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UNIVERSITY OF LOUISVILLE

"THE OXIDATION OF AMINO ALCOHOLS"

A Dissertation

Submitted to the Faculty
Of the Graduate School of the
College of Liberal Arts
In Partial Fulfillment of the
Requirements for the Degree
Of Master of Arts

Department of Chemistry

by

Loran S. O'Bannon

1933

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INTRODUCTION

INTRODUCTION

The mono-, di-, and tri-ethanolamines are three different members of the homologous series of the hydroxyethyl alkylamines and are best prepared by the addition of ammonia or the corresponding primary and secondary amines to ethylene oxide in aqueous solution (1). Although they are comparatively easy to prepare commercially, they are not common compounds, but on the other hand, neither are they extremely rare. These amino alcohols, as a general rule, are only relatively stable and are easily decomposed upon contact with strong oxidizing agents in the presence of suitable and appropriate catalytic agents. During this process of oxidation, the amino group almost without variation is removed entirely from the mono-ethanolamine (2) and ammonia is liberated as a by-product of the reaction. Since the mono-, di-, and tri-ethanolamines are of the same homologous series and are prepared in similar manners (1), it is only reasonable and under-

standing to assume that they possess similar chemical characteristics and properties. It is only reasonable and understanding, therefore, to assume that the amino group will be removed from the di-ethanolamine and the tri-ethanolamine, an apprehension that will be proved at a later point in this dissertation. For the most part, these reactions between the amino alcohols and the oxidizing agents should take place with comparative ease (2).

The oxidation of the most simple and elementary of these amino alcohols affords an excellent example of this particular type of reaction. When mono-ethanolamine is treated with hydrogen peroxide in the presence of ferrous sulphate at a medium temperature of 30-50° C., the simplest of the aldoses, glycolic aldehyde, which is sometimes known as glycol aldehyde, is formed (2), as is shown by the following equation:

Glyoxal (I) contains an aldehyde group, as is shown by its formula, and shows quite distinctly the properties of the aldehydes, as for instance

in its extreme ease of oxidation (3).

As the oxidation continues, the glycolic aldehyde is decomposed to the di-aldehyde, glyoxal (2), which is also known as oxaldehyde. This transformation is illustrated by the following equation:

Under ordinary laboratory conditions, glyoxal (I) is obtained in the liquid form. It possesses a melting point of 15° C., and a boiling point of 50.5° C. It has a molecular weight of 58.02, and its specific gravity is 1.14. It is very soluble in water and is soluble in alcohol and ether in ordinary quantities (4).

Thus, it becomes quite obvious to the understanding that the assemblage of nitrogen and hydrogen atoms forming the amino radicals of the amino alcohols are to be found considerably less stable and resistant to the breaking force of certain oxidizing agents of sufficient strength than the alcoholic groups of the same alcohol.

In view of these properties and characteristics, it shall be the object and intention of this investigation to determine and bring to

light some method, either direct or indirect, by which the mono-, di-, and tri-ethanolamines may be oxidized and at the same time retain the amino group in combination with the final acids formed.

THEORIES

THEORIES

MONO-ETHANOLAMINE

Mono-ethanolamine (5), which is also known as amino-ethyl alcohol, aminoethane, or hydroxyethylamine, possesses the empirical formula, $\text{CH}_2(\text{OH})\text{CH}_2\text{NH}_2$, and a structural arrangement,

It has a boiling point of 171°C . (6), and is best prepared by the addition of ammonia or the corresponding primary and secondary amines to ethylene oxide in aqueous solution (1).

When mono-ethanolamine is treated with hydrogen peroxide in the presence of a suitable catalytic agent such as ferrous sulphate, glycol aldehyde is formed, and upon further oxidation glyoxal (2) is produced as is shown by the following equations:

A medium temperature of 30-50° C. should be maintained during the course of this reaction.

When mono-ethanolamine is treated with an acid such as hydrochloric acid and a solution of sodium nitrite, ---acetaldehyde, ammonium nitrite and sodium chloride will form as the products of the equation (7):

Thus, it becomes obvious that whenever mono-ethanolamine is brought in contact with a strong oxidizing agent in the presence of the appropriate catalysts, the alcohol is oxidized readily and at the same time the nitrogen is liberated from the compound either in the form of free ammonia or some ammonium salt. Consequently, it is quite obvious that in order to oxidize this amino alcohol, it will be necessary to protect the amino group or to strengthen it to such an extent that it will be much more stable than the alcoholic group of the alcohol and will, therefore, be strong enough to resist the action of the oxidizing agents. When this reaction takes place,

it may be assumed that the hydroxyl group will then undergo the oxidizing process, while the amino radical will remain intact.

