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NRL Report 5746

A REVIEW OF MONOETHANOLAMINE CHEMISTRY

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June 1, 1962



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CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION	1
PHYSICAL PROPERTIES	1
COMMERCIAL PREPARATION	4
ACTION OF BACTERIA ON MEA	6
PHARMACOLOGY OF MEA	7
PHYSICAL CHEMISTRY OF MEA	8
Structure of Liquid MEA	8
Viscosity and Dielectric Constant of MEA	12
Solubilities of Salts in MEA	13
Basic Function of MEA	14
Thermodynamics of Ionization	17
Heat of Vaporization of MEA	20
CHEMICAL REACTIONS	21
Addition or Salt Formation	22
Reaction with Nitrous Acid	24
Acylation	24
The Formation of Piperazine	27
Cyanoethylation of MEA	27
Reaction of MEA with Aldehydes and Ketones	28
Reaction of MEA with Carbon Dioxide	30
Double Salts	37
Reaction of Iron and MEA	37
Complex Formation of MEA with the Heavy Metals	39
Reducing Action of MEA	41
Reaction of MEA with Oxygen	43
ANALYTICAL	44
Summary of Analytical Methods Pertaining to Amines	44
Isocyanide Test	45
Hofmann's Mustard Oil Reaction	45
Separation of the β -Amino Alcohols	46
Quantitative Estimation of the β -Amino Alcohols	46
Purification of MEA	46
Potentiometric Titration of Free Amine and Amine Carbonate in Carbonated MEA Solutions	46
REFERENCES	47

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ABSTRACT

Monoethanolamine, MEA, is currently the absorbent chemical employed in carbon dioxide scrubbers aboard nuclear submarines, but it is sometimes unstable under operating conditions. This report, part of a more extended effort to improve the operative stability of MEA, is a review of the physical properties and chemical reactions of monoethanolamine and its degradation products.

Among the topics discussed are a compilation of 27 different and suitably referenced physical and chemical properties of MEA, its commercial preparation, action of bacteria on MEA, pharmacology of MEA, physical chemistry of MEA, chemical reactions of MEA, and a section on the analytical processes applicable to MEA. The section on the physical chemistry of MEA is further subdivided into the structure of liquid MEA, viscosity and dielectric constant of MEA, solubilities of salts in MEA, basic function of MEA, thermodynamics of ionization, and the heat of vaporization of MEA. The section on the chemical reactions of MEA is further subdivided into addition or salt formation, reaction with nitrous acid, acylation, the formation of piperazine, cyanoethylation, reaction of MEA with aldehydes and ketones, reaction of MEA with carbon dioxide, double salts, reaction of iron and MEA, complex formation of MEA with the heavy metals, reducing action of MEA, and the reaction of MEA with oxygen.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

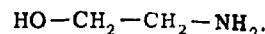
NRL Problem C08-05A
Project SF 013-08-03, Tasks 4092, 4093, 4094, 4095

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A REVIEW OF MONOETHANOLAMINE CHEMISTRY

INTRODUCTION

Monoethanolamine, known as 2-aminoethanol, β -aminoethanol, β -amino ethyl alcohol, ethylal amine (1), and hereafter referred to as MEA, is a 2-hydroxyethyl derivative of ammonia. MEA is usually represented by the formula



Although bifunctional in nature, it enters predominantly into reactions that are characteristic of amines and ammonia. The term "ethanolamines" is commonly used to designate the series of mono-, di-, and trisubstituted 2-hydroxyethyl substituted-ammonias.

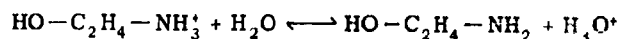
MEA is presently the only absorbent chemical employed in carbon dioxide scrubbers aboard nuclear submarines (38). This chemical is an efficient regenerative absorber of acid anhydride gases, but suffers from the liability of being unstable under scrubber operating conditions. Any improvement of MEA stability is logistically important (34). This report, part of a more extended effort to improve the operative stability of MEA, is a review of the physical and chemical properties and reactions of MEA and its degradation products.

PHYSICAL PROPERTIES

The ethanolamines are colorless, viscous, hygroscopic liquids which are miscible in all proportions with water, and the lower alkanols, but are almost insoluble in non-polar solvents (1-4). The physical and chemical constants of MEA are

1. Mol wt: 61.08; C = 39.33%, H = 11.55%, N = 22.93% (8).
2. Specific gravity: 1.0179^{20/20} (5).
3. a. Density: 1.022^{20/4} g/ml (3,4,9); 1.01170²⁵, 1.00775³⁰, 0.99983⁴⁰, 0.99182⁵⁰, 0.98366⁶⁰, 0.97551⁷⁰, 0.96749⁸⁰, (6,10); 1.0180^{20/4} (1); 1.0170²⁰, 0.9785⁷⁰ (19);
D = 1.03188 - 0.0008038t, t = °C (10).
b. Density of aqueous solutions of MEA at 25°C in g/cc: 0.998^{0.5N}, 0.9992^{2.0N}, 1.0025^{5.0N}, 1.0079^{9.5N}, 1.010^{12.5N}.
4. Melting point: 10.54°C (17); 10.5°C (1,5,6); 10.51°C (10).
5. Boiling point: 172.2°C^{760mm} (1); 171°C^{757mm} (4); 171.0°C^{760mm} (5); 170.8°C, 171.1°C (6).
6. Index of refraction: n_D²⁰ = 1.4539 (1,3,4,6,8,9,17).
7. Solubility: H₂O = ∞, CH₃-OH = ∞, C₂H₅-OH = ∞, (C₂H₅)₂O = 0.72 g/100 g MEA, benzene = sl. sol.; CHCl₃ = sol.; for detailed data on concentration and identity of other organic compounds acting either as solutes or solvents Ref. (7).
8. Azeotropic mixtures with organic liquids: Ref. (7).

9. a. Vapor pressure at 20°C: 0.36 mm Hg (5);
 b. Vapor pressure 100% MEA in mm Hg: 10^{68°C}, 50^{100°C}, 760^{171.0°C} (5b); 24^{87.5°C}, 41^{95.7°C}, 59^{101.8°C}, 76^{107.5°C}, 122^{118.5°C} (60);
 c. Heat of vaporization, $\Delta H_v = 355$ Btu/lb at 1 atm (5b); 12,780 cal/mole (temperature = 50 \rightarrow 180°C) (60); $\log P_{mm} = 2.791$ 1/T + 9.160 (T = °K; 50 \rightarrow 180°C) (60).
10. Flash point = 93.3°C (5); 92°C (8).
11. pK_B of MEA in H₂O solution: 4.498^{25°C} (15); 4.55^{25°C} (11); 4.56^{25°C} (12).
12. pK_A of monoethanolammonium ion in H₂O solution: 9.4980 + 0.0009^{25°C} (15); 9.500^{25°C} (10b); 9.45^{25°C} (13); 9.55^{20°C} (14). $-\log K_A = 2677.91$ 1/T + 0.3869 + 0.0004977T (15). For T = (0 \rightarrow 50°C).
13. pH of 2.5N MEA (commercial grade) solution in H₂O: 12.1 + 0.1^{25°C}, 10.6 + 0.5^{90°C} (20).
14. Hammett Acidity Function: 5% aqueous solution = 12.05, 100% MEA = 15.35 (18).
15. Thermodynamic values for the monoethanolammonium ion,



	Ref. 15	Ref. 16
ΔF°_{298}	+54.205 joule/mole	+12.882 + 0.020 kcal/mole
ΔH°_{298}	+50.540 joule/mole	+12.070 + 0.020 kcal/mole
ΔS°_{298}	-12.29 joule/°K mole	-2.7 + 1 cal, K mole
ΔC_p	-4.9 joule/°K mole	+4 cal/°K mole.

16. Specific conductance (100% MEA): 1.25 $\times 10^{-5}$ mhos at 30°C (17). Specific conductance (100% MEA) ($\times 10^5$): 1.37^{10°C}, 1.93^{20°C}, 2.51^{30°C}, 3.37^{40°C}, 4.34^{50°C}, 5.47^{60°C}, 6.41^{70°C} (53).
17. Dielectric constant (100% MEA): 37.72 at 25°C (17b).
18. Dissociation constant (100% MEA) (18): $K_a = [\text{HO}-\text{C}_2\text{H}_4-\text{NH}_2] [\text{O}-\text{C}_2\text{H}_4-\text{NH}_2] = 10^{-5.1}$ at 20°C.
19. Surface tension (100% MEA), $\gamma =$ dynes/cm: 48.30^{25°C}, 47.79^{30°C}, 46.59^{40°C}, 45.59^{50°C}, 44.41^{60°C}, 43.29^{70°C}, 42.18^{80°C} (6); 49.24^{20°C}, 43.58^{70°C} (19).
20. Surface tension of dilute aqueous MEA solutions at 25°C (10)

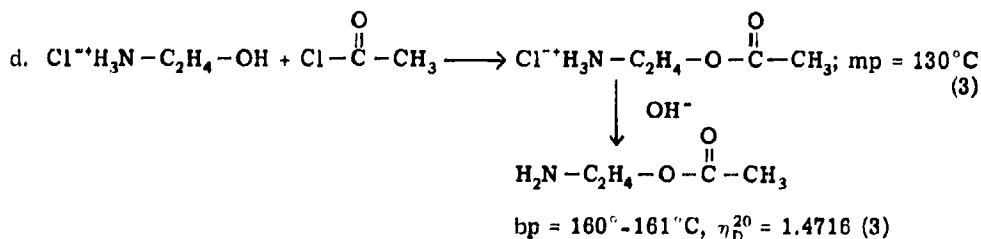
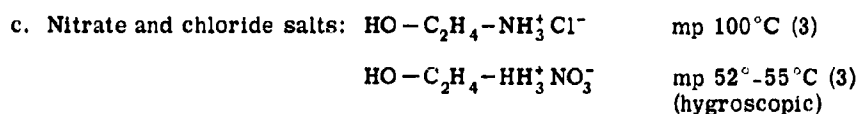
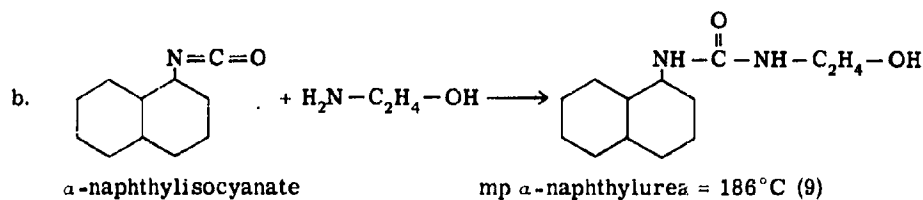
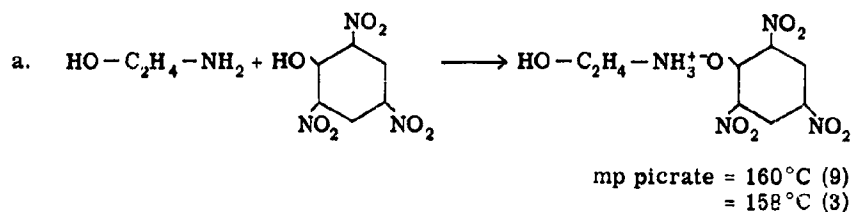
Molal conc	γ , dynes/cm
0.00100	71.37
0.01950	71.37
0.03000	71.35
0.06000	71.26
0.10000	71.00

21. Total surface energy (100% MEA) $\mu =$ ergs: 81.61^{25°C}, 81.65^{30°C}, 81.57^{40°C}, 81.69^{50°C}, 81.62^{60°C}, 81.62^{70°C}, 81.63^{80°C} (10).

22. Parachor: $P = \gamma^{1/4} M / (d_1 - d_v)$: 159.1²⁵°C, 159.4³⁰°C, 159.6⁴⁰°C, 160.0⁵⁰°C, 160.3⁶⁰°C, 160.6⁷⁰°C, 160.9⁸⁰°C (10).

23. Viscosity: 0.19346 poise at 25°C (17b); 24.1 cps at 20°C (5b).

24. Derivatives for the identification of MEA:



25. Beilstein reference: Vol. IV p. 274 (21).

26. C_p of MEA-aqueous solutions in kcal/kg°C (22).

T(°C)	8% Solution	18% Solution
20	0.795	0.752
30	0.802	0.763
40	0.802	0.774
50	0.814	0.786
60	0.820	0.797
70	0.826	0.809
80	0.832	0.820

27. Coefficient of thermal conduction in kcal/meter-hr-°C (22)

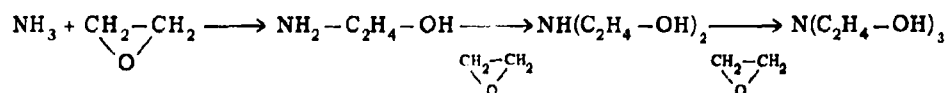
T(°C)	8% Solution	18% Solution
20	0.468	0.422
30	0.478	0.431
40	0.488	0.441
50	0.498	0.449
60	0.508	0.458
70	0.517	0.466
80	0.525	0.472

COMMERCIAL PREPARATION

MEA was first produced commercially in 1931 (2) by the reaction of ammonia with an ethylene halohydrin.



Patents utilizing this process have been assigned to the Girdler Corporation (39) and to the Nitrogen Division of the Allied Chemical Corporation (40). It is currently being manufactured, under patents assigned to Carbide and Carbon Chemicals Company, by the ammonolysis of ethylene oxide (41,42). A small amount of water is essential to the reaction. The proportion of mono-, di-, and triethanolamine present in the reaction mixture as products depends on the ratio of the reactants used. A large excess of ammonia favors the formation of MEA.

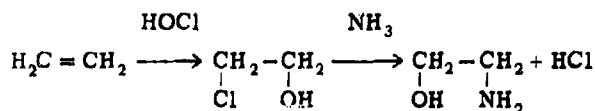


Specifications of the MEA produced by this method and offered for sale by Carbide and Carbon Chemicals Company in 1946 are listed in Table 1.

Table 1
Properties of Commercial MEA

Density = 1.017-1.027 ^{20 20}
Boiling Range = 160°-176°C
Purity 98% by weight min
Color (APHA) = 20 max

The Jefferson Chemical Company produces MEA by the ammonolysis of ethylene chlorohydrin obtained as an intermediate in the separation of ethylene from natural gas (81).



Their product is described (82a) as a clear, water white, hygroscopic liquid with a distinct ammoniacal odor and possessing an equivalent weight of 61.0-63.0. The other specifications are listed in Table 1. The Dow Chemical Corporation is also a major producer and supplier of MEA (82b) (the specifications of Dow MEA offered for sale in 1961 is listed in Table 2) as is the Olin Mathieson Chemical Corporation.

Table 2
Dow Chemical MEA

Colorless liquid
Boiling Range (5-95% MEA at 760 mm) = 170°-172°C
Sp. Gr. = 1.015 ^{25/25}
Refractive Index = 1.453 ^{25°C}
Freezing Point = 10.3°C
M.W. = 61.1

However, MEA purchased by the Department of Defense must conform to Military Specification MIL-E-50011 as amended 21 July 1959, Table 3.

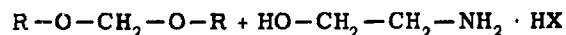
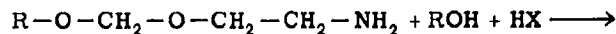
Table 3

$d_{20}^{20} = 1.017-1.021$
Distillation Range = 165°-175°C (90% min by vol.)
Color APHA = 20 max
Equivalent wt = 61-63
H ₂ O content = 1.0% by weight max
MEA content = 98% by weight min
DEA content = 1.5% by weight max
TEA content = 1.0% by weight max
Fe = 0.003% by wt max

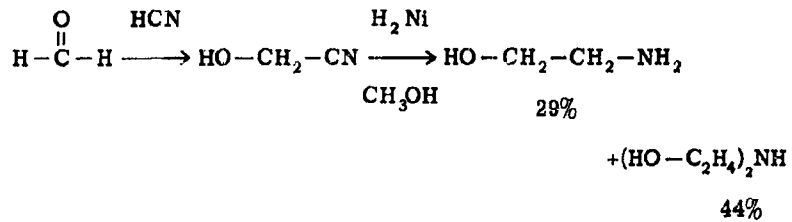
Sharples Chemicals has patented a process wherein a mixture of ammonia and ethylene oxide, in the ratio 15:1, are pumped into a reaction chamber at 130°C and 1600 psi to obtain a reaction product consisting of 78.3% MEA, 16% DEA, and 4.4% TEA (43).

