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Spectrophotometric Study of Dehalogenation of Benzyl Halides with Nickel in Aprotic Dipolar Solvents in the Presence of Oxygen

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Abstract—Oxidative dissolution of nickel in the benzyl halogenide – dipolar aprotic solvent system in the presence of air oxygen proceeds with the formation of benzaldehyde, benzyl alcohol, 1,2-diphenylethane, and trace amounts of 4,4'-ditolyl. Spectrophotometry studies have revealed that the oxidation products are formed in the solution rather than at the nickel surface. It has been shown that the oxygen adsorbed at the nickel surface practically does not pass into the solution.

Keywords: nickel, benzyl halide, oxygen, dipolar aprotic solvent, spectrophotometry

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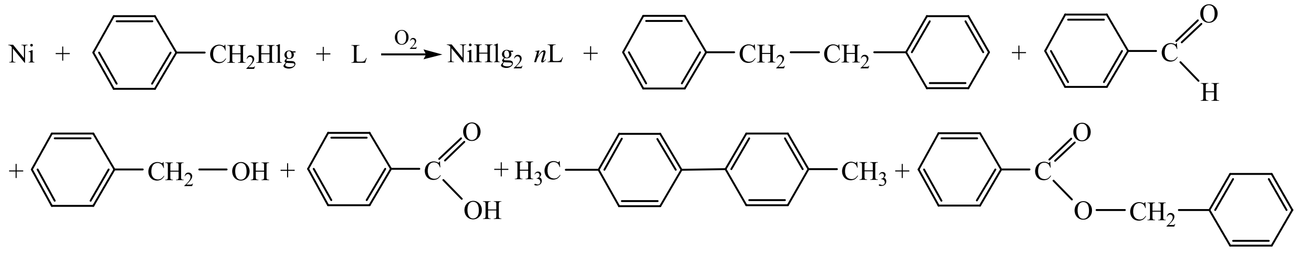
Nickel complexes with organic ligands have been used for modification of polymers to prepare the materials with desired properties. They have been often used as efficient light stabilizers of different polymers [1]. Halogenated nickel complex compounds are generally prepared via direct dissolution of the metal in the organic halide – dipolar aprotic solvent system under inert atmosphere. Carbon tetrachloride and benzyl halides have been used [2] as the halide component. Performing these processes in the presence of oxygen has been scarcely studied, their mechanism has not been established, and the kinetic features have not been determined; this has prevented scaling up of these reactions to be used in industry.

In this work, mechanism of the benzyl halides reaction with nickel in dipolar aprotic solvents in the presence of oxygen was studied aiming to develop the "green" technology for preparation of the nickel complex compounds.

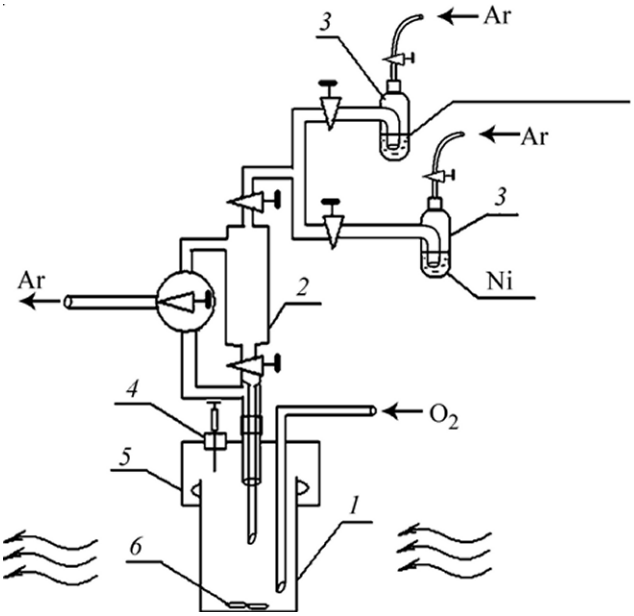
The analysis of the products by chromato–mass spectrometry revealed that the organic products of the reaction of fine-disperse nickel powder of the "PNE–1. Lux" grade with benzyl halides were 1,2-diphenylethane, benzaldehyde, and benzyl alcohol, on top of trace amounts of 4,4'-ditolyl, benzoic acid, and benzyl benzoate. Oxidative dissolution of nickel in the benzyl halide–dipolar aprotic solvent–oxygen system proceeded according to the Scheme 1.

Treatment of the reaction mixtures containing benzyl bromide with diethyl ether gave the nickel(II) complex compounds: $[Ni(DMF)_6]Br_2$ and $[Ni(DMSO)_6]Br_2$.

