calculated from the elemental analyses giv-

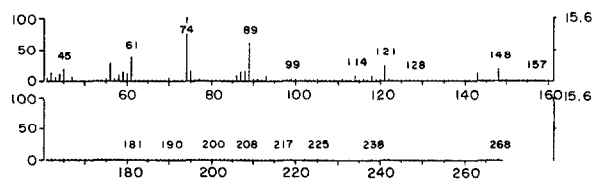


Fig. 6. EI mass spectrum of the solid.

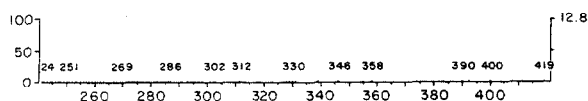
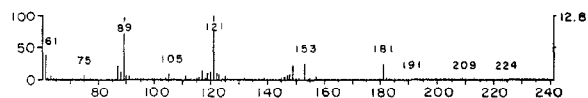


Fig. 7. CI mass spectrum of the solid.

en in Table II. For examples, in the solid generated in the runs at 180°C, the C/S, C/H, C/N, S/O, N/O, C/O, H/N and H/O ratios are 2.93, 0.50, 17.50, 5.09, 0.85, 14.93, 34.57 and 29.48, respectively. These ratios represent approximately an empirical formula of  $C_{15}H_{30}NOS_5$  (empirical weight 400). The high empirical weight of the solid is consistent with its high melting point.

Solid-probe EI and CI mass spectral analyses were performed on the solid product to determine the fragmentation pattern and the molecular weight; the results are shown in Figs. 6 and 7, respectively. The CI mass spectrum shows successive losses of ions of masses 28 and 32. As the solid is rich in sulphur, the ion of mass 32 is most likely sulphur. The ion of mass 28 could either be a carbonyl group ( $C=O$ ) or an ethenyl ( $C_2H_4$ ) group. However, the very low oxygen to sulphur ratio in the solids, the almost equal number of losses of masses 28 and 32 and the high carbon content of the solids point to an ethenyl group as the fragmenting group with mass 28 (IR analysis discussed below did not show any  $C=O$  bonding). It is difficult to identify a molecular ion peak from the CI trace because of the low abundances of the high-molecular-

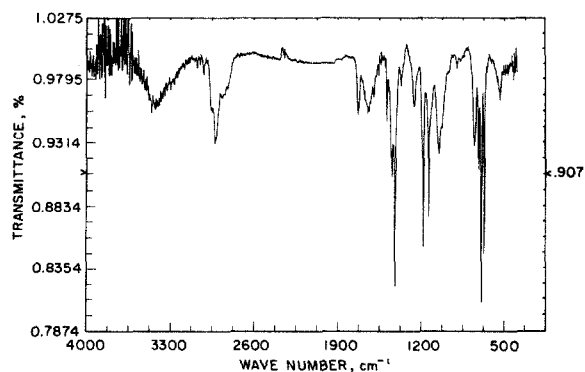


Fig. 8. Infrared trace of the solid.



TABLE III  
FUNCTIONAL GROUP ASSIGNMENTS FOR THE SOLID

Literature IR [26,27]		Sample IR	
Group	Band (cm <sup>-1</sup> ) <sup>a</sup>	Band (cm <sup>-1</sup> ) <sup>a</sup>	Assignment
CH <sub>2</sub> SCH <sub>2</sub>	670– 760 (m)	672, 698 (m)	CH <sub>2</sub> SCH <sub>2</sub>
SH	815– 930 (w)	910 (w)	SH
	2420–2600 (w)	2500 (w)	SH
(CH <sub>2</sub> NHCH <sub>2</sub> )	3100–3500 (m)	3422 (w–m)	(CH <sub>2</sub> NHCH <sub>2</sub> )
	1480–1580 (w)	1492 (w)	
	1100–1200 (m)	1187 (m)	
	1080–1150 (m)	1143 (m)	
–(CH <sub>2</sub> ) <sub>1</sub>	770– 785 (w–m)		
–(CH <sub>2</sub> ) <sub>2</sub>	735– 745 (w–m)	754 (w)	–(CH <sub>2</sub> ) <sub>n</sub>
–(CH <sub>2</sub> ) <sub>3</sub>	725– 735 (w–m)	721 (w–m)	(2 ≤ n ≤ 4)
–(CH <sub>2</sub> ) <sub>4</sub>	720– 725 (w–m)	721 (w–m)	
(CH <sub>2</sub> OH)	1400–1460 (w)	1424 (m)	CH <sub>2</sub> OH
	1260–1350 (w)	1264 (w)	
	1010–1090 (s)	1053 (w)	
	3100–3500 (s)	3422 (w–m)	

<sup>a</sup> The letters, m, s and w refer to absorbances of moderate, strong and weak intensity, respectively.

weight ions. The most abundant peak has a mass of 121, suggesting a molecular weight of 120. The high melting point of the solids is inconsistent with this molecular weight. Further, the absence of ions of mass 149 (M + 29) makes a molecular mass of 120 very unlikely.

