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Kinetics and Mechanism of Benzyl Chloride Reaction with Zinc in Dimethylacetamide

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Abstract—Oxidative dissolution of zinc in the system of benzyl chloride–dimethylacetamide was investigated. The reaction stereochemistry as well as intermediates and reaction products formed were studied. The kinetic and thermodynamic parameters of the process were measured. The process was shown to follow the Langmuir–Hinshelwood mechanism with the formation of benzyl radicals and mono-solvated organozinc compound on the zinc surface. The components of mixture are adsorbed at various sites of the zinc surface, while recombination and the isomerization of the benzyl radicals occurs in solution.

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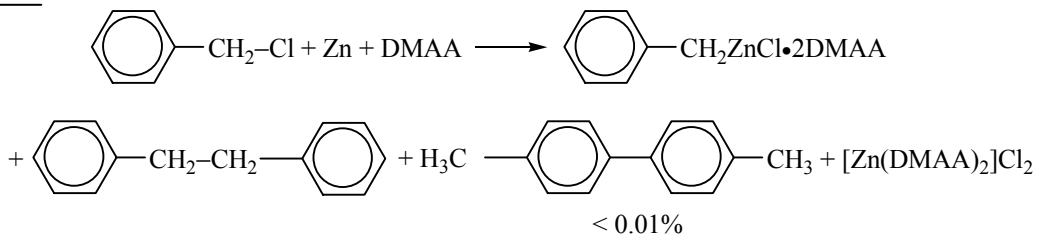
The organozinc compounds and the zinc complexes with organic ligands are widely used in industry as catalysts for the polymerization of lactones, lactides and various aldehydes [1].

The most promising method of the synthesis of complex metal compounds is the interaction of a metal with organic halide in a dipolar aprotic solvent [1]. This method allows performing the processes with high selectivity and under mild conditions without the use of toxic substances, and also makes it possible to produce simultaneous organometallic compounds. Due to this advantage, the studies on the oxidation of zinc with organic oxidants in various non-aqueous media with the donor–acceptor properties are carried out in our country and abroad.

In this work we investigated the mechanism of the reaction of zinc with benzyl chloride to provide an environmentally safe technology for producing benzylzinc chloride of the concentration up to 7 M and the zinc complex compounds with organic ligands.

The reaction of zinc with benzyl chloride in dimethylacetamide (DMAA) in an inert atmosphere leads to the formation of organozinc compounds and coordination compounds of zinc, as well as of 1,2-diphenylethane and trace amounts of 4,4'-dimethylbiphenyl (< 0.01%):

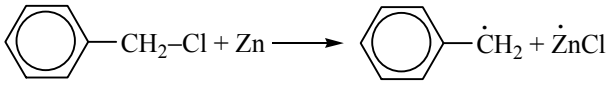


The oxidative dissolution of zinc proceeded selectively. Organozinc compound and 1,2-diphenylethane yields were 92% and 8%, respectively.

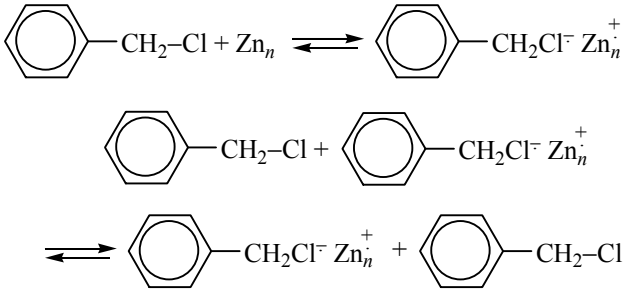
It is known that the mechanism of the metal reaction with various reagents in dipolar aprotic solvents depends on the nature of the metal, the reagent, and the solvent. These reactions as a rule occur on the metal surface and proceed by the radical, ion-radical, or carbanion mechanism [1–4]. The presence in the reaction mixtures of 1,2-diphenylethane and trace amounts of 4,4'-dimethylbiphenyl suggests that the reaction proceeds by a radical mechanism through the formation of the radical pair [1, 4–6].

To identify the reaction intermediates [1, 5], we registered the ESR spectra at 77 K of the films of jointly condensed zinc and benzyl chloride in the ratio of 1:50 in accordance with the method [7]. Zinc was evaporated from the corundum crucible in a vacuum (570–600 K, 10^{-4} mm Hg) and condensed as a molecular beam with benzyl chloride vapor on a quartz finger cooled to 77 K. The ESR spectra of the benzyl chloride–zinc condensate are multiplets with a total width of about 55 gauss and the *g*-factor 2.002±0.001.

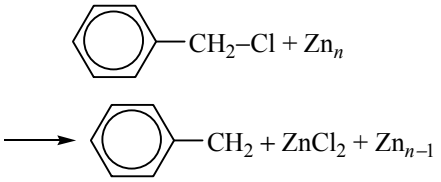
Based on comparison with published data, the obtained ESR spectra were assigned to the spectra of the benzyl radical [4–6, 8, 9] formed at the elimination of halogen atoms from the initial benzyl chloride by the atomic zinc [1]:



In the ESR spectra of the condensate of benzyl chloride with the atomic zinc (the metal atom is in the ground state) were observed the signals of two kinds: triplets or quartets or multiplets with the superposition of a singlet, with half-width 8±2 G [1]. Based on the literature data [10, 11], the singlet was assigned to the ion-radical pair $PhCH_2Cl^{\cdot-}Zn_n^{+}$ ($n \geq 1$), the absence of hyperfine structure was associated with the exchange processes [10–12]:

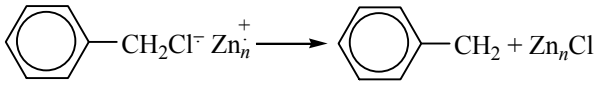


In the ESR spectra of the condensate of atomic zinc in the ground state with benzyl chloride the signals of the $^{\cdot}Zn_nCl$ radicals ($n \geq 1$) were not observed, due to the fast reaction of these radicals with a large excess of benzyl chloride already at 77 K [1]:



At the condensation of benzyl chloride on the compact zinc film the loss of superhigh frequency in the sample increases due to the increase in the electric conductivity, leading to a significant loss in the the ESR spectrum quality, but at 77 K the spectrum is not diffuse [1, 5]. The ESR spectra in these cases consist of a triplet of quartets (benzyl radicals) with a superimposed singlet of the ion-radical pair $PhCH_2Cl^{\cdot-}Zn_n^{+}$. However, the $PhCH_2\ Cl^{\cdot-}Zn_n^{+}$:$Ph^{\cdot}CH_2$ ratio increases ~3.5 times.

Thus, when compact metal is used in the reaction stabilization occurs of ion-radical pairs due to the charge distribution over the whole group of metal atoms [1, 5]. At the temperatures of 93–110 K the revealed radical ions completely disintegrate as follows [1, 5].



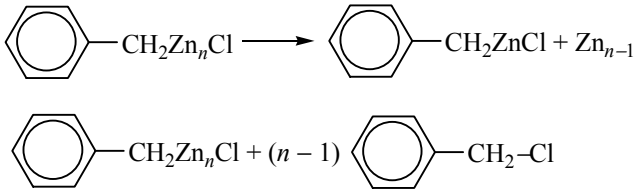
$n \geq 1$.

In the combined condensation of benzyl chloride and dimethylacetamide on the surface of a compact zinc the ESR signals are observed only at 77 K, and belong only to the ion-radical pairs indicating that the stabilization of the latter occurs not only by the metal surface but also by the dipolar aprotic solvent disintegrate as follows [1, 5]. Besides, the dipolar aprotic solvent adsorbed on the compact metal film facilitates the transfer of an electron from the metal surface to the organic halide. At increasing the temperature to 93 K the signals of benzyl radical (triplet of quartets) appear in the ESR spectrum, therewith, the ratio $PhCH_2Cl^{\cdot-}Zn_n^{+}$:$Ph\dot{C}H_2$ becomes equal to 5:1. With further increase in temperature to 110 K the signals of the ion-radical pair disappear.

