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Kinetics and mechanism of the reaction of benzyl halides with zinc in dimethylformamide

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ABSTRACT: The reaction of metal zinc with various benzyl halides in dimethylformamide has been studied. The low-temperature ESR-spectroscopy is used to show that reaction of zinc with benzyl bromide and benzyl iodide occurs to form benzyl radicals. Benzyl chloride reacts with zinc at 77 K to form benzyl radicals and ion-radical pairs $RX^{\overline{\cdot}} - Zn^{\overset{+}{\cdot}}$. Nevertheless these pairs disappear at temperatures higher than 110 K. The investigation of the reaction stereochemistry and the use of a radical trap provide evidence in favor of a radical mechanism. The optical activity has been proved in the course of the formation of organozinc halide from (+)-R-1-halogen-1-phenylethane at low temperature. The kinetic features of the reaction have been studied. Benzyl iodide reacts with zinc at transport-controlled rate. The reaction of zinc with benzyl chloride and benzyl bromide in DMF occurs according to Langmuir–Hinshelwood scheme, the adsorption of reagents taking place on similar active centers of metal. The kinetic and thermodynamic parameters of the reaction have been clarified. The comparison of kinetic parameters with those reported in literature evidences that the limiting step of reaction is halogen atom transfer (inner sphere electron transfer). Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: zinc; benzyl halides; dimethylformamide; benzylzinc halides; mechanism; ESR spectra; kinetics; stereochemistry; halogen atom transfer; inner-sphere electron transfer; benzyl radicals; ion-radical pairs; Langmuir–Hinshelwood scheme; adsorption

INTRODUCTION

Organozinc halides have been proved to be preparatively useful for a number of reactions.[1,2] However, the mechanism of their formation is uncertain and the kinetic and thermodynamic parameters are poorly investigated.[3] The experimental conditions normally used in carrying out the reaction reflect the accumulated experience of synthetic chemists.[1,2] The lack of information prevents wide application of benzyl zinc halides for industrial purposes. In this paper the mechanism of benzyl halide reaction with zinc in dimethylformamide (DMF) has been investigated. The kinetics of this reaction have been studied in detail.

EXPERIMENTAL

Equipment and analytical measurements

^{1}H-NMR spectra were recorded on a Jeol LTD FX-90 Q spectrometer using 25–30% solutions in $CDCl_3$. Chemical shifts are given in ppm relative to tetramethylsilane as internal standard. The accuracy of chemical shifts was ±0.01 ppm. Elemental analyses were carried out on 'Carlo Erba 1100' instrument according to standard procedure.[4] The ESR spectra were recorded at 77 K on a Radiopan radiospectrometer in films of zinc co-condensates with benzyl halides (1:50) according to literature[5,6] at frequency of 9 GHz without saturation and amplitude broadening. Zinc vapor was prepared by evaporating the purified metal from corundum crucible at 570–600 K 10^{-5} mm Hg. The rate of evaporation of Zn was 0.2 mmol min^{-1}. Benzyl halides were evaporated at 273–308 K. The IR spectra were measured on an IMPACT 400 d (NICOLET) and Perkin–Elmer 325 spectrophotometers; the samples were prepared in KBr and in suspension in mineral (vaseline) oil. Specific polarized light plane rotation was measured on an A-1 EPO automatic polarimeter ($\delta = 0.01°$).

The purity of initial substances was monitored and the quantitative analysis of organic reaction products was carried out using gas chromatography (GC). The conditions of GC analysis were described previously.[7] The reaction products were isolated by preparative liquid chromatography (LC) on a Tsvet-304 chromatograph equipped with a UV detector ($\lambda = 254$ nm) using steel column ($l = 250$ mm, $d = 4$ mm). Silasorb 600 (Chemapol, Czech Republic, particle sizes 15–25 μm)

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was used as the sorbent; a 5:1 hexane–diethyl ether mixture was used as the eluent. The reaction products in gaseous phase were analyzed by GC with Tsvet-800 instrument equipped with a thermal conductivity detector and a steel column ($l = 2$ m, $d = 3$ mm), packed with molecular sieves 4A (0.25 mm fraction). The column temperature was 50 °C; argon was used as the carrier gas (the flow rate was 100 mL min^{-1}).

Organic reaction products were analyzed on a Hewlett–Packard GC MS instrument (HP 5972 mass-selective detector, HP 5890 chromatograph) using a capillary column ($l = 30$ m, $d = 0.25$ mm) with a diphenyl (5%) stationary phase supported on polydimethylsiloxane. The column temperature was 40–250 °C; the heating rate was 30°/min. Helium was a carrier gas (the carrier-gas flow rate was 1 mL min^{-1}). The injector temperature was 250 °C, and the detector temperature was 280 °C.

Inorganic reaction products (Zn(I) and Zn(II) cations) were determined by ion chromatography on a Tsvet-3006 chromatograph by using Diacat-3 columns (Elsiko, Moscow; $l = 150$ mm, $d = 3$ mm). An aqueous 4 mM ethylenediamine, 5 mM citric acid, and 5 mM tartaric acid solution was used as an eluent. The rate of elution was 15 mL min^{-1}. The sample volume was 100 μL (after 1:1000 dilution with water). The anions were analyzed on a steel column ($l = 2$ m, $d = 4$ mm). Khiks-1 (Institute of Chemistry of the Academy of Sciences of Estonia, particle size 15 μm) was used as the sorbent. A 0.03 M Na_2CO_3 solution in water was used as the eluent (flow rate was 2 mL min^{-1}). The volume of sample was 10 μL. Zinc sample purities were verified by atomic absorption spectrometry on a GBC-908 AA (Australia) equipment according to standard procedure.

Reagents

Zinc powder (Aldrich Chemicals Co Ltd. of >99.998% purity, 100 mesh) was commercially obtained. In order to investigate low temperature reaction of benzyl halides with atomic zinc, the metal was purified by a sevenfold sublimation *in vacuo* (10^{-3} mm Hg) at 920–930 K.

A zinc wire (Goodfellow Corporation, ZN005090 zinc, $d = 0.05$ mm, Zn content of 99.0% and ZN005115 zinc, $d = 0.25$ mm, Zn content of 99.99%) was exposed to concentrated nitric acid for 5–10 sec, and washed with water, acetone, and then DMF. The entire operation was carried out in oxygen-free argon.

All organic compounds were commercially obtained. The purity of commercial samples (Aldrich Chemicals Co. Ltd.) of benzyl chloride and benzyl bromide was checked by GC compounds which contained toluene or were less than 99% pure were purified by low-temperature fractional recrystallization or by fractional distillation.

Benzyl iodide was prepared according to a known procedure,[8] the yield was 90%. B.p. 61–62°/3 mm Hg (lit[8] b.p. 60–62 °C/3 mm Hg). ^{1}H NMR δ (ppm): 4.19 (s, 2H, CH_2), 7.03 (m, 5H, Ph).

Synthesis of (+)-R-1-chloro-1-phenylethane was carried out by interaction of (−)-S-1-phenylethanol with $POCl_3$ in the presence of pyridine in pentane.[9] Yield 76%. B.p. = 80–81 °C/17 mm Hg, α_D^{25} + 94.1° ($l = 1$). Lit. data: b.p. = 78–82 °C/17 mm Hg, α_D^{25} + 125.4° ($l = 1$, 100%).[9] ^{1}H NMR ($CDCl_3$):1.68 (d, 3H, CH_3), 4.86 (dd, 1H, CH), 7.14 (m, 5H, Ph).