The E. I. du Pont de Nemours Company is not an active commercial producer of MEA; however, they possess a number of patents for its manufacture. Several of these patents are outlined below:

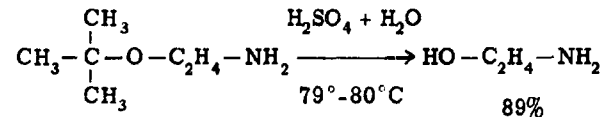
1. By treatment of an amino acetal or formal with an alcohol and acid (83a)



2. By the catalytic reduction of an aldehyde or ketone cyanohydrin in the presence of an inert solvent (83b).



3. By hydrolysis of an ether (83c)



ACTION OF BACTERIA ON MEA

MEA is composed of the elements most essential to life and may, therefore, be expected to be either a metabolic product or precursor. It may be formed in mammalian tissues by the enzymatic decarboxylation of serine, and decarboxylases occur widely in microorganisms (23, pp. 499 and 502). Oxidation of the MEA carbinol group will yield glycine, an essential amino acid. The ability of microorganisms to oxidatively ferment amino alcohols to the corresponding acid has been employed. For example, high yields are claimed for acetobacter seeded suspensions of amino alcohols that are aerated with oxygen-rich gases (27). Most bacteria cannot oxidize MEA in their resting phase. However, pseudomonas aeruginosa shows a high rate of oxygen consumption, even in its resting phase. This high rate has been considered "not so much as due to respiration (metabolic processes) as to multiplication - which is possible even on such simple media" (28).

Some bacteria do not oxidize MEA to glycine. The following are reported to degrade MEA anaerobically to form ethylene glycol and ammonia (29).

1. *Cl. flabelliferum*
2. *Cl. hystoliticum*
3. *Cl. acetobutylicum*
4. *Cl. iodophilum*
5. *Cl. butyricum*
6. *Cl. saccharobutyricum*
7. *Cl. tetani*
8. *Cl. perfringens*
9. *Bacillus teras*

The Following species were investigated and found to be inactive in the anaerobic degradation of MEA.

1. *Cl. sporogenes*
2. *Bacillus saprotoxicus*
3. *Cl. tetanomorphum*
4. *Bacillus indolicus*
5. *Proteus vulgaris*

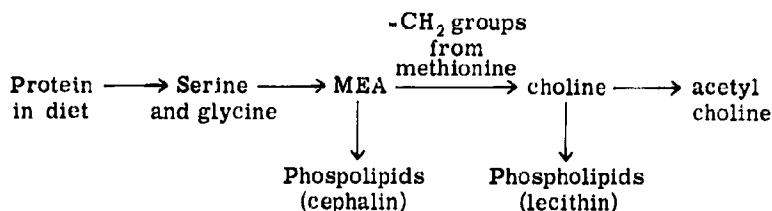
It is interesting to note that freshly prepared MEA solutions in submarine carbon dioxide scrubbers, after periods of nonuse have sometimes lost their ability to absorb carbon dioxide and released ammonia to the atmosphere when started again. However, the possibility of a bacterial degradation mechanism has not been investigated (30).

PHARMACOLOGY OF MEA

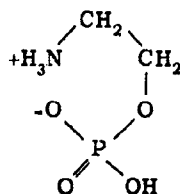
The ethanolamines show marked physiological activity. MEA is believed to inhibit cell growth, produce constriction of the blood vessels, convulsions, dyspnea, increased blood pressure, and stimulation of the heart (2). Toxicological data on MEA, using rats and rabbits as test animals have been published by Union Carbide and Chemicals Corporation (5b). The single oral dose that was lethal to 50% of the exposed rats (LD_{50}) varies from 2.14 to 2.74 grams MEA per kilogram rat body weight. Single skin absorption, a 24-hour skin contact with the liquid chemical, on rabbits proceeded to the extent of one-milliliter MEA for every kilogram of body weight. Single inhalation of the saturated mist from air saturated by MEA vapor at 170°C killed 1/3 of the test rats in a four-hour period. In rabbit eyes, addition of liquid MEA produced severe surface damage to the eyeballs.

B. H. Caminita (86) performed an extensive literature search on the toxicology of MEA in 1956. Although the toxicological effects of MEA on various mammals, including man, are discussed, only a digest of the effects on humans will be reported.

MEA is a normal intermediate in mammal metabolism; however, the various species differ in the manner in which anabolism and catabolism proceed. Consequently, only those studies performed on homo sapiens or possibly primates are of value. The following general metabolic mechanism has been postulated for mammals.



Free MEA is excreted in the urine and through the sweat glands as a waste product to the extent of 0.162 ± 0.088 mg/day/kg body weight for male and 0.491 ± 0.182 mg/day/kg body weight for female humans. An unknown quantity is excreted with the feces and any remainder is "incorporated" into various metabolic intermediates. It exists in tissues as the ethanolanmonium phosphate ester, EAP.



MEA salts are considered to be less toxic than the free base. It is claimed that internal administrations of 2.050 grams of MEA to a "normal" male produced no adverse effects but resulted in increased urinary excretions of the free base and increased activity of fecal thiaminase. The same quantity administered to a terminal case of heptamona over a six-hour period resulted in increased urinary secretion of MEA. The gross autopsy "showed

nothing of note" except an enlarged liver and death was attributed to bronchopneumonia and pulmonary edema. An aqueous solution of MEA oleate containing "free" MEA and benzyl alcohol is administered intravenously as a sclerosing agent in the treatment of varicose veins. No toxic effects have been reported and all deaths occurring during treatment have been attributed to allergic or induced allergic reactions. One autopsy showed pulmonary congestion with edema, a congested liver, an enlarged spleen, and no evidence of emboli. Eosinophilia and an increase in band cells have been found in another patient undergoing (a possibly successful) treatment. MEA is narcotic in high concentrations. No studies were reported of the tolerance of humans for MEA in the air.

The tolerance of dogs, cats, guinea pigs, rabbits, rats, and mice to MEA vapor concentrations in air that ranged up to 2.47 milligrams per liter was recently investigated (84). Rats, rabbits, and mice were less susceptible than guinea pigs but more susceptible than cats and dogs to MEA vapor in the air. MEA vapor produced, in the exposed animals, respiratory disturbances which varied in severity according to the concentration of the vapor in the air. However, ocular irritation was negligible. Post-mortem examination of the animals that died (no dogs and cats) revealed acute pulmonary irritation characterized by edema, hyperemia, extravasation of erythrocytes, and emphysema. Other visceral lesions, among which nonspecific degenerative changes in the liver and kidneys were prominent, were also present. Animals that survived, but were killed for examination several days after exposure had lesions of acute bronchitis and pneumonia superimposed upon those of injury to pulmonary tissue. The operator of the animal test chamber complained of nausea and mild conjunctivitis.

PHYSICAL CHEMISTRY OF MEA

Structure of Liquid MEA

MEA is composed of a polar hydroxyl group and a polar amino group joined by a two-carbon alkyl chain. A salient property of such functional groups is their ability to hydrogen-bond to like and unlike polar groups. These polar groups may be expected to control the physical properties of the compound. For example, Fisher-Hirschfelder ball atomic models of the molecule, Figs. 1-3 suggest highly probable configurations (i.e., with C-H, O-H, and N-H bonds so spatially oriented so that the molecule occupies a minimum energy state) favoring intermolecular hydrogen-bonding. However, a configuration equally as probable, results in the possibility of intramolecular hydrogen-bonding and five membered ring formation (Fig. 4). Such five membered ring formation on the part of a major portion of the molecular population would if it occurred decrease the intermolecular bonding energy and be reflected in the values of viscosity, boiling point, and density of MEA.

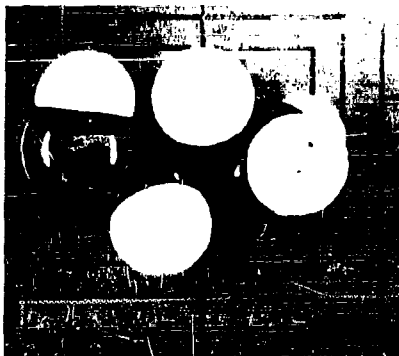


Fig. 1 - Fisher Hirschfelder Model of extended form of MEA (side view)

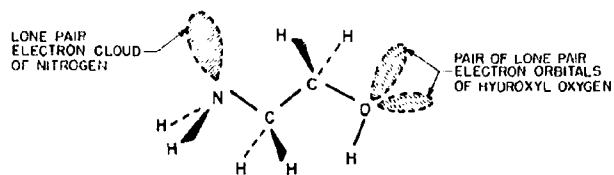
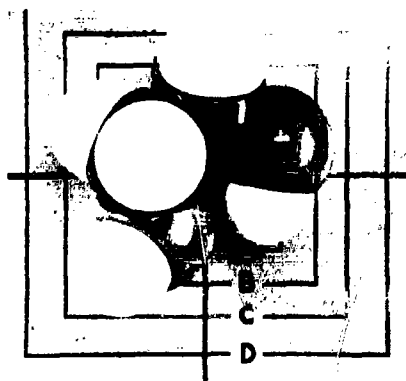
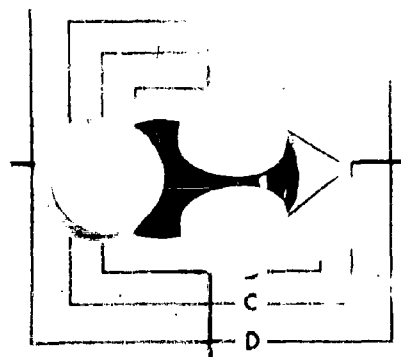
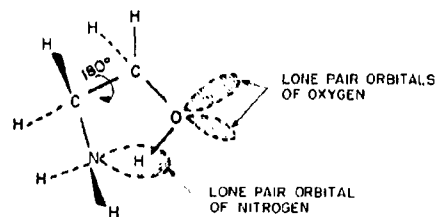


Fig. 2 - Skeletal configuration of molecule in Fig. 1

Fig. 3 - Molecule of Fig. 1 rotated 90° (bottom view)



(a)



(b)

Fig. 4 - Rotation of C-NH₂ fragment of molecule in Fig. 1 180° about C-C bond superimposes nitrogen lone pair electrons on hydroxyl hydrogen atom

It is possible to obtain an insight into the structure of liquid MEA by an examination of the trends exhibited by the values of density, boiling point, and viscosity of n-butane and a series of derivatives in which either one or both of the n-butane terminal methyl groups have been substituted by hydroxyl or amino groups (Table 4). Compounds 1-6 have similar molecular weights. By assuming that the van der Waals interactions are similar for the entire group, any deviations of the physical properties mentioned become a function of the polar end-groups.

Table 4
Physical Properties of Substituted n-Butanes

Compound	Mol wt	Density (g/cm ³)	Boiling point (°K)	Viscosity (cps)
1. CH ₃ -CH ₂ -CH ₂ -CH ₃	58.2	0.60 ^{0°C}	272.5	—
2. CH ₃ -CH ₂ -CH ₂ -NH ₂	59.1	0.718	322.6	0.35 ^{25°C}
3. CH ₃ -CH ₂ -CH ₂ -OH	61.1	0.804	370.9	2.26 ²⁰
4. NH ₂ -CH ₂ -CH ₂ -NH ₂	61.1	0.900	390.1	1.54 ²⁵
5. HO-CH ₂ -CH ₂ -OH	62.1	1.113	470.5	19.9 ²⁰
6. HO-CH ₂ -CH ₂ -NH ₂	61.1	1.022	{ 444.1 (171.0°C)	19.3 ²⁵
7. HO-CH ₂ - $\overset{\text{C}_2\text{H}_5}{\text{CH}}$ -NH ₂	89.1	0.944	(174.8°C)	—
8. H-O-H	18.0	1.000	373.1	1.00

The density and boiling point data of Table 4 are presented graphically in Fig. 5, in which the respective boiling points or densities are plotted against the number of CH₃ groups in n-butane that have been replaced by -OH or -NH₂ groups. The fact that the increases in both boiling point and density observed in the hybrid MEA are higher than the averages of the corresponding increases in glycol and ethylenediamine respectively suggests that the presence of the unlike polar groups enhances intermolecular interaction. The alternative intramolecular interaction to cause ring closure might increase liquid densities, but would not be expected to cause an abnormal increase in the boiling point.

The density changes may also be discussed in terms of the increments to molecular volume observed in passing from -OH substitution to -NH₂ substitution in a given molecule. Between n-propyl alcohol and n-propylamine this difference is 6.3 cm³/mole, and between glycol and ethylenediamine it is 12.0 cm³/mole (or 6.0 cm³ per -NH₂ group). On passing from n-propyl alcohol to MEA, however, the increment is only 4.0 cm³/mole, which again indicates enhanced molecular interactions for the hybrid molecule.

The effect of the heterofunctional substitution in MEA on viscosity is more spectacular than the effects on the boiling point and density. The viscosity of MEA is not the average of the viscosities of ethylenediamine and glycol (1.54 cp at 25°C and 19.9 cp at 20°C, respectively) but is actually greater (19.3 cp at 25°C or >20 cp at 20°C) than that of glycol. This evidence supports the conclusion that strong intermolecular bonding rather than intramolecular ring closure is the preponderant type of interaction between the polar groups of MEA.

These conclusions are also supported by an infrared study of solutions of MEA in carbon tetrachloride, coupled with measurements of colligative properties (47). It was concluded that MEA showed only intermolecular H-bonding in such systems.

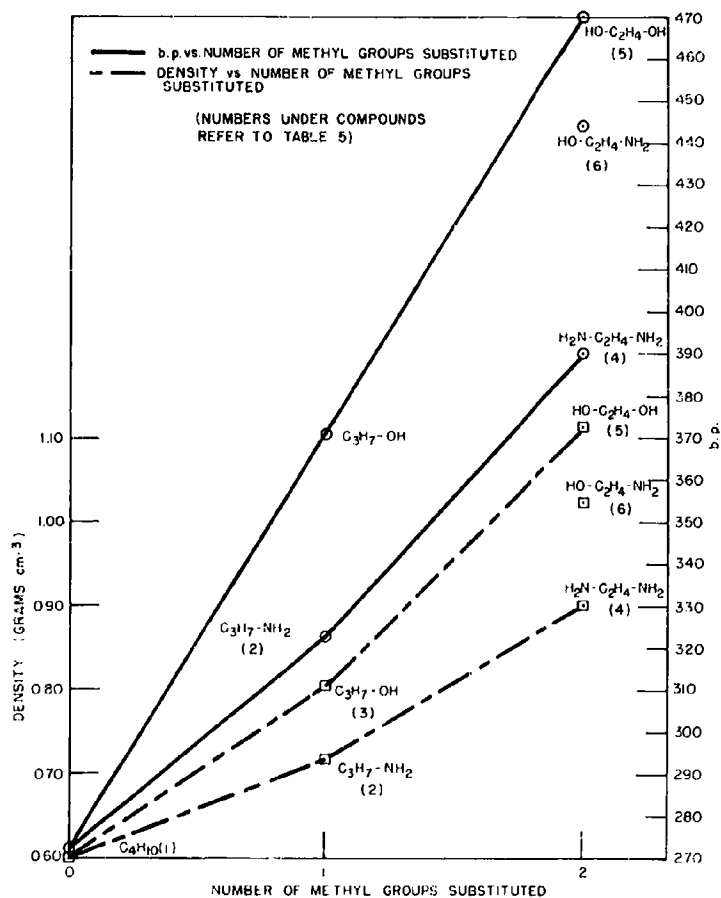


Fig. 5 - Trends in the boiling point and density of the compounds formed when the terminal methyl groups of n-butane are variously substituted with hydroxyl and amino groups

Recently the parachor method, based on Gibling's predictions, has been applied to the study of liquid MEA (48). Gibling, who obtained the parachors of a homologous series of primary, secondary, and tertiary amines, ethers, alkyl chlorides, concluded that the configuration of an alkyl chain is determined primarily by the polarity of that part of the molecule to which it is attached (49). The following values were obtained for MEA.

$$d^{20} = 1.0170 \quad \gamma^{20} = 49.24$$

$$d^{70} = 0.9785 \quad \gamma^{70} = 43.58$$

$$P = \frac{\gamma^{1/4} M}{(d_1 - d_v)} = 159.1^{20}, 160.5^{70}$$

These values of the parachor correspond closely to those obtained by an earlier investigation: 159.1²⁵, 160.67⁰ (1⁰). On the basis of the experimental parachor of MEA coupled with Gibling's predictions it was postulated that the molecules are associated in the liquid state. The parachor of MEA, using Sugden's values (85) for the individual atomic parachors is 161.8.

