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Liquid Phase Amination of 1-Bromobutane under High Temperature and High Pressure

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The amination of 1-bromobutane in an aqueous ammonia solution of 50 wt% ammonia using a high-pressure coiled-tube flow reactor was examined. The temperature range studied was from 343 to 403 K and the reaction pressure was 13 MPa. The major reaction products were *n*-butylamine and di-*n*-butylamine, but higher amines, such as tri-*n*-butylamine, were detected only in trace amounts. Based on a second order consecutive reaction model for the formation of *n*-butylamine and di-*n*-butylamine, the reaction rate of amination of 1-bromobutane was determined. Arrhenius parameters for the rate constant of the first reaction step to form *n*-butylamine were found to have an activation energy of 87.9 kJ/mol and pre-exponential factor of 1.03×10^9 mol/(dm³ s), and those for the second reaction step to form di-*n*-butylamine were found to have the activation energy of 84.3 kJ/mol and pre-exponential factor of 4.30×10^9 mol/(dm³ s).

1. Introduction

Amines are important organonitrogen compounds used in petrochemistry. Aliphatic monoamines, diamines, and polyamines are important intermediates, not only in the manufacture of textile, paper, agricultural chemicals, and chelating agents but also in the polymerization and vulcanization of natural and synthetic rubber^{1),2)}. Among the technologies being used to prepare alkylamines, the amination of alkyl halide is the oldest one, and it is still of commercial importance for the manufacture of allylamines and select mixed alkylamines. For example, ethylenediamine and other members of the amine series are prepared commercially by treating ethylene dichloride with ammonia under high pressures in the temperature range from 100 to 150°C. The synthetic studies of amines based on the amination of alkyl and aryl halides in aqueous ammonia and alcoholic ammonia have been performed by several researchers^{3)–5)}. Curme and Lommen⁶⁾ patented the processes for the production of ethylene diamine by amination of ethylene dichloride in liquid ammonia. Braun⁷⁾ prepared alkylamines by action of liquid ammonia on alkyl bromides at room temperature. Shreve and Rothenberger^{8),9)} investigated the reaction between alkyl halides and sodium amide in liquid ammonia in the temperature range from –70 to –34°C. Krishna Murthy¹⁰⁾ studied the amination of ethylene dichloride in liquid ammonia at 110°C, while Asami^{11),12)} studied the amination of alkyl halides using caustic alkali in liquid ammonia at room temperature.

Temperature used in the above studies is lower than that being used in the present commercial amine production processes.

Now many of the commercial processes for amine production use a tube reactor. To design, to develop, and to study reaction conditions of commercial amination processes, accurate reaction rate data covering a wide range of temperature are required. However, in most of the previous studies only batch reactors have been used. Since the effect of ammonia vaporization on the reaction temperature can not be ignored in a batch reaction, kinetic parameters of amination of alkyl and aryl halides at high temperatures could not be determined accurately in the batch reactor.

Typical initial reaction conditions of alkyl and aryl halide amination processes are usually temperature of about 340 K, NH₃/halide ratio of about 20, NH₃ concentration in aqueous solution of about 50 wt%, and pressure at 10 MPa. These conditions have been selected specifically based on such factors as the maximum temperature limit for the reactor (about 473 K for the titanium tube reactor), solubility of the electrolyte byproducts (NH₄Br), phase behavior of the NH₃ + H₂O mixture, and prevention of undesirable reactions, *e.g.*, formation of polyamines. It has been known that separation of water and unreacted NH₃ from the effluent liquid mixture and recycling NH₃ are the most energy consuming steps in amination processes. If higher reaction temperatures could be used, the NH₃/halide ratio can be reduced to about 5–10. Higher temperatures are also known to be suitable to prevent the formation of cyclic polyamines. The reduction in the amounts of NH₃ and water can significantly contribute