In order to bring about the stabilization of the amino group, it is necessary that some preliminary reaction take place in which the amino group is involved; a reaction in which one or both of the hydrogen atoms of the amino group will be replaced by a more complicated carbon chain. By a careful investigation of the various reactions of the amino groups of the mono-, di-, and tri-ethanolamines, it is found that such a stabilization may be obtained through the process of acetylation. In other words, we know that the reaction will take place at the weakest part of the structure of the molecule, and the weakest part of the molecule almost invariably has the simplest structure. Therefore, by acetylation we may be able to complicate the structure surrounding the nitrogen atom to such an extent as to prevent any reaction at this point in the arrangement of the molecule (8).

The acetylation takes place very readily when one part of the mono-ethanolamine is treated with four parts of acetyl chloride, the entire reaction taking place under the cooling effects of chipped ice (9). When the reaction is com-

plete, the white solid substance which should be formed should be washed thoroughly in acetone for purification. A large mass of short white crystals begin to crystallize out, immediately deliquescing upon their exposure to the atmosphere. This white solid substance is known as N-acetyl- β -aminoethyl alcohol. The reaction is shown by the following equation:

Thus, we are able to see how the acetyl group replaces one of the hydrogen radicals of the amino group. When this new acetyl-amino group is placed in contact with an oxidizing agent, its ready resistance to any reaction demonstrates that it is much more stable than the original amino group. When this new compound is treated with a weak or only a moderately strong acid or oxidizing agent, no reaction will take place. This statement must be proved later by experiment. But whenever a strong oxidizing agent is placed in contact with the N-acetyl- β -aminoethyl alcohol, the new acetyl-amino group should still resist all attempts at oxidation and force the oxidizing reaction to take place with the alcoholic radical.

Now, since it is seen that the acetyl-amino group of the N-acetyl- β -aminoethyl alcohol should be more stable than the alcoholic radical, the next step is to select a suitable method of oxidation.

The oxidation of an organic compound may involve the addition of oxygen or of a hydroxyl group to an unsaturated linkage, the removal of hydrogen, the replacement of a hydrogen or other atom by oxygen or hydroxyl, the breaking of a carbon to carbon linkage and the subsequent addition of oxygen or hydroxyl, or the increase in the valence of carbon or other element (10).

There are five important considerations that should be borne in mind when selecting a reagent to bring about an oxidation. (a) The reagent must be strong enough to accomplish the desired results. (b) It must be of such a nature that the reaction may be stopped at the desired stage. (c) It should give a minimum amount of side reactions. (d) The products of the reaction should and must be separable from the organic product. And (e) the agent should be as inexpensive as possible and easily used, and should require as little apparatus as is consistent with the meeting of other requirements (10).

One of the most powerful oxidizing agents

with which we are acquainted is potassium permanganate when used in either acid or basic solution. More oxygen, however, is liberated in the acid solution. The equations for these reactions are as follows: (11)

Thus, when N-acetyl- β -aminoethyl alcohol is treated with an acid solution of potassium permanganate, the oxygen liberated by the permanganate should react with the alcohol to oxidize it to N-acetyl- β -aminoacetic acid as is shown by the equation:

By saponification, the acetyl group will be liberated to form acetic acid while at the same time the original amino group will be regenerated (8).

The white precipitate should be very carefully washed in ethyl alcohol and ether, and then the purified glycine should be very carefully and

thoroughly dried.

Glycine (I) crystallizes in colorless, monoclinic crystals which, when heated, darken at about 228° C., and melt with the evolution of a gas at $232-236^{\circ}$ C. It possesses a specific gravity of 1.1607 and is soluble in 4.3 parts of cold water and in 930 parts of ethyl alcohol (specific gravity, 0.828), but is totally insoluble in absolute ether (12). When heated with barium hydroxide, it breaks up into methylamine and carbon dioxide; nitrous acid converts it into glycollic acid. Ferric chloride imparts an intense red coloration to glycine solutions; acids discharge this, but ammonia restores it.

DI-ETHANOLAMINE

Di-ethanolamine (13), which is also known as imino-ethyl alcohol or imino-diethyl alcohol, is a thick, heavy, syrupy liquid that appears to be slightly yellowish in color. It possesses a melting point of 28° C., and a boiling point of 270° C. It has a molecular weight of 105.1, and possesses an empirical formula, C₄H₁₁O₂N, and possesses the following structural formula,

Like mono-ethanolamine, di-ethanolamine is a relatively stable compound, but during its interaction with certain chemical compounds it is noticed that the imino group is almost invariably attacked and the nitrogen removed almost without variation (2), as is illustrated by the following equation:

Therefore, it again becomes necessary to bring about the stabilization of the amino group if we desire the reaction to take place with the alcoholic groups rather than with the amino-radicals. Like mono-ethanolamine, it is found that such a stabil-

ization may be obtained through a process of acetylation.