Viscosity and Dielectric Constant of MEA

High dielectric constant organic solvents such as acetonitrile ($\text{CH}_3-\text{C}\equiv\text{N}$, $D = 36$) and nitromethane (CH_3-NO_2 , $D = 37$) have been found to be strong ionizing solvents. Since MEA possesses a similar dielectric constant and two functional groups capable of solvating ions, it would also be expected to be a strong ionizing solvent. However, conductivity measurements of variously substituted methylammonium chlorides and picrates (including a quaternary picrate and nitrate) yielded equivalent conductivity versus concentration curves typical of weak electrolytes and dissociation constants that ranged from 10^{-5} to 10^{-8} . Some of these binary salts were reported to be much stronger electrolytes in nitromethane and acetonitrile. Conductivity measurements reflect ion mobility, which in turn is a direct function of the solvent viscosity. The viscosity of MEA (19.35 centipoises at 25°C) is 32 times that of nitromethane, 65 times that of acetonitrile, and 19.3 times that of water. In dilute solution it was found that the Debye-Huckel equation reduced to $\log f_{\pm} = -1.532 \sqrt{c}$, where c is the stoichiometric concentration. This, the investigators concluded, implies complete dissociation, since the stoichiometric concentration is substituted for the ionic concentration (17b).

The depressant effect of viscosity on the conductivities of nominally strong electrolytes in anhydrous MEA was observed in later investigations with inorganic salts (53,54). Generally, temperature-induced decreases in dielectric constants are compensated by parallel increases in degrees of dissociation and in solvent fluidities. The effect of temperature on the specific conductivities of solutions of yttrium acetate, $\text{Y}(\text{C}_2\text{H}_3\text{O}_2)_3$, in MEA and ethylenediamine may be observed in Table 5.

Table 5
Variation of Specific Conductivity of $\text{Y}(\text{C}_2\text{H}_3\text{O}_2)_3$ with Temperature

T°C	Specific Conductivity			
	$\text{H}_2\text{N}-\text{C}_2\text{H}_4-\text{NH}_2$ ($D = 16$, $\eta = 1.54$)		$\text{HO}-\text{C}_2\text{H}_4-\text{NH}_2$ ($D = 37.72$, $\eta = 19.34$)	
	Pure Solvent	0.60N Salt Soln.	Pure Solvent	0.48N Salt Soln.
20	3.53×10^{-6}	0.98×10^{-5}	1.93×10^{-5}	1.61×10^{-3}
70	4.94×10^{-6}	1.62×10^{-5}	6.41×10^{-5}	4.43×10^{-3}

It was further postulated that the addition of small quantities of water to the anhydrous solution will substitute solvent molecules in the solvation shell of the cation to create a smaller and more mobile species (53).

None of the electrolyte solutions in MEA studied in these investigations (17b,53,54) displayed minima in their equivalent conductivity versus concentration curves. Fuoss and Kraus have interpreted such minima as ion pair association (+-) followed, at higher concentrations, by triplet ion formation (+-, +--). They further postulated that in solvents with dielectric constants exceeding 40 (MEA: 37.72) there is a minimum probability of ion pair formation (55).

Many salts which coordinate strongly with water form addition compounds with the lower alcohols including MEA (2). Metallic halides which react in this manner are soluble in the alcohol. Typical coordination compounds of alcohols are decomposed on the addition of water, which displaces the alcohol from the coordination sphere of the cation.

Solubilities of Salts in MEA

In this review the physical properties of MEA are interpreted in terms of substituted water and ammonia joined by a dimethylene bridge. The solubilities of inorganic salts in this solvent, in the prototypes water and ammonia, and in the analogs ethyleneglycol and ethylenediamine are given in Table 6 for comparison.

Table 6
Solubilities

Salt	Grams Salt/100 Grams Solvent				
	H ₂ N C ₂ H ₄ NH ₂ D = 16.0	MEA D = 37.72	HO C ₂ H ₄ OH D = 37.7	NH ₃ D = 16.9	H ₂ O D = 78.5
25°C (56)					
NaCl	0.33	1.86	7.15	3.02	35.98
NaBr	54.4	33.6	35.4	138.0	94.6
NaI	34.6	22.0	107.4	161.9	183.7
KCl	0.014	0.27	5.18	0.04	35.85
KBr	0.78	3.27	15.5	13.50	68.3
KI	74.9	42.3	49.9	182.0	148.7
NaClO ₃	52.8	19.7	16.0		106
NaClO ₄	30.1	90.8	75.5		209.6
KClO ₃	0.145	0.30	1.21	2.52	8.6
KClO ₄	2.81	1.36	1.03		2.07
LiCl	1.39	30	14.3	1.41 ^{0°C}	84.66
LiBr	2.41	60	39.4		170
CaCl ₂	0.00	14.0	20.6		83
SrCl ₂	0.00	19.5	36.4		55.8
BaCl ₂	0.22	45.2	36.8	0.00	37.2
HgCl ₂	0.4	decomposed			7.2
Hg(C ₂ H ₃ O ₂) ₂	0.186	decomposed	17.8		25 ^{10°C}
30°C (53)					
La(NO ₃) ₃	2.45	7.75			
NdBr ₃	0.936	3.20			
NdI ₃	2.53	1.93			
Nd(C ₂ H ₃ O ₂) ₃	7.81	18.4			151 (1)
Y(C ₂ H ₃ O ₂) ₃	6.26	17.6			

As would be expected from the interpretation of the structure of liquid MEA (vide ante), solubilities in this solvent tend to occupy a position intermediate between those in ethylenediamine and ethylene glycol. For the less soluble salts the values approximate the geometric mean of the solubilities in the latter two solvents. For the more soluble salts the solubilities are unpredictable. Lithium salts form solutions of extraordinary viscosity (56). Solubilities of the alkaline earth metal chlorides reflect the formation of addition compounds with -OH groups. Mercury compounds are reduced by MEA to metallic mercury (see MEA as a reducing agent). The acetates listed are covalent compounds and their solubilities reflect the solvent dielectric constant (53). A comparison of the dielectric constant of MEA with those of related compounds is given in Table 7.

Table 7
Dielectric Constants

Compound	Dielectric Constant 25°C
$\text{CH}_3-\text{O}-\text{H}$	32.63
$\text{CH}_3-\text{CH}_2-\text{O}-\text{H}$	24.30
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{O}-\text{H}$	20.1
$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$	16.0
$\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$	37.7
$\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_2$	37.72
NH_3	16.9
$\text{H}-\text{O}-\text{H}$	78.5
CH_3-NH_2	9.4

Basic Function of MEA

The basicity of the amino functional group of an alkyl amine is a function of the availability of the nitrogen lone pair electrons. This availability is in turn influenced by inductive effects acting on the carbon-nitrogen bond. The dipole moment of the C-N bond is 0.4 Debyes in the direction of the more electronegative nitrogen. It may be postulated, a priori, that an alkyl amine possessing radicals exhibiting positive inductive effects (+I) on the C-N bond will influence the pK_B of the amino group in a positive manner. Similarly, any radical exhibiting a negative inductive effect (-I) will decrease the nitrogen basicity. Alkyl radicals such as the methyl and ethyl groups have a +I effect, while -OH and -NH₂ groups have a -I effect when in proximity to the C-N bond. A study of the influence of these radicals on pK_B when substituted on the α and/or β carbon hydrogens in ethylamine has been made (11). Table 8 contains an expanded version, viz., the effect on pK_B of methylamine when one to three of its hydrogens are variously substituted with methyl ethyl, hydroxymethylene, etc., radicals. The decreased basicity of MEA over that of ethylamine is primarily due to the -I effect of the β -hydroxy group.

Further evidence for the basicity depressant effect of an hydroxyl group in proximity to an amino group was obtained by an investigation of a series of straight chain amino alkanols with two to six methylene groups separating the polar ends (14). The pK_A values

Table 8
Effect of Structure on pK_B of Amines

Compound	Reference	pK_B (25°C)
$H-CH_2-NH_2$	4	3.36
$CH_3-CH_2-NH_2$	11	3.25
$H_2N-CH_2-CH_2-NH_2$	13	3.92 (pK_{B1})
$HO-CH_2-CH_2-NH_2$	11, 13	4.55
	12	4.56
$\begin{array}{c} C \\ \\ HO-C-C-NH_2 \end{array}$	11	4.57
$\begin{array}{c} C \\ \\ C \\ \\ HO-C-C-NH_2 \end{array}$	11	4.48
	12	4.45
$\begin{array}{c} C \\ \\ HO-C-C-NH_2 \\ \\ C \end{array}$	11	4.28
	12	4.29
$\begin{array}{c} OH \\ \\ C \\ \\ HO-C-C-NH_2 \\ \\ C \end{array}$	11	5.24
$\begin{array}{c} OH \\ \\ C \\ \\ HO-C-C-NH_2 \\ \\ C \\ \\ C \end{array}$	11	5.20
$\begin{array}{c} OH \\ \\ C \\ \\ HO-C-C-NH_2 \\ \\ C \\ \\ OH \end{array}$	11	5.97

(Table 9) of the corresponding ammonium ions were determined potentiometrically at 20°C, and an empirical relation describing pK_A as a function of the distance d , in angstrom units, between O and N was derived.

$$pK_A = 11.3 - \frac{7.3 A}{d} \quad (20^\circ C)$$

As the distance between O and N is increased, pK_A for an ω -amino-n-alcohol approaches 11.3 asymptotically. To emphasize the -I effect of the hydroxyl group, consider hydroxylamine ($\text{HO}-\text{NH}_2$), a compound lacking an insulating methylene group. The covalent inter-nuclear distance between O and N is 1.36 Å.

$$pK_A = 11.3 - \frac{7.3 \text{ \AA}}{1.36 \text{ \AA}} = 11.3 - 5.37 = 5.9$$

which corresponds to a pK_B value of 8.1 ($pK_W = 14.0$). pK_B for hydroxylamine (4, p. 1382) is 7.97 at 25°C; compare with pK_B (NH_3) whose value is 4.74 (Table 10).

Table 9
 pK_A Values of Homologous
 ω -Amino-n-Alcohols

Compound	pK_A (20°C)
$\text{HO}-\text{C}_2\text{H}_4-\text{NH}_2$	9.55
$\text{HO}-\text{C}_3\text{H}_6-\text{NH}_2$	10.16
$\text{HO}-\text{C}_4\text{H}_8-\text{NH}_2$	10.35
$\text{HO}-\text{C}_5\text{H}_{10}-\text{NH}_2$	10.52
$\text{HO}-\text{C}_6\text{H}_{12}-\text{NH}_2$	10.62

Table 10
 pK_B of Various Substituted
Ammonias

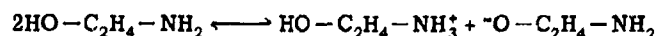
Compound	pK_B
$\text{H}-\text{NH}_2$	4.74
CH_3-NH_2	3.36
$\text{CH}_3-\text{CH}_2-\text{NH}_2$	3.25
$\text{HO}-\text{NH}_2$	7.97
$\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_2$	4.55

Table 11
 K_A of Alcohols

Compound	K_A
$\text{H}-\text{OH}$	1.8×10^{-16}
CH_3-OH	1×10^{-17}
$\text{CH}_3-\text{CH}_2-\text{OH}$	7.3×10^{-20}

We have seen that the positive inductive effect of an alkyl group on a substituted ammonium ion resolves itself by decreasing the acid dissociation constant of that ion. An identical mechanism is operative in an alkyl substituted water as Table 11 indicates (48, p. 139). It is evident from Table 10 that the positive inductive effect of an ethyl group is compensated by the negative inductive effect of the hydroxyl group on the β -carbon. Similarly, the K_A of the MEA hydroxyl group closely approximates that of its prototype, water. Release of a proton, upon autoionization, implies the presence of a base

capable of accepting it to form a conjugate acid, and in pure water, H_2O fills that role. However, MEA possesses a basic substituent that is much stronger than ethyl-substituted water, so that ionization in 100% MEA follows the scheme.



Such ionization may be termed a "push-pull" effect on the part of $-\text{NH}_2$ group. The ionization constant K_S for anhydrous MEA was determined electrometrically at 20°C (18).

$$K_S = [\text{HO}-\text{C}_2\text{H}_4-\text{NH}_3^+][^-\text{O}-\text{C}_2\text{H}_4-\text{NH}_2] = 10^{-5.1} \quad \text{dielectric constant} = 37.72$$

Compare with pure water

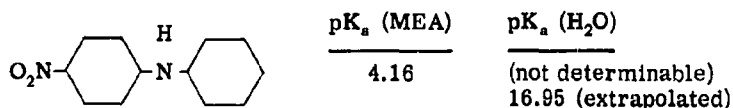
$$K_W = [\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14.2} \text{ at } 20^\circ\text{C} \quad \text{dielectric constant} = 80.36$$

Also it was postulated that K_a of the MEA hydroxyl group was of the order of 10^{-17} . Since the amphoteric properties of MEA are dominated by the amine functional group, bulk MEA provides a more basic solvent environment than that of water.

The Hammett acidity function H_- has been defined as the ability of a particular solution to accept a proton from a specified reference indicator acid (52). In dilute aqueous solution the acidity function is equal to the pH value.

$$H_- = \left[-\log [H^+] \frac{f_{A^-}}{f_{HA}} \right] = pK_a + \log \frac{[A^-]}{[HA]}$$

where; f represents the activity coefficient (ratio fixed for all acids of same charge type; Hammett postulate), $[HA]$ and $[A^-]$ represent concentrations of the indicator acid and its conjugate base anion, and pK_a is the negative logarithm of the acid dissociation constant of the indicator acid. H_- varies from 12.05 for 5% aqueous MEA to 15.35 for 100% MEA at 20°C (18). For comparison, the pH of a 2.5% aqueous MEA (commercial grade) solution at 25°C is 12.1 (20). The ionization constants K_a of acids too weak to be affected by H_2O may be determined by using $Na^+ \cdot O-C_2H_4-NH_2$ in anhydrous MEA and extrapolating pK_a in MEA to pK_a in H_2O . For example



Thermodynamics of Ionization

The ionization of the ammonium ion of MEA into the corresponding base and hydronium ion has been investigated by a calorimetric method (16) and a potentiometric method (15) to yield similar values for the thermodynamic parameters, ΔF° , ΔH° , and ΔS° at 298.1°K (Table 12).

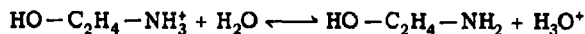


Table 12
Thermodynamic Values of MEA

	(Ref. 15)	(Ref. 16)
ΔF°_{298}	12,970 cal/mole	12,882 cal/mole
ΔH°_{298}	12,080 cal/mole	12,070 cal/mole
ΔS°_{298}	-2.939 cal/mole-°K	-2.72 cal/mole-°K
ΔC_p_{298}	-1.17 cal/mole-°K	+4 cal/mole-°K
K_A_{298}	3.18×10^{-10}	—
K_B_{298}	3.18×10^{-5}	—

The values from Ref. 16 have not been corrected to infinite dilution; it was assumed that the resulting error was small. The potentiometric results of Ref. 15 were extrapolated to zero ionic strength. The general equation used to express such results (70) is

$$-\ln K_A = \frac{A}{T} + B - \frac{\Delta C_p}{R} \ln T$$

This expression was modified to

$$-\log K_A = \frac{A}{T} + B + CT$$

from which form the other thermodynamic parameters may be derived.

$$\Delta F^\circ = 2.3026 R (A + BT + CT^2)$$

$$\Delta H^\circ = 2.3026 R (A - CT^2)$$

$$\Delta S^\circ = 2.3026 R (-B - 2CT)$$

$$\Delta C_p^\circ = 2.3026 R (-2CT)$$

The empirically derived expression for the ionization constant of the ammonium ion of MEA is

$$-\log K_A = 2677.91/T + 0.3869 + 0.0004277T$$

and the value of pK_B of MEA may be obtained from the expression

$$pK_B = -\log K_w + \log K_A$$

which at 25°C is 4.498

A rarely used technique for the evaluation of ionization constants is the measurement of the electrical conductance of aqueous solutions of MEA hydroxide at 25°C and extrapolating to infinite dilution (10b). K_B is evaluated from

$$K_B = \frac{C x^2 f_i^2}{1 - x} = K_B' f_i^2$$

where K_B and K_B' are the thermodynamic and stoichiometric basic ionization constants, respectively, x is the degree of dissociation, C is the molar concentration of MEA hydroxide, and f_i is the mean activity coefficient of the ions. The empirical values of 3.19×10^{-5} and 9.500 for K_B and pK_A , respectively, correspond closely to those obtained by the potentiometric method (3.18×10^{-5} and 9.498).

