
TECHNICAL NOTE

KINETICS OF BENZYL CHLORIDE PRODUCTION IN A BENCH REACTOR UNDER PRESSURE WITH STIRRER

S. H. Noie and B. Jajuee

Department of Chemical Engineering, Faculty of Engineering, Ferdowsi University of Mashhad
P.O. Box 91775-1111, Mashhad, Iran, noie@ferdowsi.um.ac.ir

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Abstract Benzyl chloride is economically one of the most important starting materials for a large number of industrial syntheses. Far too much money is now spent to buy and import this valuable product. The production of benzyl chloride has been recognized as one of our national projects and budgeted by the National Iranian Petrochemical Organization in order to economize on the country's foreign exchange. It is certain that obtaining a broad spectrum of scientific information must take priority. A part of this information consists of the kinetics of the reaction, resistance of the used materials, the proper gas-liquid ratio for efficient production, the best range of temperature, etc. Much attention has also been paid to the development of kinetic models, to the design of the reactor, the effects of agitators and inhibitors. The kinetics of thermal chlorination of toluene without catalyst in a semi-batch reactor in a temperature range of 80-100°C and a pressure range of 1-3atm has been investigated. The reactor had an approximate volume of 7 liters. It was equipped with condenser and electric heater and necessary measuring instruments. The reactor was made of SS-316. Since certain metallic impurities such as iron act as a catalyst for ring chlorination and self-condensation, their presence must be avoided. Consequently, a special resistant lining, PTFE, was used for coating the reactor interior. The rate of initial reactants conversion and the production of benzyl chloride in a temperature range of 80-100°C and a pressure range of 1-3atm with an optimized situation consideration and maximum efficiency of production have been determined.

Key Words Kinetics, Benzyl Chloride, Toluene, Bench Reactor

چکیده در این مقاله سینتیک کلراسیون تولوئن بدون کاتالیزر در یک راکتور نیمه پیوسته بررسی شده است. به کمک نتایج آزمایشها، سرعت تبدیل مواد اولیه و تولید بنزیل کلراید در گستره دمای هشتاد تا یکصد درجه سانتیگراد و فشار یک تا سه اتمسفر تعیین شده است. راکتور مورد نظر دارای حجم هفت لیتر و مجهز به چکالنده، گرماساز برقی و وسایل اندازه گیری مورد نظر می باشد. بدنه این راکتور و دیگر اجزای آن از جنس فولاد زنگ نزن نوع SS-316 است. از آنجایی که ناخالصیهای فلزی همچون آهن بعنوان کاتالیزور در واکنشهای کلراسیون حلقه ای و چگالش خودبخودی عمل می کند باید از حضور آنها در محیط جلوگیری شود. در نتیجه یک روش مقاوم برای پوشش دیواره داخلی راکتور استفاده شده است. به کمک نتایج حاصله سرعت تبدیل مواد اولیه به محصول بنزیل کلراید در گستره دمایی هشتاد تا یکصد درجه سانتیگراد و فشار یک تا سه اتمسفر با در نظر گرفتن شرایط بهینه و بالاترین بازدهی محصول بدست آمده است.

1. INTRODUCTION

Although benzyl chloride is structurally the simple side chain chlorinated derivative of toluene, economically is important as a starting material for a large number of industrial syntheses. Benzyl chloride is mainly used to produce plasticizers (e.g., benzyl butyl phthalate), benzyl alcohol, and phenyl acetic acid and benzyl cyanide (for

production of penicillin). It is also used to produce quaternary ammonium salts (as disinfectants and phase transfer catalysts), benzyl esters (benzyl benzoate and benzyl acetate for the flavor and perfume industry), dyes of the triphenyl methane series, dibenzyl disulfide (antioxidant for lubricants) and benzyl phenol and benzyl amines on a smaller scale [1]. Benzyl chloride can be obtained with sulfuryl chloride and zinc chloride as chlorinating

agents in the laboratory. In commercial practice benzyl chloride is manufactured by thermal or photochemical chlorination of toluene at 80-100°C. At lower temperatures the amount of ring-chlorinated byproducts is increased [2].

To acquire the know-how of benzyl chloride production on a pilot plant scale, a bench reactor with volume of 7 liters has been designed and constructed. The reactor was used as a basis for getting fundamental information for pilot plant design.