Synthesis of (+)-R-1-bromo-phenylethane was carried out by interaction of (−)-S-1-phenylethanol with $POBr_3$ in the presence of pyridine in pentane.[10] Yield 74%. B.p. = 86–87 °C/11 mm Hg, $[\alpha]_D^{25}$ + 73.3° ($l = 1$) (From Ref. 10, b.p. = 86–87 °C/11 mm Hg, $[\alpha]_D^{25}$ + 96.3° ($l = 1$, 100%)). ^{1}H NMR ($CDCl_3$): 1.68 (d, 3H, CH_3), 4.86 (dd, 1H,CH), 7.14 (m, 5H, Ph).

Synthesis of (−)-S-1-phenylethanol was carried out as described in literature.[11,12] Yield 55%. B.p. = 94–95 °C/14 mm Hg, $[\alpha]_D^{25}$ − 37.65° ($l = 1$). Lit. data: b.p. = 94–95 °C/14 mm Hg, $[\alpha]_D^{25}$ − 44.2° ($l = 1$).[12] ^{1}H NMR ($CDCl_3$):1.21 (d, 3H, CH_3), 3.78 (q, 1H,CH), 7.06 (m, 5H, Ph).

Synthesis of gaseous DCl was carried out by interaction of sulfuric acid-d_2 (Aldrich Chemicals Co. Ltd., 98%) with NaCl in the presence of DCl (37% solution in D_2O, Aldrich Chemicals Co. Ltd.).

All solvents were purified according to standard procedures.[13] All organic compounds were freed from dissolved gases by repeatedly freezing and thawing at reduced pressure and stored in ampoules in the absence of air.

Reaction of benzyl halides with zinc, general procedure

A solution of 21.5 mmol $PhCH_2Hal$ (Hal = Br, I) in 11 mL DMF was slowly added (1/each 5 sec) to 1.7 g (26 mmol) of zinc powder at 0 °C, which had been activated according to procedure.[14] After 2 h of stirring at 5 °C the mixture was filtered. The filtrate was treated with 50 mL benzene. Precipitated white crystals were filtered off, washed by hexane and then evacuated. The reaction of zinc with $PhCH_2Cl$ in DMF was carried out by a similar procedure, except that the reaction mixture was stirred at 40 °C for 12 h.

$[Zn(DMF)_2Cl_2]$. Yield 48%, m.p. 117–118 °C (lit[15] m.p. = 118 °C). Analysis: $C_6H_{14}N_2ZnCl_2O_2$ calculated: C 25.51, H 5.00, Cl 25.10, N 9.92, O 11.33, Zn 23.15%. Found: C 25.53, H 5.02, Cl 25.07, N 9.98, O 11.29, Zn 23.11%. IR (KBr), $\nu = 1670$ (C=O), 1510 (C—N), 1430 (CH_3), 1255 (C—N), 1122 (C—N), 695 (OCN) cm^{-1}. IR (mineral oil), $\nu = 384$ (Zn—O), 335 (Zn—Cl), 299 (Zn—Cl) cm^{-1}.

$[Zn(DMF)_2Br_2]$. Yield 47%, m.p. 119–120 °C (lit[15] m.p. = 120 °C). Analysis: $C_6H_{14}N_2ZnBr_2O_2$ calculated: C 19.41, H 3.80, Br 43.03, N 7.54, O 8.62, Zn 17.60%. Found: C 19.43, H 3.77, Br 43.05, N 7.51, O 8.60, Zn 17.64%. IR (KBr), $\nu = 1670$ (C=O), 1500 (C—N), 1430 (CH_3), 1255

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(C—N), 1123 (C—N), 698 (OCN) cm^{-1}. IR (mineral oil), $\nu = 384$ (Zn—O), 258 (Zn—Br), 299 (Zn—Br) cm^{-1}.

The residue was poured into a 20% solution of HCl. Organic products of reaction were extracted with benzene (50 mL). Toluene, 1,2-diphenylethane and 4,4′-dimethylbiphenyl were found as products and benzyl halides and DMF were found as remaining starting materials. The yields of resulting compounds are recorded in Table 1.

Toluene. b.p. = 109–110 °C, $n_D^{20} = 1.4969$. (lit[13] m.p. = 110 °C, $n_D^{20} = 1.4969$). MS (EI, 70 eV): calculated *m/z* = 92.06 (M), found *m/z* = 92 $[M]^+$ (71.8), 91 $[M—H]^+$ (100), 90 $[M—2H]^+$ (5.1), 65 $[M—C_2H_3]^+$ (12.8), 63 $[M—C_2H_4]^+$ (10.3).

1,2-Diphenylethane. m.p. = 51–52 °C (lit[16] m.p. = 51–52 °C). ^{1}H NMR ($CDCl_3$): $\delta = 2.82$ (s, 4H, —CH_2—), 7.02 (m, 10H, -Ph.) ppm. MS (EI, 70 eV): calculated *m/z* = 182.11 (M), found *m/z* = 182 $[M]^+$ (23), 91 $[M/2]^+$ (100).

4,4′-Dimethylbiphenyl. MS (EI, 70 eV): calculated *m/z* = 182.11 (M), found *m/z* = 182 $[M]^+$ (100), 167 $[M—CH_3]^+$ (56), 152 $[M—2CH_3]^+$ (15).

Identification of radical species in solution

The reaction in a fivefold excess of a radical trap was studied similarly to the general procedure. Dicyclohexyl deuterophosphine (DCPD) was used as the radical trap.[17,18] The residues of benzyl chloride and DMF, as well as 1,2-diphenylethane and α-deuterotoluene, were detected in the benzene solutions. Table 1 summarizes the yields of organic reaction products.

α-Deuterotoluene. ^{1}H NMR ($CDCl_3$): $\delta = 2.32$ (m, 2H, —CH_2—), 7.15 (m, 5H, -Ph.) ppm. MS (EI, 70 eV): calculated *m/z* = 93.07 (M), found *m/z* = 93 $[M]^+$ (100), 92 $[M—H]^+$ (93), 91 $[M—D]^+$ (46), 66 $[M—H—C_2H_2]^+$ (9), 65 $[M—C_2H_2D]^+$ (11).

Study of the reaction kinetics

The reactions of zinc with benzyl halides in DMF were studied by the resistometric method[19] according to the published procedure[20] in a water- and oxygen-free atmosphere of argon. The kinetics of the reaction were studied by monitoring the electrical resistance of species during experiments. Species were zinc wire (diameters were 0.25 and 0.05 mm and lengths were 100 and 6.25 mm). Consequently, an increase in species electrical resistance reflects a decrease in the thickness of the wire.

To obtain kinetic and thermodynamic parameters of the process, three series of experiments were carried out. The first one was carried out at initial $C_{RHal} = 0.5\,mol\,L^{-1}$ and initial C_{DMF} was changed from 0.2 to 7 mol L^{-1} (Fig. 1, curve 1). The second series was realized at initial $C_{DMF} = 0.5\,mol\,L^{-1}$ and initial C_{RHal} was changed also from 0.2 to 7 mol L^{-1} (Fig. 1, curve 2). We made the third series at initial $C_{DMF} = 2\,mol\,L^{-1}$. In this case the initial C_{RHal} was changed from 0.2 to 7 mol L^{-1} (Fig. 1, curve 3). Benzene was used as a neutral solvent for determination of the kinetic characteristics of the reaction of zinc with benzyl chloride in the presence of DMF.[18] The reaction was studied in the kinetic mode, as evidenced by the independence of the rate of zinc dissolution in the test medium from the rate of stirring. Benzyl iodide reacts with zinc at a transport-controlled rate. Tables 2 and 3 summarize the results of this study.

