



Efficient reduction of nitroarenes using supercritical alcohols as a source of hydrogen in flow-type reactor in the presence of alumina

V.P. Sivcev^a, D.V. Korchagina^b, E.V. Suslov^b, K.P. Volcho^b,
N.F. Salakhutdinov^b, V.I. Anikeev^{a,*}

^a Borekov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Prosp. Akad. Lavrent'eva 5, Novosibirsk 630090, Russian Federation

^b Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, Prosp. Akad. Lavrent'eva 9, Novosibirsk 630090, Russian Federation

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ABSTRACT

Reduction of nitroarenes using supercritical alcohols as a source of hydrogen was studied in a flow reactor in the presence of alumina at temperatures 515–615 K and residence times not exceeding 6 min. In the reaction of nitrobenzene reduction by 4-methylpentan-2-ol in supercritical (sc) CO₂, the selectivity for aniline reached 95% with a conversion of 71%. If methanol was used as the reducing agent, the main reaction product was *N,N*-dimethylaniline. It was shown that the use of scCO₂ co-solvent had a significant impact on the course of the reduction process including secondary and side reactions. The conditions for the reduction of halogenated nitroarenes into respective amines with high conversion and nearly 100% selectivity almost without dehalogenation were found.

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1. Introduction

Aromatic amines are widely used as intermediates for the production of polymers, pigments, pesticides, dyes, and pharmaceuticals [1,2]. In practice, aromatic amines are produced mainly by the reduction of respective aromatic nitro compounds which are usually readily available. Metals (Zn, Sn, Fe) in the presence of acids can be used as the reducing agents [1]. The methods of catalytic hydrogenation [3–5], including those using supercritical co-solvent CO₂ [6] are applied. In recent years, considerable attention has been focusing on the reduction of nitroarenes to amines with the use of catalytic hydrogen transfer systems including alcohols, hydrazine hydrate, triethylammonium formate, etc. as the hydrogen donors [7]. The catalysts are Ru/C [8], Au/TiO₂ [9,10], Au/C [11], Cu–MgO–Al₂O₃ [12], KOH–NiO–Al₂O₃ [13], KOH–ZrO₂–NiO [14], etc.

As shown in our recent studies of 4-nitrobenzaldehyde **1** and 4-nitroacetophenone **2** reduction in a flow reactor in sc-CO₂/isopropanol solvent in the presence of Al₂O₃ [15,16], the reduction of carbonyl groups is accompanied by partial reduction of nitro-groups to amine-groups (Scheme 1). In these reactions,

isopropanol acts both as solvent and hydrogen donor and converts to acetone (contact time ≤ 6 min).

The use of this simple and readily up-scalable catalytic system for the reduction of nitroarenes to amines seems quite promising although the selectivity to aminoarenes in [15,16] was low.

The present work is focused on the development of efficient method for selective production of aminoarenes from nitrocompounds in a flow reactor using reducing system alcohol/alumina.

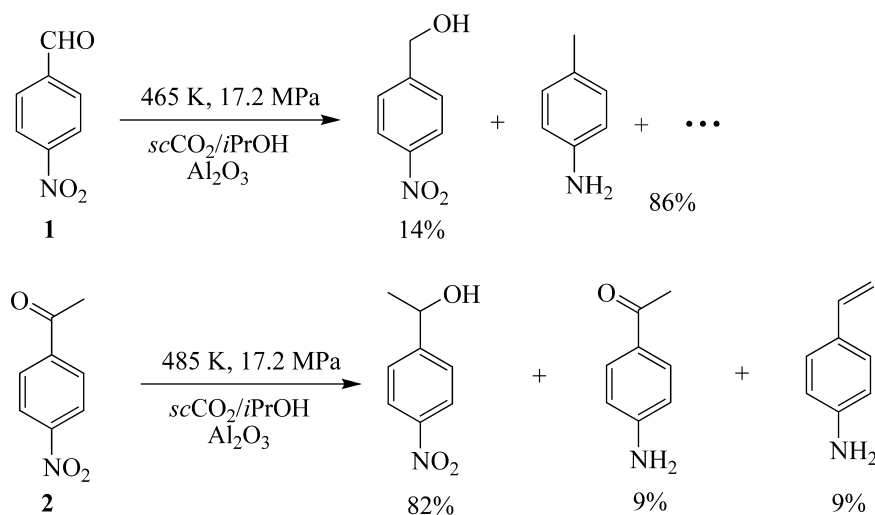
2. Experimental

Commercially available nitroarenes and 4-methylpentan-2-one **14** (see Scheme 5), Aldrich were used as received without purification. *N*-Isopropylaniline **7** (see Scheme 2) was synthesized in accordance with article [17]. The supplied isopropyl alcohol and methanol contained no less than 99.8 wt.% of the main substance and no more than 0.05 wt.% of water. CO₂ was a stated purity of 99.9 vol.% and contained no more than 0.02 vol.% water. The reactor was loaded with γ-Al₂O₃ (Macherey–Nagel, pH 7 ± 0.5, free BET surface area ~130 m²/g) of 50–200 μm particle size without pre-treatment.

