Kinetics and mechanism of the reaction of substituted benzyl chlorides with copper in dimethylformamide

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ABSTRACT: The reaction of copper metal with various substituted benzyl chlorides in dimethylformamide was studied. The kinetic and thermodynamic parameters of the reaction was clarified. Hammett plots of $\log(k/k^0)$ vs the substituent constant σ gave a good correlation ($\rho = 0.43$, $S_\rho = 0.05$, $r = 0.960$). The structure of the organic group has little effect on the rate of reaction of substituted benzyl chlorides with copper. In the absence of atmospheric oxygen, the oxidative dissolution of copper proceeded via a single-electron transfer mechanism with formation of 1,2-diphenylethanes and copper(I) complexes. The stereochemistry and intermediate compound were also studied. The reaction mechanism is discussed. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: substituted benzyl chlorides; dehalogenation; mechanism; ESR spectra; copper; kinetics; dimethylformamide; stereochemistry

INTRODUCTION

Ullmann chemistry along with copper-catalyzed cross-coupling[1,2] serves well for CN, CS, CO, CC and some other bond formation reactions.[3–5] Classical Ullmann coupling has proved to be of general synthetic utility for forming both symmetric and asymmetric biaryls. The reaction has been well studied and its mechanism has been investigated.[6] The mechanism of the reactions of copper metal with organic halides, which are characterized by low energies of cleavage of the carbon–halogen bond, remains obscure.

The present paper expands classical Ullmann coupling in the area of alkyl halides as initial reagents. The kinetics and mechanism of the reaction of copper with substituted benzyl chlorides in the presence of dimethylformamide (DMF) were studied in detail. This work provides sufficient evidence that excludes the occurrence of many transition states expected in the rate-limiting step of the reaction of substituted benzyl chlorides with copper.

EXPERIMENTAL

Equipment and analytical measurements

^{1}H NMR spectra were recorded on a Jeol LTD FX-90 Q spectrometer using 25–30% solutions in CDCl3. 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 a 'Carlo Erba 1100' equipment according to standard procedures.

ESR spectra were recorded at 77 K on a Radiopan radiospectrometer in films of copper co-condensates with benzyl chloride and DMF (1:50:50) according to the literature[7] at a frequency of 9 GHz without saturation and amplitude broadening.

Low-frequency IR spectra were measured on a Perkin-Elmer 325 spectrophotometer; the samples were prepared as suspensions in mineral (vaseline) oil.

The purity of the initial substances was monitored and the quantitative analysis of organic reaction products was carried out using gas chromatography (GC). The conditions of GC analysis have been described previously.[8]

The reaction products were isolated by preparative liquid chromatography (LC) on a Tsvet-304 chromatograph equipped with a UV detector (254 nm) using a steel column (250 × 4 mm i.d.); Silasorb 600 of particle size 15–25 µm) (Chemapol, Czech Republic) was used as the sorbent; hexane–diethyl ether (5:1) was used as the eluent.

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

Specific polarized light plane rotation was measured on an A-1 EPO automatic polarimeter ($\delta = 0.01°$).

Inorganic reaction products [Cu(I) and Cu(II) cations] were determined by ion chromatography on a Tsvet-3006 chromatograph by using Diacat-3 columns (150 × 3 mm i.d.) (Elsiko, Moscow, Russia). An aqueous 4 mM ethylenediamine, 5 mM citric acid and 5 mM tartaric acid solution was used as the eluent at a flow-rate of 15 ml min^{-1}. The sample volume was 100 μl (after 1:1000 dilution with water).

Reagents

Copper powder of >99.99% purity was prepared by the reduction of CuSO$_4$ (analytical grade) with magnesium powder (MP-1, Khlorvinil, Ukraine) in oxygen-free argon.

A copper wire covered with a varnish film (GOST 7262-54, Russia; Cu content 99.99%) 0.2 mm in diameter was held in DMF for 24 h. Just before the experiment, the sample was mechanically purified to remove the swollen insulating film, exposed to concentrated nitric acid for 5–10 s and washed with water, acetone and DMF. The entire operation was carried out in oxygen-free argon.

