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## Kinetics and Mechanism of Nickel Reaction with Benzyl Bromide in Dimethylformamide

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**Abstarct**—The reaction of nickel with benzyl bromide in DMF has been studied. The reaction intermediates were investigated by different methods and the kinetic and thermodynamic parameters were determined. The reaction of benzyl bromide with nickel was shown to occur on the metal surface by the Langmuir-Hinshelwood scheme, with the formation of benzyl radicals which are recombined and isomerized in solution to form 1,2-diphenylethane and trace amounts of 4.4'-dimethylbiphenyl.

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In the plastics industry, to prepare technically valuable products various additives are introduced into polymers. For example, halogenated nickel complex compounds are effective light stabilizers for various polymers [1].

Nickel complex compounds are obtained in onestep by the reaction of carbon tetrachloride with specimens of active nickel in dipolar aprotic solvents [2]. Now it is established that carbon tetrachloride is an ozone depleting compound and its industrial use is forbidden. Therefore, it became necessary to find a substitute for it in different chemical processes. In the present paper, the mechanism of the reaction of nickel with benzyl bromide was studied aiming at elaboration of the environmentally friendly technology for preparation of the nickel complex compounds with organic ligands without the use of carbon tetrachloride.

To study the products of the reaction, we have performed the reaction of nickel powder with benzyl bromide in dimethylformamide in an atmosphere of pure dry argon at 80°C at stirring. After complete dissolution of nickel, a complex compound hexakis(dimethylformamide)nickel(II) bromide [Ni(DMF)<sub>6</sub>]Br<sub>2</sub>, 1,2-diphenylethane, and less than 0.1% of 4,4'-dimethybiphenyl were isolated from the reaction mixture:



Using the method of ion chromatography we found that only nickel(II) cations were present in solution, while nickel(I) and nickel(III) were not formed in the reaction under investigation. Analysis of the reaction mixtures by the use of chromatomass spectrometry has shown that 1,2-diphenylethane and trace amounts of 4,4'-dimethylbiphenyl are the only organic products of the reaction. The molar ratio 1,2-diphenylethane: dissolved nickel of 1:1 suggests that the reaction products are formed not due to catalytic coupling of benzyl bromide but by the radical mechanism, via the formation of a radical pair [3]:



The absence of toluene in the reaction products allows a conclusion that in the reaction of benzyl bromide with nickel in dimethylformamide the benzyl radical does not abstract hydrogen atom from the solvent.

One of methods which allows to check the suggestion of the radical mechanism of a reaction is investigation of the stereochemistry of the process. The presence of the reaction center in the methylene fragment of the benzyl bromide molecule makes it possible to generate an asymmetric center in this place. (+)-R-1-Bromo-1-phenylethane was synthesized by the known procedure [4] from the phosphoryl tribromide and (-)-S-1-phenylethanol in the presence of pyridine in 74% yield and 76% optical purity. In turn, (-)-S-1-phenylethanol was prepared by asymmetric reduction of acetophenone [5, 6]. The reaction of (+)-R-1-bromo-1-phenylethane with nickel in dimethylformamide in an atmosphere of pure dry argon at 80°C proceeded with the loss of optical activity:



All organic products were isolated by preparative liquid chromatography and identified by different methods. The ratio of RS,RS-2,3-diphenylbutane and RR,RR-2,3-diphenylbutane was 1.04:1, that in conjunction with the detection of equal amounts of styrene and ethylbenzene is typical for reactions with optically active 1-phenylethyl radicals [7]. Recombination and disproportionation of 1-phenylethyl radicals occurs in solution in the cage of the solvent [8].

Identification of radical intermediates was performed at 77 K in films of cocondensates of nickel with benzyl bromide (the ratio of nickel:benzyl bromide 1:50) according to the protocol described in [9]. Nickel was evaporated from a corundum crucible at 1650–1700 K,  $10^{-4}$  torr). Nickel and benzyl bromide were cocondensed in the regime of molecular beams onto a quartz finger cooled to 77 K. ESR spectrum of the cocondensate of nickel with benzyl bromide at 77 K represents a triplet of quartets with full width  $\sim$ 55 G and g-factor of  $\sim$ 2.002, its parameters are given in Table 1. Comparison of the obtained spectra of cocondensates with the literature data [9, 12, 13] on the ESR spectrum of the benzyl radical allows to assign these spectra to the ESR spectrum of the benzyl radical in solid matrix; no ion-radical pairs were detected.