Scheme 1.



Hlg = Br, Cl; L = DMF, DMSO, $n = 3, 6$.



The setup for investigation of oxidative dissolution of nickel in the benzyl halide–solvent–oxygen system by spectrophotometric method. (*1*) quartz cuvette (*l* = 2 cm), (*2*) dropping funne, (*3*) Schlenk tube, (*4*) input for selection of the reaction mixture, (*5*) a cover of polyamide-6 with a rubber sealing gasket, and (*6*) micromixer.

After oxidative dissolution of nickel in the benzyl chloride–DMSO–oxygen system, $[Ni(DMSO)_6][NiCl_4]$ and $[Ni(DMSO)_6]Cl_2$ were isolated from the reaction mixture in the ratio depending on the concentration of DMSO and the temperature.

Similar results were obtained using nickel nanopowder of Hongwu International Group Ltd (China) production or of the oxygen-stabilized nanoparticles (oxygen content <0.15 %) from “Advanced Powder Technologies” (Russia).

Dissolution of nickel nanopowders stabilized with carbon (carbon content 0.08%) or oxygen (oxygen content > 1 %), in the benzyl halide – dipolar aprotic solvent – oxygen systems proceeded with substantial inductive period, owing to the presence of dense oxide or carbide film at the nanoparticle surface. However, the ratio of the products was always the same. Except for fine-disperse nickel powder “PNE–1. Lux,” all the used nanopowders formed floating suspensions in the dipolar aprotic solvents, making the dosing procedure easy. Therefore, we used the nickel powder produced in argon atmosphere or stabilized with oxygen (oxygen content < 0.15 %) for the spectrophotometry studies.

The presence of 1,2-diphenylethane and trace amounts of 4,4'-ditolyl in the products suggested the radical reaction mechanism with the formation of benzyl radical as the intermediate, its recombination and isomerization occurring in the radical pair [3]. On top of that, benzaldehyde and benzyl alcohol were isolated, apparently, the products of benzyl radical oxidation with oxygen [4].

Benzyl radical was detected in the reaction mixture using a chemical radical trap – dicyclohexyldeuterophosphine (DCPD) [2, 4]. When performing the reaction in the presence of DCPD (molar ratio Ni : DCPD = 1 : 5), α-deuterotoluene and trace amounts of 1,2-diphenylethane were detected in the reaction mixture. Benzaldehyde, benzyl alcohol, benzoic acid, benzyl benzoate, and 4,4'-ditolyl were absent, indicating the reaction mechanism via the formation of benzyl radical [2, 4].

Oxidation of benzyl radical might occur both in solution and at the nickel surface. In order to identify the reactive site, we investigated the nickel–benzyl halogenide–dipolar aprotic solvent–oxygen system by means of spectrophotometry.

It is known that certain dipolar aprotic solvents form charge transfer complexes (CTC) with molecular oxygen [5]. It was found that for CTC between DMSO (DMF) and oxygen could be identified by the appearance of the absorption band at 256 (264) nm [6, 7].

The interactions in the nickel–benzyl halide–dipolar aprotic solvent–oxygen system were investigated using the setup depicted in the figure.

The setup was made on the basis of standard quartz cell placed in a cell holder of CF-26 spectrophotometer, allowing for unambiguous detection of appearance and disappearance of the absorption bands of CTCs between oxygen and dipolar aprotic solvent, as well as for performing the experiments in the semi-automated mode.

In the first series of the experiments, oxygen was passed through the solvent till the appearance of the absorption band characteristic of the CTC between DMSO (DMF) and oxygen [5–7]. Then, nickel nanopowder prepared in argon atmosphere or the oxygen-stabilized nanopowder (oxygen content <0.15 %) was added. The absorption bands instantly disappeared, likely due to fast adsorption of oxygen at the nickel surface. After addition of benzyl bromide to the reaction mixture and carrying out the reaction during 2 h, the reaction products were analyzed.

The chromato–mass spectrometry showed that in the both cases the products of the reaction were 1,2-diphenylethane (99.9 %) and trace amounts of 4,4'-ditolyl (<0.1 %). Similar results were obtained for benzyl chloride. Noteworthily, the same products were formed in the course of oxidative dissolution of nickel in the benzyl halide – dipolar aprotic solvent systems in the absence of oxygen [8]. However, the metal dissolution was much faster in the presence of small amounts of oxygen. The absence of the products of oxidation of benzaldehyde, benzyl alcohol as well as even trace amounts of benzoic acid and benzyl benzoate in the first series of the experiments, along with disappearance of the absorption band, suggested that oxygen was adsorbed at the nickel surface and practically did not pass to the solution; no oxidation with oxygen occurred at the metal surface.