Studies of the reaction of atomic zinc with benzyl halides at low temperature

Co-condensation of zinc with benzyl halides. Studies of the low-temperature reaction of zinc with benzyl halides were carried out in a vacuum apparatus similar to that reported previously.[21] The reagents were evaporated in an evacuated (10^{-4} mm Hg) reactor ($V = 10$ L) and condensed on the reactor surface cooled with liquid N_2. Atomic zinc was prepared by evaporating

Table 1. Product composition in the oxidative dissolution of zinc in benzyl chloride-DMF systems in the presence (and in the absence) of radical trap

					Yield, %		
N	RHal	DCPD/RHal[a]	*T* (K)	Time (h)	R–H	R–D[b]	R–R[c]
1	RCl	0:1	313	12	96	—	4
2		5:1	313	12	44	56	—
3		5:1	313	15	44	56	—
4	RBr	0:1	278	2	95	—	5
5		0:1	313	0.5	78	—	22
6		5:1	313	0.5	32	68	—
7	RI[d]	0:1	278	2	85	—	15

[a] impurity of dicyclohexyl phospine 1%.
[b] impurity of toluene 1%.
[c] impurity of 4,4′-dimethylbiphenyl < 0.1%.
[d] Benzyl iodide decomposes at higher temperature to form iodine.

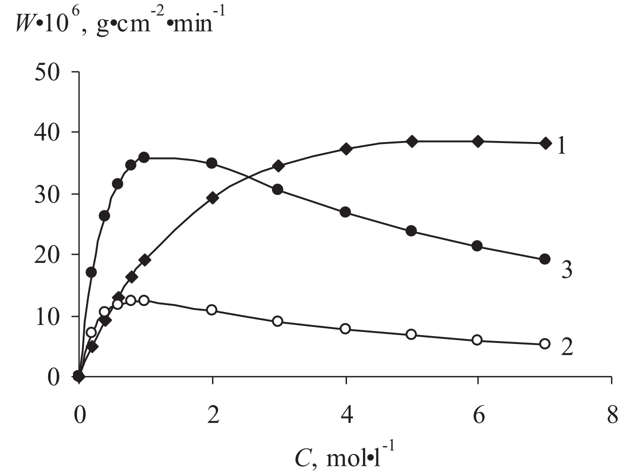

Figure 1. Rates (w) of the zinc reaction with benzyl chloride in DMF as a function of initial concentrations (C) of mixture components in benzene at 283 K. W-dependence on: (1) C_{DMF}, $C_{RHal} = 0.5$ mol L^{-1} (the initial C_{DMF} was ranged from 0 to 7 mol L^{-1}, the initial C_{RHal} is kept constant); (2) C_{RHal}, $C_{DMF} = 0.5$ mol L^{-1} (the initial C_{RHal} was ranged from 0 to 7 mol L^{-1}, the initial C_{DMF} is kept constant); (3) C_{RHal}, $C_{DMF} = 2$ mol L^{-1} (the initial C_{RHal} was ranged from 0 to 7 mol L^{-1}, the initial C_{DMF} is kept constant)

the purified metal from a corundum crucible at 570–600 K.[22] The rate of evaporation of Zn was 0.2 mmol min^{-1}. Benzyl halides were evaporated at 273–308 K ($PhCH_2Hal$:Zn = 50–100:1). The duration of co-condensation was 2–4 h.

Acidolysis of reaction products at 160 K. After completion of the co-condensation of zinc with benzyl halides, the samples were heated to 160 K, kept at this temperature for 20 min, and then cooled down to 77 K. DCl (50 g) was condensed on their surfaces. After the end of the evacuation, the reactor was filled with dry and pure Ar (760 mm Hg). The samples were heated to 160 K (at this temperature the film melted and decolorized) and kept at this temperature for 20 min. The excess of DCl was removed at 190–200 K (100 mm Hg). The reaction mixtures were heated to 298 K. The liquid (298 K) and gaseous (160 K) phases were analyzed by GC. Reaction products were isolated by preparative LC. Yields are shown in Table 4.

Acidolysis of reaction products at 298 K. Once co-condensation of zinc with benzyl chloride and DMF was completed and evacuation terminated, the reactor was filled with dry pure Ar (760 mm Hg). The samples were heated to 298 K. At this temperature the film melted and decolorized. The reaction mixtures were treated with 20% solution of DCl in D_2O (99.5 atom. % D, Aldrich) at 298 K in pure, dry Ar. The liquid and gaseous phases were analyzed by GC. The reaction products were isolated by preparative LC. The results are given in Table 4.

Detection of benzylpolyzinc hydrides. After completion of co-condensation of zinc with benzyl halides, the samples were heated to 160 K, kept at this temperature for 20 min, and then cooled down to 77 K. CCl_4 was condensed on their surfaces. The CCl_4-containing samples were kept at 160 K for 1 h. Acidolysis of the samples was carried out at 160 and 298 K. The liquid and gaseous phases were analyzed by GC. Reaction products were isolated by preparative LC. Yields are shown in Table 4.

Chloroform. MS (EI, 70 eV): calculated $m/z = 117.91$ (M), found $m/z = 118$ $[M]^+$ (1), 117 $[M—H]^+$ (0.7), 83 $[M—Cl]^+$ (100), 82 $[M—H—Cl]^+$ (4), 70 $[Cl_2]^+$ (1), 47 $[M—H—2Cl]^+$ (36), 36 $[HCl]^+$ (1).

Study of stereochemistry

A solution of 50 mmol (+)-R-1-bromo-1-phenylethane in 50 mL DMF was slowly added at −15 °C to 100 mmol zinc powder, which had been activated according to the

Table 2. Kinetic and thermodynamic parameters of the oxidative dissolution of zinc in the benzyl chloride–DMF system calculated using the Langmuir–Hinshelwood mechanism with adsorption of the reagent and the solvent at identical active centers of the metal

Parameter	$k \cdot 10^3$ (g cm^{-2} min^{-1})	K_1 (L mol^{-1})	K_2 (L mol^{-1})
T (K)			
283	0.413 ± 0.004	1.20 ± 0.01	0.273 ± 0.002
293	1.13 ± 0.01	0.864 ± 0.008	0.195 ± 0.002
303	2.55 ± 0.02	0.639 ± 0.005	0.138 ± 0.001
313	6.02 ± 0.05	0.471 ± 0.004	0.0979 ± 0.0008
323	12.2 ± 0.1	0.369 ± 0.002	0.0715 ± 0.0006
333	27.4 ± 0.2	0.274 ± 0.002	0.0548 ± 0.0005
r^a	0.999	0.999	0.999
E_A (kJ mol^{-1})	64.9 ± 2.0		
ΔH°_{RHal} (kJ mol^{-1})		-22.9 ± 0.8	
ΔH°_{DMF} (kJ mol^{-1})			-25.5 ± 0.8
ΔS°_{RHal} (J mol^{-1}K^{-1})		-79 ± 4	
ΔS°_{DMF} (J mol^{-1}K^{-1})			-101 ± 7

[a] Sample correlation coefficient.