The stability of different materials for the reactor body, the reactor kinetics and some of the optimization processes have been considered in this reactor. By setting an elevated temperature (80-100°C) and pressure 1-3atm, the kinetics of the thermal chlorination of toluene has been studied.

Although much research has been done in order to enhance the efficiency of the benzyl chloride production, the confidential nature of this information necessitates duplication of related research [3-8]. In this research the kinetics of thermal chlorination of toluene and optimal situation of maximum efficiency of production have been investigated.

2. BENCH REACTOR

The bench reactor had a volume of 7 liters approximately with a 14.5-cm internal diameter and a 41.5-cm-height (Figure 1). It was equipped with a condenser and electric heater and other measurement instruments. The materials of construction of the reactor body and its accessories were made of SS-316. A special resistant covering, PTFE, covered the inside wall of the reactor. The reactor system was designed and constructed such that to provide the following conditions for performing the gas-liquid reactions: Temperature range: 65-160°C; Pressure: up to 3 atm; Stirrer speed: up to 1000 rpm. The stuffing box constructed around the stirrer shaft is one of the most important parts of the system in testing at pressures up to 3 atm pressure.

3. PHYSICAL COEFFICIENTS

In order to design a proper bench reactor for obtaining the kinetic data of chlorination of toluene, the physical

coefficients are required. In the absence of toluene, physical absorption will be predominant, and therefore the physical coefficients can be obtained by the relevant equation. To get an effective dispersion, the proposed relations offer 258 rpm as the minimum theoretical impeller speed and 450 rpm as practical [9-10]. Considering the viscosity, density, surface tension of gas-liquid phase, the evaluated volumetric gas flow rate per orifice at the reaction temperature ($Q_g=2.22 \times 10^{-5} \text{ m}^3/\text{s}$), the impeller speed ($N = 450 \text{ rpm}$), and its diameter ($D_i = 8 \text{ cm}$), the power delivered to the gas mixture by the impeller was $P_G = 9.3W$.

4. INITIAL PREREQUISITES

Substitution of chlorine for hydrogen in the aliphatic side-chain occurs by way of a radical chain mechanism. This chlorination is highly exothermic (96-105 kJ/mol chlorines). Since the mechanisms of side-chain chlorination and nuclear chlorination are fundamentally different, selectivity can be readily achieved. The prerequisites for high side-chain chlorination efficiency are as follows:

Elimination of components capable of destroying the radical chain Oxygen, a well-known radical scavenger, greatly reduces the consumption of chlorine; its presence is therefore undesirable [11-12]. Toluene can be freed of oxygen, for example, by purifying with an inert gas such as nitrogen.

Elimination of Components Conducive to Other Side Reactions The experiments showed that the presence of water leads to the formation of aqueous hydrochloric acid (indicated by cloudiness) and possibly to the hydrolysis of the chlorinated toluene and thus the used chlorine was freed from water by means of silica gel as an industrial dryer.

Achievement and Maintenance of an Optimal Radical Concentration Chlorine radical formation can be promoted by the addition of a radical forming agent such as 2,2 Azobis (isobutyronitrile) or AIBN, benzoyl peroxide, or