All organic compounds were obtained commercially. The purity of commercial samples (Aldrich Chemical) of benzyl chloride, 3-methylbenzyl chloride, 4-methylbenzyl chloride, 3-methoxybenzyl chloride, 4-fluorobenzyl chloride, 3-fluorobenzyl chloride, 3-chlorobenzyl chloride, 4-methoxybenzyl chloride and 4-chlorobenzyl chloride was checked by GC. Compounds which contained toluene or were <99% pure were purified by low-temperature fractional recrystallization or by fractional distillation in the case of liquids or by recrystallization from ethanol in the case of solids.

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. Yield 76%; b.p. 80–81 °C/17 mmHg, $[\alpha]_D^{25}$ +94.1° ($l = 1$). Lit. data: b.p. 78–82 °C/17 mmHg, $[\alpha]_D^{25}$ +125.4° ($l = 1$, 100%).[9] ^{1}H NMR (CDCl$_3$): δ1.68 (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 the literature.[10,11] Yield 55%; b.p. 94–95 °C/14 mmHg, $[\alpha]_D^{25}$ −37.65° ($l = 1$). Lit. data: b.p. 94–95 °C/14 mmHg, $[\alpha]_D^{25}$ −44.2° ($l = 1$).[11] ^{1}H NMR (CDCl$_3$): δ 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 Chemical, 98%) with NaCl in the presence of DCl (37% solution in D$_2$O; Aldrich Chemical).

3-Methylpyridine (Janssen) was dried with fused KOH and distilled twice over KOH in an inert gas atmosphere; b.p. 143.7–144 °C; $n_D^{20} = 1.5067$ (lit.[12] b.p. 144.0 °C; $n_D^{20} = 1.5068$).

All solvents were purified according to standard procedures.[13] They 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 chloride with copper; general procedure

A 1 g portion of Cu powder was dissolved in 10 ml of DMF and 5 ml of benzyl chloride in an argon atmosphere at 70 °C. After 5 h, the white precipitate formed (which rapidly became green in air) was filtered off in an atmosphere of oxygen-free argon. Recrystallization from 3-MePy yielded 4.90 g (83%) of yellow crystals of tris-3-methylpyridine copper(I) chloride [Cu(3-MePy)$_3$Cl], which were stable in air.[14] Analysis: C$_{18}$H$_{21}$N$_3$CuCl calculated, Cu 16.49, Cl 9.37, C 57.14, H 5.59, N 11.10; found, Cu 16.50, Cl 9.32, C 56.88, H 5.68, N 11.06%. IR (mineral oil), $\nu = 475$ (m, Cu–N), 420 (w, Cu–N), 350 (s, Cu–N), 320 (s, Cu–Cl), 292 (s, Cu–Cl), 230 (vs Cu–N) cm^{-1}.

Organic products of reaction were extracted with diethyl ether (20 ml). The residues of benzyl chloride and DMF, and also 1,2-diphenylethane and 4,4′-dimethylbiphenyl, were detected in the ether solution. The isolated yield of 1,2-diphenylethane was 1.37 g (96%); m.p. 51–52 °C (lit.[15] 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 182 [M]$^+$ (23), 91 [M/2]$^+$ (100).

4,4′-Dimethylbiphenyl, MS (EI, 70 eV): calculated m/z 182.11 (M), found 182 [M]$^+$ (100), 167 [M−CH$_3$]$^+$ (56), 152 [M−2CH$_3$]$^+$ (15).

