Nitrobenzene Hydrogenation to N-phenylhydroxylamine: a New Approach to the Selectivity

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Abstract

A new approach to resolve the problem of selectivity with respect to N-phenylhydroxylamine in nitrobenzene hydrogenation is proposed. N-phenylhydroxylamine only is the final product of nitrobenzene electroreduction in aprotic media. In this case nitrobenzene reduction carries out by alternation of electrochemical (electron transfer) and chemical (species formed protonation) stages *i.e.* by so-called EC mechanism. Such mechanism realization in nitrobenzene hydrogenation is possible if i) a catalyst activates hydrogen as "hydrogen electrode" *i.e.* serves electrons source; ii) a reaction media contains limiting proton concentration. These limitations are discharged in the media of aprotic dipolar solvent, which solvated both positive and negative species. Really, in aprotic dipolar solvents over reduced platinum complexes or low-percentage (≤1 wt.%) platinum, iridium or osmium catalyst nitrobenzene is hydrogenated with process discontinuance after nitrobenzene total consumption. Nitrobenzene hydrogenation yields N-phenylhydroxylamine as the main (the yield is 98%) product. As these low-percentage catalysts, complex catalyst *in situ* is heterogeneous *i.e.* it represents a platinum colloid (particle size ~ 40 nm) stabilized by aprotic dipolar solvent. So, process of nitrobenzene hydrogenation, which is similar to nitrobenzene electoreduction, can is created.

A kinetic scheme proposed is analyzed and kinetic equation for initial reaction rate, which is conformed to kinetic data, is obtained.

Introduction

An abundant literature is devoted to catalytic hydrogenation of nitrobenzene into aniline. Metals used as catalysts include nickel, platinum, palladium, rhodium and ruthenium. In liquid phase the mechanism of nitrobenzene hydrogenation and the obtained products are known to depend strongly on the solution acidity [1]. Nitroarenes substituted into aromatic ring by electron deficient groups (*e.g.* by halogen, –C≡N or –COOR), are hydrogenated with N-arylhydroxylamine accumulation. The accumulation degree in such nitroarenes hydrogenation was 70-80% over Raney Ni in ethanol solution [2,3]. This value is higher (up to 93%) over iridium catalysts under special conditions in propan-2-ol solution, but N-phenylhydroxylamine (PHA) accumulation is not observed [4]. High (up to 70%) yield of PHA in nitrobenzene (NB) hydrogenation over platinum supported on activated carbon cloths was observed, but reaction mixture along with PHA contained both 15% of initial NB and 15% of aniline. The total consumption of NB was observed when the relative concentration of PHA was 60% [5]. Therefore, approach for PHA production when hydrogenation is forcedly stopped in a moment when the concentration of PHA is maximal but the concentration of NB is minimal (for example, [4]), is used. This approach has poor processability as a batch reactor is used and the reaction mixture monitoring is needed. PHA is the final product of NB electroreduction in aprotic dipolar media. The elecroreduction of NB is carried out as a succession of alternate electron transfer (electrochemical) and protonation (chemical) stages, *i.e.* by so-called EC mechanism [6]. This looks tempting to design NB hydrogenation process similar to NB electroreduction in aprotic dipolar media [6]. Really, as first example of this approach use, NB hydrogenation to PHA as a final product with the high (98%) yield catalyzed by complex $Pt(DMSO)_2Cl_2$ reduced by $NaBH_4$ in DMSO was reported [7].

In the present paper kinetic data on hydrogenation of NB in the media of aprotic dipolar solvents are analyzed.

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Experimental

Complexes $Pt(DMSO)_2Cl_2$ (I), $Pt(DMS)_2Br_4$ (II), $Pt(Pq)_2Cl_2$ (III), $Pt(Ml)_2$ (IV) and $Pt(Aq)_2$ (V), where DMS – dimethyl sulfide, Pq – 9,10-phenantheren-quinone, Ml – 3-hydroxy-2-methyl-γ-pyrone (maltol), Aq – 1,2-dihydroxy-9,10-anthraquinone (alizarin), were used. The complexes (III), (IV) were prepared as described in [8], (V) — in [9]. Preparations of (I), (II) and basic experimental methods were reported in [7]. Complexes (I), (II) were reduced before use by $NaBH_4$ (molar ratio $NaBH_4/Pt = 3$), (III)-(V) — by H_2 at room temperature for 15 min. Solutions of the complexes change color after reduction to more intense and become mahogany.