When the cocondensates of nickel with benzyl bromide were warmed to 120 K only the ESR signals of the PhCH<sub>2</sub> radicals were observed, and a gradual decrease in the intensity of the triplet of quartets occurred with growing temperature. At 130-150 K further decrease in the intensity of the ESR signals and substantial deterioration of the resolution of ESR spectra caused apparently by overlapping of signals from radical pairs of the PhCH<sub>2</sub><sup>--</sup>CH<sub>2</sub>Ph type.

These data allow a conclusion that nickel atoms react with benzyl bromide with formation of the benzyl radical by a single electron transfer mechanism with abstraction of the halogen atom:

$$\bigcirc$$
  $CH_2$   $Br$  +  $Ni$   $\checkmark$   $CH_2$  +  $\dot{N}iBr$ 

In the cocondensate, the radicals are in the cage of solid benzyl bromide (molar ratio  $PhCH_2Br : Ni = 50:1$ ), that is why the radical Ni+Br at 77 K does not disproportionate but rather reacts with the second molecule of benzyl bromide by abstraction of the halogen atom:

$$\bigcirc$$
 -CH<sub>2</sub>-Br +  $\dot{N}iBr$  -  $\dot{C}H_2$  + NiBr<sub>2</sub>

For detection of radical intermediates at 298 K we used the spin trap method. As a spin trap, we used the stable radical 2,2,6,6-tetramethylpiperidine-1-oxyl (TMPO) [14,15]. It was added into the reaction mixture (the ratio nickel:benzyl bromide:dimethyl-

**Table 1.** Parameters of ESR spectrum (a/G) of the benzyl radical in solid matrices

g-Factor	$a_{\rm CH2}^{\rm H}{ m G}$	$a_o^{\mathrm{H}}, \mathrm{G}$	$a_m^{\rm H}, {\rm G}$	$a_p^{\mathrm{H}}, \mathrm{G}$	References
$2.002 \pm 0.001$	16.5±0.5	5.5±0.5	_	5.5±0.5	а
$2.002 \pm 0.001$	16.4±0.5	5.5±0.5	_	5.5±0.5	[9]
$2.002 \pm 0.001$	16.4±0.5	5.5±0.5	_	5.5±0.5	[12]
2.0026	16.34	5.13	1.77	6.17	[13]

<sup>a</sup> From the present work.

formamide was 1:5:8) placed in an ampoule in the spectrometer resonator. The ESR spectrum of the reaction mixture was assigned to the spectrum of the nitroxyl radical by comparing to the literature data [16]. During the reactions, the ESR signals of the introduced stable radical (TMPO) disappear. Further treatment of the reaction mixtures with hydrogen peroxide in an alkaline medium does not lead to restoration of the ESR signals, which is indicative of the presence of radical intermediates in solution [14, 15].

Investigation of the process by the ESR method in the presence of TMPO allowed us to establish the nature of the reaction under consideration but did not allow to determine the nature of the radical intermediates. The reaction of the benzyl radical with dicyclohexyldeuterophosphine (Cy<sub>2</sub>PD) is known to proceed by the following scheme [12]:



Therefore, we have carried out the reaction of nickel with benzyl bromide in DMF in the presence of  $Cy_2PD$ :

$$\underbrace{Cy_2PD}_{CH_2 \longrightarrow Br} + Ni + DMF$$

$$\underbrace{Cy_2PD}_{Ni(DMF)_6}Br_2 + \underbrace{O}_{CH_2D}CH_2D$$

For the Ni:Cy<sub>2</sub>PD ratio of 1:5, instead of the expected 1,2-diphenylethane and 4,4'-dimethylbiphenyl, the equivalent amount of  $\alpha$ -deuterotoluene was isolated from the reaction mixtures. This is indicative of the fact that benzyl radicals move from the metal surface into the solution, where their recombination and isomerization in the radical pair occur.