The pattern of successive losses of masses 28 and 32 in the CI mass spectra suggests a fragile linear structure containing several covalent bonds with sulphur interspersed between the ethenyl groups. The ease of bond breakage is, perhaps, the reason for not having a prominent molecular ion peak.

To gain an insight into the functional groups in the compound, IR absorption traces were obtained using potassium bromide pellets in a Bomem–Michelson 100 spectrophotometer. The resulting trace is shown in Fig. 8. It should be noted that the absorbances are of weak to medium intensities. Table III shows the assignment of functional groups to the absorption bands in the IR trace.

The analyses conducted allowed the identification of the fragments or functional groups that constitute the solid product. The insoluble nature of the solid and its level of purity were handicaps that prevented further analysis and a more conclusive identification.

The present results are at variance with previous

findings of Orbach and Selleck [11] and Pearce *et al.* [12]. However, it is important to note that the degradation reactions were slow. Even under severe conditions (40% DEA, 180°C), only the low-boiling degradation compounds were formed in appreciable amounts within the first 6 h. At 120°C, only the low-boiling degradation compounds were detected within the first 24 h. As pointed out earlier, perhaps the inability of the previous investigators to detect degradation compounds in COS–DEA systems was due to the short experimental durations and inadequate analytical techniques.

#### Practical implications

The practical significance of COS-induced DEA degradation stems from the fact that degradation affects the absorption of acid gases, plant corrosion, equipment fouling and solution foaming. The major degradation compounds include MEA, BHEED, BHEP, HEOD, HEI, THEED and BHEI. Except for BHEI and HEOD these compounds are known to absorb acid gases (especially CO<sub>2</sub>) and their presence will alter, but not eliminate, the absorptive capacity of DEA solutions. As MEA and diamines are known to be particularly corrosive at high temperatures, hot spots in the plant should be avoided. The most susceptible areas are the reboiler

and the rich side of the lean-rich DEA heat exchanger.

Formation of solid products may also create fouling deposits in piping, heat exchangers and reboilers. As a result, pressure drops will rise and heat-transfer coefficients will fall, leading to overall energy costs for the plants. Cleaning of piping and heat exchangers is also expensive. It is therefore advisable to provide efficient filtration systems.

There is a trend towards utilizing mixtures of alkanolamines for the removal of impurities from gas streams. The results of this study show that if the mixture consists of a primary and a secondary alkanolamine such as MEA and DEA, more degradation products will be formed compared with the single amine system. The increased degradation needs to be taken into consideration in deciding which alkanolamines are to be mixed.

#### CONCLUSIONS

COS can cause degradation of aqueous DEA solutions. Products not previously identified as degradation compounds in CO<sub>2</sub>-DEA systems were detected. This is an indication that COS-induced degradation does not result, entirely, from CO<sub>2</sub> formed by the hydrolysis reaction. The degradation is slow, but may become significant under typical plant conditions, especially over extended periods of time. In addition to the water-soluble degradation compounds, a polymeric, insoluble, sulphur-rich solid product was formed.

#### ABBREVIATIONS

BHEED	Bis(hydroxyethyl)ethylenediamine
BHEI	Bis(hydroxyethyl)imidazolidone
BHEP	Bis(hydroxyethyl)piperazine
DEA	Diethanolamine
EAE	Ethylaminoethanol
EDEA	Ethyldiethanolamine
ETAHEAME	Ethane thioic acid S-[(2-hydroxyethyl)amino]methyl ester
HEA	Hydroxyethylacetamide
HEI	Hydroxyethylimidazolidone
HEOD	Hydroxyethylloxazolidone
HEP	Hydroxyethylpiperazine
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
TEA	Triethanolamine

THEED	Tris(hydroxyethyl)ethylenediamine
TSIM	Trimethylsilylimidazole

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