

# PREPARATION OF ETHYLENEDIAMINE BY AMMONOLYSIS OF 1,2-DICHLOROETHANE IN NONAQUEOUS MEDIA

Rahimizadeh, Mohammad\*  
Rajabzadeh, Ghadir

Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad,  
P.O.Box 91735-654, Mashhad Iran.

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**ABSTRACT :** *Kinetic parameters of the ammonolysis reaction of dichloroethane in nonaqueous media are studied and the optimum reaction conditions are reported. A suitable reactor for running the reaction under high pressure in the range of 50 to 500°C is designed. Kinetic behaviour of the system is studied and other reaction parameters such as rate constant, kinetic order, and activation energy are determined. Gas-liquid chromatography with internal standard method was used for analyses of the samples under the optimized conditions.*

**KEY WORDS :** *Ethylenediamine, Preparation, Kinetic, Ammonolysis, Nonaqueous.*

## INTRODUCTION

Ethylenediamine is a compound of ethyleneamine homologous series which is widely used in chemical laboratories and industries. This compound has also been used as an intermediate in the synthesis of other chemicals.

Laboratory preparations of ethylenediamine (EDA) are as follows: Gabriel synthesis [1], ammonolysis of  $\alpha$ -chloroacetyl chloride

followed by reduction of the product [2], ammonolysis of ethanolamine [3], and ammonolysis of a mixture of formaldehyde and cyanic acid followed by catalytic hydrogenation of the product [4]. In industry this compound is prepared from ammonolysis of dichloroethane (DCE) in aqueous or nonaqueous media [5].

Many attempts have been made for the industrial preparation of ethylenediamine and

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\* To whom correspondence should be addressed

consequently quite a large number of reports have been appeared in the literature. *Leszczynski* and his co-workers have performed the ammonolysis of DCE by the mole ratio of 20:1 for  $\text{NH}_3$ : DCE and obtained the optimum temperature in the range of 90-100°C. Aqueous ammonia (50% by weight) has been used in this process and 48% conversion of DCE has been reported [6]. *Roupyzinski et al* have studied the same reaction by the mole ratio of 2:1 to 10:1 for  $\text{NH}_3$ : DCE in the range of 80 to 160°C. They concluded that increasing the temperature and molar ratio increases the conversion of dichloroethane [7]. *Nunes* and his co-worker have investigated the effect of molar ratio of  $\text{NH}_3$ : DCE on the products of the reaction; they observed that, increasing the molar ratio of  $\text{NH}_3$ : DCE leads to increased formation of ethylenediamine relative to higher molecular weight ethylene amines. With respect to the type of products obtained, this reaction could be classified as  $\text{S}_{\text{N}}2$  reaction [8]. Researchers at *Farben Fabriken Bayer Aktiengesellschaft* company in Germany have found that solubility of the anhydrous ammonia in dichloroethane is high and hence it paves the way for performing the reaction in a homogeneous media and so the difficulty of mass transfer is eliminated [9].

The kinetic and thermodynamic parameters of this reaction in aqueous media have been investigated by *Dutkai* [10]. In their procedure the EDA was prepared at 140°C and under 15 atmospheres. Different components of the product have been separated by fractional distillation and the amount of unreacted DCE has been determined. In *Dutkai's* study, the reaction constant has been calculated for the assumed orders of 1 and 0.5. Fig. 1 shows that the logarithm of rate versus logarithm of concentration is nonlinear. So, he concluded that the synthesis of EDA is not a simple reaction and could not have an integer kinetic order.

Following this work, *Dutkai* used *Ulrich* and *Dietze* equation for determining apparent kinetic order and the rate constant of the reaction in a

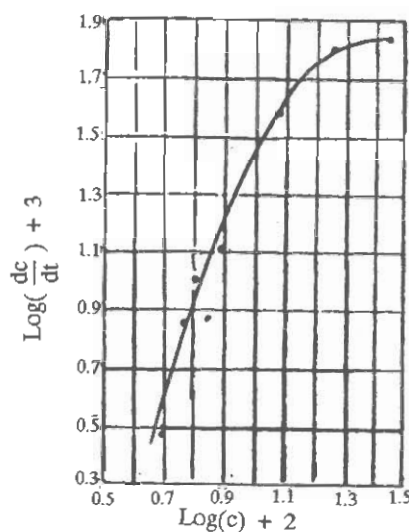


Fig. 1: Log of the rate of EDA formation versus log of DCE concentration.

homogeneous liquid phase [11]. They observed %90 conversion for DCM. The half life ( $t_{\text{H}}$ ) of this reaction was 2.9 min and the apparent kinetic order is determined to be 0.5. The calculated amount for the apparent rate constant was  $0.148 \text{ mol}^{1/2} \cdot \text{L}^{-1/2} \cdot \text{min}^{-1}$ .

These kinetic results are obtained in aqueous media and analogous results for nonaqueous media are not reported. Thus, in this paper the ammonolysis reaction of DCE in anhydrous ethanol is reported. In a systematic manner, the effects of molar ratios of  $\text{NH}_3$ :DCE, temperatures, and time are studied and the optimum conditions for the production of ethylenediamine are obtained. The activation energy and the kinetic order of the reaction are also determined.

## EXPERIMENTAL

Our initial investigations, showed the optimum temperature to be in the range of 100-140°C. At this temperature range and atmospheric pressure, the concentration of ammonia in liquid phase is too low, hence there is not any significant conversion of DCE, even after a long period of time, while for obtaining a good yield and high purity of ethylenediamine a

high molar ratio of  $\text{NH}_3$ : DCE is required. For this purpose a suitable reactor was designed. This reactor was equipped with pressure and temperature controls (between 50 to 500°C), sampling gauge, and ammonia inlet system. The schematic of the reactor is shown in Fig. 2.