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Table 3. Kinetic and thermodynamic parameters of the oxidative dissolution of zinc in the benzyl bromide–DMF system calculated using the Langmuir–Hinshelwood mechanism with adsorption of the reagent and the solvent at identical active centers of the metal

Parameter	$k \cdot 10^2$ (g cm^{-2} min^{-1})	K_1 (L mol^{-1})	K_2 (L mol^{-1})
T (K)			
283	1.05 ± 0.01	1.85 ± 0.01	0.272 ± 0.002
293	1.90 ± 0.01	1.21 ± 0.01	0.194 ± 0.002
303	3.72 ± 0.02	0.893 ± 0.007	0.132 ± 0.001
313	6.41 ± 0.05	0.646 ± 0.006	0.0986 ± 0.0008
323	11.5 ± 0.1	0.477 ± 0.003	0.0719 ± 0.0007
333	18.8 ± 0.1	0.355 ± 0.003	0.0548 ± 0.0004
r[a]	0.999	0.999	0.999
E_A (kJ mol^{-1})	45.6 ± 1.4		
ΔH°_{RHal} (kJ mol^{-1})		-25.5 ± 1.0	
ΔH°_{DMF} (kJ mol^{-1})			-25.3 ± 0.8
ΔS°_{RHal} (J mol^{-1}K^{-1})		-85 ± 6	
ΔS°_{DMF} (J mol^{-1}K^{-1})			-100 ± 7

[a] Sample correlation coefficient.

procedure described in Ref. 14. After 3.5 h of stirring at $-15\,^\circ$C the mixture was filtered. The filtrate was treated with 50 mL benzene. Precipitated white crystals were filtered off, washed by hexane and then evacuated. The reaction of zinc with (+)-R-1-chloro-1-phenylethane in DMF was carried out by a similar procedure, except that the reaction mixture was stirred at 30 °C for 10 h. The residue was poured into 20% solution DCl in D_2O (99.5% D). Organic products of reaction were extracted with benzene (50 mL). Yields are shown in Table 5. The reaction products were as follows:

Mixtures of RS-1-phenylethane-1D and phenylethane (1 and 4). ^{1}H NMR ($CDCl_3$): $\delta = 1.20$ (d, 3H, CH_3) (**1**), 1.24 (t, 3H, CH_3) (**4**), 2.62 (q, 1H, CH) (**4**), 2.66 (m, 2H, CH_2) (**1**), 7.19 (m, 5H, -Ph.) ppm.

RR,SS-2,3-Diphenylbutane (2). B.p. 130–132 °C/7 mm Hg, $n_D^{20} = 1.5557$. ^{1}H NMR ($CDCl_3$): $\delta = 1.17$ (d, 6H, $2CH_3$), 2.76 (m, 2H, CH—CH), 7.24 (m, 10H, 2Ph.) ppm (From Refs. 23 and 24 data: b.p. 130–132 °C/7 mm Hg, $n_D^{20} = 1.5557$.).

RS,RS-2,3-Diphenylbutane (3). B.p. 144–149 °C/12 mm Hg, m.p. 126–127 °C. ^{1}H NMR ($CDCl_3$): $\delta = 1.03$ (d, 6H, $2CH_3$), 2.75 (m, 2H, CH—CH), 7.24 (m, 10H, 2Ph.) ppm (From Refs. 23 and 24, b.p. 144–149 °C/12 mm Hg, m.p. 126–127 °C.).

Styrene (6). ^{1}H NMR ($CDCl_3$): $\delta = 5.20$ (m. 1H, CH_2=), 5.70 (m. 1H, CH_2=), 6.69 (m. 1H, —CH=), 6.90 (m. 5H, Ph). MS, m/z (%): 104 $[M]^+$ (100), 103 $[M—H]^+$ (40), 102 $[M—H]^+$ (12), 78 $[M—C_2H_2]^+$ (32), 77 $[M—C_2H_3]^+$ (24), 51 $[M—C_4H_5]^+$ (28).

The co-condensation of (+)-R-1-halogen-1-phenylethane with zinc (10:1) was carried out according to co-condensation of zinc with benzyl halides. Acidolyses of products at 160 and 298 K were similar to those of products in the case of unsubstituted benzyl halides.

Table 4. Composition of reaction products obtained by acidolyses of zinc co-condensates with benzyl halides

			Yield, % mol						
RHal	RHal/Zn	T (K)[a]	R–R	R–D	D_2[b]	$CHCl_3$	Zn/RD	Zn/D_2	n[c]
RCl	50	160	16.7	75.7	7.6	0.05	1.10	11	1.10
	50	298	35.6	64.4	—	—	1.00	—	1.00
	100	160	34.5	62.4	3.1	0.01	1.05	21	1.05
	100	298	44.2	55.8	—	—	1.00	—	1.00
RBr	50	160	32.7	67.3	—	0.001	1.00	—	1.00
	50	298	40.0	60.0	—	—	1.00	—	1.00
	100	160	44.4	55.6	—	—	1.00	—	1.00
	100	298	49.0	51.0	—	—	1.00	—	1.00
RI	50	160	58.8	41.2	—	—	1.00	—	1.00
	50	298	73.5	26.5	—	—	1.00	—	1.00

[a] The acidolysis was carried out at temperatures listed.

[b] D_2 contains trace amounts HD.

[c] n is the amount of Zn atoms in $PhCH_2Zn_nCl \cdot DMF$.

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Table 5. Yields of products **1–5** (%) in the stereochemical study of the Zn-benzyl halide reaction

			Yields of products, % (optical purity, %)				
RHal	T (K)	Solvent	**1**	**2**	**3**	**4**	**5**
Cl	303	DMF	90.4	4.1	4.0	1	0.5
	160[a]	—	52.8 (18.5)	23.8	23.1	0.3	—
	298[a]	—	34.8 (7.4)	31.0	30.0	2.2	2.0
	160	—	40.5	29.5	28.6	0.8	0.6
	298	—	15.8	40.4	39.1	2.4	2.3
Br	258	DMF	78.3	10.3	10.0	0.9	0.5
	160[a]	—	35.7 (3.7)	32.5	31.2	0.4	0.2
	298[a]	—	22.0	37.2	36.1	2.4	2.3
	160	—	28.9	35.1	34.1	1	0.9
	298	—	7.4	44.4	43.1	2.6	2.5

[a] Benzyl halide was condensed on zinc film surfaces.

RR,SS-, RS,RS-diphenylbutanes, styrene, (+)-S-1-phenylethane-1-D were found as products.

(+)-S-1-Phenylethane-1D (1). B.p. 135–136 °C, $n_D^{20} = 1.4954$, $[\alpha]_D^{20} + 0.06$ ($l = 0.1$). ^{1}H NMR (CDCl$_3$): $\delta = 1.23$ (d, 3H, CH$_3$), 2.62 (q, 1H, CH), 7.20 (m, 5H, -Ph.) ppm (From Refs. 23 and 24, b.p. 135–136 °C, $n_D^{20} = 1.4919$, $[\alpha]_D^{20} + 0.81$ ($l = 0.1$).).

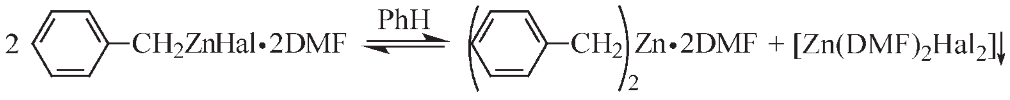
Studies of the low-temperature reactions of compact zinc with (+)-R-1-halogen-1-phenylethane were carried out in an apparatus similar to that reported previously.[21] Zinc was evaporated in an evacuated (10^{-4} mm Hg) reactor (10 L) from corundum crucible at 570–600 K and condensed on the reactor surface cooled with liquid N$_2$. (+)-R-1-Halogen-1-phenylethane was condensed on the zinc film surfaces (RHal:Zn = 1:1). Acidolysis of products at 160 and 298 K were similar to those of the products in the case of unsubstituted benzyl halides. RR,SS-, RS,RS-diphenylbutanes, styrene, (+)-S-1-phenylethane-1-D were found as products.