This acetylation (2), if it is found practicable, should take place with comparative ease when one part of the di-ethanolamine is treated with approximately four parts of acetyl chloride. This entire reaction, as was done in the case of mono-ethanolamine, should take place under the cold and chilling influence of water that contains a large quantity of chipped ice. A heavy white precipitate should form upon the completion of the reaction. This precipitate is known as N-acetyl- β -iminoethyl alcohol. Its formation during the reaction is shown by the following equation:

The precipitate (I), N-acetyl- β -iminoethyl alcohol, which has been formed during the reaction, is now thoroughly washed in acetone which has previously been purified, and a large mass of short, white crystals begin to form, which liquefy immediately upon the absorption of moisture from the atmosphere. To prevent deliquescence, these crystals must be

preserved in an air-tight sample tube or a vacuum dessicator.

Thus, it is apparent as to how the hydrogen atom is replaced by the acetyl group. When this new acetyl-amino group is subjected to the oxidizing powers of some strong oxidizing agent, its ready opposition toward any reaction illustrates that it is much more stable than the original imino-group. Thus, whenever an oxidizing agent of sufficient strength that will cause any reaction whatever to take place with this new compound is placed in contact with it, the N-acetyl- β -iminoethyl alcohol, the acetyl-amino group should still resist oxidation and force the reaction to take place with either one or both of the hydroxyl groups of the alcohol.

As used with theoretical success in the oxidation of the N-acetyl- β -aminoethyl alcohol, and since it fulfills all requirements for a satisfactory agent to bring about the oxidation, an acid solution of potassium permanganate is again employed to oxidize the alcohol. Theoretically, the reaction should take place in stages with only one of the alcoholic radicals reacting at a time, and should be able to be stopped at the completion of the oxidation of one of the alcoholic radicals, as is illustrated

by the equations:

(I)

Upon saponification, the acetyl group will be removed from the N-acetyl- β -iminoacetic acid (I) to form acetic acid while at the same time the imino group will be regenerated. The equation for the reaction is as follows:

The white precipitate should be washed very

thoroughly in ethyl alcohol and ether, and immediately following this procedure, the purified imino-acetic acid should be very carefully dried and placed in a very clean and air-tight sample tube.

Imino-acetic acid (14) is also known as imino-diacetic acid and diglycolamic acid. It melts at approximately 225° C., and is obtained, as a general rule, in colorless, rhombic crystals. Imino-acetic acid is very slightly soluble in water and is totally insoluble in alcohol and ether. It has a molecular weight of 133.06, and forms salts when reacted with both acids and bases.

(15)

TRI-ETHANOLAMINE

Tri-ethanolamine (16) is also recognized as nitriloethyl alcohol, azoethyl alcohol, and amino-triethyl alcohol. It is a thick, heavy, oily appearing substance that is colorless when obtained in a pure state and which turns to a light yellow color when it becomes slightly aged. It has a molecular weight of 149.12, and possesses an empirical formula, $C_6H_{15}O_3N$, and a structural formula,

Similarly to mono-ethanolamine and di-ethanolamine, the tri-ethanolamine is a comparatively stable compound, but whenever the substance is placed in contact with certain chemical reagents, it is again noticed that the amino group is the weakest point in the structure of the alcohol and the nitrogen is almost invariably removed from the original position upon the completion of the reaction. Therefore, it again becomes a necessity to reinforce the amino group in order to compel the oxidizing action to attack the alcoholic radicals

of the alcohol, rather than the amino group. This may be accomplished, as in the cases of the mono-ethanolamine and the di-ethanolamine, through the process of acetylation.

Again, as in the cases of the mono-ethanolamine and di-ethanolamine, the acetylation of the tri-ethanolamine will take place with great ease when one part of the alcohol is treated with approximately four parts of pure acetyl chloride, the reaction taking place under the decidedly necessary cooling effects of iced-water. A heavy white precipitate should be formed upon the completion of the reaction. This precipitate is known as N-acetyl- β -triethanolamine. Its formation during the reaction is illustrated by the following equation:

The precipitate (I), N-acetyl- β -triethanolamine, which has been formed during the reaction, is now

thoroughly washed in acetone which has previously been purified, and an abundant quantity of white crystals take form, which liquefy immediately upon the absorption of moisture from the atmosphere. To prevent deliquescence, these crystals must be preserved and protected in an air-tight sample tube or vacuum dessicator.