Study of the reaction kinetics

The reactions of copper with nine benzyl chlorides in DMF were studied by the resistometric method[16] according to the published procedure[17] in an atmosphere of water-free argon freed from oxygen. The reaction kinetics were studied by monitoring the electrical resistance of species during experiments. Species were copper wire (diameter 0.2 mm and length 100 mm). Consequently, an increase in 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 was carried out at initial $C_{RCl} = 0.5$ mol l^{-1} with
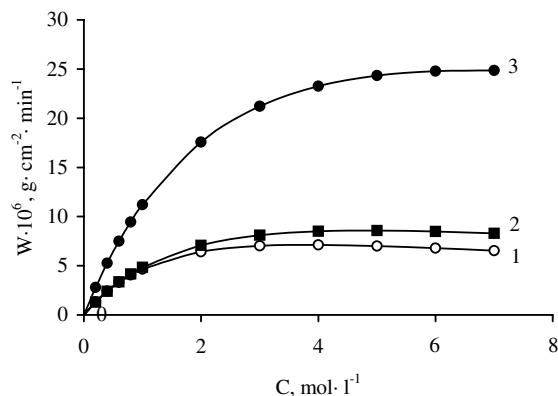
Figure 1. Reaction rate (w) as a function of initial concentrations (C) of mixture components in benzene at 353 K. Curve 1: w dependence on C_{DMF}, $C_{RCl} = 0.5$ mol l^{-1} (the initial C_{DMF} ranged from 0 to 7 mol l^{-1}, at constant initial C_{RCl}). Curve 2: w dependence on C_{RCl}, $C_{DMF} = 0.5$ mol l^{-1} (the initial C_{RCl} ranged from 0 to 7 mol l^{-1}, at constant C_{DMF}). Curve 3: w dependence on C_{RCl}, $C_{DMF} = 2$ mol l^{-1} (the initial C_{RCl} ranged from 0 to 7 mol l^{-1}, at constant initial C_{DMF})

initial C_{DMF} varied 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} with initial C_{RCl} varied from 0.2 to 7 mol l^{-1} (Fig. 1, curve 2). We performed the third series at initial $C_{DMF} = 2$ mol l^{-1} with initial C_{RCl} varied from 0.2 to 7 mol l^{-1} (Fig. 1, curve 3).

Benzene was used as a neutral solvent for the determination of the kinetic characteristics of the reaction of copper 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 copper dissolution in the test media from the rate of stirring.

Reaction of copper with benzyl chloride and DMF at low temperature

Co-condensation of copper with benzyl chloride and DMF.
Studies of the low-temperature reaction of copper with benzyl chloride were carried out in a vacuum apparatus similar to that reported previously.[19] The reagents were evaporated in an evacuated (10^{-4} mmHg) reactor (10 l) and condensed on the surface cooled with liquid N_2. Copper vapor was prepared by evaporating the purified metal from a corundum crucible at 1400–1440 K.[20] The rate of evaporation of Cu was 0.2 mmol min^{-1}. Benzyl chloride and DMF were evaporated at 273–308 K (DMF:PhCH$_2$Cl:Cu = 0–10:10:1). The duration of co-condensation was 2–4 h.

Acidolysis of reaction products at 160 K.
After completion of co-condensation of copper with benzyl chloride and DMF, the samples were heated to 160 K, kept at this temperature for 20 min and then cooled to 77 K. DCl (50 g) condensed on their surfaces. Evacuation was then terminated and the reactor was filled with dry,

pure Ar (760 mmHg). 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 mmHg). The reaction mixtures were heated to 298 K. Reaction products were isolated by preparative LC.

Acidolysis of reaction products at 298 K.
Once co-condensation of copper with benzyl chloride and DMF was completed, evacuation was terminated and the reactor was filled with dry, pure Ar (760 mmHg). The samples were heated to 298 K. At this temperature the film melted and decolorized. The reaction mixtures were treated with a 1% solution of DCl in D_2O (99.5 at.% D, Aldrich Chemical) at 298 K in pure, dry Ar. The liquid phase was analyzed by GC. The reaction products were isolated by preparative LC.

Stereochemistry

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

The reaction products were as follows.