To determine the routes of formation of 1,2diphenylethane [17] we have studied the reaction of nickel with benzyl bromide in the presence of DMF at low temperatures by the use of high-vacuum unit for preparation of atomic metals and cryosynthesis [18]. Cocondensation of nickel with benzyl bromide and DMF (molar ratio 1:10:0-10, respectively) was carried out in the regime of molecular beams onto the surface of the reactor cooled to 77 K. First on the surface of the reactor pink films of cocondensates were formed, which quickly turned colorless. Pink color of the samples suggests the presence of  $\pi$ -complexes of nickel with benzyl bromide [19]. Low melting point of DCl allowed to perform acidolysis of the reaction mixture both at 160 and at 298 K (Table 2):

 $CH_2 - NiBr + DCl$ 



As can be seen from Table 2, the organonickel compounds are more stable at low temperatures. Increase of the DMF content results in a negligible stabilization of benzylnickelbromide. Analysis of the gas phase showed that in no case hydrogen or its deuterated analogs were formed in the course of acidolysis of the reaction mixtures, which is indicative of the absence of benzylnickelhydride intermediates in the reaction mixture. Therefore, the main amount of 1,2-diphenylethane is formed by recombination of benzyl radicals in solution rather than decomposition of organonickel compounds.

The kinetic parameters of the reaction were determined by a resistometric method [12, 20, 21] suitable for investigation of processes occurring on a metal surface. The use of an inert solvent (benzene,  $DN_{sbC15} = 0.42 \text{ kJ mol}^{-1}$  [22]) allowed to obtain the dependences of the rate of dissolution of the metal both on concentration of benzyl bromide and of dipolar aprotic solvent. The kinetics was studied in a wide range of concentrations (0–7 M) at 313–353 K.

The rate dependences on the initial concentrations of the components (see figure) are smooth curves with maxima. The curves start from the origin, that is, the

**Table 2.** Reaction products found in the reaction mixtures after their treatment with DCl at 160 and 298 K

N. D. CH D. DME	τV	Yield, $\% \pm 1\%$		
NI:PhCH <sub>2</sub> Br:DMF	1, К	PhCH <sub>2</sub> CH <sub>2</sub> Ph <sup>a</sup>	$PhCH_2D^b$	
1:10:0	160	96	4	
	298	99	1	
1:10:5	160	92	8	
	298	98	2	
1:10:10	160	90	10	
	298	98	2	

 $^{a} < 0.1\%$  of 4,4'-dimethylbiphenyl.  $^{b}$  2% of toluene.

rate of the nickel reaction with benzyl bromide in the absence of DMF (in benzene) is lower than the threshold of the sensitivity of the instrument. Such a shape of the curves is characteristic of the reactions proceeding on the metal surface by the Langmuir-Hinshelwood mechanism provided that the components are adsorbed on the same active centers of the metal surface [23].

$$(\bigcirc -CH_2 - Br + S \xrightarrow{K_1} (\bigcirc -CH_2 - Br) S, (1)$$

$$DMF + S \xrightarrow{K_2} (DMF)S, (2)$$

$$(\bigcirc -CH_2 - Br) S + (DME)SH.$$

 $W \times 10^5$ , g cm<sup>-2</sup> min<sup>-1</sup>

30



Reaction rate (*w*) of the reaction between nicket and benzyl bromide in DMF as a function of initial concentrations of the components at 353 K in the presence of an inert solvent (benzene): (1) c(DMF) = 0.5 M;  $c(PhCH_2Br)$  varied from 0 to 7.0 M and (2)  $C(PhCH_2Br) =$ 0.5 M; c(DMF) varied from 0 to 7.0 M.

where S are active surface centers on which benzyl bromide and DMF are adsorbed,  $K_1$  and  $K_2$  are the adsorption constants for adsorption of benzyl bromide and DMF onto the metal surface,  $k_3$  is the rate constant of the rate-determining step.

The equation for the reaction rate (W) includes the degrees of covering of the surface obtained from the Langmuir isotherm for adsorption of each component and has the following form:

$$W = k \frac{K_1 K_2 [\text{PhCH}_2 \text{Br}] [\text{DMF}]}{(1 + K_1 [\text{PhCH}_2 \text{Br}] + K_2 [\text{DMF}])^2}, \qquad (4)$$

where  $k = KN^2$ , N is the number of active centers of the metal surface on which benzyl bromide and DMF are adsorbed.

