

Reductive amination of cyclopentanone

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Abstract

The kinetics of heterogeneous catalytic reductive amination of cyclopentanone has been studied on a pilot plant PARR autoclave. *N*-cyclopentyliminocyclopentane was detected as the main intermediate in a reaction mixture. It was found that, at the given conditions, the main intermediate does not form the undesirable *N,N*-dicyclopentylamine but undergoes slow hydrolysis, and the desired product, cyclopentylamine, results in a good yield. Slight amounts of by-products such as cyclopentanol and *N,N*-dicyclopentylamine were obtained. The experimental data were confronted with the suggested kinetic model.

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1. Introduction

Cyclopentylamine is an important industrial intermediate, e.g. in production of the fungicides based on *N*-benzylcycloalkylamines [1]. The respective industrial manufacturing process (used in BorsodChem s.r.o., Ostrava, The Czech Republic) is based on reductive amination of cyclopentanone catalysed by powdered Raney nickel (Ra–Ni) and carried out in an autoclave. This reaction belongs among the group of reductive alkylations of amines [2]. It is known that hydrogenation of the imine (prepared in situ by condensation of a ketone with ammonia) occurs at room temperature and at atmospheric pressure in ethanol in the presence of catalyst (5% palladium on charcoal). Raney nickel in ethanol at 326–363 kPa is an alternative catalyst, where reductive amination of ketone preferably occurs and parallel hydrogenation of ketone also takes place [3].

Since the process consists in bimolecular reactions on the catalyst surface, the yield of cyclopentylamine strongly depends on the reaction conditions. Moreover, the amine primarily produced competes with ammonia in the carbonyl

condensation step. A proper choice of concentrations of the reagents can lead to the desired product (primary amine) in a high yield [2].

The use of a large excess of ammonia gives the primary amine as the predominant product. An excess of carbonyl compound gives the symmetrical secondary or tertiary amines. The preparation of cyclopentylamine by reductive amination of cyclopentanone over Raney nickel catalyst was described by Corrigan et al. [4], Plate et al. [5] and Xing et al. [6].

The procedure described in the patent [6] uses ammonia/cyclopentanone in the molar ratio 4/1; the catalyst used is a mixture of Ra–Ni and MgCl₂; the reaction pressure is 5–11 MPa, the reaction temperature is 120–180 °C. The declared conversion of the ketone is 99%, selectivity 96% and the yield of amine is 89%.

Other ways of reductive amination have also been developed, e.g. by Panfilov et al. [7] and Johansson et al. [8], where sodium borohydride and borane-dimethylsulphide complex were used as a reducing agents. However, these procedures are only convenient for laboratory purposes because of the very expensive reducing agents.

The aim of this present work is a kinetic study of the reductive amination of cyclopentanone in a laboratory

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PARR autoclave (BorsodChem) which should provide a kinetic model of the process as well as kinetic data useful for industrial purposes.

2. Experimental

2.1. Apparatus

The reductive amination was carried out in a PARR 4522 autoclave from Parr Instrument Company. The reactor of total volume 2 dm³ was equipped with the mechanic stirrer, inlet of gases, outlet and the sample port (Fig. 1).

2.2. Process of reductive amination

The reactor was filled with 0.95 kg cyclopentanone (11.29 mol, commercial sample from Rhodia Organique), and 0.95 g powdered Ra–Ni (commercial sample from Endelhard De Meern B.V.) was added. Then, the reaction vessel was closed and loaded with 0.37 kg liquid ammonia (21.73 mol); the starting temperature was 20 °C and the initial pressure was 1 MPa. The starting liquid reactants (mixture of ammonia and cyclopentanone) occupied ca. 80.3% of total reactor volume. Subsequently, the reactor was heated to the experimental temperature (80–150 °C) and hydrogen was introduced to reach and maintain the desired constant experimental pressure (4–9 MPa).

At definite time intervals, reaction samples (1.5 cm³) were taken and cooled to the laboratory temperature (22 °C), their residual free ammonia was volatilised, the catalyst was filtered off, and the samples were analysed by gas chromatography.

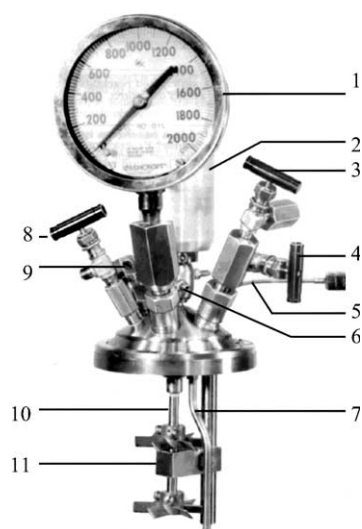


Fig. 1. Scheme of the PARR reactor used. (1) Pressure gage; (2) stirrer drive system; (3) gas inlet valve; (4) liquid sampling valve; (5) thermocouple; (6) water cooling channel; (7) dip tube; (8) gas release valve; (9) safety rupture disc; (10) stirring shaft; (11) lower guide bearing.

2.3. Gas chromatography

Gas chromatography (GC) was performed on a Hewlett Packard 6890 apparatus equipped with a 25 m capillary column HPI-dimethylsilicon with the inner diameter of 0.2 mm and the film width of 0.25×10^{-6} m. A temperature gradient of $30 \text{ }^\circ\text{C min}^{-1}$ from 60 to 250 °C was used for the analysis. Helium 30 mL min^{-1} was used as a carrier gas. A volume of 0.2×10^{-6} L sample was injected without dilution at the temperature of 60 °C. Chromatographic responses of analysed compounds were detected at 250 °C with FID Hewlett Packard detector.

Concentrations of compounds were determined by comparing with chemical standards of cyclopentanone, cyclopentylamine and cyclopentanol supplied from Aldrich (99%). The other components (*N*-cyclopentyliminocyclopentane, *N,N*-dicyclopentylamine and 2-cyclopentylcyclopentanone) were identified by GC–MS (for the spectra, see Chapter 3) before they were isolated from the reaction mixtures by means of fraction distillation. Chromatographic responses were converted to mass%.

2.4. GC–MS

The chromatographic apparatus consisted of a Hewlett Packard HC 5890 pump, a 30 m capillary column HPI-dimethylsilicon with an inner diameter of 0.25 mm and the film width of 0.25×10^{-6} m. A temperature gradient of $30 \text{ }^\circ\text{C min}^{-1}$ from 60 to 250 °C was used for the analysis. Helium 0.5 mL min^{-1} was used as a carrier gas. The chromatographic responses of analysed compounds were detected by means of a 5971A MS detector.

The quadrupole mass spectrometer with EI probe was used for all the measurements. The EI ion source temperature was set at 250 °C.

2.5. Calculations

All the calculations such as linear regression and non-linear fits of measured data were performed on PC using commercial software Microsoft Excel 97 SR-1.

3. Results and discussion

Reductive amination of cyclopentanone to cyclopentylamine catalysed by powdered Raney nickel (Ra–Ni) was carried out in a laboratory autoclave (Fig. 1) and can be described by the total chemical equation (Fig. 2).

All the experiments described in this work were carried out at a constant concentration of catalyst Ra–Ni (1 g per



Fig. 2. Synthesis of cyclopentylamine (C₅H₁₁N) from cyclopentanone (C₅H₈O).

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