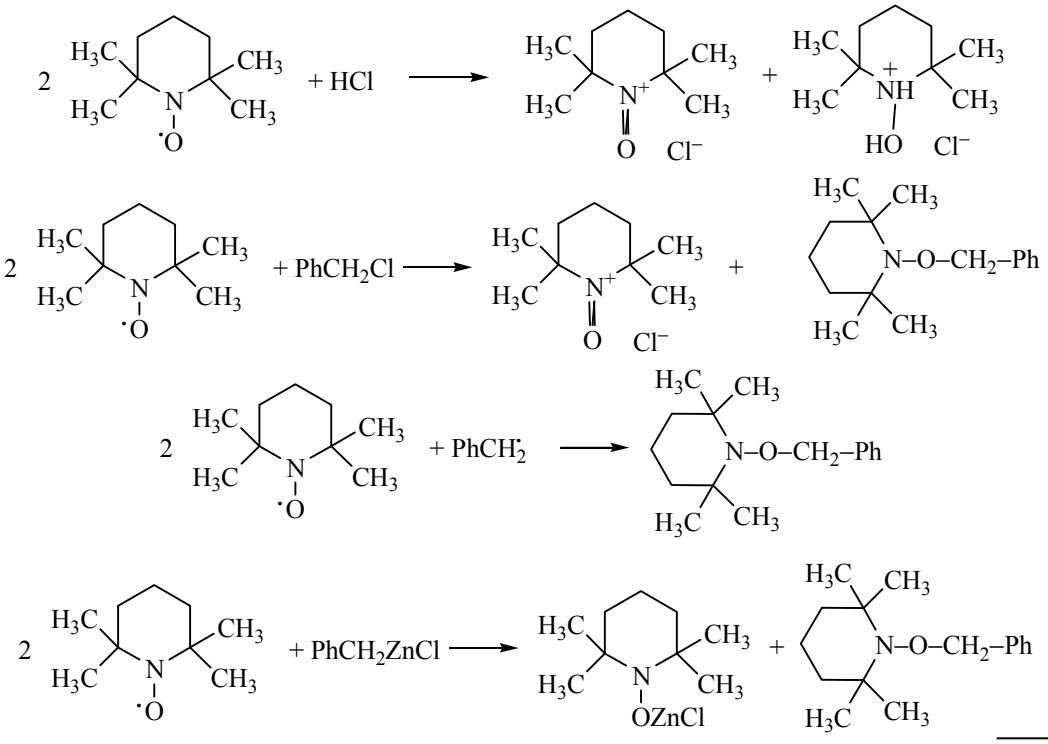
It was found in [1, 5] that the reaction of benzyl chloride with zinc occurs mainly at the C–X bond, and the low value of the energy of this bond cleavage prevent the insertion of zinc in the C–H bond, that is, benzylzinc hydrides and benzylpolyzinc chlorides are not practically formed.

A method of detection of the radical intermediates in solution is the ESR study of the reaction at 273 K [4, 13] using a spin trap. As a spin trap for the benzyl radicals, we used 2,2,6,6-tetramethylpiperidine 1-oxyl, which does not react with zinc or organozinc compounds. The ESR spectrum of a mixture containing zinc or an organozinc compound, benzyl chloride, DMAA, and 2,2,6,6-tetramethylpiperidine 1-oxyl

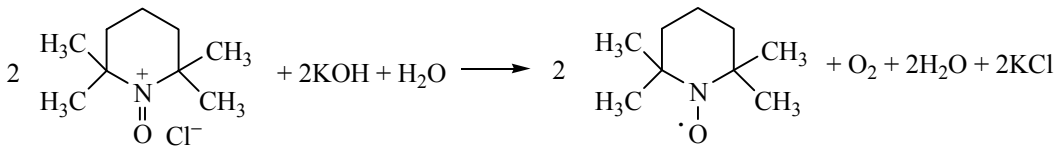
(1:5:8:0.2 ratio) is a triplet of 55 gauss width with the *g*-factor 2.0055±0.0002, which corresponds to the interaction of the electron with the nucleus of the nitrogen atom in the nitroxide group. Parameters of the ESR spectrum and literature data [14] are listed in Table 1. A comparison with the data [14] allows the assignment of the resulting ESR spectrum to that of the nitroxyl radical.



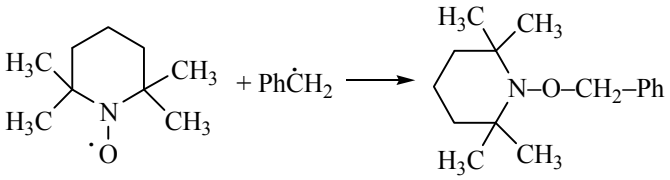
During the reaction of zinc with benzyl chloride in DMAA the signal of the added stable radical 2,2,6,6-tetramethylpiperidine 1-oxyl disappears from the ESR spec-trum of the reaction mixture. 2,2,6,6-Tetramethylpiperi-dine 1-oxyl can react with traces of the formed hydrogen chloride, the parent benzyl chloride, and benzyl radicals [1]:



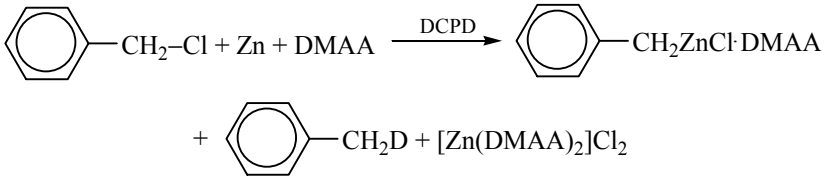
Therewith, the tetramethylpiperidine oxide salt can be reduced by hydrogen peroxide in alkaline medium to afford the corresponding radical [4, 15]:



The treatment of reaction mixtures with hydrogen peroxide in alkaline medium [4, 15] did not result in restoring the ESR signal, indicating the presence of radical intermediates in solution [15]. It is likely that benzyl radicals are formed and react with the trap along the scheme:



To test this hypothesis, we attempted to detect the benzyl radicals in solution using a spin trap. As the chemical trap for the benzyl radical we used dicyclohexyldeuterophosphine (DCPD), which did not react with organozinc compounds or zinc powder:



After separation of $[Zn(DMAA)_2]Cl_2$, the reaction mixture was treated with 20% HCl in H_2O. The yield of the organozinc compound is equal to the amount of the formed toluene:

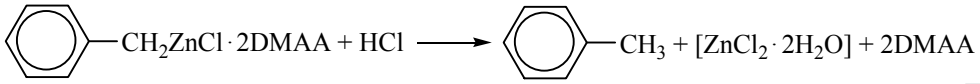
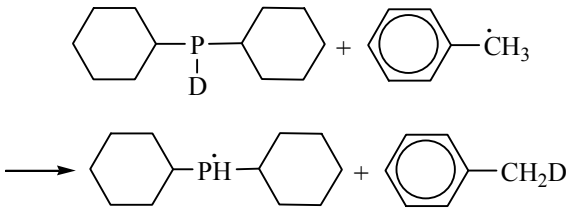


Table 2 lists the yields of the organic products of oxi-dativ dissolution of zinc in the benzyl chloride–dimethylacet-amide system in the absence and the presence of DCPD.

The presence in the reaction mixtures of α-deutero-toluene can be associated only with the presence of benzyl radicals in the solution:



The benzyl radicals leaving the zinc surface are captured by DCPD. Thus, the recombination and isomerization of benzyl radicals in solution leads to the formation of 1,2-diphenylethane and 4,4'-dimethyl-biphenyl. Nevertheless, the amount of detected α-deuterotoluene exceeds the amount of isolated 1,2-diphenylethane. This means that at least 50% of benzylzinc chloride is formed in the reaction of $^{\bullet}ZnCl$ with benzyl radicals that are released into the solution and return to the zinc surface.

To study the pathways of the formation of reaction products and to confirm experimentally the retention of optical activity at the asymmetric center at the formation of the zinc–carbon bond, we synthesized (+)-*R*-1-chloro-1-phenylethane and investigated the stereochemistry of its reaction with metallic zinc in dimethylacetamide.