The catalysts Pt/C, Ir/C, Pd/C and Os/C (metal content 1 wt.%) and Raney's Ni were prepared according to [10]. H_2O and D_2O were purified from catalytic poisons by boiling over 5 wt.% Pt/C. Kinetics measurements were carried out at 40°C and hydrogen pressure 0.1 mPa, the complexes concentration was 4×10^{-3} M.

Results and discussion

Nitrobenzene anion-radical NB⁻ is the product of first reduction stage as in NB electroreduction [6]. $PhNO_2H^{\cdot}$ radical formed after irreversibly protonation of nitrobenzene anion-radical NB⁻ by a proton donor B^-H^+ with the acidity constant K_a *i.e.* by a dissociated form of proton donor whereas another proton source is absent and proton concentration is limited. The catalyst K activates molecular hydrogen with electron accumulation and forms catalyst active form K*. Nitrobenzene NB adsorbed on catalyst surface oxidizes catalyst active form K*. Nitrobenzene anion-radical NB⁻ adsorbed on catalyst surface is an intermediate product in this process. Nitrobenzene anion-radical NB⁻, which was observed in liquid phase [7], is probably the result of K-NB⁻ dissociation. This nitrobenzene anion-radical NB⁻ adsorbed on catalyst surface is irreversibly protonated by a proton donor B^-H^+ with the acidity constant K_a with adsorbed $PhNO_2H^{\cdot}$ radical (PK) being formed. PK is the limiting stage product as stated elsewhere [11]. As result NB hydrogenation process similar to NB electroreduction [6] is realized as:

$$K + H_2 \xrightarrow{K_1} K^* + 2H^+$$

$$K^* + NB \xrightarrow{K_2} K\text{-}NB^{\cdot}$$

$$K\text{-}NB^{\cdot} + B^-H^+ \xrightarrow{k_3} PK + B^-$$
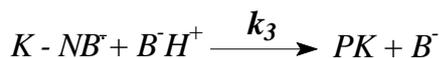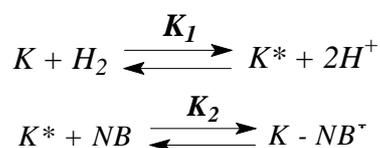
The analysis of this scheme in the framework of quasistationary concentrations method assuming that $[K\text{-}NB^{\cdot}] \ll [NB]_0$ results to the equation for the initial rate of NB hydrogenation:

$$W_0 = \frac{K_1 K_2 k_3 [K]_0 [NB]_0 [BH]_0 [H_2]_0}{K_a [BH]_0 + K_1 [H_2]_0 + K_1 K_2 [NB]_0 [H_2]_0} \quad (1)$$

As seems, NB hydrogenation in DMF, dimethyl-acetamide (DMA), DMSO, pyridine (Pyr) or hexamethylphosphoramide (HMPT) catalysed by product of reduction of platinum complexes, realizes by proposed above scheme.

Product of reduction of complexes I–V in DMF, DMA, DMSO, Pyr or HMPT catalyzes nitrobenzene hydrogenation. The observed kinetic curve is characterized by a breakdown time and is S-curve (Fig. 1). These facts point to the autocatalytic character of NB hydrogenation in aprotic media. After NB depletion the reaction is completed (Fig. 1). PHA (98%) is the main product of NB hydrogenation in aprotic media. The second minor hydrogenation product is azoxybenzene. The presence of azoxybenzene probably points to an intermediate formation of nitroso-benzene, which interacts with PHA extremely readily to form azoxybenzene. The specific catalytic activities are symbate with respect to solvent donor number (Table 1).
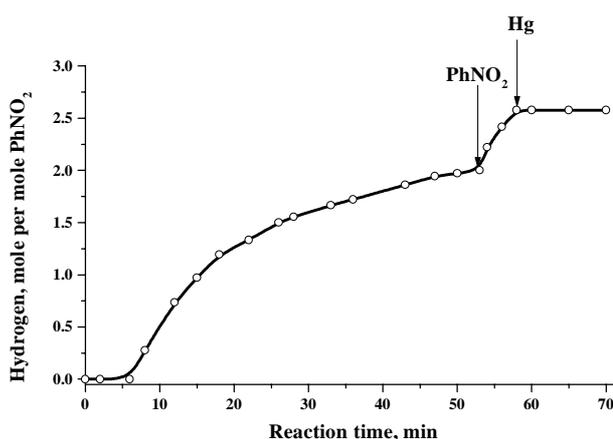

Fig. 1. Kinetic curve of hydrogen consumption in NB hydrogenation (NB initial concentration $[NB]_0$ is equal of 0.066 M) in DMSO solution (volume 10 ml) catalyzed by reduction product of complex I (platinum concentration [Pt] is equal of 2×10^{-2} M). Arrows indicate NB and Hg inlets.