(+)-S-1-Phenylethane-1D (1). $[\alpha]_D^{20} + 0.15$ and $[\alpha]_D^{20} + 0.03$ ($l = 0.1$) (From Refs. 23 and 24 $[\alpha]_D^{20} + 0.81$ ($l = 0.1$)).

RESULTS AND DISCUSSION

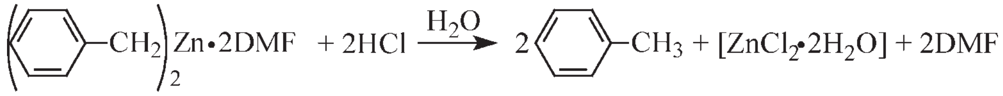
The reaction of zinc with benzyl halides and DMF is outlined in Scheme 1.

While benzene is added to the reaction mixture, white crystals of [Zn(DMF)$_2$Hal$_2$] (47–48%) are formed:

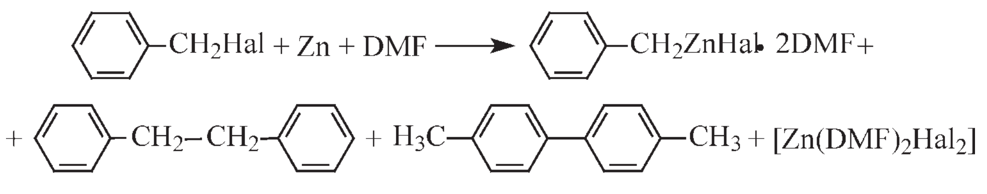


Hal = Cl, Br, I

The residues are treated with 20% solution HCl in H$_2$O. Thus the yield of toluene reflects that of benzylzinc halides. Hydrogen was not observed in the gaseous phase.



The analysis of water solutions demonstrated that the samples contained Zn^{2+} cations and halide anions, whose ratio corresponded to the formula ZnHal$_2$ (Hal = Cl, Br, or I). Zn (I) was not found. The evaporation of solvents *in vacuo* gives colorless crystals of ZnHal$_2 \cdot$ 2H$_2$O. Organic



Scheme 1. Hal = Cl, Br, I

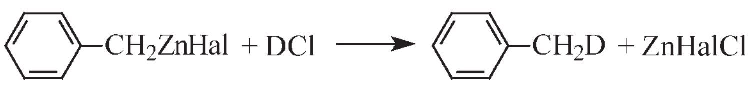
products yields are given in Table 1. The total amount of organic products corresponds to 100%. As expected, the order of decreasing halide reactivity is I, Br, Cl. The reaction of zinc with benzyl iodide is facile at low temperature. However, benzyl iodide provides lower yield of organozinc compounds (Table 1) than benzyl bromide and benzyl chloride do. As illustrated in entries 4 and 5, the yield of benzylzinc halides is temperature dependent. Significant amounts of organozinc compounds are found in entries 1 and 4. 1,2-Diphenylethane and 4,4′-dimethylbiphenyl were found as side products and 4-benzyl-1-methylbenzene was not detected. It may be reasonable to assume that the reaction proceeds according to the radical mechanism. In this case isomerization of benzyl radical occurs only in the radical pair.[25]

The paramagnetic particles that formed in the reaction of zinc with benzyl halides were studied by ESR-spectroscopy. The ESR spectrum of the co-condensate of zinc with benzyl bromide at 77 K shows a triplet of quartets with width of about 50 G and g factor of 2.002 ± 0.002, $a^{H}_{CH_2}$ of 16.6 ± 1.0 G, a^{H}_{o} of 5.5 ± 0.6 G, a^{H}_{p} of 5.5 ± 0.6 G. The ESR spectrum of the co-condensate of zinc with benzyl iodide is analogous to that of the co-condensate of zinc with benzyl bromide. However, the former is more poorly resolved. The comparison of the parameters of the typical ESR spectrum obtained in this research with those of benzyl radicals in solid matrices allows the assignment of the signals of this spectrum to benzyl radical.[7,18,26]

The ESR spectrum of the co-condensate of zinc with benzyl chloride is a superposition of the triplet quartets (which is similar to the spectrum of zinc co-condensate with benzyl bromide and benzyl iodide) and a singlet with a half-width of 8 ± 2 G. The ESR spectra are similar for reactions of benzyl chloride with magnesium[7] and zinc. We may conclude that the singlet with a half-width of 8 ± 2 G corresponds to the ion-radical pair of the $RX^{\cdot -} - Zn^{\cdot +}$ type and the absence of hyperfine structure is related to exchange processes.[7] According to ESR spectra, the total fraction of paramagnetic species in the samples at 77 K amounts to 9, 12, 22% for Cl, Br, I of the amount of precipitated zinc atoms and depends on the energy of the carbon–halogen bond in the starting benzyl halide (95, 69 and 45 kcal mol^{-1}).[27] Examination of the ESR spectra recorded at different temperatures provides data on the stability and conversion of the reaction intermediates. The intensity of the ESR signal gradually decreases as the co-condensate of Zn with benzyl halides are heated to 100 K. In the case of Zn co-condensates with benzyl chloride the signal of the ion-radical pair (singlet) decreases more rapidly than that of benzyl radical and completely disappears at 110 K. At temperatures higher than 130–150 K, the resolution of the ESR-spectra is substantially impaired, apparently due to the overlap of the signals of benzyl and 4-tolyl radicals, as well as of the signals of the corresponding radical pairs. The ESR signal of zinc co-condensates with benzyl chloride disappears at 170 K. In that of benzyl bromide and benzyl iodide the ESR signal disappears at 185 and 210 K, respectively.

While excess of benzyl halide is settling on to the zinc film surface (the thickness of the film is about 10^{-4} mm), UHF power dissipation increases. The consequent decreases of ESR spectrum resolution can be attributed to increases in the zinc film electroconductivity. The paramagnetic particles appearing in benzyl halide compact zinc systems are identical to the particles formed when atomic zinc films are used. The ESR spectrum of benzyl chloride-compact zinc film is similar to the low-intensity spectrum of zinc co-condensate with benzyl chloride, with the ratio singlet:triplet of quartets being increased by two- to threefold. The main cause of this increase is the stabilization of ion-radical pairs by charge distribution among the whole group of zinc atoms.

Mono- and polyorganomagnesium compounds can be formed as a result of the decay of ion-radical pairs $RX^{\cdot -} - Mg_n^{\cdot +}$. The mechanism of this reaction also depends on the bond-breaking energy of the carbon–halogen bond of the starting benzyl halide.[7,28] The spectra obtained show that ion-radical pairs are possible intermediates in the formation of organozinc halides from benzyl derivatives. The reaction mechanism seems to be dependent on the type of halogen in the benzyl halide. The composition of organozinc compounds was determined by acidolysis co-condensates of zinc with benzyl halides (1:50–100). The ratio metal:matrix of 1:100 leads to approximately 85% of atomic and 15% of dimeric metal. The ratio metal:matrix 1:10 000 results in atomic metal.[7,22] The low melting point of DCl made it possible to detect the reaction products both before (159 K) and after (298 K) defrosting of the sample. Organozinc compounds have been observed reacting with DCl according to the scheme:



As represented in Table 4 the benzyl chloride shows high yield of benzylzinc halides (75.7%) at 160 K. When the RHal/Zn ratio was increased to 100, the yield of organozinc compounds was reduced to 62.4%. For the reaction of zinc-benzyl bromide, observations are similar to those for benzyl chloride: 67.3 and 55.6%. The comparison of the results in Table 4 shows that the rise of temperature causes an increase in the yield of homo-coupled product and a decrease that of benzylzinc halides.