(+)-(S)-1-Phenylethane-1D (**1**). B.p. 135–136 °C, $n_D^{20} = 1.4954$, $[\alpha]_D^{20}$ +0.05 ($l = 0.1$). ^{1}H NMR (CDCl$_3$): δ 1.23 (d, 3H, CH$_3$), 2.62 (q, 1H, CH), 7.20 (m, 5H, Ph.) ppm. Lit. data: b.p. 135–136 °C, $n_D^{20} = 1.4919$,[21] $[\alpha]_D^{20}$ +0.81 ($l = 0.1$).[22]

Mixture of (RS)-1-phenylethane-1D and phenylethane (**1** and **4**), 1:1. ^{1}H NMR (CDCl$_3$): δ 1.20 (d, 3H, CH$_3$) 50%, 1.24 (t, 3H, CH$_3$) 50%, 2.62 (q, 1H, CH) 50%, 2.66 (m, 2H, CH$_2$) 50%, 7.19 (m, 5H, Ph.) ppm.

(RR,SS)-2,3-Diphenylbutane (**2**). B.p. 130–132 °C/7 mmHg, $n_D^{20} = 1.5557$. ^{1}H NMR (CDCl$_3$): $\delta = 1.17$ (d, 6H, 2CH$_3$), 2.76 (m, 2H, CHCH), 7.24 (m, 10H, 2Ph.) ppm. Lit. data: b.p. 130–132 °C/7 mmHg,[21] $n_D^{20} = 1.5557$.[22]

(RS,RS)-2,3-Diphenylbutane (**3**). B.p. 144–149 °C/12 mmHg, m.p. 126–127 °C. ^{1}H NMR (CDCl$_3$): δ 1.03 (d, 6H, 2CH$_3$), 2.75 (m, 2H, CHCH), 7.24 (m, 10H, 2Ph) ppm. Lit. data: b.p. 144–149 °C/12 mmHg,[21] m.p. 126–127 °C.[22]

Identification of radical species in solution

The reaction in the presence of a radical trap was studied similarly to the general procedure. Dicyclohexyldeuterophosphine (DCPD) was used as the radical trap.[23]

The residues of benzyl chloride and DMF, and also 1,2-diphenylethane and α-deuterotoluene, were detected in the diethyl ether solutions. Summarizes the yields of organic reaction products.

α-Deuterotoluene, ^{1}H NMR (CDCl$_3$): δ 2.32 (m, 2H, CH$_2$), 7.15 (m, 5H, Ph.) ppm. MS (EI, 70 eV): calculated m/z 93.07 (M); found 93 [M]$^+$ (100), 92 [M$-$H]$^+$ (93), 91 [M$-$D]$^+$ (46), 66 [M$-$H$-$C$_2$H$_2$]$^+$ (9), 65 [M$-$C$_2$H$_2$D]$^+$ (11).
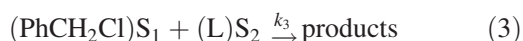
RESULTS AND DISCUSSION

Kinetic studies

The reaction kinetics of the oxidative dissolution of Cu in the benzyl chloride–DMF system was 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.[18,24]

To determine the kinetic characteristics of the process, the reaction was performed in a neutral solvent, benzene ($DN_{SbCl_5} = 0.42 \, \text{kJ mol}^{-1}$).[19]

Figure 1 shows the kinetic curves with maxima. An increase in the concentration of DMF from 0.5 to 2 mol l^{-1} did not change the shape of the curves, indicating the dependence of the reaction rate on the concentration of benzyl chloride. This indicates that the process proceeds by the Langmuir–Hinshelwood mechanism with adsorption of the reagent and solvent at identical active centers of the metal surface.[25]

$$PhCH_1Cl + S \underset{}{\overset{K_1}{\rightleftharpoons}} (PhCH_2Cl)S \tag{1}$$

$$L + S \underset{}{\overset{K_2}{\rightleftharpoons}} (L)S \tag{2}$$

$$(PhCH_2Cl)S_1 + (L)S_2 \overset{k_3}{\rightarrow} products \tag{3}$$

where L is DMF, K_1 and K_2 are the equilibrium constants of benzyl chloride and DMF adsorption, respectively, k_3 is the rate constant of the chemical process and S is the active center 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 an expression for the reaction rate (w) is given as

$$w = \frac{kK_1K_2[\text{PhCH}_2\text{Br}][\text{DMF}]}{\left(1 + K_1[\text{PhCH}_2\text{Br}] + K_2[\text{DMF}]\right)^2} \tag{4}$$

where $k = k_3N^2$ and N is the number of active centers of the metal surface at which the adsorption of benzyl chloride and DMF takes place.