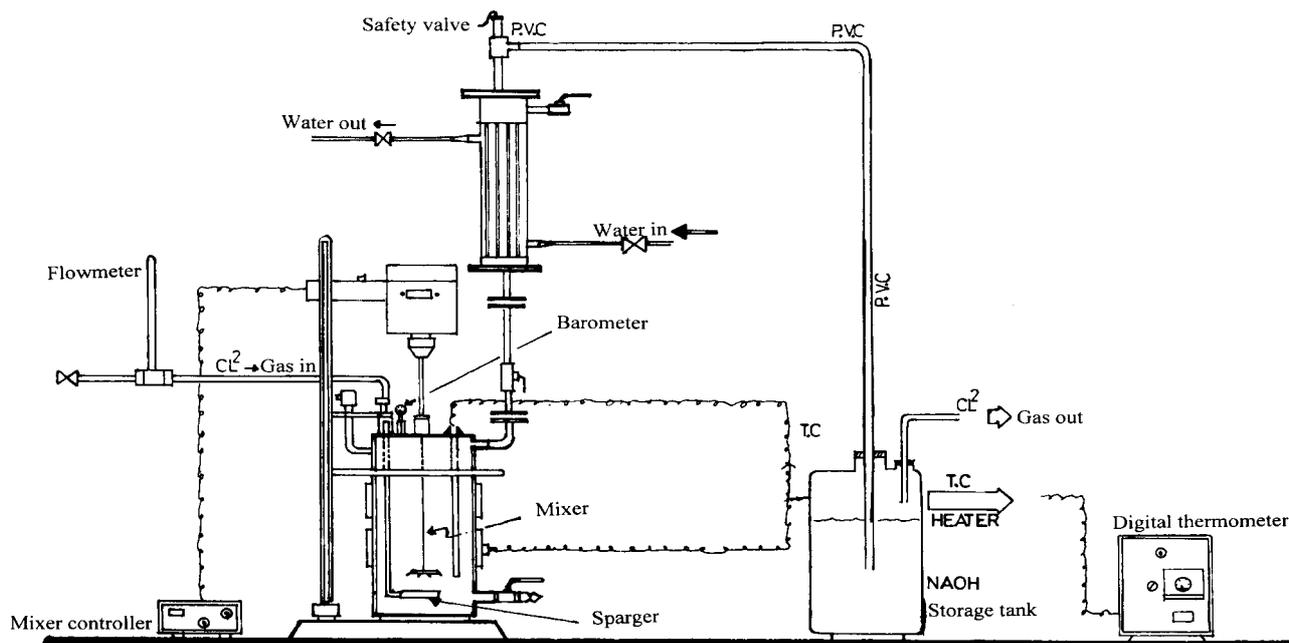


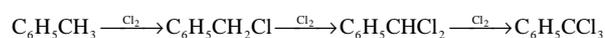
Figure 1. The gas-liquid bench reactor with its accessories.

hexaphenylethane. Such compounds are consumed in the reaction, however, and thus have to be added repeatedly. For the same reason, two other methods, singly or in combination, are of greater importance, particularly in industrial chlorination; irradiation (ultraviolet light, radiation) and the use of an elevated temperature. In both cases, the effect is the result of excitation of chlorine molecules. In this research the optimal temperature was used to form an optimal radical concentration.

Elimination of Components that Might Impart an Electrophilic Course to the Reaction During the experiments, we found that formation of Friedel-Craft catalysts cause nuclear chlorination. For this reason, ensure that toluene is free of dissolved iron salts and rust particles. By extension, steel, including stainless steel is unsuitable as a reactor material. The preferred reactor materials are glass, enamel and polytetrafluoroethylene (PTFE)

Initial Precautions that would Encourage Radical Reactions or Suppress Electrophilic Reactions Different experiments showed adverse effects caused by excessive chlorine concentrations (especially nuclear chlorination, both addition and substitution).

In the course of radical chlorination of toluene, all three hydrogen atoms of the side-chain are successively replaced by chlorine. As a result, mixtures of the three expected compounds are obtained: benzyl chloride, benzal chloride, and benzotrichloride.



The change in the composition of the mixture as a function of the number of mole chlorine that has reacted is shown in Figure 2. [1]

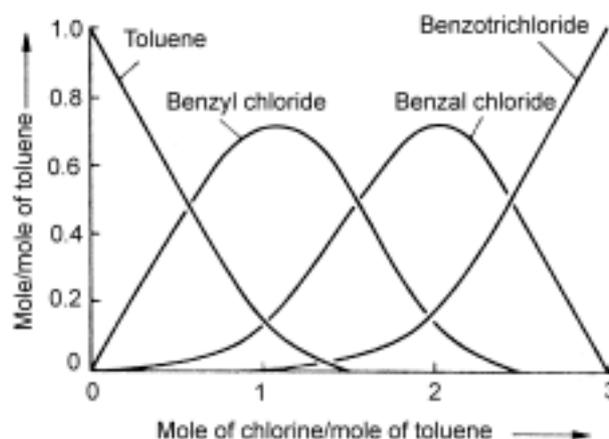


Figure 2. Progression of toluene chlorination.