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to the efficiency of the process. Therefore, we are planning to operate the amination reaction under higher temperatures than those now used. To do it, we have to develop a simulation method to predict a temperature profile and a thermal runaway limit of tube reactors for liquid phase amination of alkyl and aryl halides under high temperatures and high pressures. One of the characteristics of amination is a large evolution of heat. In almost all amine production processes, the reaction products consist of a mixture of primary, secondary and tertiary amines. Since the product distribution can easily be affected with the temperature profile along the tube reactor, the maximum yield of the desired amine can be obtained by proper adjustment of the ratio of the reactant and the reactor temperature profile¹³⁾. Thus, for the optimum design of a reactor, kinetic parameters for the amination of alkyl halides and aryl halides under high temperatures and high pressures are indispensable. However, kinetic parameters for amination of alkyl halides and aryl halides under high temperatures and high pressures are unavailable in the literature. The objective of the present study is to determine the reaction rate constant of amination of 1-bromobutane in the temperature range higher than that in previous studies and also to develop a reliable method to estimate the rate constant up to about 473 K. This paper reports the results of liquid phase amination of 1-bromobutane in an aqueous ammonia solution of 50 wt% ammonia in the temperature range from 343 to 403 K and pressure at 13 MPa. The reaction pressure was chosen to ensure reaction in the liquid phase at the highest reaction temperature condition and the composition of the liquid mixture. While higher pressures above 13 MPa are available for commercial amination processes, the pump system for the aqueous ammonia solution is not economically available. Lower pressures below 13 MPa are generally not recommended both for the vapor phase formation and salt crystallization in the reactor.

Measurements were made with a high-pressure coiled-tube flow reactor. From a temporal variation of the concentration of 1-bromobutane and reaction products, the reaction pathway was ascertained, and the rate constants were determined.

2. Experimental Section

2.1. Experimental Apparatus

Figure 1 shows a schematic of the high-pressure flow reactor system used in this study. It consisted of a feed system, an oil bath, a coiled-tube reactor, influent heat exchangers (preheaters), an effluent collection device, pressure measurement and control devices, and a temperature measurement and control systems.

An aqueous ammonia solution of 50 wt% ammonia and 1-bromobutane were fed separately and mixed at

the inlet of the coiled-tube reactor. The aqueous ammonia solution was fed to a 1700 cm³ stainless steel tank fitted with a high-pressure tubing and a shut-off valve. The tank was set upside down on the electronic balance to feed a liquid sample directly to the reactor and also to determine its mass flow rate. The feed tank for 1-bromobutane was a 500 cm³ glass measuring cylinder, which was also set up on an electronic balance. The feed rate of sample and molar ratio of 1-bromobutane/ammonia were determined from the balance readings, which were made periodically during the experiment.

Two HPLC plunger pumps (Shimadzu, Model LC-9A for 1-bromobutane and Model LC-6AD for aqueous ammonia solutions) were used to pressurize the samples, whose pressure was measured with Bourdon-tube gauges. The plunger head of the LC-6AD pump was cooled with chilled water circulated in the water jacket. Peek packing was used for sealing the plunger head of the LC-6AD pump. All high-pressure connections located downstream of the pump discharge were Swagelok SUS316 fittings. The high pressure line and coiled tube reactor were both 3.15-mm-o.d. SUS316 tubing with 0.89-mm wall thickness, and the preheaters were all 1.65-mm-o.d. SUS316 tubing with 0.51-mm wall thickness. The high pressure lines between the stop valve, V-1 and V-2, of the preheaters were controlled to the reaction temperature with an electric heater and heat insulator.

Pressurized feed samples, prior to entering the reactor, were heated in preheater immersed in an oil bath prior to entering the reactor. The basic design of the preheater was similar to that of the mixing flow cell proposed by Tomaszewicz and Randzio¹⁴⁾. The preheater was a coiled tubing of about 2-m length wound into grooves machined on a 20-mm-o.d. and 400-mm length copper rod and fixed with a thermal cement. The copper rod and tubing were placed inside a copper shell.

The oil bath 1-m-o.d. and 1-m depth was made from SUS304. It was a double-walled stainless steel vessel and was evacuated to about 1 kPa to reduce heat losses and to improve temperature stability. Silicon oil was used as the bath fluid. The temperature of the oil was regulated within 0.01 K with toluene-mercury temperature controller and measured with a platinum resistance thermometer. The uncertainty in the overall temperature measurements was estimated to be 0.02 K.