To determine the rate constants k and equilibrium constants for adsorption of benzyl bromide and DMF on the metal surface ( $K_1$  and  $K_2$ ) the algorithm was established involving linearization of the experimental dependencies in the coordinates ( $CW^{-1}$ )<sup>0.5</sup> vs. f(C). Investigation of the reaction kinetics at various temperatures (313–353 K) provided a possibility to determine the energy of activation  $E_a$  of the chemical process as well as the enthalpies and entropies of adsorption of benzyl bromide and DMF on the nickel surface. The Langmuir–Hinshelwood scheme for the process under consideration suggests that the rate-determining step is the interaction of the surface of the oxidized metal, that is, a chemical reaction on the surface [20, 23].

As can be seen from Table 3, both benzyl bromide and dimethylformamide have large negative values of

 Table 3. Kinetic and thermodynamic parameters of the nickel reaction with benzyl bromide in DMF<sup>a</sup>

Т, К	$k \times 10^4$ , g cm <sup>-1</sup> min <sup>-1 b</sup>	$K_1$ , $1 \text{ mol}^{-1 \text{ c}}$	$K_2$ , 1 mol <sup>-1 d</sup>
313	2.23±0.01	3.12±0.03	3.08±0.01
323	4.39±0.01	2.39±0.01	2.44±0.01
333	8.21±0.02	1.93±0.01	1.99±0.01
338	10.7±0.1	1.72±0.01	$1.77 \pm 0.01$
343	15.8±0.1	$1.51 \pm 0.01$	$1.64 \pm 0.01$
353	27.7±0.2	1.21±0.01	1.33±0.01

<sup>a</sup>  $E_a$  57.8±2.5;  $\Delta H_{\text{RHal}}^0$  -21.5±1.0;  $\Delta H_{\text{DMF}}^0$  -19.1±0.7 kJ·mol<sup>-1</sup>; at 298 K  $\Delta S_{\text{RHal}}^0$  -59.2±3.4; and  $\Delta S_{\text{DMF}}^0$  -51.7±2.3 J mol<sup>-1</sup> K<sup>-1</sup>. Selected correlation coefficient for the dependence ln Y = f(1/T). <sup>b</sup> R = 0.998 (Y = k). <sup>c</sup>  $R = 0.998 (Y = K_1)$ . <sup>d</sup>  $R = 0.999 (Y = K_2)$ . enthalpy and entropy of adsorption. This can be due to a large heat evolution during the adsorption or by interaction between the adsorbate and the metal leading to deformation or dissociation of the adsorbed molecules. Large negative values of the entropy of adsorption of benzyl bromide and DMF suggest that they do not dissociate on the nickel surface during adsorption.

The detailed analysis of the obtained results shows that the first steps of the nickel reaction with benzyl bromide in DMF are nondissociative adsorption of the reagent and the solvent on the same active centers of the nickel metal surface. Apparently, benzyl bromide is adsorbed so that the benzene ring is oriented parallel to the surface [24–27]. Only after that, benzyl bromide reacts with nickel with elimination of bromine and formation of benzyl radical.

The second molecule of benzyl bromide attacks  $Ni_nBrDMF$  (part of the nickel surface) by the Langmuir–Hinshelwood or Eley–Rideal mechanism to form the second benzyl radical and a solvated molecule of  $NiBr_2$  (Scheme 1).

Benzyl radical reacts with Ni<sub>n</sub>Br DMF to form organonickel compounds.

Organonickel compounds are decomposed by the known scheme [17]. (Scheme 2)

Benzyl radicals in solution recombine with the formation of 1,2-diphenylethane and isomerize to form the traces of 4,4'-dimethylbiphenyl.

## **EXPERIMENTAL**

Analysis of the reaction products and quantitative determination of admixtures in the reagents was performed by the GC method on a Tsvet-800 chromatograph, the details were published earlier [9]. Analysis by the method of ion chromatography was done on a Tsvet-3006 chromatograph with electro-conductivity detector using a "Diakat-3" (Elsiko, Moscow, l 150 mm, d 3 mm) or a "Hiks-1" column (Institute of Chemistry, Estonian Academy of Sciences, particles of 15  $\mu$ m size) by the earlier described procedure [9].