The analysis of the experimental relations (Fig. 1) using Eqns (1)–(3) allowed the determination of the equilibrium constants of benzyl chloride and DMF adsorption on the surface of copper (K_1 and K_2, respectively) and the rate constant k of the chemical reaction. The study of the reaction kinetics at different temperatures provided E_A for the chemical reaction and the enthalpies and entropies of adsorption of the reactants on the copper surface. Table 1 summarizes the results.

Comparison of the results with previously published data[21] on the oxidative dissolution of copper in the I$_2$–DMF system showed that $\Delta H_{\text{ads DMF}}$ at the surface of copper remained almost unchanged ($-27.1 \pm 1.7 \, \text{kJ mol}^{-1}$) when I$_2$ is substituted for PhCH$_2$Cl, whereas the corresponding values for an organic halide changed considerably (from -70 ± 8 to $-24.6 \pm 1.5 \, \text{kJ mol}^{-1}$). This indicates the selective adsorption of a dipolar aprotic solvent, which participates in the reaction, on the surface of copper.

Nechaev's group have shown that the adsorption of organic compounds on a metal surface depends on their ionization potential only.[26–29] PhCH$_2$Cl and DMF have similar ionization potentials and this is why they have similar ΔH_{ads} values.

The Langmuir–Hinshelwood scheme for the test process suggests that the interaction of adsorbed reactant

Table 1. Kinetic and thermodynamic parameters of the oxidative dissolution of copper in the benzyl chloride–DMF system calculated using the Langmuir–Hinshelwood mechanism from the adsorption of the reagent and the solvent at identical active centers of the metal

Parameter		$k \times 10^5$ (g cm^{-2} min^{-1})	K_1 (l mol^{-1})	K_2 (l mol^{-1})
T, K	313	0.60 ± 0.02	0.701 ± 0.021	0.943 ± 0.028
	318	1.10 ± 0.03	0.598 ± 0.018	0.792 ± 0.024
	323	1.90 ± 0.06	0.527 ± 0.016	0.662 ± 0.020
	333	5.3 ± 0.2	0.409 ± 0.012	0.517 ± 0.016
	343	11.4 ± 0.3	0.315 ± 0.009	0.366 ± 0.011
	353	27.1 ± 0.8	0.235 ± 0.007	0.290 ± 0.009
r^a		0,999	0,998	0,998
E_A (kJ mol^{-1})		86.6 ± 5.1		
$\Delta H^\circ_{\text{RCl}}$ (kJ mol^{-1})			-24.6 ± 1.5	
$\Delta H^\circ_{\text{DMF}}$ (kJ mol^{-1})				-27.1 ± 1.7
$\Delta S^\circ_{\text{RCl}}$ (J mol^{-1} K^{-1})			-81.2 ± 5.2	
$\Delta S^\circ_{\text{DMF}}$ (J mol^{-1} K^{-1})				-86.8 ± 5.6

^{a} Sample correlation coefficient.

Table 2. Relative reactivities of substituted benzyl chlorides towards copper in DMF at 80 °C

Substituent	$k \times 10^4$	σ^{30a}	k/k^{0a}
m-Cl	3.93 ± 0.11	0.37	1.45
m-F	3.63 ± 0.10	0.34	1.34
p-Cl	3.87 ± 0.11	0.23	1.43
m-OMe	2.92 ± 0.08	0.12	1.08
p-F	3.14 ± 0.08	0.06	1.16
H	2.71 ± 0.08	0	1
m-Me	2.63 ± 0.08	−0.07	0.97
p-Me	2.46 ± 0.07	−0.17	0.91
p-OMe	2.01 ± 0.06	−0.27	0.74

[a] σ is the Hammett substituent constant and k^0 is the rate constant for reaction of copper with unsubstituted benzyl chloride in DMF.

molecules with the metal surface, viz. a surface chemical reaction, is a rate-limiting step of the reaction.