The thermodynamic parameters of MEA are considered to be similar to those of ammonia (Table 13).

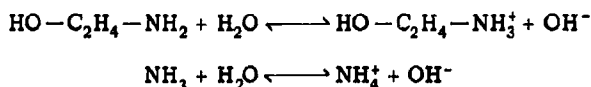
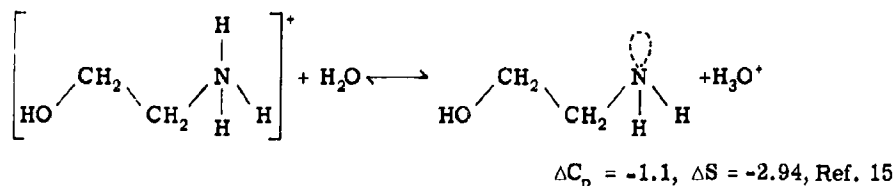
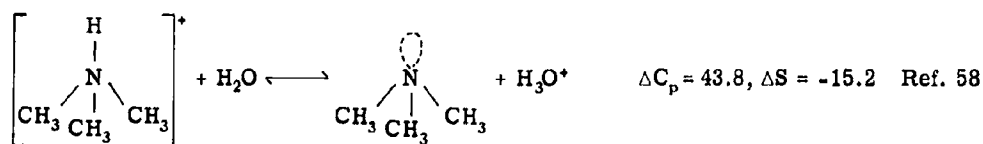
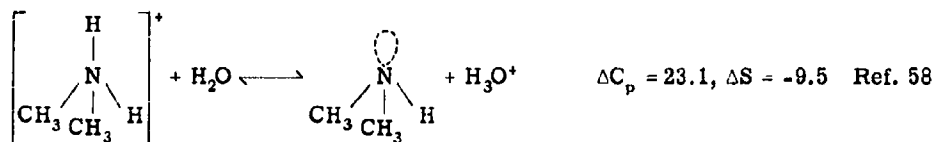
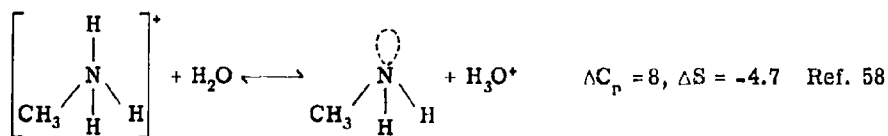
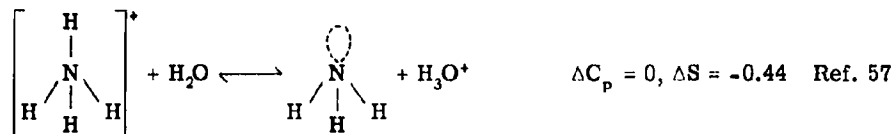


Table 13
Basic Ionization of MEA and NH_3

	MEA (15)	NH_3 (57)
ΔF°_{298}	25,675 joules/mole	27,111 joules/mole
ΔH°_{298}	6,023 joules/mole	4,345 joules/mole
ΔS°_{298}	-65.9 joules/mole-°K	-76.4 joules/mole-°K
$\Delta C_p^\circ_{298}$	-190 joules/mole-°K	-195 joules/mole-°K

The dissociation of an ammonium ion to the conjugate base and hydronium ion represents an isoelectric reaction, e.g., a proton is shifted but no new electrostatic charge is created. It has been postulated that ΔC_p° for such a process should be zero (58), which value has been confirmed for ammonium ions (57). However, the ionizations of the substituted ammonium ions yield large positive numbers for ΔC_p° .



ΔC_p and ΔS are expressed in calories/mole- $^\circ\text{K}$.

The large positive values of ΔC_p for the substituted ammonium ions have been interpreted on the basis that a hydrogen atom, capable of hydrogen bonding with water, has been substituted by a hydrophobic alkyl group in the base (59). It must be borne in mind that ΔC_p reflects a change of the number of degrees of freedom over which energy can be absorbed as $1/2 kT$ in the system (molecular),

$$\Delta C_p \, dT = d(\sum \Delta E_{\text{trans}} + \sum \Delta E_{\text{rot}} + \sum \Delta E_{\text{vib}})$$

and that ΔS reflects the number of possible ways to distribute a given quantity of energy. MEA undergoes a slight reduction in ΔC_p upon ionization although it possesses a dimethylene bridge between the polar groups.

Heat of Vaporization of MEA

A reliable value of the heat of vaporization of MEA could not be obtained from the literature survey. Union Carbide Chemicals Corp. published a value of 355 Btu/pound at one atmosphere (5b) which may be converted to 12.1 kcal/mole. C. Blachly of this Laboratory, at the author's request, determined the vapor pressure of MEA as a function of temperature using a Podbelniak distillation column of 150 theoretical plates and containing a purified constant boiling point fraction of MEA. These values were combined with those published in Ref. 5b and the best possible curve drawn (Table 14, Figs. 6,7).

Table 14
Vapor Pressure vs Boiling Point of MEA

C. Blachly		Ref. (5b)	
P _{vap} (mm Hg)	Temp (°C)	P _{vap} (mm Hg)	Temp (°C)
24	87.5	10	69
41	95.7	50	100
59	101.8	760	171.0
76	107.5	—	—
122	118.5	—	—

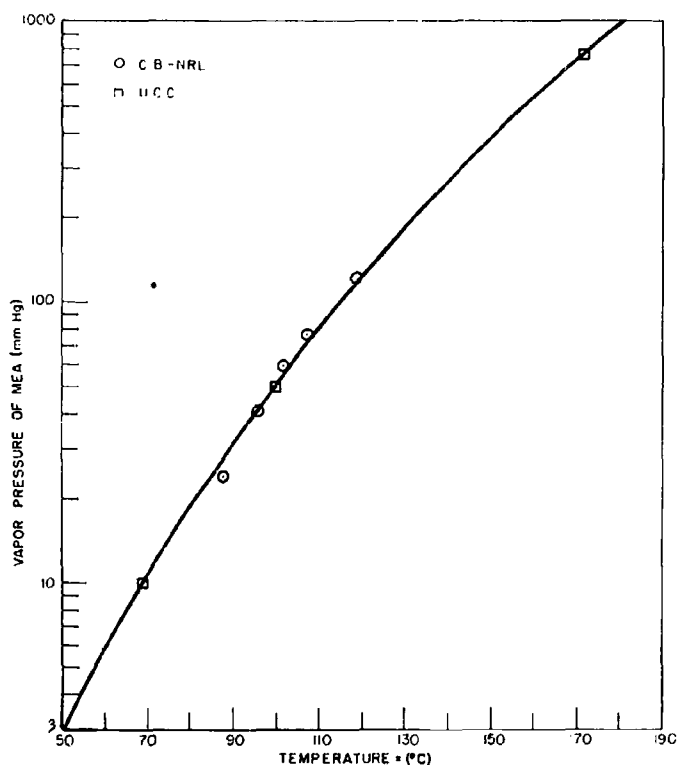


Fig. 6 - Empirical vapor pressure vs temperature diagram of MEA

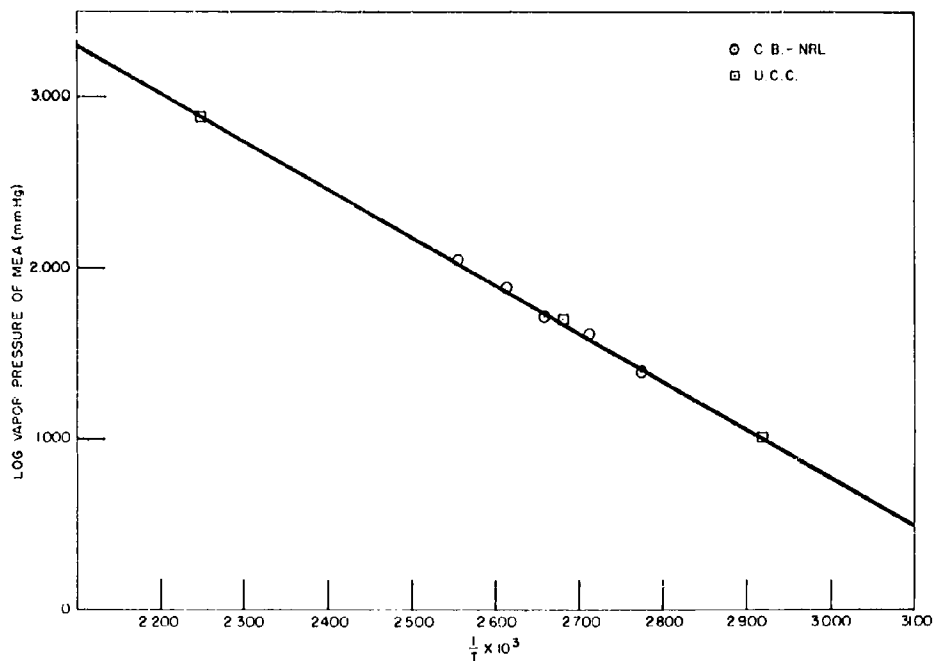


Fig. 7 - Log of the empirical vapor pressure of MEA vs the reciprocal of the absolute temperature

The heat of vaporization, ΔH_v , as determined from the Clausius-Clapeyron equation (Fig. 7) is 12,780 cal/mole. ΔH_v is assumed constant over the temperature range indicated on Fig. 7 (50° - 180°C). For comparison, the heat of vaporization of water at 100°C is 9,720 cal/mole and of ammonia at 760 mm, 5,564 cal/mole. The Clausius-Clapeyron equation,

$$\ln P_{\text{mm Hg}} = - \frac{\Delta H_v}{RT} + C$$

that best fitted the curve of Fig. 7 has the form

$$\log P_{\text{mm}} = - \frac{12,780 \text{ cal/mole}}{2.303 R} \cdot \frac{1}{T} + 9.160$$

or

$$\log P_{\text{mm}} = - 2.791 \frac{1}{T} + 9.160$$

where T is the absolute temperature.

CHEMICAL REACTIONS

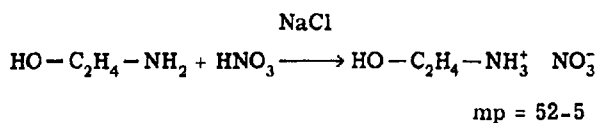
Although bifunctional in nature, the ethanolamines enter predominantly into reactions characteristic of amines and ammonia to give derivatives of the amine group. In the

paragraphs that follow, the known chemical reactions of amines applicable to, or characteristic of, MEA or its oxidation or carbon dioxide reaction products will be described.

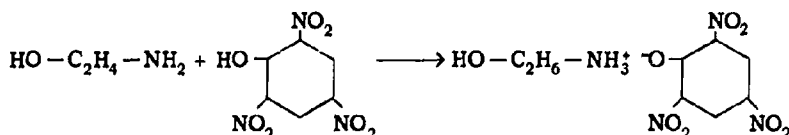
Addition or Salt Formation

MEA readily undergoes addition to the amino functional group with a number of inorganic and organic acids to yield salts (2,23). Acids capable of existing in reversible aqueous equilibrium with their sparingly soluble gaseous anhydrides, form salts with MEA which can be dissociated at elevated temperatures into the free base and the gaseous acid anhydride. The employment of MEA as a gas scrubbing agent for CO_2 and H_2S and its regeneration depends on the action of this equilibrium mechanism and the high partial vapor pressure of the gaseous anhydride at the regeneration temperature (31).

Salts formed with strong acids may be employed for the qualitative and quantitative characterization of the amine. When, for example, nitric acid and MEA are brought together in the cold, with sodium chloride present, the nitrate is formed (3).



However, the salt is hygroscopic. The picrate, which is a preferable derivative, has a melting point of 160°C (3,9).

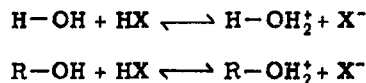


The ethanolamines combine readily with fatty acids, such as oleic and stearic acids, to form soaps whose consistency depends more upon the fatty acid employed than upon the particular ethanolamine. The saponification reaction takes place without the evolution of water, usually at room temperature. Many stable o/w emulsions of oils, fats, and waxes can be prepared with these soaps (2). The stability of salts of MEA and weak acids are a direct function of the dielectric constant of the medium, being greatest in solvents such as water.

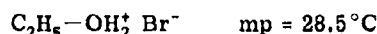
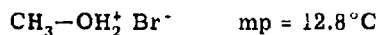
Trace organic acid components in the gas being scrubbed, in addition to accumulating and contributing to nonregenerable salt formation, have been the cause of foaming. Such foaming may seriously decrease the gas handling capacity of the absorber even though the concentration of the foaming agent is small. Fortunately, it has been found that the addition of small quantities of suitable antifoaming agents (long chain alkyl alcohols, oleyl alcohol, silicone antifoamer) will overcome the foaming tendency of such solutions (31).

By virtue of the MEA carbinol group, the alkaline earth metal halide salts form addition complexes with MEA similar to those formed with alcohols (2).

Acids react rapidly with alcohols, as they do with water, to form a positively charged oxonium ion and the acid derived anion (48).



For example, methanol (mp: -97.8°C) and ethanol (mp: -117.3°C) react with hydrogen bromide (mp: -88.5°C) in a 1:1 molar ratio to form the corresponding oxonium bromides (48).



The corresponding water derivative, hydronium bromide ($\text{H}_3\text{O}^+\text{Br}^-$), has never been isolated and exists only in solution. The solubilizing power exercised by oxonium ion formation is illustrated by butyl alcohol which is more soluble in concentrated hydrochloric acid than in pure water. Sparingly soluble amines behave in a similar manner.

Oxonium ion formation involving MEA has not been reported in the literature. However, abnormal solubilities of CO_2 in aqueous solutions of ethanolamines have been reported (50,51). "It is . . . interesting to note that the absorption (curve of CO_2) in many cases proceeds far beyond the point corresponding to the conversion of the base to the carbonate and even beyond the point of conversion to the bicarbonate and furthermore no break, indicative of compound formation occurs at these points" (51). Data relating the number of moles of CO_2 absorbed per mole of MEA as a function of the partial pressure of CO_2 for 0.5M aqueous solutions at 0°C is given in Table 15 (51).

Table 15
Pressure Dependence of CO_2 Absorption

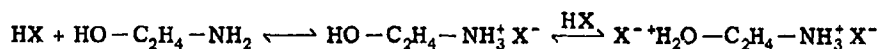
P_{CO_2} (mm at 0°C)	Mole CO_2 /Mole MEA Absorbed in 0.5M MEA
—	*
10.6	0.675
45.3	0.817
256.3	0.990
—	†
745.8	1.110
—	‡

*Max for carbonate or carbamate absorption = 0.500.

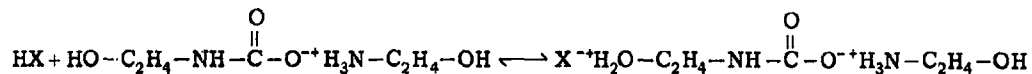
†Max theoretical absorption, e.g., $\text{R}-\text{NH}_3^+\text{HCO}_3^- = 1.000$.

‡Solubility CO_2 in pure H_2O when $P_{\text{CO}_2} = 760$ mm at $0^{\circ}\text{C} = 0.076$ mole/l.