Figure 2 shows the details of the reactor. Liquid ammonia and 1-bromobutane were mixed at the tee connector C-1 and the reaction was then started. For complete mixing of the two liquids, a static mixer of 1.734-mm-i.d., 3.15-mm-o.d. and 150 mm length with 27 mixing elements (Noritake Co., Ltd., Model-T) was connected to the tee connector. A platinum resistance thermometer (Okazaki Co., Ltd., SUS316 sheath,

① HPLC-pump for 1-bromobutane (Shimadzu LC-9A), ② Measuring cylinder for 1-bromobutane, ③ Electric balance, ④ HPLC-pump for aqueous ammonia solution (Shimadzu LC-6AD), ⑤ Feed tank for aqueous ammonia solution, ⑥ Stop valve (V-1 and V-2), ⑦ Bourdon pressure gauge, ⑧ Heat insulator, ⑨ Preheater, ⑩ Static mixer, ⑪ Coiled-tube, ⑫ Oil bath, ⑬ Stirrer, ⑭ Platinum resistance thermometer, ⑮ Heat exchanger, ⑯ Filter, ⑰ 3-Way valve, ⑱ Product accumulator (R-1 and R-2), ⑲ N₂ gas cylinder, ⑳ Plunger pump, ㉑ Flow control valve, ㉒ Gas bubble meter.

Fig. 1 Experimental Apparatus for 1-Bromobutane Amination

① Platinum resistance thermometer, ② Tee(C-1), ③ Static mixer, ④ Coiled-tube.

Fig. 2 Details of the Coiled-tube Flow Reactor

model R35) was inserted at the top part of the tee to determine the fluid temperature in the reactor inlet section. The same type of platinum resistance thermometer was inserted near at the effluent end of the reactor. Temperatures of the two liquids at inlet and outlet sections were almost the same in most of the experiments. The average temperature of the two liquids was taken as the reaction temperature. Coiled-tube reactors of different lengths in the range from 0.2 to 3 m were used to provide variable residence times. In order to terminate the reaction, a heat exchanger was located closely above the silicon oil surface, and water cooled to about 0°C was circulated in it. In this study, we assumed that reactions began at the tee connector C-1 and ended at the silicone oil surface.

The cooled effluent then passed through a 0.1-mm SUS316 filter and then through two accumulators (R-1 and R-2) consisting of two 500 cm³ high pressure vessels connected in parallel. Accumulator R-1 was used for collecting the effluent obtained under transient conditions, and the other accumulator R-2 for collecting the effluent obtained under steady-state conditions. The contents of R-2 were used for composition analysis. The lines from the top of the accumulators were

Table 1 Experimental Conditions ($P = 13$ MPa, mole ratio of 1-bromobutane to ammonia is 3.3 : 96.7)

T [K]	Mass flow rate range [g/min]		Residence time range [s]
	1-Bromobutane	Aqueous ammonia soln.	
343.15	0.229-0.972	0.632-7.003	46.2-247.4
358.15	0.115-0.939	0.849-6.969	45.4-288.5
373.15	0.113-0.959	0.830-7.065	5.1-163.5
388.15	0.165-0.959	0.951-7.098	6.4-104.8
403.15	0.129-1.115	0.972-8.227	4.1-34.4

connected to a pressure gauge, nitrogen gas cylinder, a plunger hand pump, and a flow control valve.

2. 2. Experimental Procedure

Prior to running a series of experiments, a 50 wt% aqueous ammonia solution was prepared in the feed tank as follows: Distilled water was introduced into the tank after it was evacuated, and it was then cooled by submerging in cooled methanol. Next, ammonia was introduced into the feed tank by distillation from an ammonia bomb. The total amount of ammonia and water used to prepare the solution, whose composition was determined by weighing, were about 600 g. Mass determinations were made to 10 mg by difference. Finally, nitrogen gas was applied to the feed tank to 0.3 MPa higher than the vapor pressure of the aqueous ammonia solution to provide a back pressure sufficient for the HPLC pump. The feed tank was connected to the feed line to the pump, which was placed upside down on the electric balance. The 1-bromobutane was introduced into a glass cylinder and nitrogen was then bubbled into it to purge oxygen dissolved therein.

Meanwhile the system was thermally conditioned to the desired temperature. Stop valves, V-1 and V-2, were closed and the system downstream from them was evacuated for 30 min and then nitrogen gas from a nitrogen cylinder was introduced into the system up to 13 MPa with the plunger pump. When all was ready, HPLC pumps were turned on, and their mass flow rates were adjusted so the mole ratio of 1-bromobutane to ammonia became 3.3 : 96.7. After the pressure of the effluents from the pumps increased to above 13 MPa, V-1 and V-2 were opened and to start the feeding of the samples into the reactor.