Thus we are able to see how the nitrogen, which in the tri-ethanolamine has a valence of three, assumes a valence of five and is consequently strengthened to such an extent that it will resist the oxidizing effects of any oxidizing agent. Therefore, when an oxidizing agent of sufficient strength is brought into contact with this new acetylated tri-ethanolamine, the alcoholic radicals will be attacked and oxidized to carboxyl groups while the amino group will remain unaffected.

Theoretically, potassium permanganate is one of the most powerful of all oxidizing agents when it is used in an acid solution. It was used to advantage in the oxidation of mono-ethanolamine and di-ethanolamine, and, therefore, it is possible that it may be used successfully in the oxidation of tri-ethanolamine. This reaction should take place in successive steps with one alcoholic group being attacked at a time, as is

(III)

At the completion of the reaction, the acetyl-group may be liberated from compound III upon saponification with sulphuric acid to form imino-triacetic acid, acetic acid, hydrochloric acid and sulphur trioxide. The reaction is shown by the following equation:

This white precipitate is purified and washed thoroughly in ethyl alcohol and ether, and immediately upon purification it is carefully and thoroughly dried.

Imino-triacetic acid (17), $C_6H_9O_6N$, known sometimes as tri-glycolamic acid, decomposes when subjected to heat at approximately 245-250° C. As a general rule, it is obtained in white or colorless crystals that are sometimes difficult to purify. It is somewhat soluble in water, but is totally insoluble in ethyl alcohol and ether. It has a molecular weight of 191, and unlike di-ethanolamine, which forms salts with both acids and bases, tri-ethanolamine will not react with either bases or acids and is relatively stable within itself (18).

GENERAL THEORIES

Theoretically, it should be practicable to halt the reaction immediately after the oxidation of the first alcoholic radical of the di-ethanolamine and immediately after the first and second alcoholic groups have been oxidized in the tri-ethanolamine. In a practical sense, however, this reaction meets with difficulty and it appears impossible to arrest the chemical transformations at the desired points. The reason for the impracticability of this theory is that each of the alcoholic groups is equally susceptible to oxidation,--and since the reaction takes place so vigorously, the alcoholic groups are either oxidized simultaneously, or are oxidized in such rapid succession as to make the passage of time imperceptible.

Another theory concerning the preparation of an acid containing one or even two unoxidized alcoholic radicals is to prepare glycine or di-glycolamic acid and in some manner substitute an ethanol group for one or both of the hydrogen atoms of the amino group. This method, also, is found to be impracticable, the reasons coming to light when a study of the reactions and properties of the amino-acids is made.

Glycine is the simplest of the amino acids and is typical of the class and hence will be used as an illustration in the discussion of the general properties of the amino acids. By reaction with nitrous acid it yields nitrogen gas and hydroxyacetic acid (19). This property is in common with the other acid-amines, because they also react with nitrous acid to produce nitrogen gas and the corresponding alcohol (alcohol-acid). In fact when an amino group is in the α position with respect to a carboxyl group, the reaction with nitrous acid takes place more easily than in the case of the ordinary amines or ammonia itself. This reaction is used in determining and studying α amino acids. The equation is shown as follows:

One of the most important characteristics of the amines is their base-forming property and their ability to form salts with acids (20). In aminoacetic acid, for example, we have an amino group that is capable of forming salts with acids, and along with it an acid group. The question naturally arises as to whether or not the acid group is able to react with the amino

group.

When ammonia is brought in contact with water, it adds hydrogen ions to some extent and leaves hydroxyl ions free in the solution. When ammonia comes in contact with an acid, it takes up hydrogen ions very rapidly, forming ammonium ions, and leaves the negative ion of the acid free in solution. The essential thing about the interaction of ammonia and acids is the addition of the hydrogen ion by the ammonia. Since hydrogen ions are free to move about independently in a solution, they should be taken up by the amino groups, no matter where the amino groups are situated with respect to the acid group from which the hydrogen ions arise. If this should happen in the case of the amino-acetic acid, the product would have the following structure:

which might be described as an ionized internal salt (21). When the term ionized is used in this connection it must be understood in a qualified sense. Ions are free to move independently and in this case the positive and negative ions are attached to each other and cannot move independently. A structure of this kind in solution would not

conduct electricity.

There seems to be ample reason for thinking that amino-acetic acid in solution exists in part in the form of the internal salt as pictured below. However, it is the salt of a weak acid and a weak base and as such is hydrolized to a greater or lesser extent, depending on the dilution. In very dilute solution it would be largely hydrolized as may be pictured in the following way:

Actually we may consider the substance to exist both as an acid and as a base in solution, and for the sake of simplicity we shall picture the reactions of the amino acids as though they exist in the free form rather than as one of the internal salts.