The reaction of (+)-*R*-1-chloro-1-phenyletane with metallic zinc in the presence of dimethylacetamide was carried out along the following scheme:

Table 1. ESR spectral parameters of tetramethylpiperidine 1-oxyl

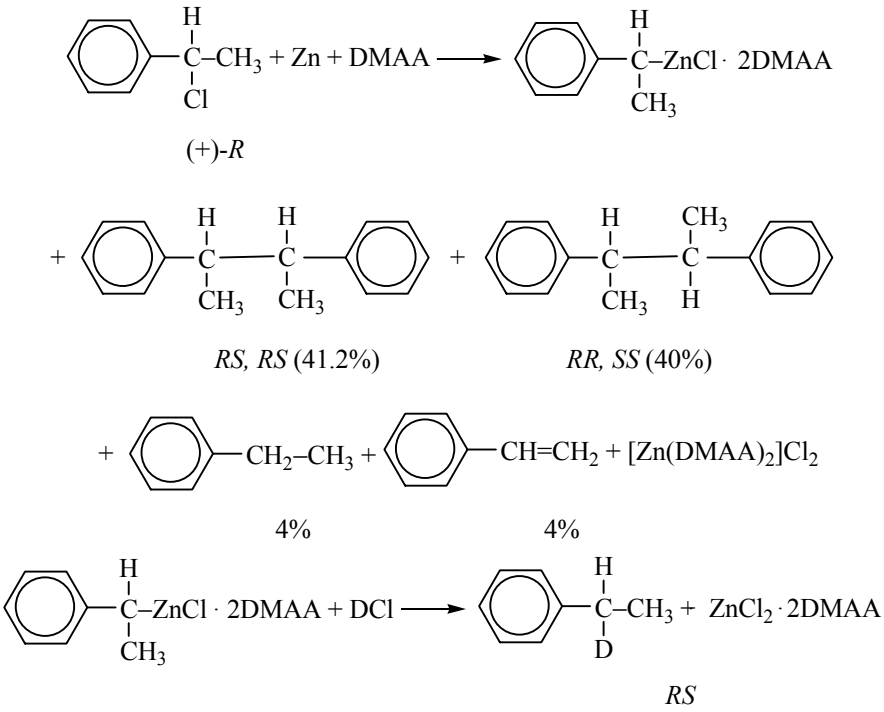
Solvent	*g*-Factor	a_N, G	a_H, G	ΔH, G
[a]	2.0055±0.0002	16.6±0.1	0.2±0.1	1.5±0.3
Beene	2.0055	15.4±0.1	0.2±0.2	1.5±0.2
Diethyleneglycol	2.0055	16.2±0.1	0.2±0.2	1.5±0.2
Formamide	2.0055	16.4±0.1	0.2±0.2	1.5±0.2

[a] Obtained in this work in the system of benzyl chloride–dimethylacetamide (molar ratio 5:8).

Table 2. Yields of organic products at the oxidative dissolution of zinc in the system benzyl chloride–dimethylacetamide without an additive and in the presence of dicyclohexyldeuterophosphine

$DCPD:PhCH_2Cl$	*t*, h	Yield,[a] mol %		
		$PhCH_3$	$PhCH_2CH_2Ph$	$PhCH_2D$
0:1	2	92	8	–
5:1	2	36	–	64

[a] The 4,4'-dimethylbiphenyl yield is less than 0.01%.



After processing the reaction mixtures with 20% DCl in D_2O racemic *RS*-1-deutero-1-phenyletane was isolated. This fact indicates stereochemical instability of the Zn–C bond and suggest a radical nature of its formation and decay. The *RS,RS*-2,3-diphenylbutane and *RR,SS*-2,3-diphenylbutane also were optically inactive, and their ratio in all cases was about 1.03:1, the styrene:ethylbenzene ratio was equal to 1:1. This ratio agrees well with published data on the behavior of 1-phenylethyl radicals in the solvent cage [16], so it can be concluded that the reaction of zinc with (+)-*R*-1-chloro-1-phenylethane proceeds by a radical mechanism through the formation of 1-phenylethyl radicals, which suffer recombination and disproportionation in the solution.

It is known that the reactions of various reagents and dipolar aprotic solvents with the metal surface, usually proceed by either the Langmuir–Hinshelwood, or Eley–Rideal mechanism.

The Langmuir–Hinshelwood mechanism [1, 17] comprises the following steps: equilibrium and independent of each other adsorption of the reagent and solvent molecules at the metal surface, which can occur either on identical or on different active sites of the metal, and the interaction of adsorbed reagent and solvent molecules with the metal surface and formation of intermediates or reaction products.

The Langmuir–Hinshelwood scheme assumes that the limiting stage of reaction is the interaction of adsorbed reagent and solvent molecules with the surface of the metal undergoing the oxidation, that is, occurs a chemical reaction on the surface.

Consider several versions of the Langmuir–Hinshelwood mechanism that are possible if this mechanism is realized.

(1) At the equilibrium adsorption of reagent and solvent at different active sites of the metal surface and their further interaction the Langmuir–Hinshelwood scheme is as follows [1]:

$$\mathrm{RHal} + S_1 \overset{K_1}{\rightleftharpoons} (\mathrm{RHal})S_1,$$

$$\mathrm{L} + S_2 \overset{K_2}{\rightleftharpoons} (\mathrm{L})S_2,$$

$$(\mathrm{RHal})S_1 + (\mathrm{L})S_2 \xrightarrow{k_3} \text{Reaction products.}$$

Here and hereinafter RHal is the organic halide, L is a dipolar aprotic solvent, S_1 and S_2 are the active sites of the metal surface where the adsorption of organic halide and dipolar aprotic solvent, respectively, occurs; K_1 and K_2 are the equilibrium constants of adsorption of organic halide and dipolar aprotic solvent, respectively, k_3 is the rate constant of the chemical process.

The nature of active sites adsorbing organic halide and dipolar aprotic solvent is not completely understood, however, due to the heterogeneity of the metal surface it contains the areas that differ in geometry and energy characteristics. The kinetic equation includes the degree of surface coverage obtained from the Langmuir isotherm for the adsorption of each component, and the expression for the reaction rate w is as follows:

$$w = \frac{kK_1K_2[\mathrm{RHlg}][\mathrm{L}]}{1 + K_1[\mathrm{RHal}] + K_2[\mathrm{L}] + K_1K_2[\mathrm{RHal}][\mathrm{L}]},$$

where $k = k_3N_1N_2$, N_1 and N_2 are the numbers of active centers of the metal surface adsorbing organic halide and dipolar aprotic solvent, respectively.

If the process proceeds according to the Langmuir–Hinshelwood mechanism with the adsorption of organic halide and dipolar aprotic solvent at different active centers of the metal, then the plots of the reaction rate *vs*. the initial concentration of the components in the mixture are smooth curves without maxima.

(2) When the equilibrium adsorption of organic halide (RHal) and solvent (L) occurs on the identical active sites of the metal surface (S) and they interact irreversibly with the metal surface resulting in the formation of intermediates or the products of the reaction, then the scheme of the Langmuir–Hinshelwood mechanism is as follows [1]:

$$\mathrm{RHal} + \mathrm{S} \overset{K_1}{\rightleftharpoons} (\mathrm{RHal})\mathrm{S},$$

$$\mathrm{L} + \mathrm{S} \overset{K_2}{\rightleftharpoons} (\mathrm{L})\mathrm{S},$$

$$(\mathrm{RHal})\mathrm{S} + (\mathrm{L})\mathrm{S} \xrightarrow{k_3} \text{Reaction products}.$$

The expression for the rate is as follows:

$$w = \frac{kK_1K_2[\mathrm{RHal}][\mathrm{L}]}{(1 + K_1[\mathrm{RHal}] + K_2[\mathrm{L}])^2},$$

$$k = k_3N^2.$$

In the process proceeding by the Langmuir–Hinshelwood mechanism with adsorption of organic halide and dipolar aprotic solvent at identical active sites of the metal surface without the formation of surface-bound intermediates, the plots of the reaction rate *vs*. the concentration of the initial components in the mixture are smooth curves with maxima (the extreme character of the curves).

(3) At the equilibrium adsorption of organic halide (RHal) and solvent (L) on the identical active sites of the metal surface (S), followed by the equilibrium formation of the surface-linked intermediates, the scheme of the Langmuir–Hinshelwood mechanism is as follows [1]:

$$\mathrm{RHal} + \mathrm{S} \overset{K_1}{\rightleftharpoons} (\mathrm{RHal})\mathrm{S},$$

$$\mathrm{L} + \mathrm{S} \overset{K_2}{\rightleftharpoons} (\mathrm{L})\mathrm{S},$$

$$(\mathrm{RHal})\mathrm{S} + (\mathrm{L})\mathrm{S} \overset{K}{\rightleftharpoons} (\mathrm{RHal})(\mathrm{L}),$$

$$(\mathrm{RHal})\mathrm{S} + (\mathrm{L})\mathrm{S} \xrightarrow{k_3} \text{Reaction products}.$$

The expression for the rate of the process is as follows:

$$w = \frac{kK_1K_2K[\mathrm{RHal}][\mathrm{L}]}{1 + K_1[\mathrm{RHal}] + K_2[\mathrm{L}] + K_1K_2K[\mathrm{RHal}][\mathrm{L}]},$$

$$k = k_3N.$$

In the process by the Langmuir–Hinshelwood mechanism with the adsorption of organic halide and dipolar aprotic solvent at identical active sites of the metal surface with the formation of the surface-bound intermediates, the plots of the reaction rate on the initial concentration of the components in the mixture are smooth curves without peaks.