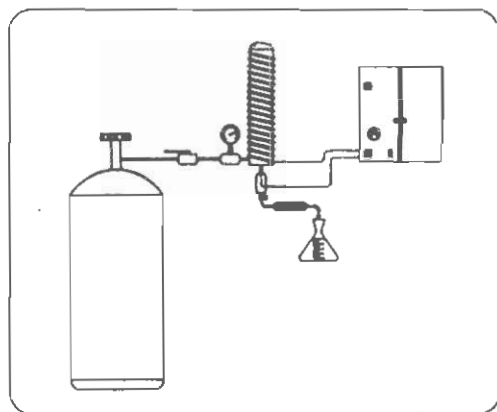


Fig. 2: Schematic of the reactor.

With this reactor, the effects of temperature, pressure, and concentration of the starting material in ethanol were investigated. At constant temperature of 120°C, the pressure variation studies showed that at 155 psi, the ammonia concentration in liquid phase reaches the saturation point. Hence, in later experiments the optimum pressure of 160 psi was used. The result of this investigation is shown in Fig. 3.

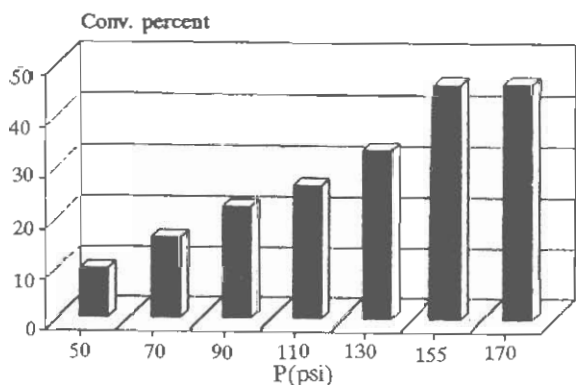


Fig. 3: Dependence of DCE conversion to the pressure of  $\text{NH}_3$  at 120°C.

At constant pressure of 160 psi, the effect of temperature variations were studied and the

optimum temperature of 120°C was obtained (Fig.4).

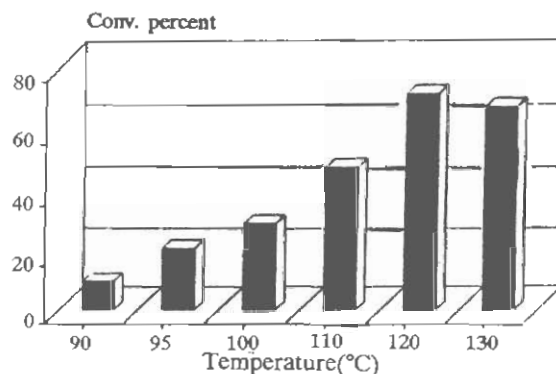


Fig. 4: Variation of dichloroethane conversion with temperature at 160 psi and after 60 min.

At the pressure of 160 psi and constant temperature of 120°C, after 60 min., the percentage of conversion was about 71.5 percent.

Variations of the logarithm of concentrations of DCE versus time at temperatures of 95, 100, 110, and 120°C are shown in Fig.5. According to these plots, the reaction is first order relative to dichloroethane. This conclusion was confirmed by performing the reaction using different initial concentrations of dichloroethane.

The apparent rate constants of the reaction at above mentioned temperatures were also determined, and were used to determine, the activation energy of the reaction (14.93 kcal/mole) (Fig. 5).

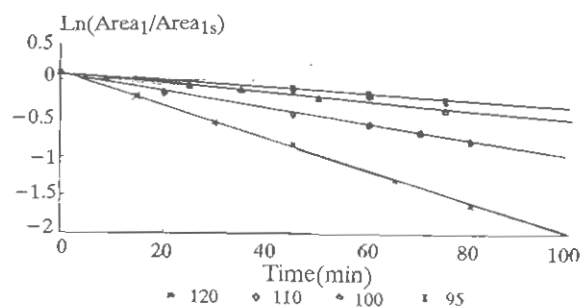


Fig. 5: Log changes of DCE concentration versus time at 95, 100, 110, 120°C.

The analysis of reaction mixture was performed with a Phillips GC PU-4500 with flame ionization detector. After preliminary investi-

gation a column containing *Chromosorb W* reacted with hexamethylene disilane and coated with 10% *Carbowax 20M* was chosen for this study. Table 1 shows the optimum results obtained in this work.

Table 1: Optimum chromatographic conditions.

Column	Chromosorb W+HMD+KOH and Carbowax 20M
Injected volume	0.1 $\mu\text{L}$
Argon flow rate	52 $\text{mL}\cdot\text{min}^{-1}$
Hydrogen flow rate	43 $\text{mL}\cdot\text{min}^{-1}$
Air flow rate	400 $\text{mL}\cdot\text{min}^{-1}$
Column temperature	60°C(3min), 60-150°C(12°C/min)
Injector temperature	140°C
Detector temperature	160°C
Sensitivity	1600
Integrator sensitivity	32

## RESULTS AND DISCUSSION

From the above studies, it can be concluded that the reaction of DCE with ammonia occurs in nonaqueous liquid phase. At pressure of 160 psi, the optimum temperature is 120°C. At temperatures above 120°C, the percentage of conversion of dichloroethane is reduced probably due to reduction in concentration of ammonia and dichloroethane in the liquid phase. Hence, in running the reaction at higher

temperatures in order to increase the rate, one should use pressures higher than 160 psi.

At the given condition (high and constant concentration of ammonia), the reaction is pseudo-first order and the mechanism is  $\text{S}_{\text{N}}2$ . The activation energy of this reaction is about 14.93 kcal/mol.

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