By analogy with the corresponding hydroxy acids, amino-acetic acid should be stronger in acid properties than acetic acid itself. Recent evidence makes it probable that this is the case in actuality but that the tendency of the amino group to take up hydrogen ions compensates for the greater tendency of the carboxyl group to throw off hydrogen ions. The result is that a solution of a simple

amino acid is practically neutral in reaction.

The amino acids are amphoteric substances, that is, they are both weak acids and weak bases. They are consequently able to form salts with either acids or bases as indicated by the following equations:

The salts formed, in both cases, are freely ionized in water solution and are soluble salts. Thus, glycine is more soluble in acid or alkaline solutions than it is in pure water. In the sodium salt, the organic ion is negative and in the hydrochloric acid salt, the organic ion is positive.

The amino acids, because of the acid group, are able to form esters (22). Esters of the amino acids are usually prepared by dissolving the amino acid in alcohol and introducing dry hydrogen chloride gas, which acts both as a dehydrating agent and as a catalyst. By this means the hydrochloride of the ester is formed and obtained from the mixture, for the ester itself is decidedly basic in water solution.

From this ester hydrochloride the free ester itself may be obtained, by careful neutralization and subsequent purification. The amino acids, like other acids, form derivatives such as acid chlorides, etc.

Thus, we are able to understand why an ester is formed when we attempt to accomplish the preparation of the acids with a mixture of carboxyl and alcoholic groups.

EXPERIMENTS

EXPERIMENTS

MONO-ETHANOLAMINE

One mole of mono-ethanolamine is placed in a flask which is partially submerged in iced-water. Four moles of acetyl chloride are measured out and added to the mono-ethanolamine in the submerged flask by means of a separatory funnel, the mixture being stirred constantly by means of an electric stirrer. Theoretically, it is an unnecessary waste of the compound to use four moles of acetyl chloride to bring about the acetylation. Practically, however, some of the mono-ethanolamine will remain unaffected unless this excess amount is used.

During the initial stages of the reaction, a heavy white gas with a very irritating odor is liberated. However, as the experiment progresses, the gas gradually decreases in quantity and a heavy white solid substance begins to form in the flask, and this white precipitate, which is produced in an unusually abundant quantity, is the acet-

ylated amino-ethyl alcohol, which is more commonly known as N-acetyl- β -aminoethyl alcohol.

The precipitate is carefully removed from the flask and is washed thoroughly with acetone that has previously been purified. The purification of the acetone is brought about in the following manner. To one cubic-centimeter of acetone add from two to three times its volume of a cold saturated solution of sodium bisulphite and shake thoroughly. The additive compound, $C_3H_6ONaHSO_3$, crystallizes out on standing. A crystal of the substance introduced into the liquid will hasten its formation immeasurably. The bisulphite solution is prepared either by dissolving sodium metabisulphite in water, or by passing sulphur dioxide into soda crystals covered with a layer of distilled water. It forms an apple-green solution smelling very strongly of sulphur dioxide. The sulphur dioxide is conveniently obtained from a bottle of the liquid, which can be purchased, or by dropping concentrated sulphuric acid on solid sodium sulphite (23). The crystalline mass, which possesses an empirical formula, $C_3H_6ONaHSO_3$, is filtered and well drained and then with a sodium carbonate solution is carefully distilled. The distillate is dehydrated over solid anhydrous calcium chloride and finally redistilled and placed

in an air-tight container until used (24).

Upon the completion of the purification of the N-acetyl- β -aminoethyl alcohol, the compound is very carefully dried and placed in a vacuum dessicator until used. By placing the substance in a dessicator, all of the atmosphere, which contains a certain indefinite amount of moisture, can be expelled and will be excluded from the acetylated alcohol and thus, deliquescence will be prevented. N-acetyl- β -aminoethyl alcohol is a very deliquescent substance, liquefying quite readily upon exposure to the moisture of the atmosphere.

The purified N-acetyl- β -aminoethyl alcohol is treated with an excess of potassium permanganate and sulphuric acid. This reaction takes place with comparative ease, the resulting products being either liquid or dissolved solid. This liquid or dissolved solid, which is colorless, is placed in a beaker or evaporating dish over a Bunsen burner and gradually heated until it begins to boil. This evaporation is permitted to continue for approximately two or three hours, or until the liquid assumes a yellowish color and the sweet smelling odor of fresh caramel. When the evaporation is nearly complete, the substance is placed in the cooling chamber of a refrigerator

and permitted to remain under the chilling effects of ice for approximately twenty-four hours.

When this yellowish and sweet-smelling liquid is permitted to stand for twenty-four hours in a cool place, a white precipitate will come down. This white precipitate is filtered off and washed very thoroughly in ethyl alcohol and ether and very carefully dried and placed in an air-tight sample tube.

