



Unique shortening of carbon chain during reduction of aliphatic nitro compounds to amines in the presence of supercritical isopropanol on alumina



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ABSTRACT

Transformations of lower aliphatic nitrocompounds in supercritical isopropanol in a flow reactor in the presence of alumina were studied. In experiments with 1-nitropropane, the dominant process was the never-before-observed formation of an amine with a shorter by one carbon atom chain as compared to the initial nitroalkane. The reaction mechanism was suggested which adequately explained the formation of all detected products. The reactions of nitroethane and nitromethane partly proceeded by a new transformation route yielding isopropylamine.

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1. Introduction

Aliphatic amines are widely used for the production of polymers, pesticides, and pharmaceuticals [1–3]. They can be produced from respective aliphatic nitro compounds by a reduction with LiAlH_4 , Zn/HCl , or by Pd-, Pt-, Ni-catalyzed hydrogenation [2,4]. Other preparation methods include the reactions of ammonia with haloalkanes or alcohols in the presence of Ni-, Co-, Cu- or Fe-based catalysts; the acid-catalyzed reactions of olefins with nitriles, followed by hydrolysis (the Ritter reaction) [2]. Unfortunately, these methods are not versatile; some of them use explosive reagents, expensive noble metals, and show low selectivity. Catalytic transfer hydrogenation of nitroarenes is currently attracting much attention as a safer and greener way than the conventional methods [5–7]. However, we found no articles on the reduction of aliphatic nitro compounds by transfer hydrogenation.

As we found recently, the use of supercritical alcohols as a source of hydrogen in the presence of alumina provides efficient reduction of nitrobenzene **1** and its halogenated or methyl-containing

derivatives to respective anilines **2** in a flow reactor at temperatures of 545–615 K and contact time not exceeding 6 min (Scheme 1) [8,9]. Transformations of polynitroarenes in this system yield the products of selective reduction of one, two or three nitrogroups depending on the reaction temperature [10]. The behavior of aliphatic nitrocompounds under these reaction conditions has not been studied previously.

The aim of the present work was to study the transformations of nitroalkanes in a flow reactor in the presence of reducing system *sc*-isopropanol/ Al_2O_3 .

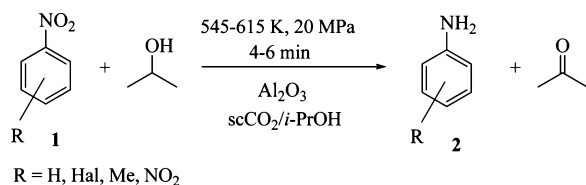
2. Experimental

Commercially available nitromethane, nitroethane, 1-nitropropane and 2-nitropropane were used as received (Aldrich) without purification. The used isopropyl alcohol contained no less than 99.8 wt.% of the main substance. CO_2 was a stated purity of 99.9 vol.%. The reactor was loaded with $\gamma\text{-Al}_2\text{O}_3$ (Macherey-Nagel, $\text{pH } 7 \pm 0.5$, free BET surface area $\sim 130 \text{ m}^2/\text{g}$) of 50–200 μm particle size without pretreatment.

Experimental studies were performed in the laboratory-scale set-up described earlier [11,12], using a tubular flow-type reactor (6.0 mm \times 0.8 mm, length 3.0 m) loaded with 42 cm^3 (39.1 g) of

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Scheme 1. Reduction of nitrobenzene and its derivatives by isopropyl alcohol in a flow reactor in the presence of alumina [8,9].

alumina. The initial mixture was fed to the reactor as two streams. The first stream – 1% substrate solution in isopropyl alcohol – was fed at a rate of 3 ml/min to a mixer at the reactor inlet. The second stream was supplied into the same mixer by a syringe pump through a heat exchanger where it was preheated to the reaction temperature. The second stream rate was 5 ml/min in case of CO₂ and 7 ml/min in case of isopropanol.

The contact time (τ) was determined as the ratio between the catalyst volume in the reactor V_c (cm³) and the total inlet rate of the mixture Q (cm³/s). Depending on the second stream rate, the contact time varied from 4.2 to 6.0 min. The reactions were performed in the temperature interval of 480–605 K at pressure $P \approx 20$ MPa.

To determine the critical parameters of the studied systems, and to find experimental conditions (temperature and pressure) providing single-phase supercritical state of the reaction mixture, thermodynamic calculations and phase diagram plotting were made using RKS EOS [13].

The reaction products were cooled at the reactor outlet, separated into the gas and liquid phases, and analyzed. The primary amines, which are formed at the reduction of nitromethane, nitroethane, 1-nitropropane and 2-nitropropane, have too low boiling temperatures that makes impossible to analyze them by gas–liquid chromatography in the presence of isopropanol. To overcome this problem, benzaldehyde, which reacts with primary amines to produce respective imines [14], was added to the reaction mixtures in the experiments with these nitroalkanes. Before analysis, these mixtures were kept at room temperature for 24 h.