By feeding the reactants into the reactor, the pressure in the product accumulators R-1 and R-2 increased. The pressure was controlled to the reaction pressure of 13 MPa by releasing the nitrogen gas into the accumulators using a flow control valve. The rate of release of nitrogen gas was observed by using a bubble flow meter. In this way, the pressure of the system could be maintained at 13 MPa with 0.02 MPa uncertainty. To attain a steady state, about 30 min were usually required. After attain it, observations on system conditions were made periodically. The effluent from the reactor during the first 45 min was considered to be the

reaction products under transient conditions, but after 45 min, they were considered to be steady state products.

Since the concentration of 1-bromobutane was low, the residence time of the reactants was calculated from the Eq. (1):

$$t = \frac{Vd}{m} \quad (1)$$

where t is the residence time in s, V the reactor volume in dm^3 , d the density of the aqueous ammonia solution in g dm^{-3} , and m the mass flow rate in g s^{-1} . The residence time was varied from 5 to 300 s by changing the reactor volume and mass flow rate. The density of the aqueous ammonia solution under temperature and pressure conditions in the reactor was calculated using the Ziegler-Trepp equation of state¹⁵⁾. The initial concentration of each component in the feed liquid was calculated from the mass flow rate and density. Experimental conditions are given in **Table 1**.

2. 3. Analytical Procedure

The composition of the reaction products withdrawn from accumulator R-2 was determined with a gas chromatography (GC) with a FID detector (Shimadzu, GC-15A) and an integrator (Shimadzu, CR-4A). In order to determine the concentrations of 1-bromobutane and reaction products with GC, a sample was prepared as follows: at first the product aqueous solution was bubbled into 37.5 cm^3 toluene to remove the unreacted ammonia, then the toluene was separated from the aqueous solution with a separatory funnel and was used for composition analysis. Since the solubility of n -butylamine in the water phase could not be neglected, the concentration of n -butylamine in the toluene phase was corrected by using the solubility ratio of the n -butylamine in the toluene + water system determined in this study. The solubility ratio of 1-bromobutane at 298.15 K was measured using 37.5 cm^3 toluene and 3-18 cm^3 water. **Table 2** and **Fig. 3** show the relationship between the solubility ratio of n -butylamine at 298.15 K and the volume of water. The experimental result of the solubility ratio can be expressed by the Eq. (2).

Table 2 Solubility Ratio of 1-Bromobutane in Water-toluene System at 298.15 K (toluene volume is 37.5 cm³)

V_w [cm ³]	n_w/n_T [—]
3.0	0.1633
6.0	0.2361
9.0	0.3119
12.0	0.3622
18.0	0.4601

$$n_w/n_T = 0.08527 V_w^{0.5828} \tag{2}$$

where n_w and n_T are the solubilities of 1-bromobutane in the water phase and in the toluene phase, respectively, and V_w is the volume of water phase in cm³. Corrections due to the solubility of *n*-butylamine and di-*n*-butylamine in the water phase were found to be negligible. The GC was equipped with a 15-m long capillary column coated PEG2000 and was run on the raising temperature mode. The heating rate was 5 K/min in the temperature range 323-343 K and 9 K/min in the temperature range 343-513 K.

2. 4. Sample

Both 1-bromobutane (research grade, purity > 99 mol%) and distilled water were purchased from Wako Pure Chem. Ind., Ltd. Ammonia (purity > 99.95 mol%) was purchased from Nippon Sanso Corp. These chemicals were used without further purification.

3. Results and Discussion

3. 1. Effects of Temperature on Molar Yields of Products

The amination of 1-bromobutane with ammonia is considered to proceed by the following consecutive reactions;

where i is 1 to 4 and k_i is k_1 to k_4 representing the rate constant for each reaction step. In the above amination reactions, 1-bromobutane reacts with ammonia to produce *n*-butylamine, which then reacts with 1-bromobutane to produce di-*n*-butylamine. Moreover, tri-*n*-butylamine and quaternary aminebase are similarly produced.

Under the experimental conditions of this study, *n*-butylamine and di-*n*-butylamine were produced as major reaction products, while tri-*n*-butylamine and

Fig. 3 Solubility Ratio of 1-Bromobutane in the Water-toluene System at 298.15 K (volume of toluene is 37.5 cm³)

quaternary aminebase were but rarely produced. Therefore, their production (Eqs. (5) and (6)) could be neglected. Thus, in this study, productions only *n*-butylamine and di-*n*-butylamine are considered.