The complexes III and IV in DMF, DMA, DMSO, Pyr or HMPT solution are totally dissociated as it was reported [8]. In these solutions the complexes III-V are dissociated too as detected by electochemical data. Used solvents having high donor property proveke an exchange of DMS, Pq, Ml or Aq ligands in initial complexes on solvent as ligand. This ligands exchange points to the similarity in the catalytic activity between III, IV or V and I or II with Pq, Ml or Aq additions in compliance with complex III–V formula (Table 1). So, specific catalytic activities are similar (Table 1).

Table 1

Specific activities of platinum catalysts in NB hydrogenation (initial concentration $c_0 = 0.1$ M) in aprotic solvents (liquid phase volume 10 ml).

Run N	Solvent	Donor number DN_{SbCl_5}	Specific activity, mol/mol Pt×min for complexes				
			I	II	III	IV	V
1	DMF	26.6	-	-	2.12	0.50	1.51
2	DMA	27.8	0.19	0.19	2.75	0.91	2.03
3	DMSO	29.8	0.37	0.37	3.38	1.50	2.56
3a	DMSO+Pq		3.29	3.26	-	-	-
3b	DMSO+Ml		1.48	1.46	-	-	-
3c	DMSO+Aq		2.57	2.53	-	-	-
4	Pyr	33.1	0.83	0.82	4.18	2.04	3.75
5	HMPT	38.8	1.00	0.99	15.04	6.23	10.26

The products of reduction of the complexes I–V in DMF, DMA, DMSO, Pyr or HMPT do not undergo sedimentation by ultracentrifugation (20000 g, 3 h) but become colorless and less their activity after a treatment by mercury (Fig. 1). Metal platinum colloid is formed evidently in complex I-V reduction. The particle size of this colloid is ≥ 40 nm by sedimentation data. A solvent stabilizes this colloid in contrast to well-known colloids. NB hydrogenation rate is directly proportional to catalyst concentration. Other platinum catalysts besides platinum colloid can be used in aprotic media for selective NB hydrogenation into PHA. Catalysts with low (≤ 1.0 wt.%) metal contents can be used in this case too. So, selectivity with respect to PHA in NB hydrogenation over 1.0 wt.% Ir (Pt or Os)/C in DMSO reaches 93-95% while over 5 wt.% Pt/C the one being 45% that is consistent with the data [5]. Palladium and nickel activate hydrogen by another way. Selectivity with respect to PHA in NB hydrogenation in DMSO over 1.0 wt.% Pd/C or Raney's nickel is less than 40%.

The initial NB concentration $[NB]_0$ dependence of the initial rate W_0 of NB hydrogenation is represented by a curve with saturation in the range of molar ratio $[NB]_0/[Pt] = 1 \div 40$ but it is linear in W_0^{-1} *vs* $[NB]_0^{-1}$ coordinates (Fig. 2). This dependence is consistent with the well-known pseudo-zero order of hydrogenation with respect to NB.

Observed breakdown time of the kinetic curve is annuled after one run of NB hydrogenation (Fig. 1). Water determines autocatalytic character of NB hydrogenation in aprotic dipolar media. So, water additions annul the observed breakdown time and accelerate NB hydrogenation. The initial water concentration $[H_2O]_0$ dependence of the initial rate W_0 of NB hydrogenation is represented by a curve with saturation but is linear in W_0^{-1} *vs* $[H_2O]_0^{-1}$ coordinates. D_2O addition gives the similar effect but NB hydrogenation rate at equal concentration is 1.4 times less than at H_2O addition (Fig. 3). This isotope effect is close to $\sqrt{2}$ that confirms a hypothesis about a role of dissociated form of water as a proton donor.