The final precipitate is believed to be glycine. It possesses a melting point of 234° C., and chars upon heating in an electric oven. A qualitative analysis shows the substance to contain quantities of carbon, hydrogen, oxygen and nitrogen. A quantitative analysis shows that the nitrogen is present in quantities amounting to 18.657 percent by weight. This analysis was made by the Kjeldahl method.

Kjeldahl's method (25) of determining the percentage of nitrogen in a compound is explained as follows. The organic compound is heated very strongly with sulphuric acid, which oxidizes the organic matter and converts the nitrogen into ammonium sulphate. The ammonia is then estimated volumetrically by distilling with caustic soda and collecting the gas, which is liberated, in standard acid. About 0.5 gram of the organic compound is accurately weighed and introduced into a round Jena

flask (500 c.c.), together with 15 c.c. of pure concentrated sulphuric acid and about 10 grams of anhydrous potassium sulphate. The object of the latter is to promote oxidation by raising the boiling point of the liquid. The flask is clamped over wire gauze and the contents boiled briskly until the liquid, which first darkens in color, becomes colorless or faintly yellow or light green. When the decomposition is complete, which takes from thirty to sixty minutes, the flask is left to cool and the contents are then diluted with two to three volumes of water. A Kjeldahl bulb, which is furnished with a rubber cork, through which a bulb adapter is inserted (to retain any alkali which may spurt upward), the latter being connected to a condenser, is placed in the neck of the flask. The end of the condenser just dips below the surface of 25 c.c. of a half-normal solution of hydrochloric or sulphuric acid, contained in a flask or a beaker. Thirty grams of caustic soda in 60 c.c. of water are carefully poured down the side of the flask so as to mix the contents of the flask as little as possible, and after introducing a few pieces of porous earthenware or granulated zinc to prevent bumping, the cork is quickly inserted. The flask is now carefully shaken to mix the contents and the liquid boiled briskly

until no more ammonia is evolved, which should take from thirty to forty-five minutes. This should be ascertained by testing a drop of the distillate with red litmus paper. If the operation is complete, the liquid is titrated with half-normal sodium carbonate solution, using methyl orange as the indicator.

This analysis proves quite conclusively that the product prepared is either glycine or some compound bearing the same empirical formula. However, as an added precaution, a derivative of the amino-acetic acid or glycine is prepared in the following manner (26). One-tenth of a gram of the substance is dissolved in one cubic-centimeter of water. A three cubic-centimeter quantity of a saturated solution of picric acid in alcohol is added to the original solution. Upon vigorous shaking, and only upon vigorous shaking, an abundant quantity of yellow crystals crystallize out. These crystals are filtered off and washed with a two cubic-centimeter quantity of 50 percent alcohol and dried thoroughly on tile at 100° C. This substance blackens and decomposes with effervescence at 203° C. This entire process was repeated several times with the same qualitative results. The quantitative results, however, were variant to a very great degree, little care being taken to pre-

serve the substance prepared in a sacrifice to purity. The percentage yield of the experiment ranged about 33.1 percent.

MONO-ETHANOLAMINE

	Number of Run			
	I	II	III	IV
Weight--Mono-ethanolamine	61.066	61.066	61.066	61.066
Weight--Acetyl Chloride	313.92	316.82	314.73	313.07
Time of Reaction*	45	48	45	50
Weight--N-acetyl- β -aminoethyl alcohol	79.013	74.391	82.654	84.085
Weight--Potassium Permanganate	163.81	167.44	169.83	172.12
Weight--Sulphuric Acid	107.36	108.43	110.02	113.12
Time of Evaporation*	150	120	210	160
Time of Precipitation**	24	28	24	23
Yield--Theoretical (gms)	75.05	75.05	75.05	75.05
Yield-Experimental (gms)	24.8416	18.3872	27.2431	28.8943
Percentage Yield	33.1%	24.5%	36.3%	38.5%

* Time in minutes

** Time in hours

All weights in grams

DI-ETHANOLAMINE

One mole of di-ethanolamine is carefully measured out and placed in a flask that has been partially submerged in a bath containing iced-water. Four moles of acetyl chloride which have been measured out and placed in a separatory funnel leading into the flask containing the di-ethanolamine, are added, drop by drop. Although it appears unnecessary and a seeming waste of the compound, four moles of the acetyl chloride must be used to insure the completion of the reaction. And unless four moles of acetyl chloride, which theoretically is considerably in excess, are used, the di-ethanolamine will not be completely acetylated. The acetyl chloride is added drop by drop because its reaction with the di-ethanolamine is extremely vigorous, and if it is added too rapidly an explosion may occur in which much of the compounds will be wasted.