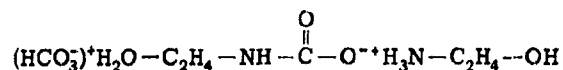
Whether the claimed enhanced solubilization mechanism is oxonium ion formation with carbonic acid, the formation of β -aminoalkyl carbonates (see absorption of CO_2 by MEA) or some other type of hitherto unreported association, or a combination of all three has not been investigated. The extent of oxonium ion formation with an alcohol, as with water, is directly dependent on acid strength.



with β -hydroxyethylcarbamate anion



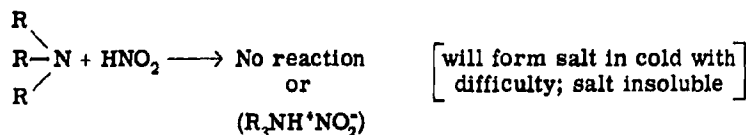
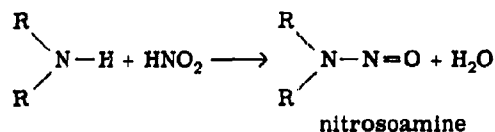
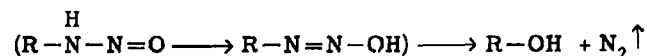
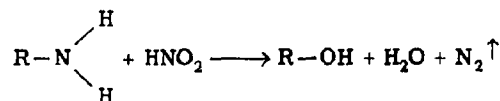
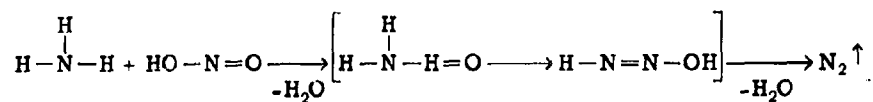
if $X = H_2CO_3$;



One should note that strong acids will decompose carbamate salt in aqueous solution. The crystalline salt $(NO_3^-)^+H_2O-C_2H_4-NH_3^+(NO_3^-)$ has been reported (3).

Reaction with Nitrous Acid

The reaction of a primary amine with nitrous acid has been described in a Girdler report (24) as a quantitative method for MEA in solution (gas burette). Nitrous acid ($NaNO_2 + HCl$) will react with ammonia and its substituted derivatives to give a variety of reaction products. The course of the reaction is dependent on the number of replaceable hydrogens on the amino functional group.



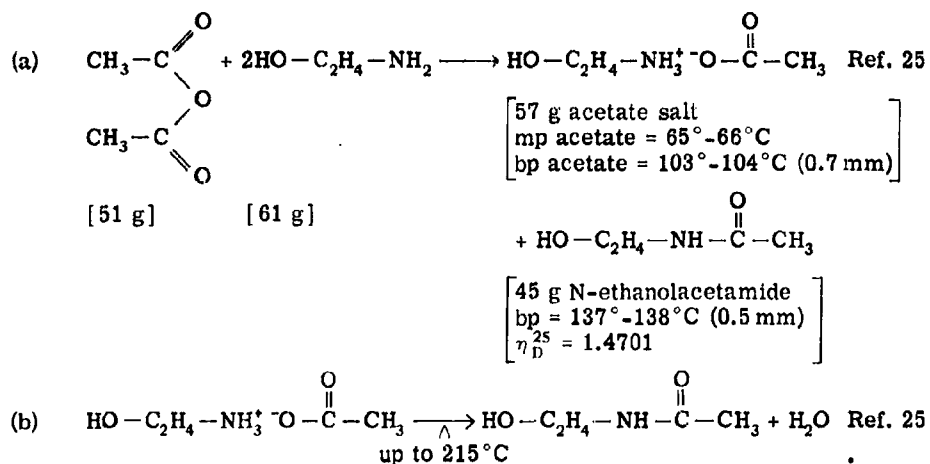
In evaluating MEA concentration by this method it is important that ammonia be absent (i.e., caution: degraded MEA may contain NH_3).

A mixture of primary, secondary, and tertiary amines may be separated by this method. The primary amino fraction is destroyed by conversion to an alcohol and its concentration determined by the nitrogen evolved. The unaltered tertiary amine fraction is removed by extraction with an ethyl ether acid mixture. The secondary amino fraction, which was converted to a neutral nitroso compound, may be regenerated by hydrolyzing with dilute hydrochloric acid and recovering the secondary ammonium chloride.

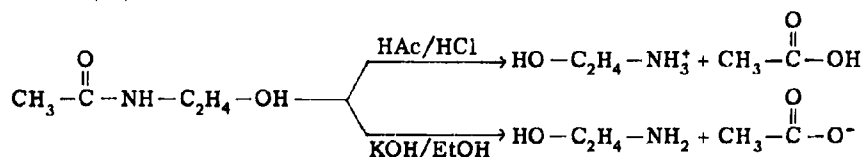
Acylation

Acylation will convert a liquid amine, having replaceable hydrogens into a solid product useful for characterization and identification. Tertiary amines, having no replaceable

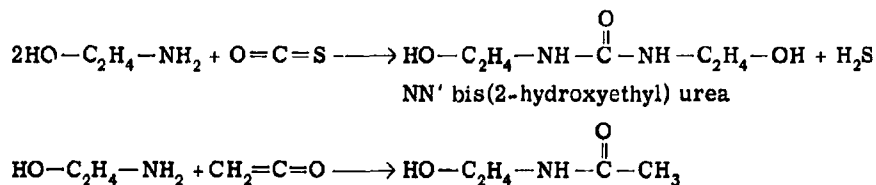
hydrogen, will not form a substituted amide. Under the proper conditions substituted amides are formed with acyl halides, acid anhydrides, alkanolic acids, alkyl sulfonates, esters, arylsulfonyl halides, etc. (2,23,25).



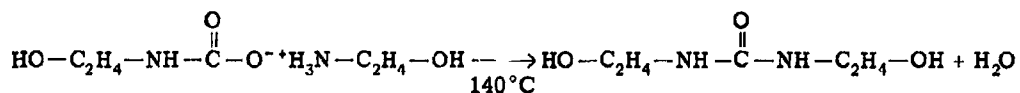
An amine salt will condense to the N-substituted amide under dehydrating conditions (reaction b). Hot spots located in the reactivator section of the gas scrubbing system might provide such a suitable environment (34,35). In contrast to the basic character of MEA, the substituted amides are neutral or feebly basic compounds. They are much less reactive than esters, and their hydrolysis proceeds smoothly, although under more drastic conditions (23).



Degradation of ethanolamine solutions by acylation, accompanied by decreased scrubbing capacity, has been reported. Diethanolamine solutions used in gas treating systems have been converted to linear carbamides (36). In another case, MEA was completely converted to diethanolurea by the reaction with carbonyl sulfide present in traces in the gas being purified. Similarly MEA was converted into N-ethanolacetamide by the reaction with ketene (31).

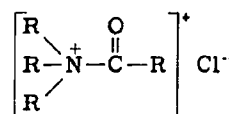


There is also evidence that at 140°C aqueous MEA loaded with carbon dioxide has, to some extent, condensed in the reboiler to form diethanolurea (31).



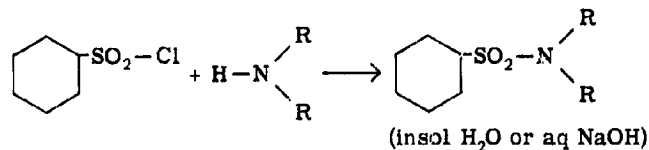
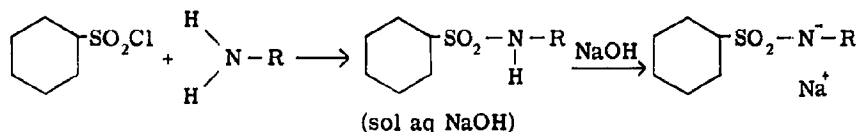
In one case the corrosion in the reactivator accompanying the degradation of the aqueous MEA solution has been ascribed to the use of high temperature oil as a heating medium with resulting high metal skin temperatures (31) [also refer to reaction between Fe and MEA].

Primary and secondary amines, like ammonia, react rapidly and exothermally with acid chlorides, less vigorously with anhydrides, and slowly with esters to form N substituted amides. Tertiary amines, having no replaceable hydrogens, do not react. Acyl halides react rapidly and often vigorously with tertiary amines to yield addition compounds of the type (48).

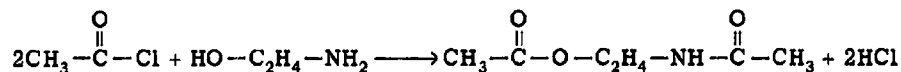
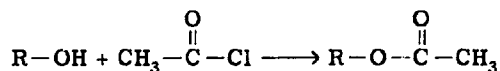


This type of compound, actually a quaternary salt, is decomposed in the presence of water to the tertiary ammonium halide and the corresponding acyl hydroxide (an acid). Consequently, acylations are especially useful for distinguishing primary and secondary amines from tertiary amines. The reaction mixture is added to water which hydrolyzes unchanged acyl halide. Any unchanged amine is converted to a salt, usually soluble, while the amides are usually very sparingly soluble. The tertiary amine may be extracted with an ethyl ether-hydrogen chloride mixture. To insure formation of insoluble amide derivatives, benzoyl chloride is the preferred reagent.

The Hinsberg test may be employed to distinguish between a primary and secondary amine. Benzenesulfonylchloride will form a derivative soluble in basic water solutions (NaOH) with a primary amine (23).

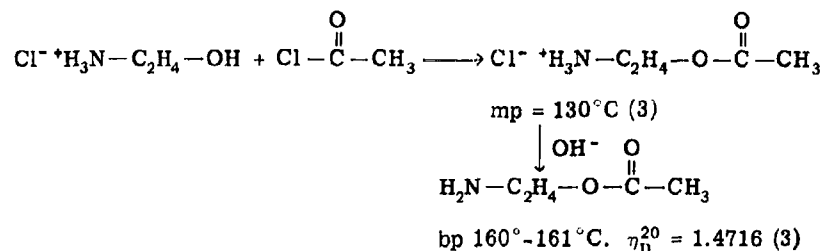


Acylation is initiated by the nucleophilic attack of a set of basic lone pair electrons (see section on cyanation) so that alcohols, like water, react (with somewhat less vigor than an amine) with acyl halides and anhydrides to form esters.



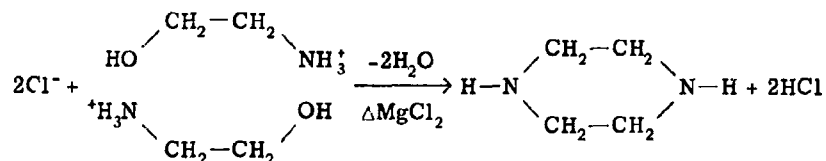
Consequently, in the acylation of an amino alcohol, care must be exercised in the choice of reagents and reaction conditions to obtain the desired derivatives.

The reaction with an acyl halide may be used as a test for the presence of a primary or secondary alcohol group. Tertiary alcohols react abnormally, with the formation of tertiary chlorides (48). Selective acylation of the carbinol group may be accomplished if the amine group is first inactivated by converting it to an ammonium (substituted) ion.



The Formation of Piperazine

Piperazine may be considered as the condensation product of two MEA molecules, and is prepared in the laboratory by heating monoethanolammonium chloride to 220°-250°C in the presence of such dehydration catalysts as the halide salts of zinc, iron, aluminum, or magnesium (32).

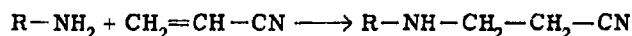


Piperazine may also be obtained, in a commercial process, by recirculating a solution of β -hydroxyethylammonium chloride in a thin layer over a large surface with rapid heating to reaction temperature (33). This method simulates conditions in reactivator units where the rich MEA solution, fresh from the scrubber, may be splashed onto hot spots (34,35). Extreme ferrous corrosion (and erosion) localized in areas containing such hot spots has been reported (35). Piperazine formed as a degradation product in MEA scrubber solutions has not been reported in the literature. However, a substituted piperazine degradation product of diethanolamine has been identified in refinery gas scrubbing solutions (36).

Replacement of two molecules of MEA by one of piperazine would have slight effect on the scrubbing capacity of the MEA solution. The basicity of the amino nitrogens of piperazine are: $\text{pK}_{\text{B}_1} = 4.19$ and $\text{pK}_{\text{B}_2} = 8.43$ (4, p. 1383), as compared to the pK_{B} of MEA of 4.50 (item 11 under Physical Properties). One of the identified degradation products of diethanolamine is 1,4 bis(2-hydroxyethyl) piperazine. This compound is still capable of salt formation with carbon dioxide, and very little loss of scrubbing efficacy is experienced even after significant amounts of the ethanolamine has been converted (36).

Cyanoethylation of MEA

The nitrogen bonded hydrogen atom in MEA and other amines may be considered to be labile. A variety of organic compounds possessing active hydrogen atoms add readily to acrylonitrile by a nucleophilic attack on the β -carbon followed by migration of the labile hydrogen. The attacking molecule acquires a cyanoethyl grouping ($-\text{CH}_2-\text{CH}_2-\text{CN}$) and the reaction is known as "cyanoethylation" (45).

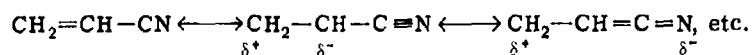


This mechanism, is typical of many amine reactions considered in this report. It involves the replacement of one or more amino group hydrogen atoms, and proceeds by a nucleophilic attack by the nitrogen lone pair electrons on a center of positive charge. Such centers of positive charge may arise from either an inductive displacement or a tautomeric equilibrium. A reaction intermediate complex, with the nitrogen possessing a formal positive charge, is formed. Migration of one of the amine group hydrogens to a center of negative charge elsewhere in the complex is followed by formation of the reaction product or products.

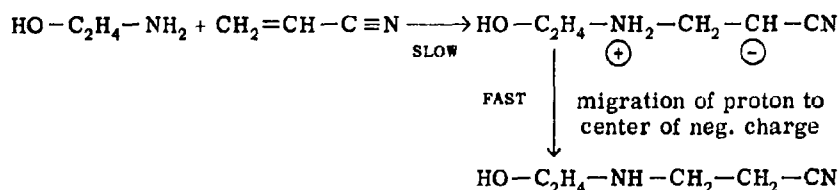
The cyanoethylation of MEA, in a buffered (pH 9.7) aqueous solution at 30°C, has recently been investigated in order to confirm this general mechanism from a kinetic standpoint as well as to identify the attacking species (46). The reaction follows a second order rate, being first order with respect to each of the two reactants.

$$\frac{dx}{dt} = k [\text{CH}_2=\text{CH}-\text{CN}] [\text{MEA}] \quad k = 3.10 \times 10^{-3} \text{ l/mole-sec} \\ \text{at pH 9.7}$$

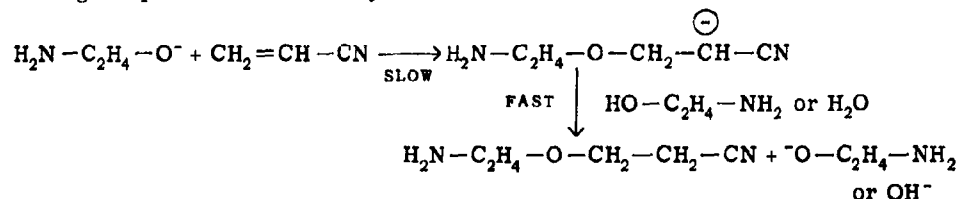
Such a rate expression agrees with a mechanism that involves a nucleophilic attack of a free amine on a center of positive charge. Acrylonitrile exists in the following tautomeric forms:



The proposed mechanism is



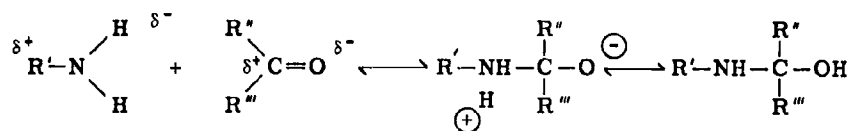
At higher pH values the concentration of the β -aminoethoxide anion increases and the following competitive reaction may occur to a limited extent.



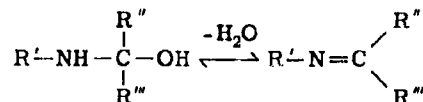
The basicity of the β -aminoethoxide anion is similar to that of methoxide (CH_3O^-). The kinetic rate constant for the second order rate reaction between sodium methoxide and acrylonitrile in methanol is 9.6×10^{-3} l/mole-sec.

Reaction of MEA with Aldehydes and Ketones

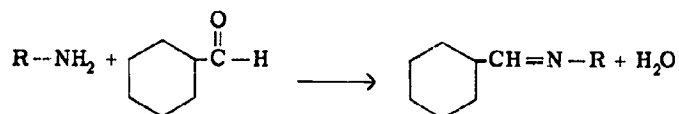
The reaction of amines with aldehydes and ketones in aqueous solutions usually results in an equilibrium mixture of amine, aldehyde/ketone, and the addition reaction product



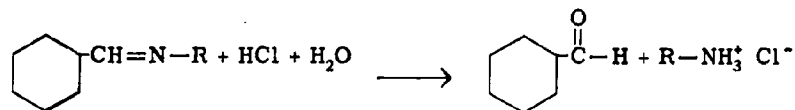
where R' is a saturated alkyl radical and R'' is hydrogen or another saturated alkyl radical. The addition product is an unstable α -amino alcohol. The reaction mechanism probably follows that discussed under the topic of cyanoethylation of MEA, namely a nucleophilic attack by the base resulting in an intermediate possessing a center of positive and a center of negative formal charges followed by migration of the active hydrogen from the amine group to the center of negative charge. Dehydration of the α -amino alcohol results in a Schiff base.