Other authors [1] have reported similar results. Extensive investigations have shown that for batch operations, it is practically impossible to alter the shape of these curves.

$$\text{toluene..gmol} = 1 \frac{\text{kmol}}{\text{m}^3} \times \frac{10^3 \text{gmol}}{1 \text{kmol}} \times 0.003 \text{m}^3 = 3 \text{gmol}$$

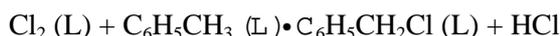
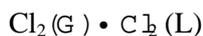
Numerous attempts have been made to produce benzyl chloride as free as possible of the secondary products benzal chloride and benzotrichloride. One possibility is to restrict the chlorination to only 30-50% of the toluene input and then to separate the resulting mixture that still has a very high toluene content by distillation. Therefore, as the experiments have shown the toluene concentration in a bench reactor, should be restricted to 1-2 kmol/m³. Consequently:

$$\text{chlorine gram} = 3 \text{ gmol (30-50\%)} \times 71 \text{ gr/gmol} \cong 100 \text{g}$$

Therefore, if the process of chlorination will be continued over these limits, the quantity of side products increase.

5. REACTION KINETICS

The overall reaction of the thermal chlorination of toluene is being explained as follows:



where (G) and (L) represent the gas and liquid phases in the reactor, respectively.

The kinetic experimental results of chlorination of toluene at 80° C have been obtained by

decreasing of pressure. This decrease happens when physical and chemical absorption begins. The liquid phase is stirred gradually while its surface is kept flat. Consequently the interfacial area would have a specific value. The solvent is chemically ineffective; therefore the initial absorption rate can be immediately measured by initial pressure decrease.

Initially 3 liters of an ineffective solvent was injected in the reactor, and the remaining volume was then filled by chlorine gas ($V_G = 3.85 \text{lit}$). Adjusting the vent pipe of the condenser and leading the outlet gas to the neutralizing tank enabled us to set the reactor pressure at the desired range of 1-3 atm. After stirring, a sudden decrease of pressure occurred and stabilized at a lower pressure. Although this state is stable in a continuous reactor, in a semi-batch reactor it will return to the first equilibrium state after a while. Table 1 shows the results of this investigation, where P_{A1} is the initial pressure, P_{A2} equilibrium pressure after time t , C_B toluene concentration and J_A the molar gas rate. The physical mass transfer coefficient was obtained by calculating the solubility ($m = C_{AL}/C_{AG}$) and the chlorine film concentration (C_{Ai}), using equation (1),

$$J_A = \frac{D_A}{\delta} (C_{Ai} - \bar{C}_A) \quad (1)$$

$$K_L = 1.4 \times 10^{-4} \text{ m/s}$$

A brief reviews of results show that J_A and P_A are in proportion. Since P_A and C_{Ai} are in the correct relation with each other, the following equation confirms completely this proportion.

$$J_A = -D_A \left(\frac{dC_A}{dx} \right)_{x=0} \equiv \frac{D_A}{\delta} C_{Ai} E_{A0} \quad (2)$$

TABLE 1. The results of kinetic experiments.

Run	$P_{A1}(\text{bar})$	$P_{A2}(\text{bar})$	$C_B(\text{kmol/m}^3)$	$t(\text{min})$	$J_A(\text{kmol/s})$
1	1	0.3	0	15.70	2.3×10^{-7}
2	1.5	0.45	0	15.73	3.45×10^{-7}
3	1	0.24	1	6.81	7.83×10^{-7}
4	1.5	0.364	1	7.60	10.4×10^{-7}
5	1	0.18	2	7.60	11.09×10^{-7}

The amount of E_A is obtained by comparison of the first and third experiments with the consideration of equations (1) and (2):

$$E_A = J_{A3}/J_{A1} = 3.4$$

On the other hand, $D_A = D_B = 7.45 \times 10^{-9}$ and by means of the amount of solubility, C_{Ai} is calculated as:

$$C_{Ai} = 0.14.$$

Thus,

$$E_{\infty} = 1 + \frac{D_B \overline{C_B}}{D_A C_{Ai}} = 1 + \frac{1}{0.14} = 8.14$$

$$\phi = \delta \sqrt{\left(\frac{2}{n+1} \times \frac{k_{n,m}}{D_A} \times C_{Ai}^{n-1} \times \overline{C_B}^m \right)} \quad (3)$$

According to the establishment of the following relation of $2 < E_A < E_{A\infty}$, the reaction is fast and then $E_A = \phi = 3.4$. The amount of the solubility calculated from experiments of 3 and 4 is different from that of 1 and 2, and ϕ in equation (3) depends on P_A in consequence.