The formation of organopolymagnesium hydrides was observed in the reactions of Mg with organic halides

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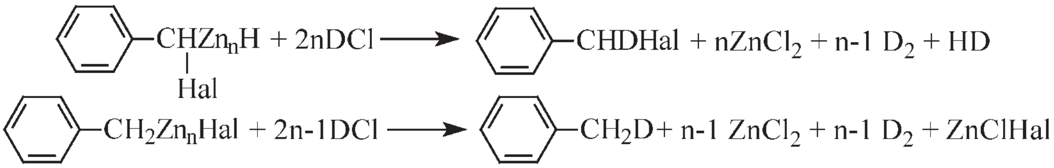
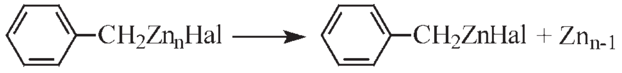
which were characterized by high energies of the cleavage of the carbon–halogen bond[28] while these products were not detected in the reactions of Mg with benzyl halides.[7] Benzylpolyzinc halides and hydrides react with DCl to form D_2:

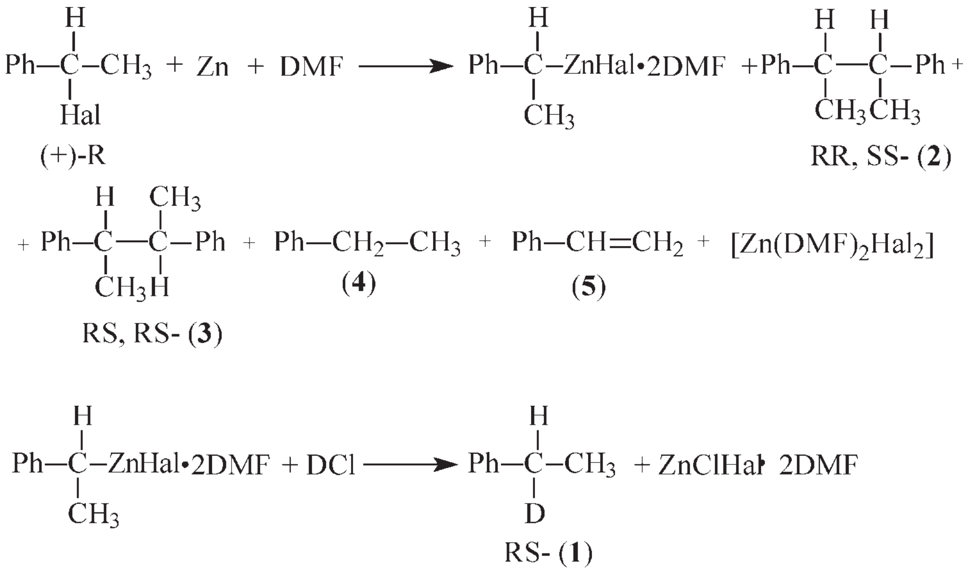


It can be seen from Table 4 that detectable amounts of D_2 were found only in the reaction of zinc with benzyl chloride. The appearance of D_2 in small amounts indicates that benzylpolyzinc halides and benzylpolyzinc hydrides are absent in the reaction mixture or present in insignificant amount at 298 K. A minor amount (<15%) of the cluster structures and their disappearance after acidolysis at 298 K can easily be explained: benzylpolyzinc halides can decompose already at 160 K to form zinc in the reaction:



The amount of hydride complexes was estimated by CCl_4 condensation on to the sample surface at 77 K before acidolysis. According to GC data listed in Table 4 the amount of chloroform in acidolysis products was about 0.05% for the case of zinc-benzyl chloride co-condensate and less than 0.01% and 0.001% for the case of systems containing benzyl bromide and benzyl iodide. Thus we can conclude that ion-radical pairs are not suitable intermediates in reaction of zinc with benzyl halides. Outer-sphere electron transfer can appear partly in the case of benzyl chloride at low temperature.

We have studied the reaction of optically active (+)-R-1-haloghen-1-phenylethane with zinc in DMF hoping to obtain experimental evidence for optical activity retention at the asymmetry center in the course of formation of organozinc compounds:



Hal = Cl, Br

Table 5 shows that this reaction results in the formation of optically inactive RS-1-phenylethane-1-D and four other unlabeled hydrocarbons **2–5**. The formation of optically inactive **2**, **3** with the ratio of **2**:**3** equal to 1.03:1 along with traces of **4** and **5**, shows that the reaction occurs according to the radical mechanism by which recombination and disproportionation of 1-phenylethyl radical can proceed after they enter the solution. However, organozinc halide racemization may proceed just after its formation. To confirm this assumption, we have studied the low-temperature reaction of zinc with (+)-R-1-halogen-1-phenylethane. The co-condensation of a zinc vapor with (+)-R-1-halogen-1-phenylethane (1:10) which were precipitated in the molecular beam mode on the surface cooled with liquid N_2 produced white films. The acidolysis was carried out by DCl at 160 and 298 K:

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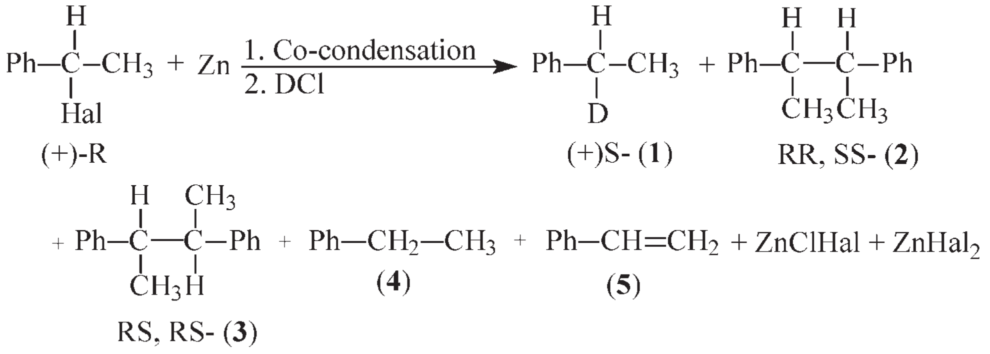


Hal = Cl, Br

It is shown in Table 5 that isolation of 52.8% the (+)-S-1-phenylethane-1-D (Hal = Cl, 160 K) with optical purity of 7.4% may be evidence for partial formation of benzylzinc chlorides on the zinc surface or by decay of ion-radical pair. The condensation of (+)-R-1-halogen-1-phenylethane on zinc film surface results in dark films. After completion of condensation of (+)-R-1-halogen-1-phenylethane the sample were heated to 160 K, kept at this temperature for 3 h and then cooled down to 77 K. The acidolysis of the samples was carried out by DCl at 160 and 298 K. The result of this reaction was formation of (+)-S-1-phenylethane-1-D with optical purity 3.7% (Hal = Br). Such optical purity of 1-phenylethane-1D does not exceed that for 1-phenylethyl radical recombination within a solvent cage. The high optical purity of (+)-S-1-phenylethane-1-D 18.5% (Hal = Cl) is associated with partial formation of ion-radical pairs in reaction of (+)-R-1-chloro-1-phenylethane with zinc at low temperatures (160 K, Table 5). Comparison of the optical purities of reaction products outlined in Table 5 and the proportion of deuterium in 1-phenylethane-1-D both lead us to conclude that the reaction of benzyl halides with Zn occurs on the metal surface. Racemization of benzylzinc halides takes place in the solution through fast structure inversion.