Hydroquinone accelerates NB hydrogenation also. The initial hydroquinone concentration $[QH_2]_0$ dependence of the initial rate W_0 of NB hydrogenation is represented by a curve with saturation, but is linear in
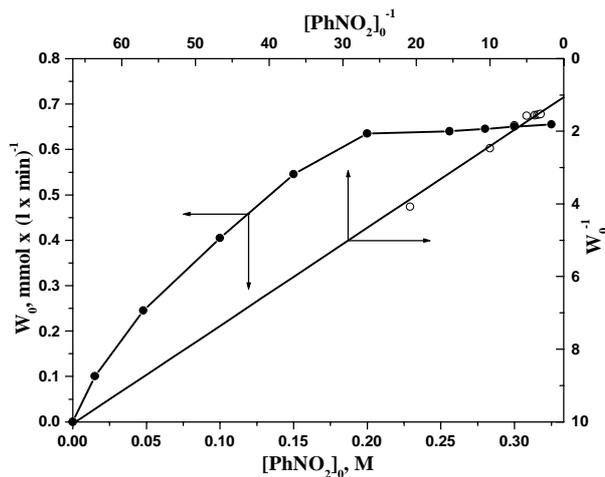
Fig. 2. NB hydrogenation initial rate W_0 at $[Pt] = 2{\times}10^{-2}$ M vs. NB initial concentration ($[NB]_0$) in the presence of 1,4-hydroquinone (1,4-hydroquinone initial concentration $[QH_2]_0$ is equal of 0.1 M) in DMSO (total volume 10 ml) and anamorphous in $W_0^{-1}\sim[NB]_0^{-1}$ coordinates.

W_0^{-1} vs $[QH_2]_0^{-1}$ coordinates as well (Fig. 4). Hydroquinones as shown are easily formed in quinone hydrogenation under these conditions; therefore, quinone addition in NB hydrogenation system results in acceleration of selective NB hydrogenation, similar to hydroquinone additions.
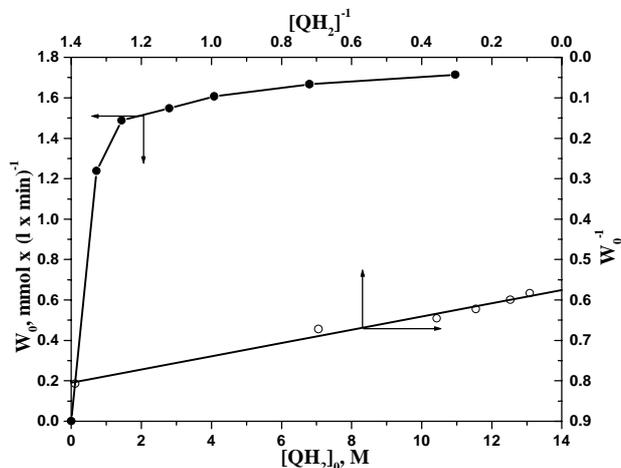

Fig. 4. NB ($[NB]_0 = 0.1$ M) hydrogenation initial rate W_0 at $[Pt] = 2{\times}10^{-2}$ M vs. 1,4-hydroquinone initial concentration ($[QH_2]_0$) in DMSO (total volume 10 ml) and anamorphous in $W_0^{-1}\sim[QH_2]_0^{-1}$ coordinates.

So, the observed linear anamorphous in $W_0^{-1}\sim[NB]_0^{-1}$ and $W_0^{-1}\sim[BH]_0^{-1}$ (Fig. 2, 3, 4) coordinates, the pseudo-zero reaction order with respect to NB and the first order with respect to H_2 are conceivable according to the equation (1).
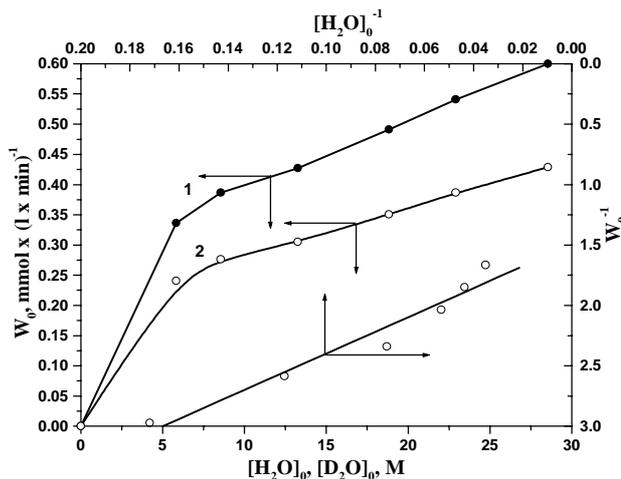
NB hydrogenation stops after aniline, not PHA,

Fig. 3. NB ($[NB]_0 = 0.1$ M) hydrogenation initial rate W_0 at $[Pt] = 2{\times}10^{-2}$ M vs. H_2O (1) or D_2O (2) initial concentration ($[H_2O]_0$ or $[D_2O]_0$) in DMSO (total volume 10 ml) and anamorphous 1 in $W_0^{-1}\sim[H_2O]_0^{-1}$ coordinates.

formation if the initial water concentration in DMF is more than 30 M. In DMSO solution the similar effect is observed when the initial water concentration is higher (near 45 M). Phenol addition results in this effect too. Hydroquinones addition in contrast to water or phenol does not to provoke the effect of final product exchange.