Using the methods of secondary ionization mass spectrometry (SIMS), X-ray photoelectron spectroscopy (XPS), near-edge X-ray adsorption fine structure (NEXAFS), temperature programmed desorption (TPD), and low-energy electron diffraction (LEED) it has been shown that the first stages of oxygen interaction with different surfaces of pure nickel are reversible chemisorption and physical adsorption [9–11]. Reversible chemisorption of oxygen at nickel surface proceeds with predominant formation of Ni_n–O–O^- and Ni_nO_2. It has been found that either reversible chemisorption of oxygen or its partial desorption from the metal surface follow the physical adsorption of molecular O_2 on Ni(100) at temperatures above 80 K [10, 11].

The results obtained in this work and the data reported in [9–11] coincided well with the data of [4], the latter demonstrating that the intermediates of the reaction of oxidative dissolution of copper in the benzyl bromide – dimethylacetamide – oxygen system are Cu_n^+–O–O^- species capable of electron transfer to benzyl bromide.

The second series of the experiments was performed similarly, but the oxygen supply was continuous. In that case, addition of the fine-disperse nickel powder led to a short-term slight weakening of the corresponding absorption band. After recovery of the band intensity, benzyl halide was added, and the process was carried out during 2 h. Addition of benzyl halide led to disappearance of the CTC absorption band, being recovered only after complete dissolution of nickel or after supply of excess oxygen. Sampling and analysis of the reaction mixtures in the first and second experiments were performed under the same conditions.

In the second experiment, the continuous supply of oxygen in the system under investigation led to the formation of the oxidation products: benzaldehyde (64.5±1.5) mol % and benzyl alcohol (31.5±1.5) mol %. On top of that, 4 mol % of 1,2-diphenylethane and trace amounts of 4,4'-ditolyl, benzoic acid, and benzyl benzoate were found in the reaction mixture, the concentration of 1,2-diphenylethane being much lower than that in the first experiment. When excess oxygen was supplied, the amount of 1,2-diphenylethane was decreased to 0.1 mol %, and that of benzoic acid increased to 1 mol %. Similar results were obtained for benzyl chloride as the substrate. The determined ratio of the reaction products suggested that the investigated process proceeded mainly via the radical mechanism (formation of benzyl radical that was rapidly oxidized with oxygen in the solution), and no formation of CTC was observed till the reaction was complete.

Comparison of the results of those experiments led to a conclusion that the formation of the reaction products (benzaldehyde, benzyl alcohol, 1,2-diphenylethane, and traces of 4,4'-ditolyl, benzoic acid, and benzyl benzoate) proceeded mainly in the solution rather than at the nickel surface. The oxygen adsorbed on the nickel surface practically does not pass to the solution.

EXPERIMENTAL

The reaction products were analyzed using an Agilent (USA) chromato–mass spectrometer (mass detector 5975C, gas chromatograph 7890A) equipped with a capillary column (l = 30 m, d = 0.25 mm), diphenyl (5%) on polydimethylsiloxane was used as the stationary phase; column temperature was of 40–250°C; heating rate was of 30 deg/min; helium (flow rate 1 mL/min) was used as the carrier gas; injector temperature was of 250°C; detector temperature was of 280°C.

Elemental analysis of deuterated organic compounds was performed using a Carlo-Erba-1100 (Carlo Erba Instruments, Italy) gas chromatograph analyzer and a Tsvet-570 (Russia) gas chromatograph as described in [12].

The absorption bands of CTC between the solvent and oxygen were observed using a SF-26 spectrophotometer by recording the spectra over the range of 186 to 1100 nm.

The following nickel powders were used: nickel powder (fraction 0.050 mm) from “Ural electrochemical plant” “PNE–1. Lux” (nickel content 99.8405%); nickel nanopowder (average particle size 70 nm, surface area 6 m^2/g) stabilized with oxygen (oxygen content <0.15 % and >1 %) from “Advanced powder technologies Ltd.;” nickel nanopowder (average particle size 40 nm) stabilized with carbon (carbon content 0.08%) from Hongwu International Group Ltd (China); nickel nanopowder (average particle size 40 nm) prepared in argon atmosphere (oxygen and carbon absent) from Hongwu International Group Ltd (China).

Benzyl chloride (“analytical pure” grade) was dried with $CaCl_2$ and distilled under reduced pressure, bp 65–66°C (11 mmHg) {bp 66°C (11 mmHg). [13]}. The organic solvents were purified by conventional procedures [14]. All the solvents and reagents were degassed by repeated freeze-thawing under reduced pressure and stored in sealed ampoules.