Experimental results at 373 and 388 K are listed in Table 3. Effects of residence time on the molar yields of reaction products at 343 and 403 K are shown in Figs. 4 and 5, respectively, where the plots are experimental data, and lines are calculated values about which will be described later. It can be seen that reaction hardly proceeded in the residence time of 250 s at 343 K, but at 403 K it proceeded almost completely in 30 s. Reaction rates and molar yields of the products increased with reaction temperature.

3. 2. Determination of Kinetic Parameters

In this study, Eqs. (3) and (4) are considered to occur as described above. The hydrogen bromide produced in each stage was immediately neutralized with the excess ammonia in the system according to the Eq. (7):

Therefore, Eqs. (3) and (4) are considered to be irreversible. By assuming that the rate constant of each stage is k_1 (Eq. (3)) and k_2 (Eq. (4)), the reaction rate of the first and second stages could be expressed by the Eqs. (8) and (9), respectively.

$$r_1 = k_1[C_4H_9Br][NH_3] \tag{8}$$

$$r_2 = k_2[C_4H_9Br][C_4H_9NH_2] \tag{9}$$

Based on the kinetic analysis of the tube reactor, the rates of formation of the 1-bromobutane, *n*-butylamine, di-*n*-butylamine, and ammonia are expressed as follows;

$$\frac{d[C_4H_9Br]}{dt} = -r_1 - r_2 \tag{10}$$

Table 3 Experimental Results at 373 and 388 K

T [K]	Residence time [s]	Molar yield [%]		
		1-Bromobutane	<i>n</i> -Butylamine	Di- <i>n</i> -butylamine
373	5.1	95.8	4.2	—
373	10.5	90.5	9.5	—
373	19.5	84.6	15.4	—
373	30.1	77.0	21.4	0.8
373	46.6	67.9	28.3	1.9
373	70.8	59.8	33.1	3.5
373	89.7	50.2	41.1	4.4
373	108.0	39.9	46.1	7.0
373	128.7	38.3	48.2	6.8
373	163.5	33.3	47.1	9.8
388	6.3	85.6	14.6	—
388	7.3	82.0	18.0	—
388	11.8	69.8	27.5	1.4
388	17.8	61.0	37.1	2.5
388	23.8	50.5	40.4	4.5
388	36.7	36.0	48.9	7.8
388	49.1	32.1	55.0	6.5
388	63.7	22.1	61.3	8.6
388	82.9	21.4	57.7	0.9
388	104.8	12.4	65.8	2.4

Fig. 4 Temporal Variation of Product Yields from 1-Bromobutane Amination in the Liquid Phase at 343.15 K and at 13 MPa

Fig. 5 Temporal Variation of Product Yields from 1-Bromobutane Amination in Liquid Phase at 403.15 K and at 13 MPa

$$\frac{d[\text{C}_4\text{H}_9\text{NH}_2]}{dt} = r_1 - r_2 \quad (11)$$

$$\frac{d[(\text{C}_4\text{H}_9)_2\text{NH}]}{dt} = r_2 \quad (12)$$

$$\frac{d[\text{NH}_3]}{dt} = -2r_1 - r_2 \quad (13)$$

These differential equations can be solved numerically using the Runge-Kutta method, and the molar yield of each product, Y_i , can be determined from the following equation:

$$Y_i = \frac{M_i}{M_0} \quad (14)$$

where M_i refers to the molar concentration of component i , and M_0 refers to the initial molar concentration of 1-bromobutane.

Since the reaction rate constants, k_1 and k_2 , are unknown parameters, the optimum values of k_1 and k_2 at each reaction temperature were determined by minimizing the sum of the relative errors between experimental and calculated Y_i . The values of k_1 and k_2 determined are listed in **Table 4**. The calculated results for Y_i with the rate constants in **Table 4** are shown by the solid lines in **Figs. 4** and **5**. As can be seen, the calculated results for Y_i are in good agreement with the experimental data at every temperature and they can satisfactorily represent the effect of the reaction temperature on molar yield.