Relative reactivities of nine substituted benzyl chlorides were obtained from the kinetic experiments, as shown in Table 2.

In Fig. 2, the logarithms of the relative rates are plotted against Hammett σ constants, and a linear relationship ($\rho = 0.43$, $r = 0.960$, $S_\rho = 0.05$) is observed. The Hammett ρ value obtained here is, however, considerably lower than the values associated with ionic reactions. The structure of organic group has little effect on the rate of reaction of substituted benzyl chlorides with copper and the differences between rate constants are very small. This indicates that the polar effect on the abstraction of chlorine atom is much smaller than in ionic reactions, although this polar effect is the crucial factor in determining the relative reactivities.

The Hammett parameters, however are similar to those reported by Blackburn and Tanner[30] ($\rho = 0.40$, $r = 0.92$, $S_\rho = 0.05$) for the reaction of tributyltin radical and benzyl chloride in benzene (Fig. 3). The abstraction of a chlorine atom from a benzyl chloride by a metal surface is probably as easy as that by a tributyltin radical. By comparison, the abstraction of a chlorine atom from substituted benzyl chlorides by a triethylgermyl radical has $\rho = 0.312$.[31]

Positive ρ values have also been obtained from kinetic studies of a number of alkyl radicals, generated in the presence of a series of substituted toluenes.[32–38]
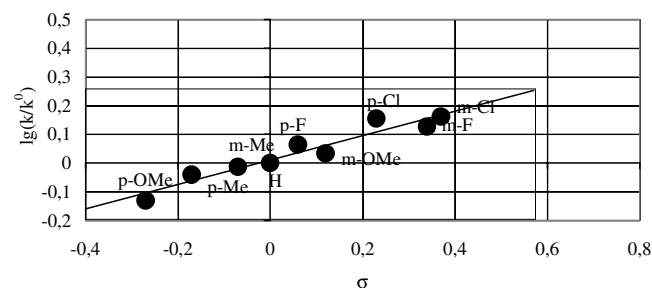
Figure 2. Hammett plot of log(k/k^0) vs substituent constant σ
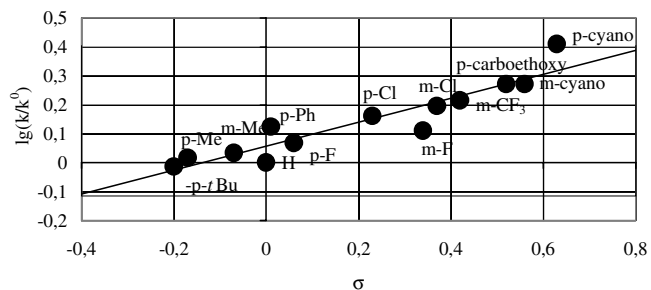
Figure 3. Hammett plot of log(k/k^0) vs substituent constant σ obtained for reaction of tributyltin radical with benzyl chlorides[30]
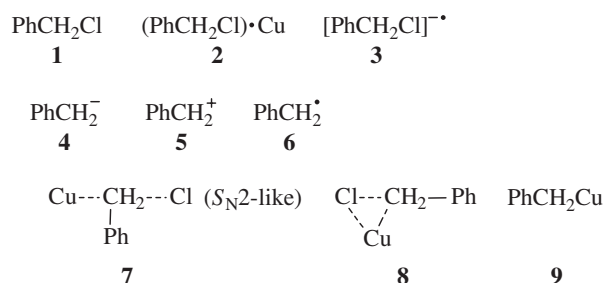
Polarographic reductions of organic halides are well known to be irreversible[39,40] and the overall two-electron transfer process leads to a carbanion, which is subsequently protonated:

$$RHal + e^- \rightarrow RHal^{-\cdot}$$

$$RHal^{-\cdot} \rightarrow R^\cdot + Hal^-$$

$$R^\cdot + e^- \rightarrow R^-$$
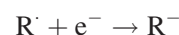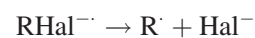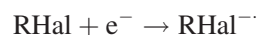
Decomposition of the radical anion is very fast or even concerted in combination with electron transfer.