If the overall reaction order is being considered as (n,m) , ϕ will be in proportion to $\sqrt{(C_{Ai}^{n-1})}$, C_B^m , if not, the ratio of J_{A4}/J_{A2} would be equal to $E_A = 3.4$.

Because of the reaction condition and variety of the consequent results, getting the real relationship between ϕ and C_{Ai} is impossible and thus there is no certainty for the order of C_{Ai} in the rate expression. This is also confirmed by the radical chain mechanism [12].

Whence p_A is proportional to C_{Ai} , it's possible to obtain C_{Ai} by equation (3) and other consequent equations as follows:

$$\frac{J_{A4}}{J_{A2}} = 3.01 = \sqrt{P_A^{n-1}} \times 3.4$$

therefore, $n \approx 0.4$

Besides, comparing of experiments 3 and 5

gives:

$$E_A = \phi \propto \sqrt{\overline{C_B}}$$

which means $m=1$.

Although results obtained from the radical chain mechanism are slightly different from this experiment (where n was computed as 0.5), but it should be noted that n was computed with some simple assumptions, and the results are completely in conformity with the theoretical work.

In any case, the experiments and the theoretical relations of the gas liquid reaction [13-14] followed a rate expression of the form:

$$\frac{d}{dt}(RCl) = k(Cl_2)^{0.4}(RH) \quad (4)$$

where RCl is the concentration of benzyl chloride and RH is the concentration of toluene.

Subsequently the rate constant was determined as follows:

By choosing suitable conditions for the reaction, the desired product would be accessible.

$$k = 6.54 \frac{m^{1.2}}{kmol^{0.4}.s}$$

Only the rate of the reaction and the nature of the observed side reactions can be shown to depend significantly on the reaction condition. Little is known with certainty about the absolute reaction rate. One reason for the scarcity of information is the fact that the actual concentration of dissolved chlorine is not accurately measurable. But more study in this area showed that if the chlorine concentration is assumed to be constant, the reaction could be taken as quasi-first order, leading to the following calculated ratios of rate constant at $100^\circ C$.

$$k_1/k_2 = 7.3$$

$$k_2/k_3 = 15.7$$

6. DISCUSSIONS AND CONCLUSION

The results of our work showed that:

1- The following prerequisites must take before

performing the experiments;

To increase the consumption of chlorine, toluene must be free from oxygen.

- The used chlorine must be free from water to avoid the formation of aqueous hydro chlorine acid.
- For optimal concentration of radicals, some specific range of temperature must be chosen.
- A special resistant covering such as polytetrafluoroethylene (PTFE) must be used to cover the inside of the reactor to ensure that toluene is free of dissolved iron salts and rust particles.
- To produce benzyl chloride that is as free as possible of the secondary products, the chlorination must be restricted to only 30-50% of the toluene input.

2- The rate expression is consistent with the first order model, while the chlorine concentration, C_{Ai} is assumed to be a function of pressure only and is constant. As a result, the reaction can be taken to be quasi-first order as follows:

$$\frac{d}{dt}(RCl) = k'(RH)$$

$$k' = kC_{Ai}^n = k \left(\frac{mP_{Ai}}{RT} \right)^n$$

where in this research "n" has been calculated at about 0.4 [11]. All investigators are unanimous about the overall order of the reaction, which with assumption of the pressure constancy was taken as first order [1,15].

7. NOMENCLATURE

A	interfacial area (m^2/m^3)
C_{Ai}	concentration of species i in the reaction phase ($kmol/m^3$)
C_B	bulk concentration of toluene ($kmol/m^3$)
D_A	mass diffusivity of dissolved gas (m^2/s)
D_B	mass diffusivity of reactant (m^2/s)
D_I	diameter of impeller (m)
E	enhance factor
J_A	molar flux ($kmol/m^2.s$)

k, k_1 , k_2 , k_3

coefficient of reaction rate

$$(m^{3(n+m-1)}/kmol^{(n+m-1)}.s)$$

K_L physical mass transfer coefficient (m/s)

m solubility

n reaction order

P_{A1} initial pressure (bar)

P_{A2} equilibrium pressure after time t (bar)

t time (s)

δ film thickness (m)

ϕ reaction characteristics

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