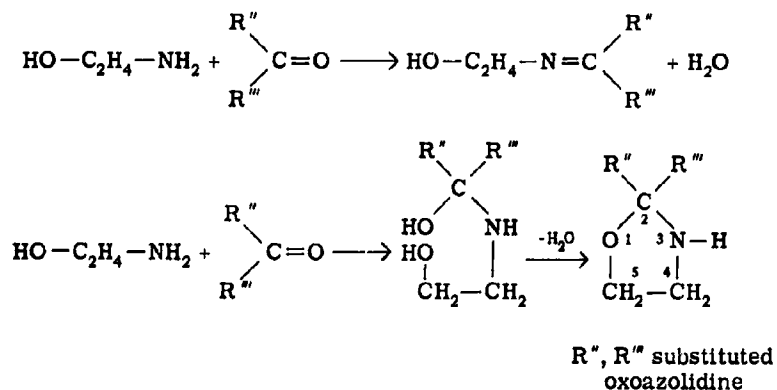
Aliphatic Schiff bases are readily hydrolyzed by water back to the aldehyde/ketone and amine. Amines reacting with benzaldehydes or α, β unsaturated aldehydes or ketones condense to Schiff bases that are stable and insoluble in water and cold dilute acids.



It is characteristic of such a double bond between carbon and nitrogen that it is easily hydrolyzed under acid conditions (48, p. 359).



The reaction products of MEA with aldehydes and ketones under dehydrating conditions have been investigated (74). Two isomeric reaction products, a Schiff base or a substituted oxazolidine, are possible.



Thermochemical calculations show that there is very little energetic differences between the two isomeric forms. The Schiff base and the substituted oxoazolidine differ in the following bonds:

C=N	94.0 kcal	C-O	70.0 kcal
O-H	110.2 kcal	C-N	48.6 kcal
		N-H	83.7 kcal
	<u>204.2 kcal</u>		<u>202.3 kcal</u>

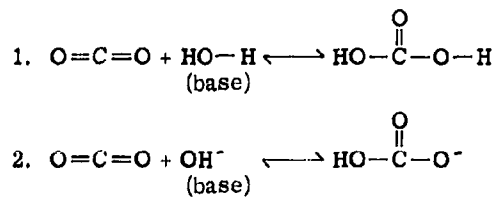
so that interconversion between the two forms is not improbable.

Examination of molar refractivities and infrared spectra showed that saturated aldehydes and ketones gave oxoazolidines except for diisobutyl ketone and isobutyl methyl ketone which form equilibrium mixtures. Aromatic and α, β unsaturated aldehydes and ketones, in general, form Schiff bases.

Reaction of MEA with Carbon Dioxide

Faurholt and his associates have, since 1921, investigated the kinetics and equilibria of the reactions between carbon dioxide and water, hydroxyl ions, alcohols, amines, etc. The following is a digest of their extensive investigations supplemented by additional source material (75).

Carbon dioxide, considered as a Lewis acid, is capable of reacting with Lewis bases to form addition products that are substituted carbonic acids or carbonates, depending upon whether the attacking base possesses a displaceable hydrogen atom or is an anion. The reaction of CO₂ with water or hydroxyl ion is typical and illustrative of this mechanism (75a, 75b, 75d).



The Bronsted acids formed in reactions (1) and (2) may either rapidly dissociate into the conjugate base and hydronium ion or react with other strong base present in the system. The kinetic velocity constants of reactions (1) and (2) reflect the base strength of water and hydroxyl ion respectively, the reaction velocity to the right being greater with the stronger base. The mechanisms illustrated in reactions (1) and (2) proceed simultaneously and independently of each other when both species are present in the same system. The kinetic rate constants of reactions (1) and (2) are illustrated respectively in (3) and (4).

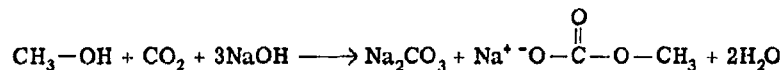
$$3. \quad \frac{d[\text{H}_2\text{CO}_3]}{dt} = k_{\text{H}_2\text{CO}_3} [\text{CO}_2] \quad (\text{pseudo 1st order})$$

$$k_{\text{H}_2\text{CO}_3} = 18 \text{ min}^{-1} \text{ at } 25^\circ\text{C}$$

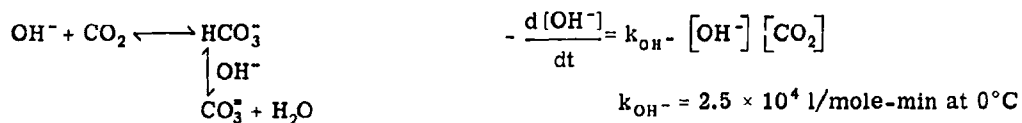
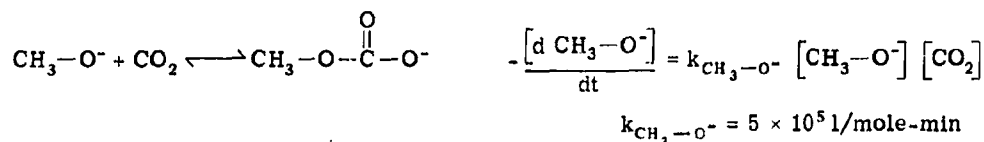
$$4. \quad \frac{d[\text{HCO}_3^-]}{dt} = k_{\text{HCO}_3^-} [\text{CO}_2] [\text{OH}^-]$$

$$k_{\text{HCO}_3^-} = 5.1 \times 10^5 \text{ l/mole-min} \\ \text{at } 25^\circ\text{C}$$

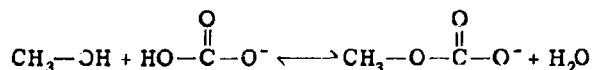
The equilibrium concentrations of reactants and products at the termination of the reaction, however, will reflect the change in free energy (between reactants and products) and conform to the law of mass action. For example, consider the reaction of carbon dioxide with methyl alcohol in basic aqueous solution at 0°C (75b).



The following reactions are proceeding simultaneously and independently of each other.



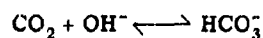
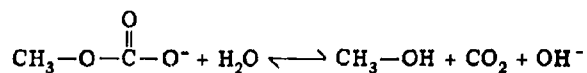
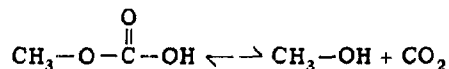
At the termination of the reaction the equilibrium constant K_{eq} for the overall reaction



is

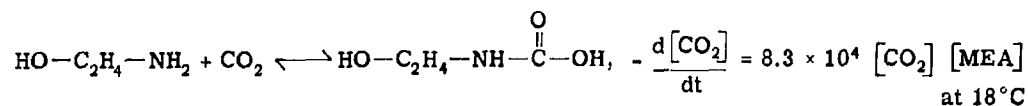
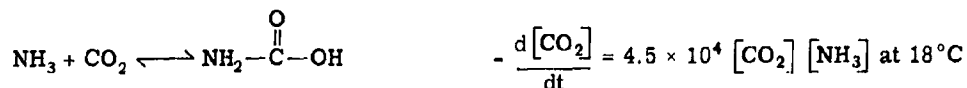
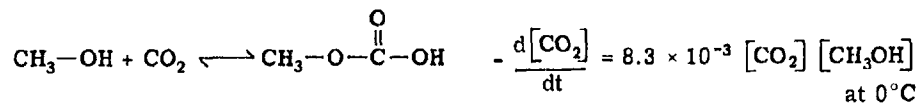
$$K_{\text{eq}} = \frac{[\text{CH}_3\text{-OH}] [\text{HCO}_3^-]}{[\text{CH}_3\text{-CO}_3^-]} = 12$$

In aqueous solutions bicarbonate ion concentrations are a function of the solution pH. Thus at "appropriate" solution pH values, Faurholt found rapid conversion of methanol into methylcarbonate ions followed by the very slow conversion of most of the methylcarbonate ions into bicarbonate ions to conform with K_{eq} (75e). All conversions from the substituted carbonic acid or carbonate ion to bicarbonate were postulated to proceed by the following two-step mechanism (75).



The alkyl carbonates were investigated at 0°C since they are unstable at higher temperatures.

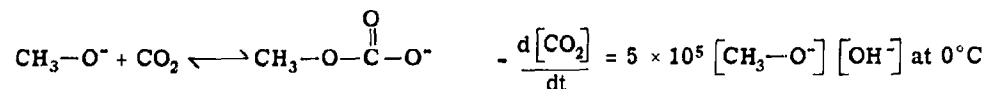
Formation of a substituted carbonic acid or carbonate ion may be accomplished by the following bases and their analogs in aqueous solution.



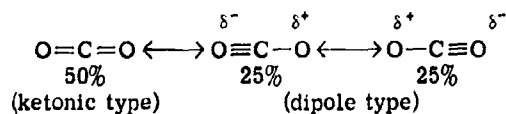
$$k_{\text{OH}} = 2.45 \times 10^4 \text{ l/mole-min at } 0^\circ\text{C}$$

$$k_{\text{OH}} = 1.05 \times 10^5 \text{ l/mole-min at } 18^\circ\text{C}$$

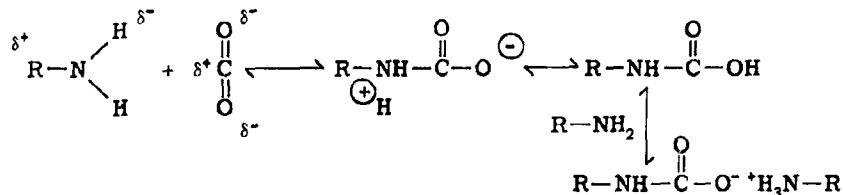
$$k_{\text{OH}} = 5.1 \times 10^5 \text{ l/mole-min at } 25^\circ\text{C}$$



Pauling (76) proposes the following resonant structures for carbon dioxide.

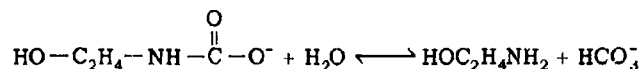


The sum of the dipole forms, accounting for 50% of the normal state of the molecule, leaves the carbon atom electropositive compared to the electronegative terminal oxygen atoms. The mechanism of formation of a substituted carbonic acid, for example, may then be postulated to be similar to that discussed for the cyanoethylation of MEA. In that reaction a nucleophilic attack by the base (with a displaceable hydrogen atom on the function group) on the center of positive charge of the Lewis acid resulted in an intermediate possessing a center of formal positive and a center of formal negative charge followed by migration of the displaceable proton to the center of negative charge.



Tertiary amines having no replaceable hydrogen atoms on the functional group do not form carbamic acids. In practice, the unstable carbamic acids formed are neutralized immediately upon formation by excess base. In summary, the type of compound immediately formed by introducing carbon dioxide into a basic solution depends on the rate of formation of carbonic acid, bicarbonate ion, the substituted carbonic acid, and the substituted carbonate ion. The concentrations of the various reaction products present at equilibrium, however, will conform to the maximum free energy decrease between reactants and products as delineated in the mass action law.

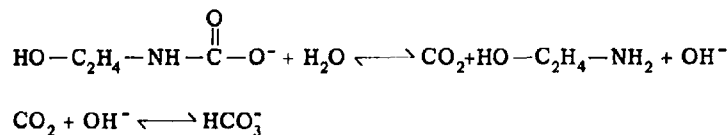
The reaction of carbon dioxide with the amine functional group of MEA at 18°C was investigated by Faurholt (77). The simultaneous reaction of the carbinol group with carbon dioxide was presumed to be negligible. The equilibrium constant K_{eq} for the reaction



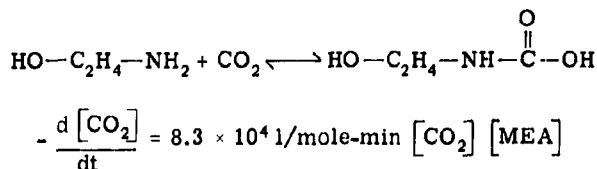
determined at a pH value of approximately 9.5 is

$$K_{eq} = \frac{[\text{HO}-\text{C}_2\text{H}_4-\text{NH}_2] [\text{HCO}_3^-]}{[\text{R}-\text{NH}-\text{CO}_2^-]} = 10^{-1.71} = 1.95 \times 10^{-2}$$

The equilibrium is attained through the two step mechanism previously described, e.g.,



The kinetic rate constant for the reaction with CO_2 is $k_{\text{MEA}} = 8.3 \times 10^4$ l/mole-min at 18°C as compared to k_{OH^-} for hydroxyl ion of 1.05×10^5 l/mole-min.



The initial rate of formation of the MEA carbamate compared to bicarbonate ion may now be calculated. A 2.5N aqueous solution of MEA was reported to have a pH of 12.0 (20), which corresponds to a molar hydroxyl ion concentration of 0.01. The ratio of carbamate ion formation to that of bicarbonate at 18°C is

$$\frac{d[\text{HO}-\text{C}_2\text{H}_4-\text{NH}-\text{CO}_2^-]}{d[\text{HCO}_3^-]} = \frac{8.3 \times 10^4 \times 2.5}{1.05 \times 10^5 \times 1.0 \times 10^{-2}} = 197^*$$

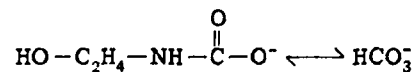
i.e., the initial rate of carbamate formation is 197* times that of bicarbonate at pH 12.0. A solution that was initially 0.1 molar in MEA, 0.14 molar in $\text{HO}-\text{C}_2\text{H}_4-\text{NH}_2^+$, and 0.02 molar in CO_3^{2-} , and with a pH of 9.5 was permitted to attain equilibrium. The reaction was followed by determining the percentage of carbonate-bicarbonate initially present that was converted to the carbamate (Table 16).

*This figure is not to be considered as empirical data but as an illustration of direction and magnitude.

Table 16
Conversion of $\text{CO}_3^{2-}/\text{HCO}_3^-$ to Carbamate

Minutes	Percent Converted to Carbamate
44	13
93	25
140	35
190	43
250	50
350	61
∞	80

If the interconversion reaction is considered as

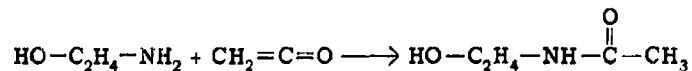
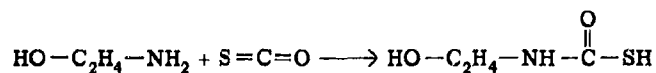
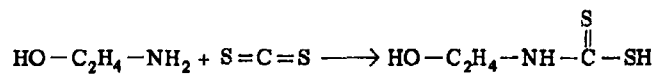


the following kinetic parameters were evaluated.