PHA formed on the catalyst can undergo other transformations besides hydrogenation to aniline, for example, disproportionation [12]. Aprotic dipolar solvent having high donor properties competes with PHA for catalyst active centers and can inhibit PHA disproportionation.

This approach is useful in the other selective hydrogenation processes, which are carried out by reduction–protonation (EC) mechanism. Carbon-carbon double bonds, $i.e.$ alkenes are reduced by the EC mechanism [6]. Alkenes, both hexene-1 and octene-1, do not hydrogenated in aprotic media over colloid platinum catalyst. Aprotic solvent (for example, Pyr and DMSO) also inhibits dehydrochlorination in chloronitroaromatics hydrogenation [13].

Conclusion

In the framework of proposed approach not only colloid catalysts which have poor processability because they are poor-pressed and not precipitated at centrifuging, but also supported metal (Pt, Ir or Os) low-percentage (≤1 wt.%) catalysts can be used. The use of the fine supported metal (Pt, Ir or Os) or reduced complex catalyst operating as a "hydrogen electrode"

or aprotic dipolar solvent alone does not perform selective hydrogenation of NB to PHA. Similarly, the use of the fine metal (Pt, Ir or Os) catalyst operating as a "hydrogen electrode" and aprotic (but not dipolar) solvent (benzene, for example) does not perform selective hydrogenation of NB too. The selectivity with respect to PHA in NB hydrogenation in DMSO over 1.0 wt.% Ir (Pt or Os)/C reaches 95-98%. Selectivity with respect to PHA in NB hydrogenation in the media of DMF, DMA, DMSO, Pyr or HMPT over colloid platinum obtained by reduction of the complexes $Pt(DMSO)_2Cl_2$, $Pt(DMS)_2Br_4$, $Pt(Pq)_2Cl_2$, $Pt(Ml)_2$ or $Pt(Aq)_2$ reaches 98%. This colloid platinum does not catalyze hydrogenation of compounds having double C-C bond (hexene-1 or octene-1 for example). In aprotic dipolar media platinum catalysts inhibit dehydrochlorination in chloronitrobenzene hydrogenation.

Acknowledgements

References

1. Haber F.Z., Elektrochem. 1898. B. 22. S. 506.
2. Studer M., Neto S., Blaser H.-U., Topics in Catal. 2000. V. 13. pp. 205-212.
3. Baumaister P., Blaser H.-U., Studer M., Catal. Lett. 1997. V. 49. pp. 219-226.
4. Savchenko V.I., Makaryan I.A., Dorohov V.G., Platinum Metals Rev. 1997. V. 41. № 4. pp. 176-183.
5. Macías Pérez M.C., Salinas Martínez de Lecea C., Linares Solano A., Appl. Catal. A: General. 1997. V. 151. pp. 461-475.
6. Organic electrochemistry (ed. M.M. Baizer), 1973, Marcel Dekker Inc., N-Y.
7. Kushch S.D., Izakovich E.N., Khidekel' M.L., Strelets V.V., Izvestiya AN SSSR. Ser. Khim. 1981. № 7. S. 1500-1505.
8. Kushch S.D., Izakovich E.N., Rashchupkina O.S. et al., Izvestiya AN SSSR. Ser. Khim. 1981. № 4. pp. 900-904.
9. Bulatov A.V., Khidekel' M.L., Trans. Met. Chem. 1980. V. 5. № 1. p. 123.
10. Organikum (ed. K. Schwetlick), 1976, VEB Deutscher Verlag, Berlin.
11. Sadler J.C., Bard A.J., J. Amer. Chem. Soc. 1968. V. 90. № 8. p. 1979.
12. Simonov V.D., Denisenko T.V., Savchenko V.I., Sklyar S.Ya., Zhurnal Organicheskoy Khimii. 1976. T. 12. № 5. p. 1036.
13. Dorohov V.G. Dissertation of Dr. of Sci., Institute of Chemical Physics USSR Academy of Sci. 1980.