After having obtained evidence for radical intermediates in the reaction of zinc with benzyl halides, next we sought for an agent to trap these radicals in the solution. We have shown[18,26] that DCPD[17] can be utilized as trapping agent for benzyl radicals. Table 1 shows the results of reaction of benzyl halides with zinc in DMF when 5 equi. of DCPD were added. Entries 2 and 3 show that DCPD does not react with benzylzinc halides during the reaction or after it was completed. Comparison of the data from entries 1,4 and 2,6 show that the radicals that escaped the zinc surface are trapped by DCPD. Thus in this case it appears that among the benzylzinc halides formed in this reaction, a minimum of 52% results from radicals that diffuse into the solution and then return to the zinc surface.

The reaction kinetics of the oxidative dissolution of Zn in the benzyl halide-DMF system has been studied using the resistometric method. This method provides an opportunity to study various kinetic features of fast heterogeneous reactions; it is characterized by high accuracy and reproducibility of results.[18,19,29] In order to determine the kinetic characteristics of the process, the reaction is performed in a neutral solvent of benzene $(DN_{SbCl_5} = 0.42\ \text{kJ} \cdot \text{mol}^{-1})^3$. The kinetic experiments were performed in pure benzene (Figs. 1 and 2, point $C_{DMF} = 0$ of curves 2, 3). The rate of the reaction in pure benzene was smaller than the sensitivity of the equipment under our conditions. Benzyl iodide reacts with zinc at a transport-controlled rate: it increases with increasing stirring rate (1000–2500 rpm). The solution exhibits new absorption band of $\lambda = 520$ nm. It may be concluded that benzyl iodide decomposes to form iodine.[30] Benzyl chloride and bromide react with zinc in DMF at a nontransport-controlled rate.

Figures 1 and 2 exhibit kinetic curves that have maxima. An increase in the concentration of DMF from 0.5 to 2 mol L^{-1} did not change the shape of the curves,

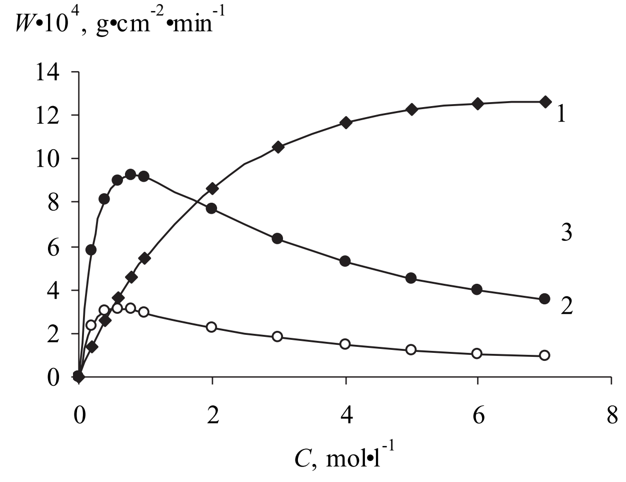


Figure 2. Rates (w) of the zinc reaction with benzyl bromide in DMF as a function of initial concentrations (C) of mixture components in benzene at 283 K. W-dependence on: (1) C_{DMF}, $C_{RHal} = 0.5$ mol L^{-1} (the initial C_{DMF} was ranged from 0 to 7 mol L^{-1}, the initial C_{RHal} is kept constant); (2) C_{RHal}, $C_{DMF} = 0.5$ mol L^{-1} (the initial C_{RHal} was ranged from 0 to 7 mol L^{-1}, the initial C_{DMF} is kept constant); (3) C_{RHal}, $C_{DMF} = 2$ mol L^{-1} (the initial C_{RHal} was ranged from 0 to 7 mol L^{-1}, the initial C_{DMF} is kept constant)

showing the dependence of the reaction rate on the concentration of benzyl halide. This indicates that the process proceeds by the Langmuir–Hinshelwood mechanism with adsorption of the reagent and the solvent at identical active centers of the metal surface[18,31]:

$$\mathrm{PhCH_2Hal} + \mathrm{S} \overset{K_1}{\rightleftharpoons} (\mathrm{PhCH_2Hal})\mathrm{S} \tag{1}$$

$$\mathrm{Solv} + \mathrm{S} \overset{K_2}{\rightleftharpoons} (\mathrm{Solv})\mathrm{S} \tag{2}$$

$$(\mathrm{PhCH_2Hal})\mathrm{S} + (\mathrm{Solv})\mathrm{S} \xrightarrow{k_3} \text{products} \tag{3}$$

Scheme 2.

where Solv is DMF; Hal = Cl or Br, K_1 and K_2 are the equilibrium constants of benzyl halide and DMF adsorption, respectively; k_3 is the rate constant of the limiting step and it corresponds to the formation of reaction products; S are the active centers at which the adsorption of benzyl chloride and DMF takes place. In this case, surface coverages derived from the Langmuir isotherms for adsorption of individual components appear in the rate equation, and the reaction rate can be expressed by Eqn (4):

$$w = \frac{kK_1K_2[\mathrm{PhCH_2Hal}][\mathrm{DMF}]}{(1 + K_1[\mathrm{PhCH_2Hal}] + K_2[\mathrm{DMF}])^2} \tag{4}$$

where $k = k_3 \cdot N^2$; N is the amount of active centers of the metal surface at which the adsorption of benzyl halide and DMF takes place. The Langmuir–Hinshelwood scheme for the test process suggests that the interaction of adsorbed reactant molecules with the metal surface, viz. a surface chemical reaction, is a rate-limiting step of the reaction.

The treatment of the experimental relations (Figs. 1 and 2) using the set of Eqns (1)–(3) allowed to determine the equilibrium constants of benzyl halide and DMF adsorption on the surface of zinc (K_1 and K_2, respectively) and the rate constant k of the chemical reaction.

The Eqn (4) can be written as

$$\frac{1}{w^{1/2}} = \frac{1 + K_1[\mathrm{PhCH_2Hal}] + K_2[\mathrm{Solv}]}{(kK_1K_2[\mathrm{PhCH_2Hal}][\mathrm{Solv}])^{1/2}}$$

When $[\mathrm{PhCH_2Hal}] = \mathrm{const}$:

$$\frac{[\mathrm{Solv}]^{1/2}}{w^{1/2}} = \frac{1 + K_1[\mathrm{PhCH_2Hal}]}{(kK_1K_2[\mathrm{PhCH_2Hal}])^{1/2}} + \frac{K_2[\mathrm{Solv}]}{(kK_1K_2[\mathrm{PhCH_2Hal}])^{1/2}}$$

where

$$\frac{K_2}{(kK_1K_2[\mathrm{PhCH_2Hal}])^{1/2}} = a$$

and

$$\frac{1 + K_1[\mathrm{PhCH_2Hal}]}{(kK_1K_2[\mathrm{PhCH_2Hal}])^{1/2}} = b$$

Then

$$\frac{[\mathrm{Solv}]^{1/2}}{w^{1/2}} = a[\mathrm{Solv}] + b$$

The similar operations for $[\mathrm{Solv}] = \mathrm{constant}$ lead to

$$\frac{K_1}{(kK_1K_2[\mathrm{Solv}])^{1/2}} = a_1$$

and

$$\frac{1 + K_2[\mathrm{Solv}]}{(kK_1K_2[\mathrm{Solv}])^{1/2}} = b_1$$

$$K_1 = \frac{a_1(a[\mathrm{Solv}] + b)}{bb_1 - aa_1[\mathrm{PhCH_2Hal}][\mathrm{Solv}]}$$