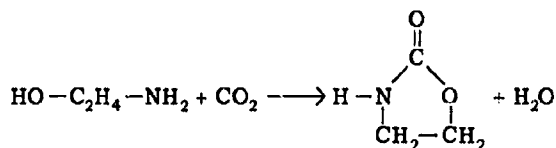
$$-\frac{d[\text{HO}-\text{C}_2\text{H}_4-\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^-]}{dt} = 3.6 \times 10^{-4} \text{ min}^{-1} [\text{HO}-\text{C}_2\text{H}_4-\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^-]$$

$$-\frac{d[\text{HCO}_3^-]}{dt} = 1.4 \times 10^{-3} \text{ min}^{-1} [\text{HCO}_3^-]$$

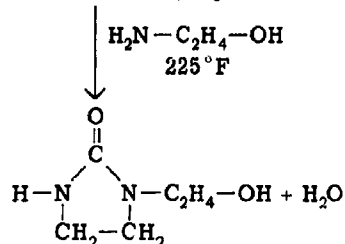
MEA reacts with other compounds whose structure and electronic distribution are similar to carbon dioxide. The reactions with carbon disulfide, carbonyl sulfide, and ketene may be represented as



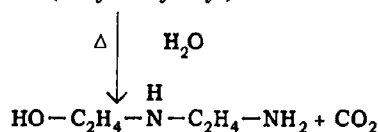
The reduction of carbon dioxide absorptive capacity of MEA scrubbing solutions has been ascribed to MEA- CO_2 condensation products which are either of limited basicity or are nitrogenous bases whose addition product with CO_2 is nonregenerative (36). The condensation reaction follows this scheme:



(a) (oxazolidone-2, mp 91.0°-91.5°C)

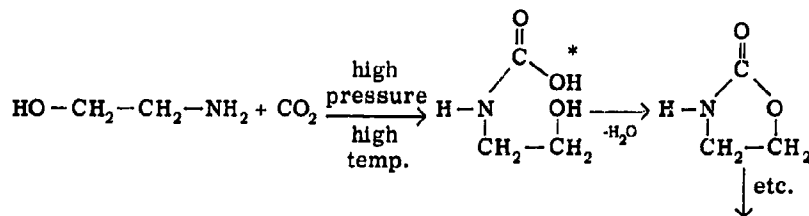


(b) [1-(2-hydroxyethyl) imidazolidone-2, mp 57°-58°C]



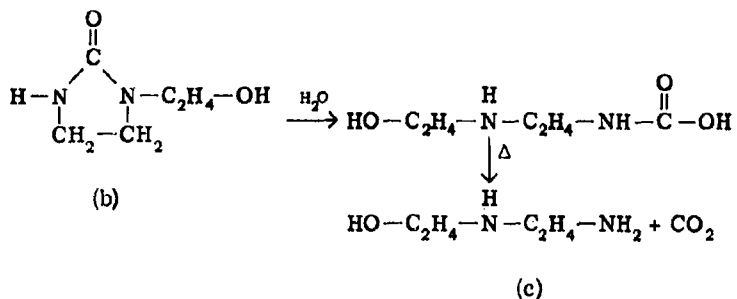
(c) [N-(2-hydroxyethyl) ethylenediamine bp 114°-115°C at 0.2 mm]

The reaction between CO_2 and MEA, under anhydrous conditions at elevated temperatures and pressures has been claimed in a recent patent (90) as a synthetic method for (a), (b), and (c).

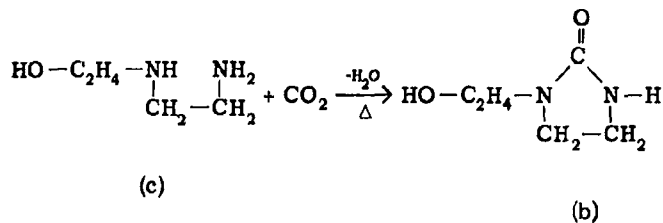


Oxazolidone-2, 1-(2-hydroxyethyl) imidazolidone-2, and N-(2-hydroxyethyl) ethylenediamine have been found in scrubbers used in natural gas treating service. Their formation is greatly enhanced by high temperatures and high carbon dioxide loadings. The desirability of employing the lowest possible reboiler temperature and pressure, consistent with good regeneration, is emphasized (36). The hydrolysis of (b) to (c) may proceed by the formation of a carbamate intermediate.

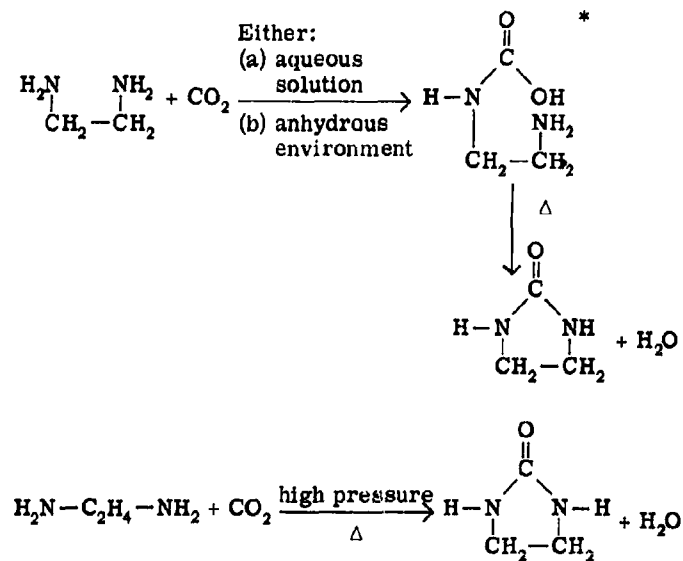
*The possible reaction intermediate.



A 7% yield of compound (b) and a 2% yield of compound (c) has been found in MEA solutions (3% H₂O) refluxed at 150°-155°C for 120 hours in a CO₂ atmosphere in the absence of air (88). The reaction between CO₂ and (c) is also postulated as occurring:



Imidazolidones have been prepared by the dehydration of the addition product of CO₂ and ethylene diamine (89).

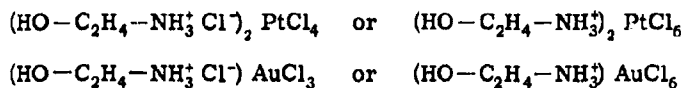


Highest yields are claimed for the latter reaction.

*The possible reaction intermediate.

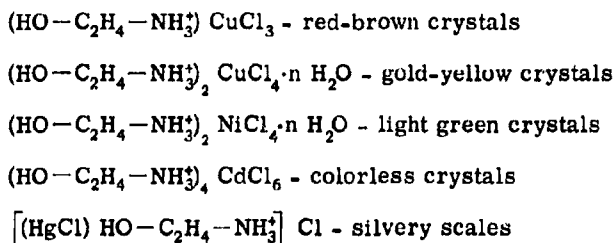
Double Salts

Ammonium halide salts form insoluble double salts with platinum chloride and auric chloride. Such double compounds may be obtained with all classes of amines and have the general formulas $Am_2 PtCl_6$ and $AmAuCl_4$, where Am represents a substituted ammonium ion. The equivalent MEA salts may be expected to be



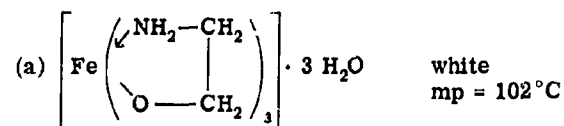
However, this reaction has not been tried with MEA. Because of the reducing action of MEA, attempts to prepare the above compounds in basic solutions may run into difficulties. Such salts, if experimentally available, serve an important analytical purpose. Ignition of a weighed sample of one of these salts in a crucible leaves a quantitative residue of platinum or gold (26).

Double salts of MEA with other heavy metal ions have been reported (64). They are prepared by mixing MEA with the metal chlorides in dilute aqueous hydrochloric acid.



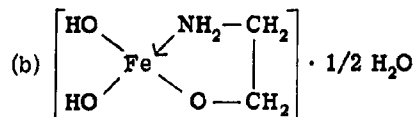
Reaction of Iron and MEA

A unique reaction between iron and MEA has been reported as a result of an investigation of deteriorated aqueous MEA solutions obtained from a CO_2 gas scrubbing plant fabricated from mild steel (61). A mixed dark-red and white crystalline precipitate and scum were observed in the degraded MEA. The white scum was separated, analyzed, and the following structure proposed.



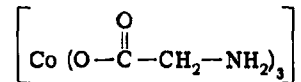
Trisethanolamino Fe(III)

(a) reacts with water, with the liberation of 2 molecules of MEA, to give dark red crystals of water insoluble (b), dihydroxoethanolamino iron (III),



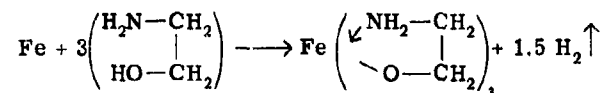
which can be reconverted to (a) by heating with excess MEA. A compound (c) of the same chemical composition and chemical behavior as (a), but with a lower melting point ($82^\circ C$)

and dehydration temperature, was prepared by refluxing a mixture of iron filings and MEA for 10 days. It was proposed that (c) is a "stereoisomeride" of (a) since Co(III) forms several tris stereoisomeric inner salt complexes with glycine



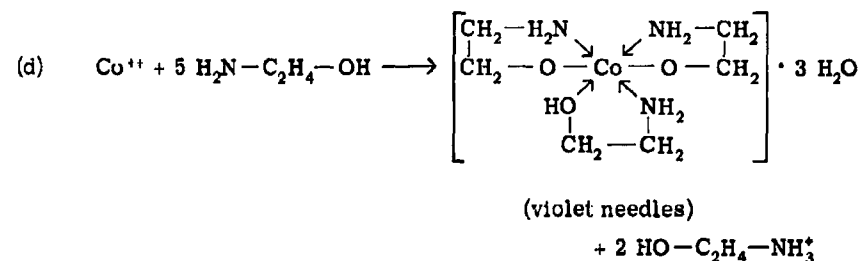
analogous to those just described for Fe(III) (62).

Most inner salt complexes are prepared by the reaction of a metal ion with an addendum in solution. The action of MEA on metallic iron, whereas in a basic solvent environment the metal is directly attacked by an acidic group with the evolution of hydrogen, was regarded as unique by the investigators.

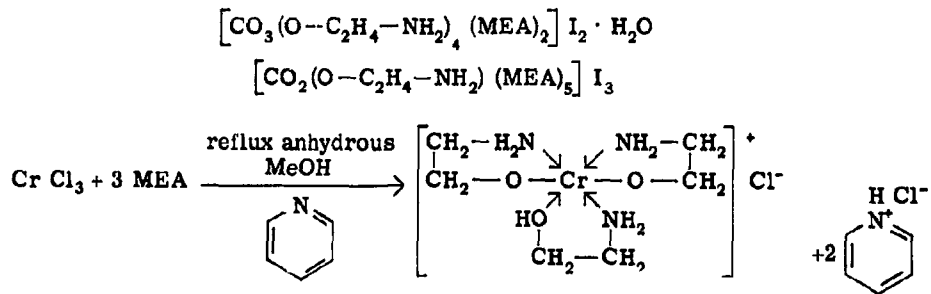


Furthermore, the existence of iron as Fe(III) in the presence of the reducing atmosphere of hydrogen was regarded as exceptional. The presence of oxygen was not considered to be necessary for the formation of the iron complex. (a) forms a 5.5% concentrated solution in MEA which may be diluted with up to 20% water without decomposition to (b). (b) does not melt on heating and is sparingly soluble in water, alcohols, and the "usual organic solvents." (a) is stable in dry air or in contact with dry organic bases but decomposes in water.

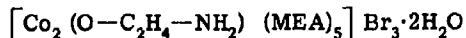
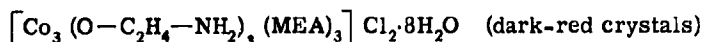
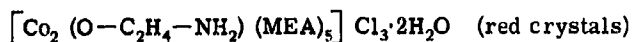
Previously the only inner salt complexes reported were those containing a maximum of two β -aminoethanolate radicals per cation. For example, if excess MEA is added to Co^{++} in aqueous solution (63).



This inner salt is stable toward cold water, acids, and alkalis, but is decomposed by hot water. If the nitrate ion is present, $[\text{Co}_2(\text{O}-\text{C}_2\text{H}_4-\text{NH}_2)(\text{MEA})_5](\text{NO}_3)_3$ is also formed. However, with CoCl_2 and CoSO_4 only (d) was identified. Reaction of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ with MEA and KI yielded (63,65,66)



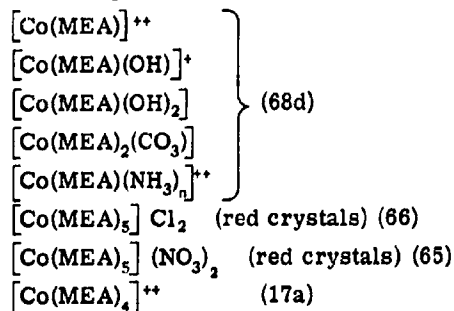
Other inner salt complexes reported (65) were prepared by refluxing the cobalt halide salt in ethanol with MEA and pyridine.



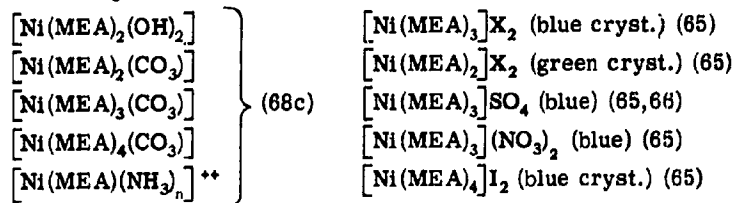
Complex Formation of MEA with the Heavy Metals

A large number of noninner salt complex compounds with the heavy metals have been reported, reflecting the bidentate character of MEA. Certain of the compounds listed below have been isolated as the crystalline salts (66,67), a few were postulated on the basis of conductance measurements during the titration of the metal chloride by MEA (17a), and the remainder of the compounds were postulated on the basis of the polarographic behavior on the metal ions in basic aqueous solutions of MEA, e.g., their existence postulated on the basis of the shift of the half-wave reduction potentials with pH (68). Due to the extreme low solubilities of the MEA-iron complexes in the solutions employed, no detailed studies of their polarographic behavior was made. However, complexes were postulated for the other ethanalamines; for example, $[\text{Fe}(\text{III})(\text{DEA})_2(\text{CO}_3)]^+$, $[\text{Fe}(\text{II})(\text{DEA})_2(\text{CO}_3)]$, etc. (68a).

(a) Cobalt Complexes

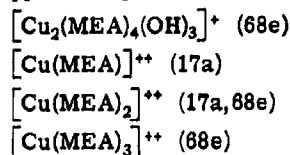


(b) Nickel Complexes

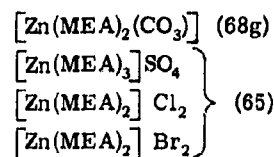


where X = Cl⁻, Br⁻, I⁻

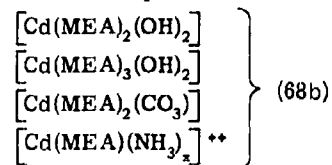
(c) Copper Complexes



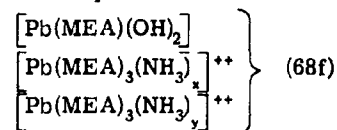
(d) Zinc Complexes



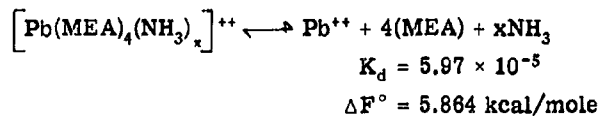
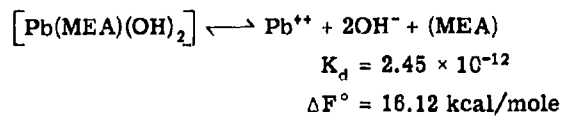
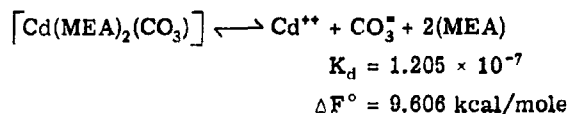
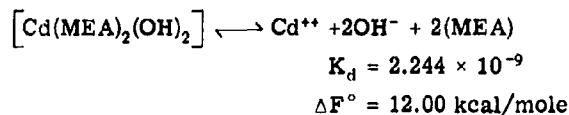
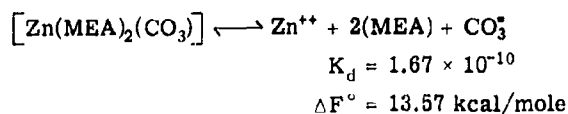
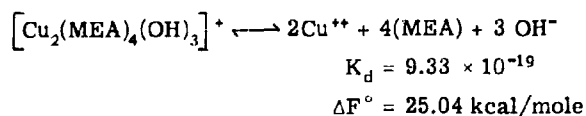
(e) Cadmium Complexes



(f) Lead Complexes



Several of the polarographic reductions (68) were reversible, permitting the calculation of the instability constants and the free energy of formation of the complexes.



It was further generalized (68g) that the bivalent metal ion-MEA complexes (including mixed ligand type complexes) had stabilities in the following decreasing order.



The pH of the solutions employed was found to be important since it reflected base concentrations, e.g., at pH values greater than 12, hydroxyl ions entered the complexing shell as did carbonate ions if present. Copper-MEA complexes in aqueous solution will absorb carbon monoxide. At cupric ion concentrations greater than 1 gm per 100 ml of solution a slow reduction to cuprous ion occurs with carbon monoxide absorption (71).

