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HIGH PRESSURE AMMONOLYSIS OF  
ETHYLENECHLOROHYDRIN

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ABSTRACT

Ethanolamines find wide applications in industry for various purposes such as emulsifiers, detergents, & corrosion inhibitors. Monoethanolamine has been prepared chiefly by the ammonolysis of ethylene oxide<sup>1-4</sup>. Very little attention has been paid to its production by the reaction of ethylene chlorohydrin and ammonia, although the raw material (chlorohydrin) is easily available as a by-product in the petrochemicals industry. Higher alkanol amines<sup>5</sup> have, however, been prepared from the corresponding chlorocompounds. Since the processes described are all patented detailed experimental conditions have not been disclosed. Hence a systematic study of the ammonolysis of ethylene chlorohydrin was taken up with a view to determining the optimum experimental conditions for obtaining high yields of monoethanolamine.

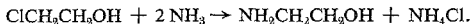
EXPERIMENTAL

The description of the apparatus used in the present investigation has been given in a previous paper by Bhrany and Rao<sup>6</sup>. The pressure reactor had a volume of 290 cc. and the stainless steel tube a volume of 180 cc.

Known quantities of ethylene chlorohydrin (B. D. H. reagent distilled at 125°C/683 mm.) and liquor ammonia (12 N) were mixed in the stainless steel tube which was placed in the reactor fitted with a calibrated pressure gauge. The reactor was then closed and the air inside flushed out with a stream of pure nitrogen. The valves were then closed and the reactor heated electrically to the desired

temperature which was maintained for known intervals of time. The reactor was then allowed to cool and the products were discharged, through the bottom valve, into two spiral glass condensers kept cooled in freezing mixture. The uncondensed gases after being scrubbed by acid were collected in a carboy over brine and analysed. In the experiments described in this paper, the residual gas was identified to be only nitrogen that was employed to replace the air in the reaction vessel. But when the temperature was raised to 150°C, the residual gas (400 cc) was found to contain 65 % hydrogen and 4 % unsaturated hydrocarbons indicating the decomposition of the chlorohydrin employed. Hence in subsequent experiments the maximum temperature of the reaction was maintained at 120°C.

The products from the condensers and the steel tube were mixed and diluted with water to a known volume. An aliquot from this was refluxed with excess of sodium hydroxide to expel the free ammonia as well as the ammonia from ammonium chloride formed during the reaction



The resulting solution was then distilled and the quantity of the amine was determined by titration with decinormal acid using methyl-orange as indicator. In order to determine whether higher ethanol amines (diethanol amine and triethanol amine) were produced during the reaction, the major portion of the distillate was neutralised with sulphuric acid and the excess of water boiled off. The concentrated solution was then mixed with the requisite quantity of alkali and distilled. It was noticed that all the liquid contents were distilled off within 170°C. Since the boiling points of diethanol amine and triethanol amine are 269° and 360°, it was concluded that monoethanolamine was the only product of the reaction. The picrate of the ethanolamine had a melting point of 158° confirming thereby that the reaction product was monoethanolamine.

## RESULTS

For investigating the effect of temperature, the reactions were carried at different temperatures employing 10 cc. of chlorohydrin and 100 cc. of 12 N ammonia. With these quantities the mol. ratio of ammonia to chlorohydrin is 7.9. The results obtained are given in Table I.

As seen from the table the yield of the ethanol amine increases with the increase in temperature with a maximum yield of 92 per cent at 120°C. After this the yield remains the same up to a temperature of 150°C. It is interesting to note that at 23°C the time taken for the maximum yield of 73 per cent is 150 hours while at higher temperatures, it is less than five hours.

The pressure of the system increases with temperature since it is dependent on the vapour pressure of ammonia. This in turn increases the activity of ammonia. It can be expected, therefore, that the increased reaction temperatures should give higher yields of the amine. The results obtained in the present case confirm this view.

TABLE I  
EFFECT OF TEMPERATURE

12 N liquor ammonia = 100 cc.       $\text{NH}_3/\text{chlorohydrin} = 7.9$   
Ethylene chlorohydrin = 10 cc.

No.	Temp. °C	Pressure psi	Time hrs.	Yield %
1	23	15	150	72.93
2	60	40	5	82.90
3	90	60	5	86.76
4	120	160	3	92.12
5	150	230	3	92.12

Since all the ammonolytic reactions are exothermic the yield of the amine should diminish at higher temperatures, but the results given in Table I indicate that this is not so, thereby indicating that this is not a case of equilibrium reaction. This is further confirmed by the fact that when additional quantities of ammonium chloride are added to the reaction mixture the yield of amine remains unaltered showing thereby the irreversibility of the reaction.

#### *Effect of ammonia ratio*

The effect of ammonia ratio was studied at the optimum temperature of 120°C by varying the quantity of liquor ammonia (12 N) and keeping a constant amount of ethylene chlorohydrin (10 cc). The results obtained are recorded in Table II.

TABLE II  
EFFECT OF AMMONIA RATIO

Chlorohydrin = 10 cc.      Temperature = 120°C  
Strength of liquor  $\text{NH}_3 = 12\text{N}$       Time = 3 hours  
Pressure = 140 psi

No.	Liquor $\text{NH}_3$ (cc.)	$\text{NH}_3/\text{chlorohydrin}$	Yield %
1	30	2.37	45.51
2	50	3.95	69.93
3	70	5.53	72.03
4	85	6.71	78.23
5	100	7.89	92.12
6	120	9.48	92.53

It is clear from the table that the yield of ethanolamine increases with increase in the ammonia ratio. In the present case a maximum yield of 92 per cent is obtained when the ammonia ratio is nearly eight. Similar observation has been recorded for the usual ammonolytic reactions.