During this entire process, the mixture is stirred constantly by means of a special stirring apparatus connected to and operated by a small electric motor. As was the case with the mono-ethanolamine, a heavy white gas with an irritating odor is liberated during the early stages of the reaction. However, as the experiment progresses, the gas decreases in quantity and a heavy white

solid substance precipitates out. This heavy white precipitate, which is produced in a very abundant quantity, is the acetylated imino-ethyl alcohol, the correct name for which is N-acetyl- β -iminoethyl alcohol.

This precipitate is very carefully removed from the flask and is washed very thoroughly in acetone, the acetone having previously been purified. The purification (24) of the acetone was thoroughly discussed in the experimental section of the discussion of mono-ethanolamine.

When the washing of the precipitate is complete, the strong and irritating odor of the acetyl chloride is entirely removed. This white precipitate is then thoroughly dried and placed in a vacuum dessicator to prevent deliquescence, which takes place quite readily when the product is placed in contact with the moisture found in the atmosphere.

This purified N-acetyl- β -iminoethyl alcohol is treated with an excess of potassium permanganate and sulphuric acid. The reaction takes place quite readily and vigorously, the final product appearing to be like sulphuric acid in appearance, inasmuch as it is a thick, heavy, oily substance. It is well to note that it gives a decidedly acidic test. This liquid is placed over a carefully regulated Bunsen burner and is

heated very gently until it begins to boil. The boiling is permitted to continue slowly for a period of two or three hours or until the liquid assumes a yellowish color and the sweet, delicious smelling odor of caramel. At this point, the heavy oily appearing substance is removed from over the flame and cooled, and finally placed in the cooling chamber of a refrigerator and permitted to stand undisturbed for approximately twelve hours or even longer. A white precipitate will eventually come down. This precipitate is filtered off, washed very thoroughly in alcohol and ether, and is carefully dried and placed in an air-tight sample tube.

The final product is believed to be the imino-acetic acid. It possesses a melting point of 225° C. (27). A qualitative analysis shows the presence of a quantity of carbon, nitrogen, oxygen and hydrogen. A qualitative analysis shows the nitrogen to be present in the compound forming 10.58 percent by weight. These analyses prove quite conclusively that the product prepared is assuredly imino-acetic acid.

This entire process was repeated several times with the same quantitative results, which are more or less sacrificed for purity. The percentage yield was approximately 15.5 percent,

which is low due to the fact that many tests were made during the process and a considerable amount of the final product was eliminated and did not continue with the experiment to completion.

DI-ETHANOLAMINE

	Number of Run			
	I	II	III	IV
Weight--Di-ethanolamine	105.098	105.098	105.098	105.098
Weight--Acetyl Chloride	312.57	313.96	315.63	314.26
Time of Reaction*	43	45	42	45
Weight--N-acetyl- β -iminoethyl alcohol	114.28	95.05	123.95	110.42
Weight--Potassium Permanganate	168.42	172.13	173.78	172.49
Weight--Sulphuric Acid	106.97	107.38	109.67	110.32
Time of Evaporation*	145	196	214	188
Time of Precipitation**	12	14	42	14
Yield--Theoretical (gm)	133.07	133.07	133.07	133.07
Yield-Experimental (gm)	21.6904	18.2306	22.8880	19.6944
Percentage Yield	16.3 %	13.7 %	17.2 %	14.8 %

* Time in minutes

** Time in hours

All weights in grams

TRI-ETHANOLAMINE

One mole of tri-ethanolamine is carefully measured out and placed in a flask which is partially submerged in a bath of iced-water. Four moles of acetyl chloride are measured out and placed in a separatory funnel which leads into the flask containing the tri-ethanolamine. Although it appears unnecessary and a seeming waste of chemicals, four moles of the acetyl chloride must be used to insure the completion of the reaction. And unless four moles of acetyl chloride, which theoretically is considerably in excess, are used, the tri-ethanolamine will not be completely acetylated. The acetyl chloride is added drop by drop because its reaction with the tri-ethanolamine is extremely vigorous, and if it is added too rapidly an explosion may occur in which much of the various compounds will be wasted.

Drop by drop, the acetyl chloride is added to the tri-ethanolamine, the mixture being stirred constantly by means of a special apparatus connected and operated by a small electric motor. As was the case with mono-ethanolamine and di-ethanolamine, a heavy white gas with a very irritating odor is liberated during the early stages of the reaction, but as the experiment progresses, however,

the gas decreased in quantity and finally a heavy white precipitate came down. This precipitate, which is produced in a very abundant quantity, is the acetylated tri-ethanolamine, the correct name of the compound being N-acetyl- β -aminotriethyl alcohol.