<sup>1</sup>H NMR spectra were taken on a Jeol LTD FX-90Q spectrometer for 25–30% solutions in deuterochloroform with hexamethyldisiloxane (HMDS) as an internal reference. The accuracy of measurement of chemical shifts was  $\pm 0.01$  ppm ( $\delta$  scale). IR spectra in



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the range of 400–4000 cm<sup>-1</sup> were taken on a IMPACT 400d (NICOLET) spectrophotometer in KBr.

Organic products of the reaction were isolated by preparative liquid chromatography on a Tsvet-304 chromatograph equipped with UV detector and steel column (l 2.5 m, d 4 mm); stationary phase Silasorb 600 (Chemapol, Czechia, size of particles 15–25 µm), eluent hexane–diethyl ether 5:1.

ESR spectra of the reaction mixtures were taken on a Radiopan SE/X-2543 spectrometer (9400 MHz) at 77 K in films of cocondensate of nickel with 50-100-fold excess of benzyl bromide by the procedure described in [9] and at 293 K by the procedure from [14, 15]. 2,2,6,6-Tetramethylpiperidyl-1-oxyl was used as a stable radical [14].

Specific rotation of the polarization plane was measured on an automatic polarimeter VNIIEKI prodmash A-1 EPO ( $\sigma$  0.01) in cells of different width.

Chromatomass analysis of the reaction products was performed on a Hewlett Packard instrument (USA) (mass detector HP-5972, chromatograph HP-5890) by the earlier described procedure [12, 23]. Quantitative analysis of admixtures in nickel was done after dissolution of the metal specimens in HNO<sub>3</sub> and neutralization of the obtained solution with 25% aqueous ammonia by atomic absorption spectrometry method on a GBC-908 AA instrument (Australia).

Nickel powder of GOST 9722-79, with nickel content of 99.8405%±2×10<sup>-4</sup>%, trademark PNE-1 "Lux" (FSUE Ural electrochemical complex, RF) was used. Nickel wire (NI005106 Goodfellow Corporation, USA, Ni 99.9804%±2×10<sup>-4</sup>%) of 0.025 mm diameter and 10 mm length was placed for 5-10 s in 20% sulfuric acid solution, washed with water, acetone and DMF (all operations were carried out in an inert gas atmosphere). All organic compounds are commercially available. Benzyl bromide (Aldrich) was dried over calcined CaCl<sub>2</sub> and distilled, bp 83.5–84°C (32 mm Hg),  $n_{\rm D}^{20}$  1.4380. {bp 83.5–84°C (32 mm Hg),  $n_{\rm D}^{20}$  1.4380 [28]}. DMF was purified by double slow vacuum distillation over large amount of P<sub>2</sub>O<sub>5</sub> [29], then refluxed for 2 h over calcium hydride and distilled in a vacuum under nitrogen. Acetone, diethyl ether, and other solvents were purified by conventional procedures [30]. Benzyl bromide and all solvents were degassed by repeated freezing and thawing under reduced pressure and stored in ampoules in the absence of air.

(+)-*R*-1-Bromo-1-phenylethane was obtained by the method described in [4] by the reaction of (–)-*S*-1-phenylethanol with phosphoryl tribromide and pyridine in pentane, and degassed by repeated freezing and thawing under reduced pressure and stored in ampoules in the absence of air. Yield 74%. Physico-chemical properties of (+)-*R*-1-bromo-1-phenylethane correspond to those in the literature [4]. (–)-*S*-1-Phenylethanol was synthesized by the procedure described in [5, 6] by the reaction of acetophenone with (+)-*S*-1-(methylamino)-1-phenylethane-*N*-aluminum hydride in diethyl ether at  $-71^{\circ}$ C. Yield 55%. Physicochemical properties of (–)-*S*-1-bromo-1-phenylethanol correspond to those in the literature [5, 6].