The ρ values calculated from the least-squares slopes of the $\Delta E_{1/2}$ vs σ^- plots were 0.5 and 0.8 for the series of benzyl bromides and chlorides, respectively chlorides ($r = 0.93$, $S_\rho = 0.10$; $r = 0.96$, $S_\rho = 0.04$). The correlation with σ substituent constants gave no correlation ($r = 0.77$, $S_\rho = 0.28$; $r = 0.78$, $S_\rho = 0.14$).[40]

To determine the rate-limiting step, nine possible limiting transition states were considered for the organic moiety summarized by structures **1–9**.[41] Here Cu represents a copper atom of a copper metal surface.

PhCH$_2$Cl   (PhCH$_2$Cl)·Cu   [PhCH$_2$Cl]$^{-\cdot}$
1   **2**   **3**

PhCH$_2^-$ PhCH$_2^+$ PhCH$_2^\cdot$
4   **5**   **6**

Cu···CH$_2$···Cl (S_N2-like)   Cl···CH$_2$—Ph   PhCH$_2$Cu
| Cu
Ph

7   **8**   **9**

Since ρ has a significantly positive value, the transition state does not resemble the starting material, and **1** can be discarded. The magnitude of ρ seems too large to be compatible with physisorption, **2**. The sign of ρ is also incompatible with an intermediate benzyl cation, **5**. Since the largest ρ values observed are similar to those for tin hydride reduction, and considerably smaller than that estimated for reactions generating benzyl anions ($\rho = 2.8$),[40] the magnitude of ρ seems to be too small for a fully formed benzyl anion, **4**. A rate-determining

step involving an intermediate (**9**) in which the carbon–copper bond is partially or fully formed is unlikely, both because this transition state bears a large negative charge on carbon and would be expected to show a large value of ρ and because the cleavage of the carbon–chlorine bond appears to be irreversible.
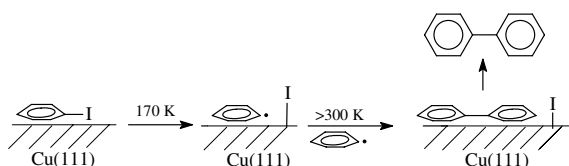
It is more difficult to differentiate between reactions leading to the three remaining limiting structures, i.e. electron transfer from copper to benzyl chloride generating the radical anion **3**, chlorine abstraction by copper forming benzyl radical **6** and insertion of copper directly into the carbon–chlorine bond of the adsorbed benzyl chloride, **7**, on the basis of the available evidence.

Xi and Bent have shown that the reaction of iodobenzene with copper occurs on a metal surface.[6,42] Adsorbed iodobenzene dissociates on Cu(111) to form iodine atoms and adsorbed phenyl radicals. The authors suggested two pathways for the reaction mechanism. The first is a low-coverage, high-temperature pathway with formation of adsorbed and subsequently coupled phenyl groups (Scheme 1).[6,42]
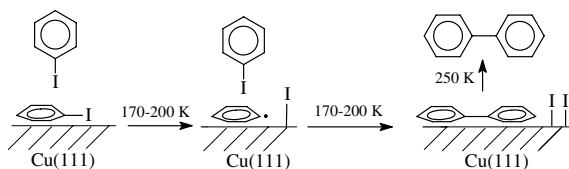
A high-coverage, low-temperature coupling reaction occurs between adsorbed phenyl radicals and molecular iodobenzene (Scheme 2).[42]

The reaction of organic halides with copper is more complex in the presence of a dipolar aprotic solvent (Scheme 3).
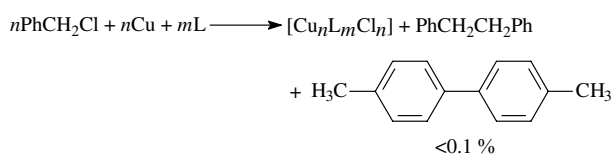
Copper salts are known to effect homocoupling of iodo derivatives. In fact, owing to the accessibility of four oxidation states from 0 to 3+ for copper, this metal can play several roles in homocoupling processes, and no external reducing or oxidizing agent is needed.[1] Analysis of reaction mixture by ion chromatography demonstrated that the samples contained Cu^+ but not Cu^{2+} and Cu^{3+} cations. The molar ratio of $[Cu_nL_mCl_n]$ and 1,2-diphenylethane agrees well with Scheme 3.