Composition of the reaction products in the liquid phase was determined by gas chromatography–mass spectrometry (GC–MS) using an Agilent 7890A gas chromatograph equipped with a quadrupole mass spectrometer Agilent 5975C as a detector. Quartz column HP-5MS (copolymer 5%–diphenyl–95%–dimethylsiloxane) of length 30 m, internal diameter 0.25 mm and stationary phase film of thickness 0.25 μ m was used for the analysis. Qualitative analysis was performed by comparing the retention indices of the components and their complete mass spectra with the corresponding data for pure compounds if any and with the data of the NIST library, the Wiley7 library of mass-spectrometric data.

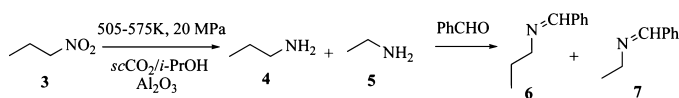
The surface areas of chromatographic peaks were determined on a gas chromatograph: 7820A gas chromatograph (Agilent Tech., USA); flame-ionization detector; HP-5 capillary column (0.25 mm \times 30 m \times 0.25 μ m), He as carrier gas (flow rate 2 ml/min, flow division 99: 1). The percentage composition of the mixtures was calculated from the surface areas of chromatographic peaks using no correction coefficients.

The gas composition was determined with the use of a gas chromatograph “Crystal 2000” equipped with a flame-ionization detector (FID), capillary column of length 30 m, internal diameter 0.25 mm, coated with Carbowax 20 M (Supelco).

¹H NMR spectra were recorded by Bruker AV-400 spectrometer (400.13 MHz (¹H)) in the CDCl₃ solutions of substances.

2.1. Synthesis of 2-phenylnitroethane **21**

Nitromethane (4.3 g) was added to the solution of benzaldehyde (7.5 g) in MeOH (25 ml) under stirring and cooling to 273 K. Then



Scheme 2. Transformations of 1-nitropropane **3**.

the solution of NaOH (4.5 g) in H₂O (40 ml) was added drop by drop. After stirring at 0 °C for 1 h, the mixture was diluted with 50 ml of H₂O and poured on ground ice with 16 ml of concentrated HCl. The obtained yellow deposit was filtered and washed with 25 ml of cooled MeOH. Thus, 7.8 g (74%) of 2-nitrostyrene was obtained.

The obtained 2-nitrostyrene (7.8 g) was dissolved in *i*-PrOH (50 ml) and CHCl₃ (250 ml), then SiO₂ (20 g) and NaBH₄ (12.0 g) were added. The mixture was stirred at room temperature for 3 h, and diluted with 100 ml of H₂O. The sediment was filtered and washed with Et₂O. The filtrate was washed 3 \times 50 ml of NaCl saturated solution and dried with Na₂SO₄. The drying agent was filtered, the solvent was distilled off, and the residue was purified by column chromatography (SiO₂, eluent hexane/ethylacetate 0–100%). Thus, 6.2 g (78%) of 2-phenylnitroethane **21** was obtained. The ¹H spectrum of compound **21** coincided with that reported in literature [15].

3. Results and discussion

We started the studies of nitroalkane transformations from experiments with 1-nitropropane **3** (Scheme 2, Table 1). At the first step of the present work, a complex supercritical solvent was used comprised of CO₂ and isopropanol. Early it was found that the use of scCO₂ as a co-solvent had a significant effect on the progress of both nitrobenzene reduction to aniline and secondary/side reactions [8]. For example, in the presence of CO₂, significant amount of *N*-alkylated derivative was formed, while without CO₂ the products of aromatic ring alkoxylation were detected in the reaction mixture. As a rule, the reduction in a complex solvent with scCO₂ was faster than in neat alcohols. It was suggested that the role of CO₂ may include the increasing in acidity of supercritical fluid which affects the reaction pathway [8].

Since 1-propylamine **4**, an expected product of 1-nitropropane **3** reduction, is a volatile compound, benzaldehyde was added to the sampled portions. It reacted with the formed amines to produce respective imines, which are readily detected by GC–MS.

At temperatures below 505 K, no conversion of compound **3** was observed (Table 1). As the temperature increased to 535 K, the conversion of 1-nitropropane **3** attained 49%, imine **7** was the main product, imine **6** – the minor one. The presence of products **6** and **7** proved that the reaction mixture contained 1-propylamine **4** and ethylamine **5**.

As neat isopropanol (Table 1) was used as the solvent instead of *i*-PrOH/CO₂, the conversion of 1-nitropropane **3** at 535 K decreased to 28%, whereas the selectivity to ethylamine **5** increased to \sim 100%.

Table 1
Transformations of 1-nitropropane **3**.

T, K	Conversion, %	Solvent	Selectivity, ^a %	
			6 (4)	7 (5)
505	0	<i>i</i> -	–	–
535	49	PrOH/CO ₂	9	91
480	0	–	–	–
505	10	<i>i</i> -	–	100
535	28	PrOH	–	100
575	71	–	19	81

^a The numbers in brackets show which amine corresponds to the imine detected in the reaction mixture after treatment with benzaldehyde.

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