Experimental studies were performed in the laboratory-scale set-up described earlier [18,19], using a tubular flow-type reactor (6.0 mm × 0.8 mm, length 3.0 m) loaded with 42 cm³ (39.1 g) of alumina. The initial mixture was fed to the reactor as two streams.

* Corresponding author. Tel.: +7 3833269434.

E-mail address: anik@catalysis.ru (V.I. Anikeev).



Scheme 1. Transformations of nitroarenes **1** and **2**.

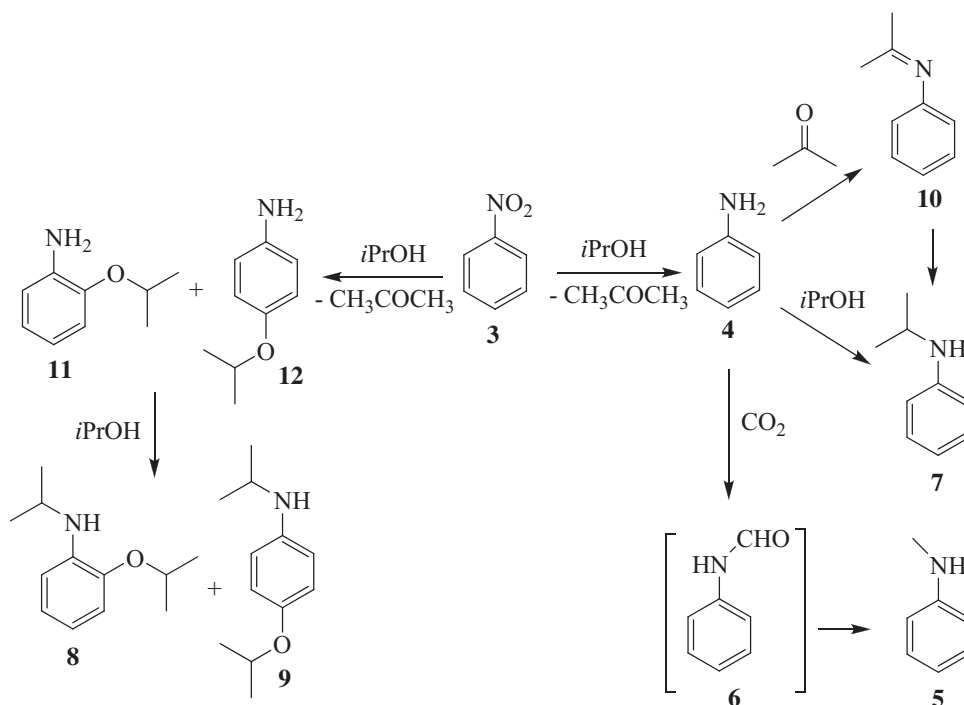
The first stream – 1% substrate solution in alcohol – was fed at a rate of 3 ml/min to a mixer at the reactor inlet. The second stream was supplied into the same mixer by a syringe pump through a heat exchanger where it was preheated to the reaction temperature. The second stream rate was varied depending on the solvent in order to provide almost the same reagent concentration in all experiments. In case of CO_2 the rate was 5 ml/min; the rates of isopropanol and methanol were 7 and 4 ml/min, respectively.

The residence time (τ) was determined as the ratio between the catalyst volume in the reactor V_c (cm^3) and the total inlet rate of the mixture Q (cm^3/s). Depending on the second stream rate, the residence time varied from 4.2 to 6.0 min. The reactions were performed in the temperature interval of 545–615 K at pressure $P \approx 20$ MPa.

To determine critical parameters of the studied systems and 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 [20]. Table 1 presents the calculated critical temperatures and pressures for the selected mixtures in comparison with respective values for CO_2 and i -PrOH.

The reaction products were cooled at the reactor outlet and analyzed. Gassing in the reaction products was not observed. 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 thickness 0.25 μm was used for the analysis. The standard deviation for chromatographic analysis is not more than 3%.



Scheme 2. Transformations of nitrobenzene **3**.

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