The Eley–Rideal mechanism [1, 17] comprises the following steps: the equilibrium adsorption of reactant molecules on the metal surface and the interaction of adsorbed molecules of reagent with the metal when the coordinating solvent molecules from the solution approach them and the reaction products are formed. Consider two versions of the Eley–Rideal mechanism which are possible at the process implementation.

(1) At the equilibrium adsorption of the reactant molecules (RHal) only on the metal surface, the Eley–Rideal scheme has the form [1]:

$$\mathrm{RHal} + \mathrm{S} \overset{K_1}{\rightleftharpoons} (\mathrm{RHal})\mathrm{S},$$

$$(\mathrm{RHal})\mathrm{S} + \mathrm{L} \xrightarrow{k_3} \text{Reaction products}.$$

The expression for the rate of the process in this case is:

$$w = \frac{kK_1[\mathrm{RHal}][\mathrm{L}]}{1 + K_1[\mathrm{RHal}]},$$

$$k = k_3N.$$

(2) At the equilibrium adsorption of the reagent (RHal) molecules as well as the solvent (L) molecules on the metal surface, followed by the reaction of the adsorbed reactant (RHal)S with the metal at the approach to them of coordinating solvent (L) molecules from the solution the Eley–Rideal scheme has the form [1]:

$$\mathrm{RHal + S} \overset{K_1}{\rightleftharpoons} \mathrm{(RHal)S},$$

$$\mathrm{L + S} \overset{K_2}{\rightleftharpoons} \mathrm{(L)S},$$

$$\mathrm{(RHal)S + L} \xrightarrow{k_3} \text{Reaction products.}$$

The equation for the process rate in this case is:

$$w = \frac{kK_1[\mathrm{RHal}][\mathrm{L}]}{1 + K_1[\mathrm{RHal}] + K_1[\mathrm{RHal}]},$$

$$k = k_3N.$$

At the implementation of the process by the Eley–Rideal mechanism the general form of the plots of the reaction rate vs. concentration of components in the mixture changes in going from the solvent (at a fixed concentration of benzyl halide) to benzyl halide (at a fixed concentration of the solvent): one plot is a straight line, and the other is a smooth curve.

To reveal the kinetic and thermodynamic characteristics of the interaction of zinc with benzyl chloride in the presence of dimethylacetamide, we used the resistometric method, which is sufficiently precise and reproducible [18–20]. The reactions were studied in an indifferent solvent benzene at the stirrer rotation rate from 2500 to 2700 rpm, which enabled to study the process in the kinetic region.

The dependence of the reaction rate of zinc with benzyl chloride in dimethylacetamide is a smooth curve in the coordinates the rate (w) is the initial concentration of the component (Fig. 1).

In [5] the dependences were reported of the zinc–benzyl chloride reaction rate in dimethylformamide on the concentration of the mixture components, which are smooth curves with extrema (Fig. 2). In this case (Fig. 2) the process obeyed the Langmuir–Hinshelwood mechanism with adsorption of organic halide and dipolar aprotic solvent on the identical active sites of zinc surface without the formation of surface-bound intermediates [5].

Comparison of the results obtained in this paper with the data of [5] show that in both cases increasing concentration of dipolar aprotic solvent from 0.5 to 2 M does not lead to a change in the form of the dependence of reaction rate on the concentration of benzyl halide, indicating that these reactions proceed by Langmuir–Hinshelwood mechanism. However, in contrast to [5] we obtained the reaction rate dependences on the concentrations of the components of zinc–benzyl chloride mixture in dimethylacetamide like smooth curves without extremal points (Fig. 1), indicating that the adsorption of benzyl halide and dimethylacetamide occurs on the different active sites of the metal surface.

Thus, the reaction of zinc with benzyl chloride in dimethylacetamide proceeds by the Langmuir–Hinshelwood mechanism, through the adsorption of the reagent and solvent at different active sites of the metal surface and their further interaction.

For processing the experimental curves, we applied the previously developed algorithms [1], which allow determining not only the rate constant k, but also the equilibrium constants of benzyl halide and solvent adsorption on the metal surface (K_1 and K_2). While investigating the reaction kinetics at different temperatures, we were able to determine the activation energy E_a of the chemical process, and the standard enthalpy and entropy of the reactant and solvent adsorption on the zinc surface.

The results of studying the reaction kinetics of zinc with benzyl chloride in dimethylacetamide are listed in Table 3.

The correlation coefficients R are close to unity, and the standard deviations are minimal that confirm the high accuracy of both the method and the data. The listed in Table 3 different values of $\Delta H^0(\mathrm{PhCH_2Cl})$ –23.1±0.9 kJ mol^{-1} and $\Delta H^0_{\mathrm{DMAA}}$ –28.2±1.4 kJ mol^{-1} indicate that benzyl chloride and dimethylacetamide are adsorbed on different active sites of zinc surface. Value of the $\Delta H^0(\mathrm{PhCH_2Cl})$ –23.1±0.9 kJ mol^{-1} for the reaction of zinc with benzyl chloride in dimethylacetamide coincides with $\Delta H^0(\mathrm{PhCH_2Cl})$ –22.9±0.8 kcal mol^{-1} [5] for the reaction of zinc with benzyl chloride in DMF, indicating that benzyl chloride is adsorbed in these reactions at the sites of the same energy and its adsorption is practically independent of the influence of the solvent.

Significant negative values of $\Delta S^0(\mathrm{PhCH_2Cl})$ –80.0±3.0 J mol^{-1} K^{-1} and $\Delta S^0_{\mathrm{DMMA}}$ –106±5 J mol^{-1} K^{-1}

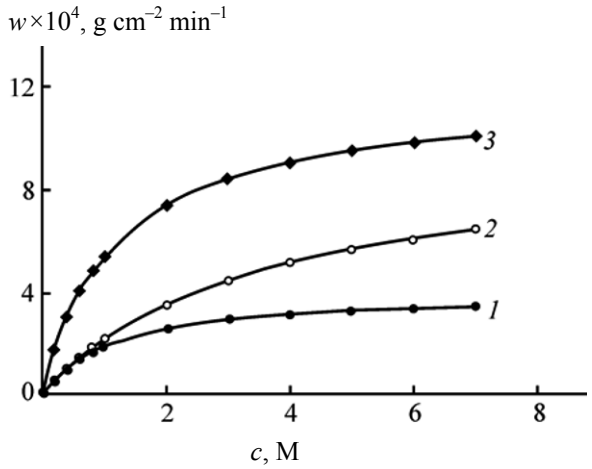


Fig. 1. Dependence of the reaction rate (w) of zinc with benzyl chloride in dimethylacetamide on the concentration of the components of the mixture at 293 K in the presence of benzene. (*1*) c_{DMAA} = 0.5 M, $c(PhCH_2Cl)$ from 0 to 7.0 M , (*2*) $c(PhCH_2Cl)$ = 0.5 M; c_{DMAA} from 0 to 7.0 M, (*3*) c_{DMAA} = 2.0 mol l^{-1}, $c(PhCH_2Cl)$ from 0 to 7.0 M.