$$K_2 = \frac{a}{b}(1 + K_1[\mathrm{PhCH_2Hal}])$$

$$k = \frac{K_2}{a^2K_1[\mathrm{Solv}]}$$

The study of the reaction kinetics at different temperatures allowed to obtain E_A of the chemical reaction and enthalpies and entropies of adsorption of the reagents on the zinc surface. As Tables 2 and 3 show, the Arrhenius plots of the rate or equilibrium constants *versus* 1/T gave good correlations ($r = 0.999$). The high accuracy of results obtained favors the mechanism (Scheme 2). Therefore, the adsorption of benzyl halides and DMF should be the first steps of the reaction. The limiting step is inner- or outer-sphere electron transfer. The equilibrium constants K_2, enthalpy and entropy for adsorption of DMF have the same values in reactions of benzyl bromide and chloride (Tables 2 and 3). The enthalpies and entropies of adsorption values obtained indicate that DMF and benzyl halides do not dissociate on zinc surface during adsorption.[32]

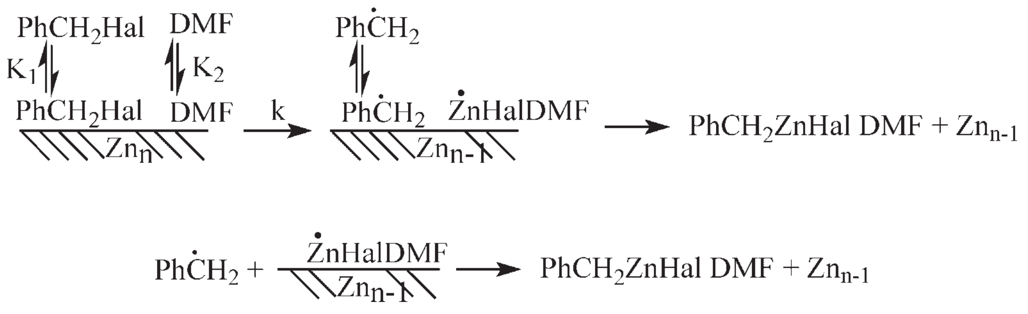
Nechaev *et al*. have shown that the adsorption of organic compounds on metal surface depends on the ionization potential of these organic compounds only.[33–36] $\mathrm{PhCH_2Hal}$ and DMF have similar ionization potentials and this is a reason why they have similar ΔH_ads values.

The rate constant ratio, $k_\mathrm{RBr}/k_\mathrm{RCl}$, may provide an independent information for the reaction mechanism. The free-radical reaction would lead to $k_\mathrm{RBr}/k_\mathrm{RCl} = 3000$–$5000$[37] and $\mathrm{S_N2}$-mechanism would lead to $k_\mathrm{RBr}/k_\mathrm{RCl} = 100$.[38] Benzyl bromide reacts much faster than benzyl chloride with zinc in DMF. The surface size of zinc wire for reaction with benzyl chloride was 80 times as much as for that of benzyl bromide. The relative rate of zinc reaction with benzyl halides in DMF $k_\mathrm{RBr}/k_\mathrm{RCl} = 773$ (318 K) and $k_\mathrm{RBr}/k_\mathrm{RCl} = 369$ (353 K) as calculated from temperature relations agree well with the order reported for halogen atom transfer rate-limited radical mechanism (760 at 318 K[39] and 496 ± 128 at 363 K[28]). The result obtained agree well with data reported in Rieke's paper. The author proposes that the electron transfer between Zn and substrates possesses an inner sphere transfer character.[40]

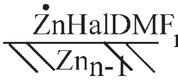
Comparison of the results with the published data[3] on the oxidative dissolution of zinc in the EtI-DMF system demonstrated that ΔH_{ads} DMF at the surface of zinc remained almost unchanged (−25.5 and −25.5 ± 0.8 kJ mol^{-1}) with replacement of EtI by $PhCH_2Hal$, whereas the corresponding values for a organic halide changed considerably (from −3.3 to −22.9 ± 0.8 and −25.5 ± 1.0 kJ mol^{-1}). This fact indicates the selective adsorption of a dipolar aprotic solvent, which participates in the reaction, on the surface of zinc.

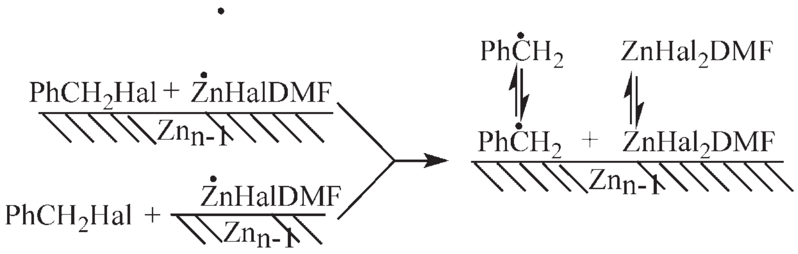
CONCLUSIONS

The results of this work indicate that the benzyl halide reaction with zinc in DMF takes place at the metal surface by halogen atom transfer mechanism (inner sphere electron transfer) via formation of benzyl radicals, which undergo recombination and isomerization mainly in solution. The reaction occurs by Langmuir–Hinshelwood mechanism (adsorption of reagent and solvent takes place at identical active centers of the metal surface) according to the following scheme.

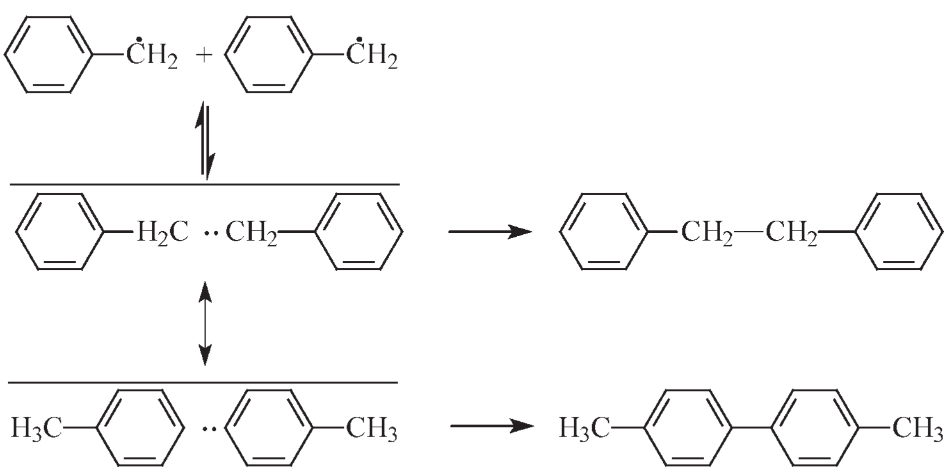


The limiting step of the reaction of benzyl halides with zinc is a halogen atom transfer to metal surface.

 react quickly with benzyl halide :



Recombination and isomerization of benzyl radicals proceed mainly in solution according to the scheme:



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The coordination compounds of zinc(II) with organic ligands in the solution are formed via the following sequence:

$$\mathrm{ZnHal_2DMF + DMF \rightarrow ZnHal_2 \cdot 2DMF}$$

$$\mathrm{PhCH_2ZnHal\ DMF + DMF \rightarrow PhCH_2ZnHal \cdot 2DMF}$$

where Hal = Cl, Br, I.

Acknowledgements

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