#### *Effect of ammonia concentration*

In the above experiments (Table II) the total volume of the liquid reactants was not constant since the same concentration of liquor ammonia (12 N) was employed. To investigate the effect of ammonia concentration, therefore, the volume of the reaction mixture was maintained constant and the strength of the ammonia was varied by suitable dilution of liquor ammonia with water. This really gives the combined effect of both the ammonia ratio and the ammonia concentration since both of them are variables. The results of this investigation are presented in Table III.

TABLE III  
EFFECT OF AMMONIA CONCENTRATION  
Chlorohydrin = 10 cc                      Temp. = 120°C  
Aqueous ammonia = 100 cc,              Time = 3 hours

No.	Normality of NH <sub>3</sub>	NH <sub>3</sub> /Chlorohydrin	Pressure psi	Yield %
1	3.6	2.37	40	61.42
2	6.0	3.95	70	68.32
3	8.4	5.53	90	72.16
4	10.2	6.71	105	79.07
5	12.0	7.89	160	92.12

As seen from the results of the Table III the yield of amine has increased both with the increase in ammonia ratio and also with the increase in ammonia concentration. But a comparison of Tables II and III will clearly indicate that the yield is independent of ammonia concentration since in all the experiments when the ratio is the same the yields obtained are nearly the same except in the first case where the ratio is 2.37. For example, when the ammonia ratio is 5.53 the 12N ammonia gives 72.03 per cent yield (Table II) and the 8.4N ammonia gives 72.16 per cent yield (Table III). It can therefore be concluded that as long as the ammonia ratio is the same the concentration of ammonia has no effect on the yield of the ethanolamine.

#### *Ammonolysis with anhydrous ammonia*

Experiments were also carried out employing anhydrous ammonia as the aminating agent. For transferring a definite quantity of anhydrous ammonia from

the cylinder to the high pressure reactor an intermediate condenser was made use of as described in an earlier paper<sup>7</sup>. The effect of temperature on the reaction was studied employing 10 cc of chlorohydrin and 20 g of anhydrous ammonia and the results are given in table IV.

As seen from the table IV, in this case also, the yield of the amine increases with the increase in temperature with an optimum yield of 35 per cent at 90°C. Further increase in temperature brings down the yield of the amine. The product obtained below 60°C was clear and there was no corrosion product whereas the product obtained above 60°C contained tarry resinous mass, the amount of which increased with the increase in temperature. A comparison of Tables I and IV clearly

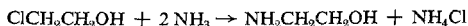
TABLE IV  
EFFECT OF TEMPERATURE ON THE REACTION  
Chlorohydrin = 10 cc.  $\text{NH}_3/\text{chlorohydrin} = 7.9$   
Anhydrous  $\text{NH}_3 = 20$  g.

No.	Temp. °C	Time hrs.	Pressure psi	Yield %
1	40	5	250	19.38
2	60	3	400	23.61
3	90	3	600	35.24
4	120	3	700	33.47

indicates that at all temperatures higher yields are obtained with aqueous ammonia than with anhydrous ammonia. Also aqueous ammonia requires comparatively easier operating conditions. Aqueous ammonia therefore offers more advantages than anhydrous ammonia for the purpose of ammonolysis of chlorohydrin.

#### DISCUSSION

Table V gives the thermodynamic data<sup>8,9</sup>, for the reaction



Since the value of free energy of formation of ethylene-chlorohydrin was not available in literature it was calculated by the method of structural modification as suggested by Parks and Huffman<sup>10</sup>. For this purpose ethane ( $\Delta F = -10,700$  cal/mole) was chosen as the basis and suitable additions were made for the replacement of two hydrogen atoms by the hydroxyl and chloride radicals. The value ( $-46,300$  cal/mole) obtained from this method is given in table V.

From the data of table V the heat of reaction, the free energy change and the equilibrium constants for the above reaction at 25°C and 120°C were calculated and the values obtained are given below

TABLE V

Compound	Heat of formation at 25°C cal/mole	Free energy of formation at 25°C. cal/mole
Ethylene dichloride (l)	-70,300	-46,300
Ammonia (g)	-11,040	-3,980
Monoethanolamine (l)	-62,520	+27,500
Ammoniumchloride (s)	-75,380	-48,730

$$\text{Heat of reaction at } 25^{\circ}\text{C} = -45,520 \text{ cal}$$

$$\text{Free energy change at } 25^{\circ}\text{C} = +33,030 \text{ cal}$$

$$\text{Equilibrium constant at } 25^{\circ}\text{C} = 6.026 \times 10^{-25}$$

$$\text{Equilibrium constant at } 120^{\circ}\text{C} = 5.164 \times 10^{-33}$$

It can be seen from these values that the reaction is highly exothermic and also that the reaction will not proceed to any considerable extent. But the experimental evidence (Table IV) shows that ammonolysis with anhydrous ammonia yields 35 per cent ethanolamine giving a value of about  $5 \times 10^4$  for the equilibrium constant at 25°C. This large deviation between the experimental and calculated values of the equilibrium constant may be due to an error in the value of the free energy of formation of chlorohydrin estimated by empirical methods. In fact the free energy of formation of chlorohydrin from the experimental value (33% yield, Table IV, equilibrium constant  $5 \times 10^4$ ) turns out to be -6849 cal/mole as against an empirical value of -46,300 cal/mole given in table V.

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