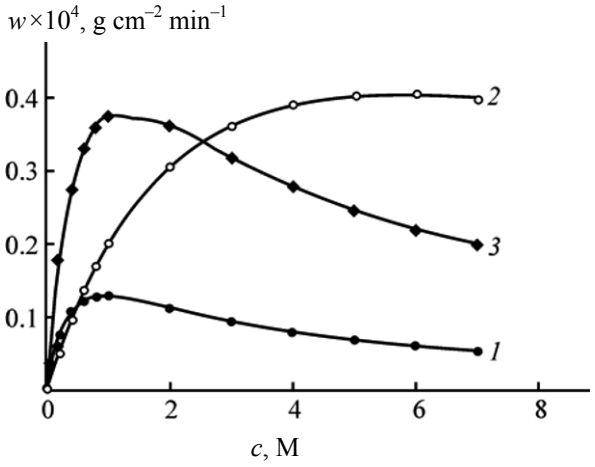


Fig. 2. Dependence of the reaction rate (w) of zinc with benzyl chloride in dimethylformamide on the concentration of the components of the mixture at 283 K in the presence of an indifferent solvent (benzene) [5]. (*1*) c_{DMF} = 0.5 M, $c(PhCH_2Cl)$ from 0 to 7.0 M, (*2*) $c(PhCH_2Cl)$ = 0.5 M; c_{DMF} from 0 to 7.0 M, (*3*) c_{DMF} = 2.0 M, $c(PhCH_2Cl)$ from 0 to 7.0 M.

shown in Table 3 indicate that there is no dissociation of benzyl chloride and dimethylacetamide during the adsorption. For comparison, the standard entropy of adsorption of the reagent and solvent for the reaction of zinc with benzyl chloride in DMF, which also do not dissociate during adsorption are: $\Delta S^0(PhCH_2Cl)$ –79±4 J mol^{-1} K^{-1}; ΔS^0_{DMMA} –101±7 J mol^{-1} K^{-1} [5].

To study quantitatively the influence of the substituents in the aromatic ring on the reactivity of benzyl chloride in the reaction with metallic zinc in dimethylacetamide, we measured the reaction rate constants with the substituted benzyl chlorides (k_s) at 293 K in the same way as were measured the rate constants of the unsubstituted substrate. The relative reactivities of the benzyl chlorides were obtained by dividing the rate constants of the substituted benzyl chloride k_s by that of the unsubstituted chloride k [1, 21]. This allowed calculating the ρ parameter of the Hammett equation. Table 4 shows the Hammett σ constants of substituents and relative reactivities of substituted benzyl chlorides at 293 K in the reaction with zinc in dimethylacetamide. Figure 3 shows the plot of the logarithms of relative rates on the σ Hammett constants of substituents. The data in Table 4 show that the dependence is a straight line with good correlation. Comparison of the kinetic parameters of the reaction shows that the nature of the substituent in

Table 3. Kinetic and thermodynamic parameters of reaction betwen zinc and benzyl chloride in dimethylacetamide[a]

T, K	$k\times10^3$, g cm^{-2} min^{-1} [b]	K_1, l mol^{-1} [c]	K_2, l mol^{-1} [d]
283	1.22±0.02	1.23±0.01	0.445±0.005
293	3.18±0.04	0.862±0.008	0.292±0.003
303	7.34±0.08	0.625±0.006	0.201±0.002
313	15.1±0.02	0.479±0.005	0.133±0.001
323	36.9±0.04	0.351±0.004	0.103±0.001
333	68.9±0.06	0.283±0.003	0.0731±0.0007

[a] E_a 63.3±2.4; $\Delta H^0(PhCH_2Cl)$ –23.1±0.9 kJ mol^{-1}, ΔH^0_{DMAA} –28.2±1.4 kJ mol^{-1} at 298 K, $\Delta S^0(PhCH_2Cl)$ –80.0±3,0 J mol^{-1} K^{-1} and ΔH^0_{DMAA} –106±5 J mol^{-1} K^{-1}. Selective correlation coefficient for the plot $\ln Y = f(1/T)$. [b] R = 0.999 ($Y = k$), [c] R = 0.999 ($Y = K_1$), [d] R = 0.999 ($Y = K_2$).

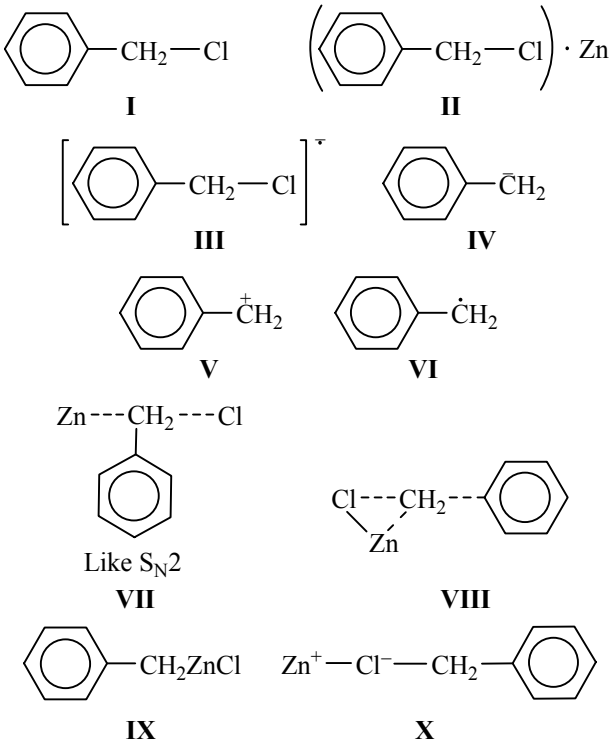
Table 4. Relative reactivity of benzyl chlorides at 293 K in the reaction with zinc in dimethylacetamide

Substituent	σ	log (k_s/k)	k_s/k	$k_s\times10^3$, g cm^{-2} min^{-1}
m-Cl	0.37	0.161368	1.45	4.61±0.04
m-F	0.34	0.149219	1.41	4.48±0.04
p-Cl	0.23	0.136721	1.37	4.36±0.04
m-OMe	0.12	0.029384	1.07	3.40±0.03
p-F	0.06	0.049218	1.12	3.56±0.04
H	0	0	1	3.18±0.04
m-Me	–0.07	–0.03152	0.93	2.96±0.03
p-Me	–0.17	–0.05061	0.89	2.83±0.02
p-OMe	–0.27	–0.13668	0.73	2.32±0.02

the aromatic ring has little effect on the reaction rate, and the rate constants k_s vary insignificantly.

Thus, the results obtained indicate that the electron-withdrawing substituents in the aromatic ring make the interaction of benzyl chloride with zinc slightly easier, while electron-releasing substituents retard the process, therewith the mechanism of these processes remains unchanged.

To determine the rate limiting steps, we considered 10 possible processes that may occur in these steps:



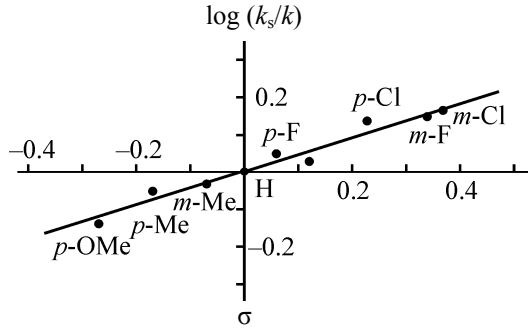


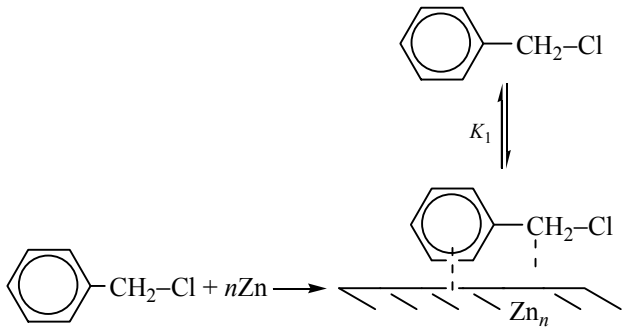
Fig. 3. Effect of substituent at the aromatic ring on the reaction of zinc with benzyl chloride in dimethylacetamide, ρ = 0.45±0.03, $S_ρ$ = 0.02, R = 0.9814, R^2 = 0.9631.

The reaction in all cases is not limited by diffusion and/or mass transfer of compound **I**. The value of ρ is too large compared to the physical adsorption of the component **II**. The sign of ρ is not typical for the processes of formation of benzyl cation **V**. The obtained ρ values are much lower than those found in the reactions with the participation of benzyl anion **IV**. The results of the study of the reaction stereochemistry of zinc with benzyl chloride allow the rejection of the processes similar to the S_N2 with intermediate **VII** and the processes that include the formation of at-complexes **X**. The rate determining step that includes the intermediate **IX** with partial or complete formation of the metal–carbon bond is hardly probable, since in this transition state there is a significant charge on carbon and a high ρ value is typical in this case. These results do not allow us to specify the reactions leading to the formation of the three remaining states: the single electron transfer with the formation of the anion radical **III**, the splittiong off the chlorine atom (the reaction product is **VI**), and the insertion of zinc atom in the C–Hal bond forming **VIII**.