Table 4 Reaction Rate Constants, k_1 and k_2

T [K]	k_1 [dm ³ /mol/s]	k_2 [dm ³ /mol/s]
343.15	4.43×10^{-5}	6.93×10^{-4}
358.15	1.86×10^{-4}	2.09×10^{-3}
373.15	3.64×10^{-4}	5.88×10^{-3}
388.15	1.27×10^{-3}	1.76×10^{-2}
403.15	5.35×10^{-3}	5.92×10^{-2}

Fig. 6 Arrhenius Plot of Rate Constants, k_1 and k_2

As shown in **Fig. 6**, Arrhenius plots of determined k_1 and k_2 are linear. By applying least squares fitting to these plots, k_1 and k_2 can be calculated by the Eqs. (15) and (16);

$$k_1 = 1.03 \times 10^9 \exp(-87.9/RT) \quad (15)$$

$$k_2 = 4.30 \times 10^9 \exp(-84.3/RT) \quad (16)$$

where R is the gas constant in kJ/(mol K). At each reaction stage, activation energy, E_1 , was 87.9 kJ/mol and that of E_2 was 84.3 kJ/mol. Also pre-exponential factors in each stage were found to be 1.03×10^9 mol/(dm³ s) and 4.30×10^9 mol/(dm³ s), respectively. The reaction rate was found to be too fast to determine the rate constant at temperatures higher than 403 K. However, the reaction rate at temperature above 403 K could be evaluated by using Eqs. (15) and (16) on the basis of the Arrhenius plots obtained from the present experimental data in the temperature range from 343 to 403 K. These equations can be applied to evaluate the temperature profile of the adiabatic-type coiled-tube reactor with an initial reaction temperature of about 383 K and with the maximum temperature of 473 K.

4. Conclusion

The amination of 1-bromobutane has been carried out with an isothermal continuous coiled-tube reactor in the temperature range from 343 to 403 K under the pressure of 13 MPa. The major products observed

were *n*-butylamine and di-*n*-butylamine, while hardly any tri-*n*-butylamine and quaternary aminebase were observed. The effect of reaction temperature on the molar yields of *n*-butylamine and di-*n*-butylamine was also investigated. From the temporal variation of the molar yields of 1-bromobutane, *n*-butylamine and di-*n*-butylamine at each reaction temperature, the reaction rate and the molar yield of each reaction product were found to increase with temperature. The kinetic equation was derived based on the second-order consecutive reaction model involving two steps accounting for the formation of *n*-butylamine and di-*n*-butylamine. Further, the value of the two rate constants for the formation of these two amines was determined by fitting the kinetic equations to the experimental data. The Arrhenius plots of the rate constants were found to be linear. From these plots, activation energies and pre-exponential factors could be determined. The temperature profile of adiabatic coiled-tube reactor for amination of 1-bromobutane is under investigation, and the simulation method for the temperature profile is under development based on the reaction rate obtained in this study. Although still in preliminary stages, fairly reliable results have been acquired from the kinetic data obtained in this study.

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Nomenclatures

d	: density of aqueous ammonia solution	[g dm ⁻³]
E	: activation energy	[kJ mol ⁻¹]
k	: reaction rate constant	[dm ³ mol ⁻¹ s ⁻¹]
M_i	: molar concentration of component i	[—]
M_0	: initial molar concentration of 1-bromobutane	[—]
m	: mass flow rate of solution	[g s ⁻¹]
n_T	: mole of 1-bromobutane in toluene-phase	[mol]
n_W	: mole of 1-bromobutane in water-phase	[mol]
R	: gas constant	[kJ mol ⁻¹ K ⁻¹]
r	: reaction rate	[mol dm ⁻³ s ⁻¹]
t	: residence time	[s]
V	: reactor volume	[dm ³]
Y_i	: molar yield of component i	[—]

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要 旨

高温高圧下における 1-ブロモブタンの液相アミノ化反応

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流通式の高圧コイル状管型反応器を用いて, 50 wt% のアンモニア水溶液中での 1-ブロモブタンとアンモニアによるアミノ化反応を行った。実験温度範囲は 343~403 K であり, 反応圧力は 13 MPa である。反応の主生成物は *n*-ブチルアミンとジ-*n*-ブチルアミンであった。トリ-*n*-ブチルアミンのような高級アミンの生成はほとんど生成しなかった。*n*-ブチルアミンおよびジ-*n*-ブチルアミンの生成機構に対して 2 次の逐次反応モ

デルを適用し, 1-ブロモブタンのアミン化反応の速度定数の値を決定した。*n*-ブチルアミンが生成する第 1 段階の反応の活性化エネルギーは 87.9 kJ/mol であり, 頻度因子は 1.03×10^9 mol/(dm³ s) であった。また, ジ-*n*-ブチルアミンが生成する第 2 段階目の反応の活性化エネルギーは 84.3 kJ/mol であり, 頻度因子は 4.30×10^9 mol/(dm³ s) であった。

Keywords

Amination, Amine, 1-Bromobutane, High pressure, Kinetics, Nitrogen compound