Nickel complex compounds were prepared by the following procedures. To 0.02 M of nickel powder 20 ml of DMF and 0.1 mol of benzyl bromide was added at 70°C in a dry argon atmosphere. After dissolution of nickel, the reaction mixture was treated with 20 ml of dry diethyl ether. The precipitated crystals of the nickel(II) complex compound were separated, washed with hexane and dried in vacuum. [Ni(DMF)<sub>6</sub>]Br<sub>2</sub>. Yield 82 %. Found (%): C 32.92, H 6.48, Br 24.35, N 12.77, Ni 8.90, O 14.57. C<sub>18</sub>H<sub>42</sub>. Br<sub>2</sub>N<sub>6</sub>NiO<sub>6</sub>. Calcd (%): C 32.90, H 6.44, Br 24.32, N 12.79, Ni 8.93, O 14.62. IR spectrum, v, cm<sup>-1</sup>: 425 (Ni-O), 465 (Ni-O), 690 (OCN), 1030 (CH<sub>3</sub>), 1070 (CH<sub>3</sub>), 1120 (CH<sub>3</sub>), 1160 (CH<sub>3</sub>), 1255 (C-N), 1387 (CH<sub>3</sub>), 1425 (CH<sub>3</sub>), 1445 (CH<sub>3</sub>), 1635 (C=O<sup>...</sup>Ni), 1650 (C=O...Ni) (KBr).

In ether solution the unreacted benzyl bromide and DMF as well as 1,2-diphenylethane and 4,4'-dimethylbiphenyl were detected by chromatomass spectrometry.

The reaction in the presence of a radical trap was investigated in a similar way as the preparation of nickel complex compounds. Cy<sub>2</sub>PD was used as a radical trap. After sedimentation of the precipitate, in ether solution the unreacted DMF and benzyl bromide as well as  $\alpha$ -deuterotoluene were detected by chromatomass spectrometry.

The stereochemistry of the reaction was studied in a similar way as the preparation of nickel complex compounds. (+)-R-1-Bromo-1-phenylethane was taken as an organyl halide. After sedimentation of the precipitate, in ether solution the unreacted DMF and (+)-R-1-bromo-1-phenylethane were detected by chromatomass spectrometry, and also RR-,SS-2,3-diphenylbutane, RS-,RS-2,3-diphenylbutane, styrene and ethylbenzene were isolated and identified. The

performed by resistometric method [12, 20, 21] using the known procedure [21] in the atmosphere of dry, oxygen free argon. The rate of the stirrer rotation was 2500 rpm. Starting from 2000 rpm, the rate of dissolution of nickel in the studied media did not depend on the rate of stirring, that was indicative of kinetic regime of the process.

yields of the reaction products are presented in the

scheme in the Results and Discussion section, physico-

chemical properties of the isolated compounds

benzyl bromide-DMF was performed in a highvacuum unit for generation of atomic metals and

cryosynthesis [18]. 1 g of compact metal produced by

vacuum melting (1650-1700 K, 0.1 torr) of nickel

metal, evaporated from a corundum crucible (1650-

1700 K,  $10^{-4}$  torr) and in the regime of molecular

beams cocondensed with the system benzyl bromide– DMF in the molar ratio 1:10:(0-10) on the surface of

the reactor cooled to 77 K by liquid nitrogen. The rate of nickel evaporation was 0.2 mmol min<sup>-1</sup>, the duration

of cocondensation 2-4 h. The specimens first turned

tained cocondensates were heated to 160 K, kept at this

temperature for 20 min, then cooled again to 77 K. On

the surface of the prepared films gaseous DCl (50 g)

was condensed. Upon heating above 160 K the

cocondensate melted and turned colorless with vellow

cocondensation was completed, the reactor was

charged with pure dry argon and allowed to warm; the

cocondensate melted at 269 K and turned light-yellow

with solid yellow inclusions. The specimen was

filtered, to the melt of cocondensate 0.1N solution of

DCl in D<sub>2</sub>O was added. From the obtained solution a

precipitate sedimented, which was separated and

cocondensate, along with DMF and benzyl bromide,

1,2-diphenylethane, traces of 4,4'-dimethylbiphenyl,

and small amounts of  $\alpha$ -deuterotoluene were detected

by the method of chromatomass spectrometry. The

After separation of the precipitate, in the melt of the

analyzed by the method of ion chromatography.

vields of the products are given in Table 2.

Acidolysis of cocondensates at 298 K. When

Acidolysis of cocondensates at 160 K. The ob-

pink, then became colorless.

inclusions.

The reaction of atomic nickel with the system

correspond to those in the literature [28, 31, 32].

As an inert solvent for determination of kinetic characteristics of the nickel reaction with benzyl bromide in the presence of DMF benzene was chosen [22].

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