Dehalogenation of benzyl halides with nickel in dipolar aprotic solvent in the presence of oxygen. 20 mL of dipolar aprotic solvent (DMF or DMSO) and 0.1 mol of benzyl halide were added to 0.02 mol of nickel powder. The reaction was carried out in the presence of dry air at 70°C. After dissolution of nickel and cooling the vessel to 20°C, the reaction mixture was treated with 20 mL of dry diethyl ether. The precipitated nickel complex compound was separated, and the ether solution was analyzed by means of chromato-mass spectrometry.

Hexakis(dimethylformamido)nickel(II) bromide $[Ni(DMF)_6]Br_2$. Yield 78 %. Found, %: C 32.92, H 6.48, Br 24.35, N 12.77, Ni 8.90, O 14.57. $C_{18}H_{42}Br_2N_6NiO_6$. Calculated, %: C 32.90, H 6.44, Br 24.32, N 12.79, Ni 8.93, O 14.62. IR spectrum, ν, cm^{-1}: 425 (Ni–O), 465 (Ni–O), 690 (OCN), 1030 (CH_3), 1070 (CH_3), 1120 (CH_3), 1160 (CH_3), 1255 (C–N), 1387 (CH_3), 1425 (CH_3), 1445 (CH_3), 1635 (C=O···Ni), 1650 (C=O···Ni) (KBr). Reference data: ν, cm^{-1}: 425 (Ni–O), 465 (Ni–O), 690 (OCN), 1030 (CH_3), 1070 (CH_3), 1120 (CH_3), 1160 (CH_3), 1255 (C–N), 1387 (CH_3), 1425 (CH_3), 1445 (CH_3), 1635 (C=O···Ni), 1650 (C=O···Ni) (KBr) [8].

Hexakis(dimethylsulfoxido)nickel(II) tetrachloronickelate(II) $[Ni(DMSO)_6][NiCl_4]$. Yield 70%, mp 122–124°C. Found, %: C 19.78; H 5.0; C1 19.40; S 26.28; Ni 16.73. $NiC_6H_{18}S_3O_3C_{l2}$. Calculated, %: C 19.70; H 4.95; C1 19.47; S 26.40; Ni 16.20. IR spectrum, ν, cm^{-1}: 425 (Ni–O), 940 (S=O···Ni) (KCl); 1000 (S=O···Ni), 1037 (S=O···Ni) (CH_3NO_2). Reference data: mp 122–124 °C [15], IR spectrum, ν, cm^{-1}: 425 (Ni–O) [15]; 940 (S=O···Ni) (KCl); 1000 (S=O···Ni), 1037 (S=O···Ni) (CH_3NO_2) [16].

Hexakis(dimethylsulfoxido)nickel(II) chloride $[Ni(DMSO)_6]Cl_2$. Yield 30%, mp 66–68°C. Found, %: C 24.06, H 6.05, Cl 11.87, Ni 9.78, O 16.08, S 32.16. $C_{12}H_{36}NiS_6O_6C_{l2}$. Calculated, %: C 24.09, H 6.06, Cl 11.85, Ni 9.81, O 16.04, S 32.15. Reference data: mp 66–68°C [15].

Hexakis(dimethylsulfoxido)nickel(II) bromide $[Ni(DMSO)_6]Br_2$. Yield 90 %, mp 83–85°C. Found, %: C 20.96, H 5.30, Br 23.23, Ni 8.57, O 13.98, S 27.96. $C_{12}H_{36}Br_2NiO_6S_6$. Calculated, %: C 20.97, H 5.28, Br 23.25, Ni 8.54, O 13.97, S 27.99. IR spectrum, ν, cm^{-1}: 444 (Ni–O), 380 (C–S–O), 347 (C–S–O), 315 (C-S-C), 306 (CH_3) (Vaseline oil); 957 (S=O···Ni) (KBr). Reference data: mp 83–85°C [15], IR spectrum, ν, cm^{-1}: 957 (S=O···Ni) (KBr) [16].

Dehalogenation of benzyl halide with nickel in dipolar aprotic solvent. *a*. Oxygen was passed for a short time through 1 mL of dipolar aprotic solvent, then 0.1 g of nickel powder (in the form of suspension in 1 mL of the corresponding solvent) and 0.5 mL of benzyl halogenide were successively added upon stirring. Reaction time 2 h.

b. Oxygen was continuously passed through 1 mL of dipolar aprotic solvent, and 0.1 g of nickel powder (in the form of the suspension in 1 mL of the corresponding solvent) and 0.5 mL of benzyl halogenide were successively added upon stirring. Reaction time 2 h.

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