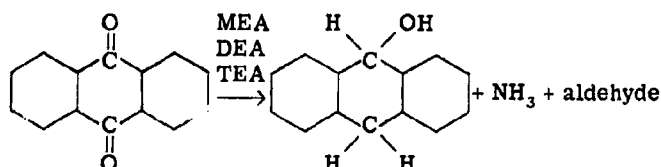
The complexes formed by MEA with heavy metals have been repeatedly reported to function as oxidation catalysts or as activators when in the presence of another MEA-heavy metal catalyst. The 3:1 complex of MEA with cupric ion is a strong catalyst for the oxidation of pyrogallol with oxygen at room temperatures. The complexes of cupric ion with such bidentate addenda as ethylene diamine and propylene diamine displayed no catalytic activity increase, while those with diethanolamine and pyridine were found to be effective catalysts (69). Kirson (72) studied catalytic hydrogen peroxide decomposition by a series of copper-amine complexes that included the $\text{Cu}(\text{MEA})_4^{++}$ ion. The amines which complexed with Cu^{++} to form effective catalysts included ammonia (72a), pyridine (72b), piperidine (72c, 72e), mono-, di-, and trimethylamine, ethylamine, butylamine, benzylamine (72e), propylenediamine, butylenediamine (72f), and various amino alcohols (72g). The ethylenediamine:copper, 2:1 complex (72d) was an ineffective catalyst. Catalytic activity was found to be dependent on the solution pH, being enhanced at the higher pH values. Alkyldiamine-copper 2:1 complexes with the bidentate ligands occupying the 1, 2 positions in the chain displayed no catalytic activity (72f); otherwise basicity, structure, and molecular weight of the amines investigated did not markedly affect the catalytic activity of the copper complexes (72e).

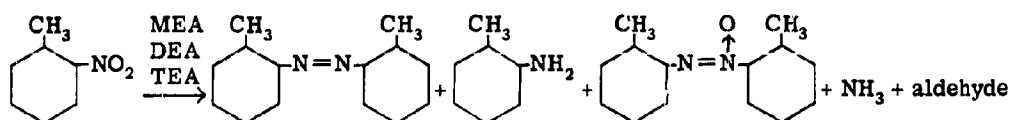
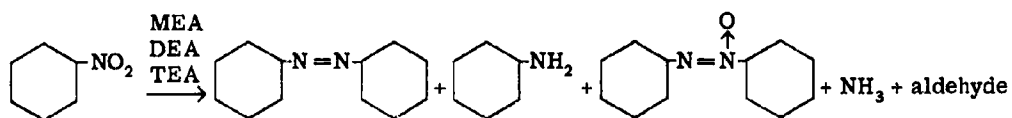
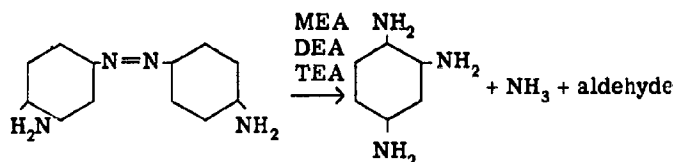
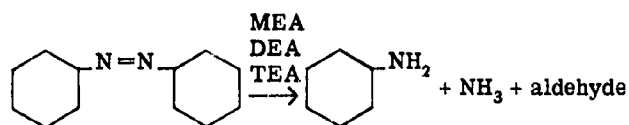
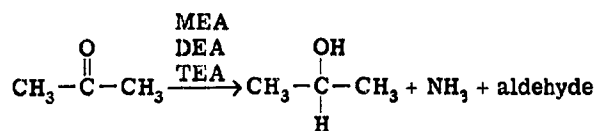
The ions Fe^{+3} , Mn^{+2} , Co^{+2} , Ni^{+2} , Zn^{+2} , and Cd^{+2} accelerated the decomposition of hydrogen peroxide by the copper-ammonia complex by either forming catalytic complexes or acting as activators to the copper-ammonia complex (72a). However, the copper-piperidine complex displayed diminished catalytic activity when the ions of nickel, cobalt, cadmium, zinc, manganese, aluminum, and chromium were present (72c).

The character of the catalase action, by which hydrogen peroxide is decomposed into water and oxygen by such catalysts as uncomplexed copper and iron ions and the copper complexes of ammonia, triethanolamine, and pyridine has been investigated. The catalytic activity of "free" iron and cupric ions was inhibited by the addition to the reaction mixture of benzene and methylmethacrylate, while the copper-amine complexes remained unaffected. A catalytic mechanism was postulated whereby the copper-amine complexes react with hydrogen peroxide to form "active" intermediates, while the uncomplexed iron and cupric ions react through a free radical chain mechanism (73).

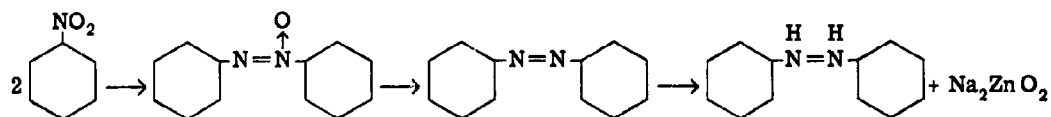
Reducing Action of MEA

The ethanolamines have been reported to be capable of reducing anthraquinone, acetone, azobenzene, chrysoidine, nitrobenzene, and 2-nitrotoluene to their various reduced forms with accompanying formation of ammonia and aldehydes (78).

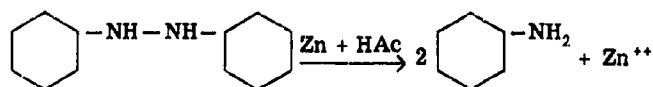




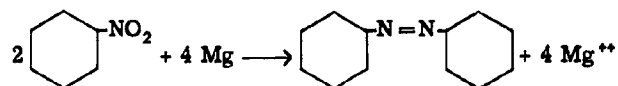
In comparison it is interesting to note that a not too vigorous reducing agent such as zinc dust in alcoholic NaOH solution will give the sequence of reactions



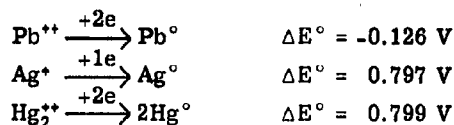
while a strong reducing agent such as zinc and acetic acid will proceed beyond the hydrazobenzene stage



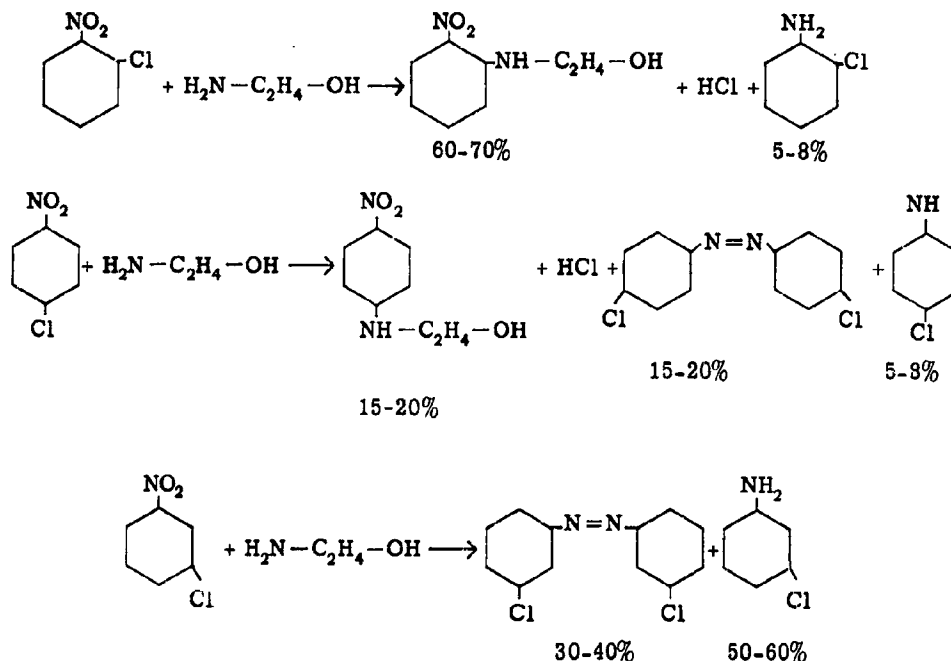
to the formation of aniline. A milder reducing agent than zinc dust in alcoholic NaOH such as metallic magnesium will proceed only as far as the formation of azobenzene (48, p. 465).



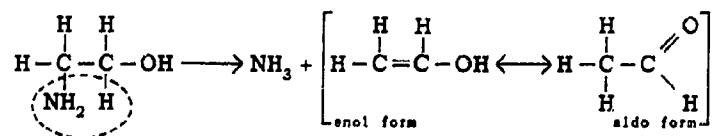
The ethanolamines are also capable of reducing lead, silver, and mercury ions in aqueous solution to the metallic state (78).



The course of reaction between MEA and a chlorine substituted nitrobenzene is influenced by the position of substitution in the nucleus (79).

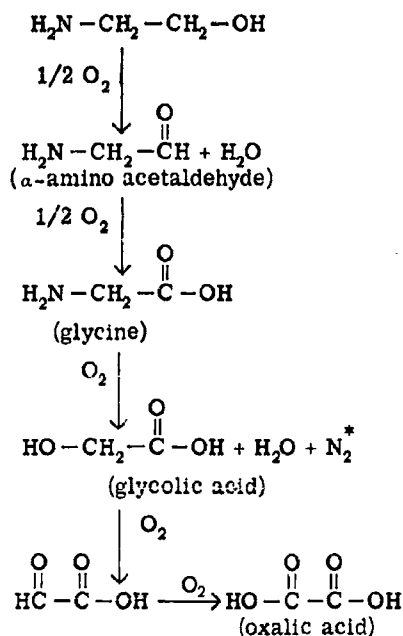


The reducing ability of a number of alkyl amino alcohols with varying numbers of C atoms separating the functional groups was investigated (80). Greatest yield of reduced forms and highest degree of reduction were obtained with the β -amino alcohols, e.g., functional groups separated by a two carbon atom chain as in MEA. The mechanism proposed for the oxidation of MEA is



Reaction of MEA with Oxygen

Jefferson Chemical Company (87) reports the following stepwise oxidation mechanism of MEA due to gaseous oxygen during carbon dioxide scrubbing operations.



Glycine, glycolic acid, and oxalic acid are said to have been qualitatively detected. During regeneration cycles with their elevated temperatures, such destruction of the amine is very much enhanced. The presence of these acids further decreases the carbon dioxide scrubbing capacity of the MEA solution by forming nonregenerative salts.

ANALYTICAL

Summary of Analytical Methods Pertaining to Amines

The following is a summary of analytical procedures which may be applied to amines and MEA. Most of the chemistry of these procedures has been outlined elsewhere in this report, except for items (1) and (3) whose chemistry is obvious.

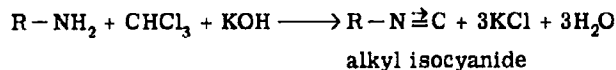
1. Titration of the purified amine base with standard acid gives its equivalent weight.
2. Ignition of the platinum or gold double salt gives the equivalent weight of the amine (Double Salts p. 37).
3. Analysis of the hydrochloride salt of an amine for the percentage chlorine gives the equivalent weight of the amine (titratable base).
4. Reaction with nitrous acid distinguishes between primary, secondary, or tertiary amines (Reaction with Nitrous Acid p. 24)
5. Only primary amines give the Isocyanide Test (p. 45).
6. Tertiary amines cannot be acetylated (Acylation p. 24).

*Release of N_2 instead of NH_3 reported.

7. Only primary amines give Hofmann's Mustard Oil Reaction (45).
8. Primary amines and ammonia may be quantitatively determined by reaction with nitrous acid (p. 24).
9. The Hinsberg test distinguishes between primary and secondary amines (Acylation p. 24).
10. Acylation forms a substituted amide of limited solubility (Acylation p.24).
11. The Kjeldahl method of analysis for total amine nitrogen. Special methods are required for nonamino nitrogen.
12. Separation of a mixture of β -amino alcohols by partitioning on columns of buffered silica gel (p. 46).
13. β -amino alcohols quantitatively estimated by periodate oxidation (p. 46).

Isocyanide Test

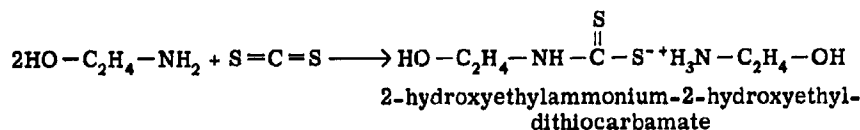
The reaction of a primary amine with alkali and chloroform yields an alkyl isocyanide which has an intolerable odor. Secondary and tertiary amines do not give this reaction and odor.



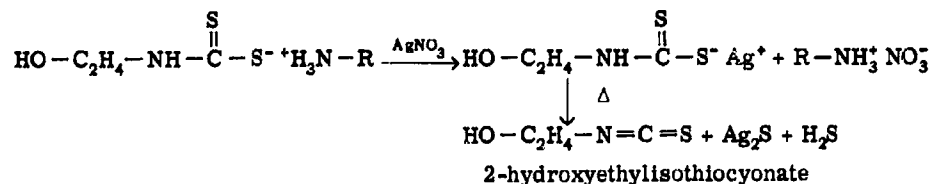
The formation of this compound therefore represents a qualitative test for primary amine (26).

Hofmann's Mustard Oil Reaction

A primary or secondary amine will react with carbon disulfide to form a salt of substituted dithiocarbamic acid.



The addition of silver nitrate, mercuric chloride, or the salt of any heavy metal capable of forming stable sulfides, accompanied by gentle warming of the solution produces a readily detectable pronounced odor of the pungent ethylisothiocyanate (ethyl mustard oil) (26).



Separation of the β -Amino Alcohols

β -amino alcohols may be separated quantitatively as the hydrochlorides on partition columns of buffered silica gel. Ethanol-chloroform mixtures are used as eluting agents. This procedure is claimed to be capable of separating β -amino-1-propanol from MEA in recoveries that vary from 96 to 100% (37). Buffered silica gel is prepared by treating silica gel with a mixture composed of equal volumes of buffer solution (pH = 4.85), ethanol, and chloroform. The buffer solution has the following composition: $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, 184.5 g; Citric acid monohydrate, 51 g; and H₂O to make one liter. The eluting solution has the following composition in parts by volume: buffer solution 1 part, EtOH 2 parts, and CHCl_3 1 part.

Quantitative Estimation of β -Amino Alcohols

A method for the quantitative estimation of β -amino alcohols obtained by the chromatographic separation described above is based on the estimation of formaldehyde released in a periodate oxidation (37). The procedure is as follows:

1. To the test sample obtained from the chromatographic column add: 0.1 ml satd. K_2HPO_4 soln.; 0.8 ml H_2O ; 1 drop periodate reagent (1.07 g NaIO_4 + 44.7 ml H_2O + 5.3 ml NaOH).
2. Oxidation is allowed to proceed four minutes. One drop of $\text{Na}_2\text{S}_2\text{O}_5$ solution is added to destroy the IO_4^- excess.
3. Chromotropic acid solution (0.1 ml) is added and mixture is cooled in an ice bath.
4. 4 ml H_2SO_4 is added, mixture shaken, and color developed by heating at 100°C (water bath) for ten minutes.
5. After cooling and dilution with 5 ml H_2O the optical density is measured at 570 $\text{m}\mu$.

Purification of MEA (10)

A sample of MEA is subjected to fractional distillation, washed repeatedly with ether, and then crystallized from an ethyl alcohol solution. This was followed by fractional distillation, care being taken to prevent the absorption of carbon dioxide. Two successive crystallizations and distillations gave a product with a constant melting point of 10.51°C (corrected) and a boiling point at 760 mm of 171.1° ± 0.1°C. Potentiometric titration against standard hydrochloric acid and a weight titration using methyl orange indicator gave results that were 99.97 and 99.96% respectively.

Potentiometric Titration of Free Amine and Amine Carbonate in Carbonated MEA Solutions

Aqueous MEA solutions containing various concentrations of carbon dioxide may be potentiometrically titrated, using glass and calomel reference electrodes, to obtain a titration curve possessing two inflection points. The first inflection point occurs at pH 7 and the second at pH 4. The carbon dioxide content of the solution may be determined by calculating the number of equivalents of titrant expended between the first and second inflection points and considering that the species being titrated in this region is the bicarbonate ion. Total concentration of nitrogen present (MEA) is represented by the number of equivalents of titrant necessary to achieve the second inflection point (44).

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Among the topics discussed are a compilation of 27 different and suitably referenced physical and chemical properties of MEA, its commercial preparation,

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