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THEORETICAL AND EXPERIMENTAL RESEARCHES OF CATALYTIC REDUCTION OF AROMATIC NITRO COMPOUNDS BY MOLECULAR HYDROGEN IN LIQUID PHASE

Abstract. Aromatic mono-, di- and polyamines are used in the production of various compounds. Synthesis of amines by catalytic hydrogenation (in the vapor or liquid phase) of the corresponding nitro compounds is the most promising and ecologically pure method. In this article issues of reduction of aromatic nitro compounds for producing amines, valuable intermediate and final products are considered. Comparative data from literary and patent sources for the last decades are given. Various variants of the mechanism of hydrogenation of the nitro group in aromatic nitro compounds are considered. Analysis of the literature shows that, most likely, regardless of the composition and methods of preparation of the catalyst, the solvent used and the presence of substituents in the nitro compound molecule, hydrogenation proceeds in accordance with the Haber-Lukashevich scheme. Nevertheless, a change in the composition of catalyst and solvent can significantly change the ratio of the rates of individual process steps.

Keywords: catalysis, aromatic nitro compounds, amines, hydrogenation, supported catalysts.

Nitro compounds: brief information. Nitro compounds are derivatives of hydrocarbons of the general formula R-NO_2 having in their composition a nitro group directly linked to an aliphatic or aromatic radical [1]. Depending on the nature of the hydrocarbon radical "R", nitro compounds are divided into aliphatic and aromatic. Aromatic nitro compounds (figure 1) are a group of organic substances, headed by nitrobenzene and formed from benzene and its homologues (toluene and xylene), naphthalene and anthracene by replacing one or more atoms with a nitro group. In aromatic nitro compounds the nitro group is bound to the aromatic ring. The nitro group can be replaced, along with halogen and some alkyl radicals, in almost any place of the ring [2].

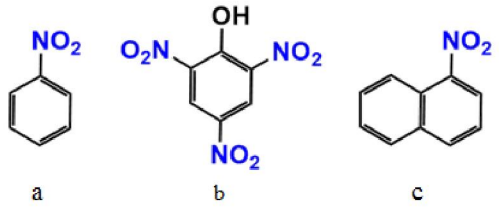

Figure 1 – Aromatic nitro compounds of different structure:
a – nitrobenzene, b – 2,4,6-trinitrophenol (picric acid), c – 1-nitronaphthalene

In the nitro group there is a π-conjugation (p-π-conjugation), as a result of which both bonds become equivalent. The structure of the nitro group can be represented by two equivalent mesomeric structures (or resonant structures). The nitro group is flat, some of its geometric parameters are given in the figure using the example of nitromethane (figure 2).

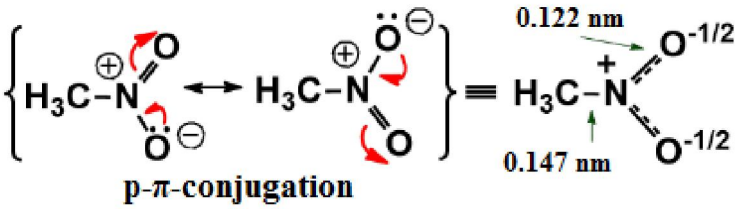

Figure 2 – Nitromethane

Nitro compounds that have the most important industrial significance include nitrobenzene, mono- and dinitrotoluenes, trinitrotoluene, tetryl, mononitrochlorobenzenes, nitroanilines, nitrochlorotoluenes, nitronaphthalene, dinitrophenol, picric acid (trinitrophenol), and dinitrocresol.

The most important property of the nitro group is its ability to be reduced to an amino group.

In the last 30-40 years, the processes of catalytic reduction of aromatic nitrocompounds by hydrogen to amines have practically superseded all other methods for the production of aromatic amines in large-tonnage plants. Aromatic mono-, di- and polyamines, due to their high reactivity, are widely used in the production of various compounds: synthetic dyes of various shades (for photography, in the paint and varnish industry, for painting natural and synthetic fibers), photochemicals, fuel stabilizers and additives lubricating oils, chemical plant protection products, synthetic fibers, sorbents, medicines, etc. [3-9]. Taking into account the extremely high volumes of commercial production of aniline and toluene diamines, the total production of which in the world is more than 3-4 million tons/year, the problem of improving the technology of obtaining these compounds can be considered actual [10].

Amines production from nitro compounds. The vapor phase and liquid-phase hydrogenation of nitro compounds hydrogenation of nitro compounds. The catalytic reduction of organic compounds, including aromatic mono- and polynitro compounds, to the corresponding amines is carried out in many variants, differing in the composition of the reaction masses, the aggregate state of the phases, the nature and type of the hydrogenation catalyst, the apparatus design of the process, the conditions of its conduct, etc. [11-40].

The reaction of reducing aromatic nitro compounds to amines by the action of ammonium sulphide on heating was discovered by N.N. Zinin in 1842 ("Zinin reaction") [12]. Zinin's reaction is a method of obtaining aromatic amines by reduction of nitro compounds (1):

$$R\text{-}NO_2 + 6H = R\text{-}NH_2 + 2H_2O. \quad (1)$$

Zinin acting on nitrobenzene with ammonium sulfide, obtained aniline (2):

$$C_6H_5NO_2 + 3(NH_4)_2S \rightarrow C_6H_5NH_2 + 6NH_3 + 3S + 2H_2O. \quad (2)$$

Later, Zinin showed that the reaction he discovered was of a general nature. The principles of the Zinin reaction form the basis for the synthesis of various aromatic amines, many of which serve as starting materials in the production of synthetic dyes, pharmaceuticals, explosives, fragrances, medicines, and other substances. The wide application of Zinin's reaction has largely determined the development of organic synthesis. With the help of Zinin's reaction, aniline and other aromatic amines were synthesized for the first time [13, 14], the foundations for the development of industrial organic synthesis of dyes, explosives and fragrances, and drugs were laid. During the time that elapsed since the discovery of the reaction of obtaining aniline from nitrobenzene by N.N. Zinin, a large number of various reducing agents were used to reduce nitro compounds: metals (Sn, Zn, Fe, etc.), metal sulfides and hydrogen sulphide, metal sulfites, hydrogen, hydrazine and its derivatives, hydrogen on catalysts [12, 14].

Amines can be obtained electrochemically by reduction of nitro compounds and nitriles of acids. The first method is usually used for the synthesis of aromatic amines and some aliphatic substituted amines,