This precipitate, the acetylated tri-ethanolamine, is carefully removed from the flask and is very carefully and thoroughly washed in acetone, the acetone having previously been purified. The strong and irritating odor of the acetyl group is removed entirely from the compound after the washing of the precipitate has been completed. The precipitate is then placed in a desiccator from which all air is expelled to prevent any possible chance of its liquefaction due to the absorption of moisture from the atmosphere, since the compound is already known to be very deliquescent.

This purified N-acetyl- β -aminotriethyl alcohol is placed in a beaker or flask and is treated with an excess of potassium permanganate and sulphuric acid. The reaction between these compounds takes place very readily and vigorously, with the production of crackling noises and the emanation of a white, cloudy-looking gas. The final product of

the reaction appears to be a heavy, oil-like substance, closely resembling sulphuric acid in external appearance. It is also well to note that this liquid gives a decidedly acidic test to methyl orange and litmus. The liquid is placed over a carefully regulated Bunsen burner and heated very gradually until it begins to boil. This evaporation is permitted to continue for two or three hours or perhaps longer until the liquid turns slightly yellowish in color and assumes the sweet-smelling odor of fresh caramel. At this point, the heavy, oily appearing substance is removed from above the flame and cooled, and finally it is placed in the cooling chamber of a refrigerator. Here it is permitted to stand for several hours, preferably overnight. After this period of time has elapsed, a white precipitate is found to have come down in the solution. This precipitate is carefully filtered off and washed very thoroughly in ethyl alcohol and ether. The washed precipitate is now carefully dried and placed in an air-tight sample tube and kept there until the analyses are ready to be made.

The final product is believed to be the imino-triacetic acid or tri-glycolamic acid. It possesses a melting point of approximately 245-

250° C. (28), at which point it appears to decompose. A qualitative analysis of these white or colorless crystals show the presence of carbon, hydrogen, oxygen and nitrogen in appreciable amounts. By making a quantitative analysis of the compound, it is found that 7.33 percent of the substance by weight is nitrogen. Solubility tests show that it is somewhat soluble in water, but is totally insoluble in ethyl alcohol and ether. From these analyses and tests, we can very well assume that the product formed is imino-triacetic acid.

TRI-ETHANOLAMINE

	Number of Run			
	I	II	III	IV
Weight--Tri-ethanolamine	149.120	149.120	149.120	149.120
Weight--Acetyl Chloride	314.34	313.28	313.63	314.03
Time of Reaction*	40	45	45	40
Weight--N-acetyl- β -aminotriethyl alcohol	208.41	203.96	211.05	209.83
Weight--Potassium Permanganate	167.64	171.63	172.15	171.93
Weight--Sulphuric Acid	108.37	110.44	110.83	111.63
Time of Evaporation*	165	170	170	190
Time of Precipitation**	15	14	29	14
Yield--Theoretical (gm)	191.08	191.08	191.08	191.08
Yield--Experimental (gm)	13.0890	12.8597	15.4010	14.6749
Percentage Yield	6.85%	6.73%	8.06%	7.68%

* Time in minutes

** Time in hours

All weights in grams

Apparatus for Acetylation

- A--Acetyl Chloride
- B--Separatory Funnel
- C--Electric Motor
- D--Glass Tube leading to Water Trap
- E--Glass Stirring Rod
- F--Stopper for sealing Flask
- G--Glass Flask
- H--Water Bath
- I--Iced Water
- J--Amino-ethyl Alcohol
- K--Glass Beaker
- L--Water (trap for fumes)
- M--Glass Funnel

CONCLUSION

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Thus, we are able to perceive how mono-ethanolamine, di-ethanolamine, and tri-ethanolamine are capable of being oxidized completely without the liberation or relinquishment of the nitrogen atom, which is the basic or fundamental constituent of the amino groups of the alcohols.

Heretofore, all reactions of an oxidizing nature brought about the surrender of the nitrogen atom by the alcohols to produce ammonia or some ammonium salt. This, we assume, is due to the fact that the amino group is less firmly established and lacks sufficient strength to resist molecular and chemical disturbances than the alcoholic radicals. In other words, the hydrogen atoms of the amino group, which are more susceptible to replacement, are superseded by a more complicated structure such as the acetyl group. When this substitution has been completed, and an oxidizing agent is then brought in contact with the alcohol, the reaction is found to take place

with the alcoholic radicals, thus proving that the original assumption concerning the strength of the amino group was correct.

In view of the properties and characteristics of the three amino-alcohols in question, the oxidation of the three alcohols in such a manner as to permit their retention of their amino groups has been accomplished.

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