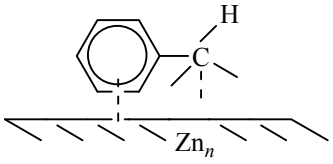
Our studies using the ESR spectroscopy, radical trapping and investigating the reaction stereochemistry showed that the reaction of zinc with benzyl chloride in dimethylacetamide proceeds by the mechanism of halogen transfer with the formation of benzyl radicals **VI**, as evidenced also by the low positive Hammett ρ value.

Based on the results obtained and literature data we assume the following mechanism of reaction of benzyl chloride with zinc in dimethylacetamide:

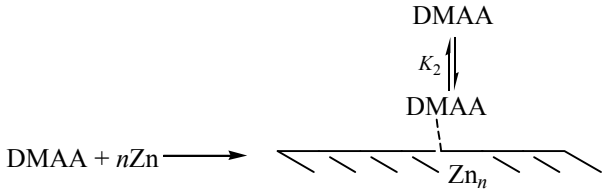
Stage I: reversible adsorption of benzyl chloride on the surface of the active sites of zinc, which have certain energy characteristics:



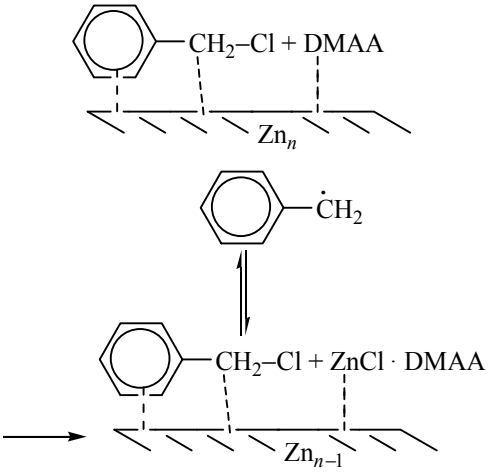
The aromatic ring is oriented parallel to the metal surface and the halogen atom is located above the plane of the ring [1]:



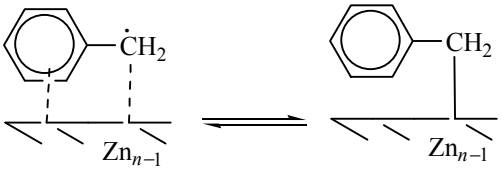
Stage II: reversible adsorption of DMAA on the active sites of zinc surface with different energy characteristics. Partial electron transfer from zinc to DMAA greatly facilitates the transfer of an electron from the surface of zinc on the benzyl chloride:



Stage III: transfer of electrons from the zinc surface in the inner sphere (the mechanism of halogen transfer). At this stage benzyl radicals are formed and solvated radical ·ZnCl·DMAA on the surface of zinc. The resulting benzyl radicals can reversibly transit to the solution. Solvated radical ·ZnCl·DMAA does not go into solution as it is part of the surface:

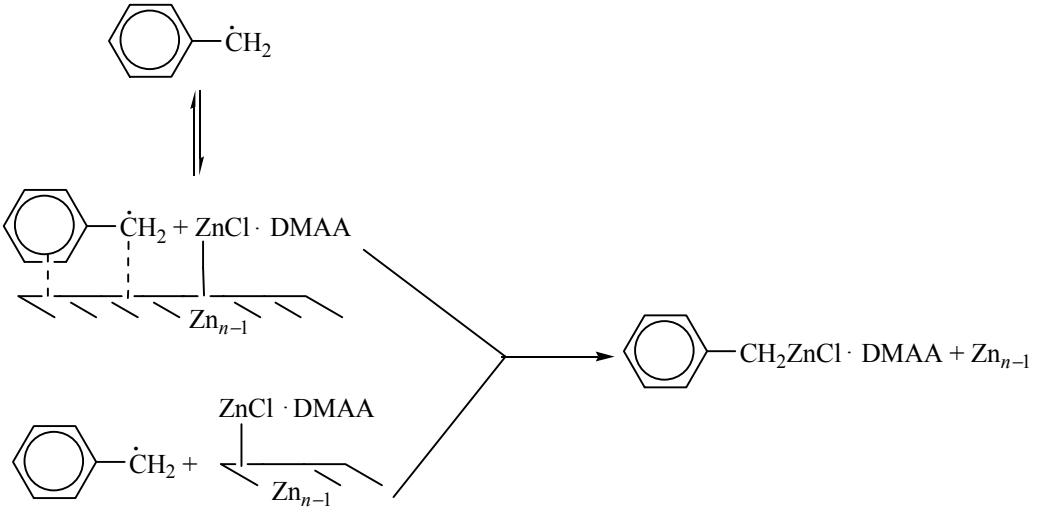


The benzyl group on the surface reversibly releases an electron. The structure of the benzyl group can be represented as follows:

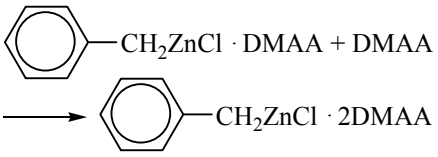


By the method of scanning tunnel microscopy it was found that aromatic radicals can move along the surface of a metal at sufficiently large distances [1].

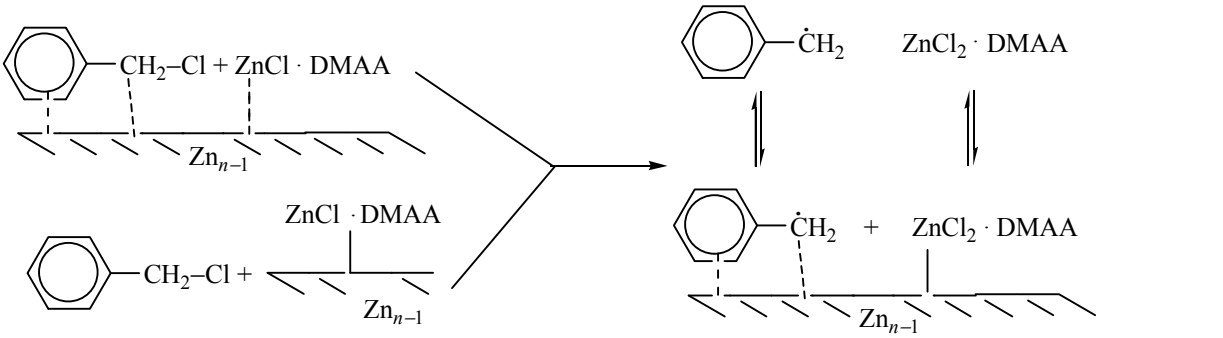
Stage IV: the interaction of the benzyl radical with solvated radical ·ZnCl·DMAA may proceed by both the Langmuir–Hinshelwood and Eley–Rideal mechanism when the radical attacks from the solution:



Stage V: solvation of the monosolvated benzylzinc chloride in the solution:

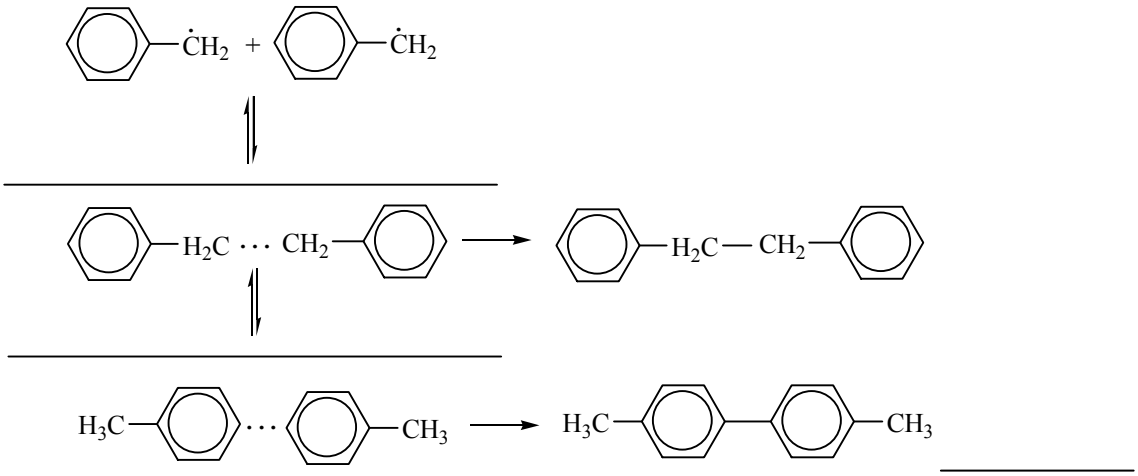


Stage VI: formation of the reaction by-products. A fast reaction occurs of solvated zinc chloride radical located on the zinc surface with benzyl chloride either on the zinc surface by the Langmuir–Hinshelwood scheme, or it is attacked with benzyl chloride from the solution by the Eley–Rideal scheme:



Stage VII: solvation of the monosolvated zinc chloride in the solution:

Stage VIII: recombination and isomerization of benzyl radicals in the solution.



The mechanism of the reaction of zinc with benzyl chloride in dimethylacetamide studied in this work is similar to the mechanism of the reaction of zinc with benzyl chloride in dimethylformamide reported in [5]. Both the mechanisms include the transfer of the halogen atom and the formation of benzyl radicals, which recombine and isomerize in solution. The difference between these mechanisms is that in the reaction with DMF the benzyl chloride and the dipolar aprotic solvent the adsorption occurs on the similar active sites of zinc surface [5], while in the case of the reaction using as solvent dimethyl acetamide the solvent and reactant adsorption occurs on different active sites of the metal surface.

EXPERIMENTAL

The purity of the starting compounds and analysis of reaction products were monitored by the methods of gas–liquid chromatography (chromatograph Tsvet-800, Russia), ion chromatography (Tsvet-3006, Russia) along the techniques described in [4]; by the NMR spectroscopy (an NMR Fourier spectrometer Jeol FX-90Q LTD, Japan), the analysis conditions have been published earlier [4]; by IR spectroscopy (a Nicolet IMPACT 400d instrument, USA) from tablets of KBr; by ESR spectroscopy (an electron spin resonance spectrometer SE/H-2543 Radiopan,

Poland) using previously described technique [4–6]; by the method of gas chromatography–mass spectrometry (mass detector HP-5972, gas chromatograph HP-5890 Hewlett Packard, USA), the conditions of analysis are described in [18, 22]; by elemental analysis (Gas chromatographic elemental analyzer Carlo-Erba-1100, Italy) by standard methods [1].

Quantitative analysis of metal impurities in zinc was carried out by atomic absorption spectrometry on a GBC AVANTA PM instrument (Australia) after dissolving the samples of the metal in nitric acid and neutralizing the resulting solution with 25% solution of ammonia [23].

Organic reaction products were separated by preparative liquid chromatography (chromatograph Tsvet-304, Russia). Conditions of analysis are described in [4]

Elemental analysis of deuterated organic compounds was carried out on a gas-chromatographic elemental analyzer Carlo-Erba-1100 (Italy) and gas chromatograph Tsvet-570 (Russia) by the method [24].

Measurement of specific rotation of the plane-polarized light was carried out on an automatic polarimeter VNIEKIprodmash A-1 EPO (Russia, σ = 0.01˚) in cells of various thicknesses.

Zinc powder PTs0 (GOST 3640-94 [25], of Belovsky Plant, Russia), fine-dispersed, was used without further purification. The particles size 63–77 μm purity 99.9806%. Zinc powder was activated with 1,2-dibromomethane. Zinc wire ZN005115 (Goodfellow Corp.), d = 0.25 mm±1%, l = 100 mm±0.05%, 99.9915% purity) prior to the experiment was cleaned mechanically to remove oxide film, then kept for 10 s in nitric acid, washed with distilled water, acetone, and dimethylacetamide.

All organic compounds were obtained from commercial sources. Benzyl chloride, analytical grade (Reahim, Russia) was dried over $CaCl_2$ and distilled in a vacuum, bp 65–66°C (11 mm Hg) The literature data: bp. 66°C (11 mm Hg) [26]. *N,N*-Dimethylacetamide (Aldrich Chemicals, 98%) was dried over P_2O_5, boiled for 2 h over CaH_2, and distilled in a vacuum in a stream of nitrogen, bp 83.8–84.0°C (32 mm Hg), n_D^{20} 1,4307. The literature data: bp 84.0°C (32 mm Hg), n_D^{20} 1.4308 [26]. Toluene, tetrahydrofuran, benzene, acetonitrile, and other solvents were purified according to conventional techniques [27]. Benzyl chloride and all solvents were freed from dissolved gases by repeated freezing in liquid nitrogen and thawing under reduced pressure, and stored in ampules without air access.

(+)-*R*-1-Chloro-1-phenylethane was synthesized along the procedure in [28] by reacting (–)-*S*-1-phenylethanol with phosphoryl trichloride and pyridine in pentane. The compound obtained was freed from dissolved gases by repeated freezing and thawing under reduced pressure and stored in ampules without air access. Yield 75%, bp 80–81°C (17 mm Hg), α_D^{25} +94.1° (neat liquid, l = 1). Published: bp 78–82°C (17 mm Hg), α_D^{25} + 125.4° (neat liquid, l = 1, for 100% optical purity) [28]. ^{1}H NMR spectrum, δ, ppm: 1.68 d (3H, CH_3), 4.86 q (1H, CH), 7.14 m (5H, arom.). Mass spectrum (EI, 70 eV), m/z (I_{rel},%): 142 $[M]^+$ (6.4), 140 $[M]^+$ (19.2), 125 $[M - CH_3]^+$ (7.7), 105 $[M - Cl]^+$ (100), 79 $[M - Cl - C_2H_2]^+$ (11.5), 77 $[M - Cl–C_2H_4]^+$ (12.8).

(–)-*S*-1-phenyletanol was synthesized along the procedure in [29] by reacting acetophenone with (–)-*S*-BINAL-H in THF at –70°C. Yield 8.16 g (68%), bp 94–95°C (14 mm Hg), α_D^{25} –42˚ (neat, l = 1), 95% optical purity; published: bp 94–95°C (14 mm Hg), α_D^{25} –44.2˚ (neat, l = 1, 100% optical purity) [29]. ^{1}H NMR spectrum, δ, ppm: 1.68 d (3H, CH_3), 4.86 q (1H, CH), 7.14 m (5H, arom.). Mass spectrum (EI, 70 eV), m/z ($I_{rel.}$, %): 186 $[M]^+$ (0,6), 184 $[M]^+$ (0.6), 105 $[M - Br]^+$ (100), 91 $[M - CH_2Br]$ (7.7), 79 $[M - Br - C_2H_2]^+$ (11.5), 77 $[M - Br - C_2H_4]^+$ (14.1), 51 $[M - Br–C_3H_6]^+$ (12.8).

Synthesis of the coordination compounds of zinc [1]. To 1.7 g (26 mmol) of zinc powder was slowly added (1 drop every 5 s) a solution of 21.5 mmol of benzyl chloride in 11 ml of dimethylacetamide. The zinc powder was pre-activated with one drop of 1,2-dibromoethane by the known method [8]. The reaction was performed in an argon atmosphere at 0°C. The mixture was stirred for 2 h and then filtered. To the filtrate was added 50 ml of water-free benzene. The precipitated white crystals were filtered off on a glass filter, washed with hexane, and then evacuated. Yield of $[Zn(DMAA)_2Cl_2]$ 49.8%, mp 119–120°C. Published: mp 119–120°C [30]. IR spectrum (KBr), cm^{-1}: ν(C=O) 1620, 1603. Found, %: C 30.95, H 5.87, Cl 22.81, N 9.01, O 10.31, Zn 21.05. $C_8H_{18}Cl_2N_2O_2Zn$. Found, %: C 30.94, H 5.84, Cl 22.83, N 9.02, O 10.30, Zn 21.07.

By gas chromatography–mass spectrometry (EI, 70 eV) in the filtrate were found unreacted benzyl

chloride, dimethylacetamide and the reaction products: toluene, 1,2-diphenylethane and trace amounts of 4,4'-dimethylbiphenyl. The characteristics of the products are as follows.

Toluene, Mass-spectrum, *m/z* ($I_{rel.}$, %): 92.06 $[M]^+$ (71.8), 91 $[MH]^+$ (100), 90 $[M - 2H]^+$ (5.1), 65 $[M - C_2H_3]^+$ (12.8), 63 $[M - C_2H_4]^+$ (10.3). *M* 92.06.

1,2-Diphenylethane, Mass-spectrum, *m/z* ($I_{rel.}$, %): 182 $[M]^+$ (23), 91 $[M/2]^+$ (100). *M* 182.11.

4,4'-Dimethylbiphenyl, Mass-spectrum, *m/z* ($I_{rel.}$, %): 182 $[M]^+$ (100), 167 $[M - CH_3]^+$ (56), 152 $[M - 2CH_3]^+$ (15). *M* 182.11.

Investigation of the reaction of benzyl chloride with zinc in dimethylacetamide in the presence of radical trap was performed similar to the synthesis of the zinc coordination compounds. Dicyclohexyldeuterophosphine was used as the radical trap, molar ratio of zinc: dicyclohexyldeuterophosphine 1: 0–5.

After the precipitate separated in the ether–alcohol solution by gas chromatography–mass spectrometry α-deuterotoluene, toluene, and unreacted benzyl chloride were detected. The yields of organic reaction products are shown in Table 2.

α-Deuterotoluene. Yield 64%, 110°C (published bp 110.6°C [26]). ^{1}H NMR spectrum, δ, ppm: 2.32 m (2H, CH_2), 7.15 m (5H, arom.). Mass-spectrum (EI, 70 eV), *m/z* ($I_{rel.}$, %): 93 $[M]^+$ (100), 92 $[MH]^+$ (93), 91 $[MD]^+$ (46), 66 $[M - C_2H_3]$ (9), 65 $[M - C_2H_2D]$ (11). Found, %: C 90.29, H 7.53, D 2.18. C_7H_7D. Calculated, %: C 90.27, H 7.56, D 2.17.

Investigation of the process stereochemistry was carried out by the method similar to the synthesis of the zinc coordination compounds. As a benzyl halide (+)-*R*-1-chloro-1-phenylethane was used. After precipitation the following reaction products were detected in ether by gas chromatography–mass spectrometry: *RS,RS*-2,3-diphenylbutane, *RR,SS*-2,3-diphenylbutane, ethylbenzene, and styrene, as well as unreacted (+)-*R*-1-chloro-1-phenylethane and dimethylacetamide. All organic reaction products were isolated by preparative liquid chromatography, yields are shown in the scheme of the reaction of (+)-*R*-1-chloro-1-phenylethane with zinc. The physicochemical properties of isolated *RS,RS*-2,3-diphenylbutane, *RR,SS*-2,3-diphenylbutane, ethylbenzene and styrene correspond to the published data [26, 31].

Investigation of kinetics of the processes. The kinetics of the reaction of zinc with benzyl chloride in dimethylacetamide was studied by a resistometric method [18–20] in the atmosphere of anhydrous argon freed from oxygen. The stirring rate was 2500–2700 rpm. At the rotation rate 2000 rpm and higher the rate of zinc dissolution in the medium under study did not depend on the stirring rate, indicating that the studied process is in the kinetic regime.

As an indifferent solvent in determining the kinetic characteristics of the interaction of zinc with benzyl chloride in dimethylacetamide was used benzene [4].

ACKNOWLEDGMENTS

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REFERENCES

1. Egorov, A.M., *Doctorate (Chem.) Dissertation*, Tula, 2008.
2. Garst, J.F. and, Ungváry, F., in *Grignard Reagents: New Developments*, Chichester: John Wiley & Sons, 2000, ch. 7, p. 185.
3. Guijarro, A., Rosenberg, D.M., and Rieke, R.D., *J. Am. Chem. Soc*., 1999, vol. 121, no. 17, p. 4155.
4. Egorov, A.M., Matyukhova, S.A., Kocherova, I.S., Novikova, A.N., and Anisimov, A.V., *Zh. Obshch. Khim*., 2009, vol. 79, no. 3, p. 455.
5. Egorov, A.M., *J. Phys. Org. Chem*., 2006, vol. 19, no. 10, p. 664.
6. Egorov, A.M., Matyukhova, S.A., and Anisimov, A.V., *J. Phys. Org. Chem*., 2005, vol. 18, no. 10, p. 1023.
7. Sergeev, G.B., Smirnov, V.V., and Zagorskii, V.V., *Vestn. Mosk. Univ., Ser. 2: Khim*., 1980, vol. 21, no. 3, p. 257.
8. *Organozinc Reagents: A Practical Approach*, Knochel, P. and Jone, R., Eds., Oxford: Oxford Univ. Press, 1999.
9. Egorov, A.M. and Anisimov, A.V., *Appl. Organomet. Chem*., 1995, vol. 9, no. 2, p. 285.
10. Sergeev, G.B., Smirnov, V.V., and Zagorsky, V.V., *J. Organomet. Chem*., 1980, vol. 201, no. 1, p. 9.
11. Sergeev, G.B, Zagorsky, V.V., and Badaev, F.Z., *J. Organomet. Chem*., 1983, vol. 243, no. 2, p. 123.
12. Mendkovich, A.S. and Gul'tyai, V.P., *Teoreticheskie osnovy khimii organicheskikh anion-radikalov* (Fundamentals of the Chemistry of Organic Radical Anions), Moscow: Nauka, 1990.

13. Golubev, V.A., Sen', V.D., and Rozantsev, E.G., *Izv. Akad. Nauk SSSR, Ser. Khim*., 1979, no. 9, p. 2091.
14. Biere, R., Lemaire, H., and Rassat, A., *Bull. Soc. Chim. France*, 1965, no. 11, p. 3273.
15. Rozantsev, E.G. and Sholle, V.D., *Organicheskaya khimiya svobodnykh radikalov* (Organic Chemistry of Free Radicals), Moscow: Khimiya, 1979.
16. Brown, W.G. and McClure, D.E., *J. Org. Chem*., 1970, vol. 35, no. 6, p. 2036.
17. Bairamov, V.M., *Osnovy khimicheskoi kinetiki i kataliza* (Fundamentals of Chemical Kinetics and Catalysis), Moscow: Akademiya, 2003.
18. Egorov, A.M., Matyukhova, S.A., and Anisimov, A.V., *J. Phys. Org. Chem*., 2005, vol. 18, no. 5, p. 456.
19. Nifontova, G.A., Echmaev, S.B., Sikorenko, Yu.B., and Lavrent'ev, I.P., *Zh. Fiz. Khim*., 1998, vol. 72, no. 1, p. 147.
20. Sergeeva, V.P., Kondin, A.V., Alyasov, V.N., and Maslennikov, V.P., *Kinetika i Kataliz*, 1993, vol. 34, no. 4, p. 615.
21. Blackburn, E.V. and Tanner, D.D., *J. Am. Chem. Soc*., 1980, vol. 102, no. 2, p. 692.
22. Egorov, A.M., Matyukhova, S.A., and Anisimov, A.V., *Appl. Organometal. Chem*., 2005, vol., 19, no. 5, p. 605.
23. *Mezhgosudarstvennyi standart GOST 23957.1–2003*, Moscow: IPK Izd. Standartov, 2005.
24. Egorov, A.M., Matyukhova, S.A., Demidova, I.S., Platonov, V.V., and Proskuryakov, V.A., *Zh. Prikl. Khim.*, 2004, vol. 77, no. 8, p. 1346.
25. *Mezhgosudarstvennyi standart GOST 3640–94*, Moscow: IPK Izd. Standartov, 1996.
26. *Svoistva organicheskikh soedinenii. Spravochnik* (Properties of Organic Compounds. Handbook), Potekhin, A.A., Ed., Leningrad: Khimiya, 1984.
27. Gordon, A.J. and Ford, R.A., *The Chemist's Companion. A Handbook of Practical Data, Techniques and References*, New York: Wiley, 1972.
28. Burwell, R.L., Shields, A.D., and Hart, H., *J. Am. Chem. Soc*., 1954, vol. 76, no. 3, p. 908.
29. Giondo, G.M., Gregorio, F.D., Palladino, N., and Marconi, W., *Tetrahedron Lett*., 1973, no. 34, p. 3195.
30. Bull, W.E., Madan, S.K., and Willis , J.E., *Inorg. Chem*., 1963, vol. 2, no. 2, p. 303.
31. Cohen, H.L. and Wright, G.F., *J. Org. Chem*., 1953, vol. 18, no. 4, p. 432.