The formation of 1,2-diphenylethane and 4,4′-dimethylbiphenyl and the absence of 4-benzyl-1-methylbenzene among the reaction products indicate that the reaction proceeds according to the radical mechanism. In this case, isomerization of benzyl radical occurs only in the radical pair.[43]

It is well known that ESR is the most reliable evidence for the existence of paramagnetic particles as intermediates in many reactions and is one of the most convenient methods for their detection.

Our study showed that the ESR spectrum of the co-condensate of copper with benzyl chloride and DMF (1:50:50) at 77 K is a triplet of quartets with full width about 50 G and a g-factor of 2.002 ± 0.001, $a_{CH_2}^H$ of 16.4 ± 0.8 G, a_o^H of 5.5 ± 0.5 G and a_p^H of 5.5 ± 0.5 G. A comparison shows that the ESR spectrum of co-condensates of copper with benzyl chloride and DMF coincides with that of the benzyl radical.[8,43,44]

When the excess of benzyl chloride and DMF (1:1) is condensed on the compact copper film (the thickness of the film is about 10^{-4} mm), the losses of UHF power in the sample increase owing to increased electroconductivity, which considerably deteriorates the resolution of the ESR spectra. Paramagnetic species that appeared in benzyl chloride-DMF–atomic Cu systems did not differ from those produced when the compact copper film was formed.

Dicyclohexyldeuterophosphine (DCPD) provides an opportunity not only for detecting radical intermediates but also for determining their concentration in solution.[23]

In the dehalogenation of benzyl chloride with copper in DMF in the presence of DCPD, the composition of the reaction products changed depending on the copper:DCPD molar ratio (Table 3). With a copper:DCPD molar ratio of 1:5, the formation of 1,2-diphenylethane was not observed (Table 3), but an equivalent amount of α-deuterotoluene was detected instead (Scheme 4).

Scheme 1

Scheme 2

Scheme 3

Table 3. Product composition in the oxidative dissolution of copper in benzyl chloride–DMF systems in the presence (and absence) of radical traps

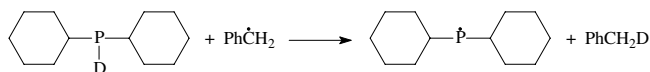| DCPD[a]: Cu (mol/mol)	Yield (mol%)	
	PhCH₂D[b]	PhCH₂CH₂Ph[c]
0	0	100
1	63	37
2	78	22
5	100	0

[a] Impurity of dicyclohexylphospine 1%.
[b] Impurity of toluene 1%.
[c] Impurity of 4,4′-dimethylbiphenyl <0.1%.

Scheme 4

Scheme 5

where $L = DMF$.

Analysis of the reaction products in the presence or absence of radical traps indicates that the process occurs by a radical mechanism via mainly formation of benzyl radical (Scheme 5).

The results of this work indicate that the dehalogenation process occurs at the surface of copper by a radical mechanism via formation of benzyl radicals. Recombination and isomerization of the benzyl radicals can proceed both on a copper surface (A-model) and in solution (D-model). The ratio between these processes depends on the ionization potential of the reagents and free radicals.[29]

At temperatures above 273 K, benzyl cuprates are known to be thermally unstable, giving the corresponding homo-coupled products in a significant yield.[45] At lower temperatures, these organocopper compounds have greater stability but react quickly with benzyl chloride with formation of corresponding coupled products.[45]

The low melting-point of DCl made it possible to detect the reaction products both before (159 K) and after (298 K) by defrosting of the sample and to observe organocopper compounds, unstable at 298 K, reacting with DCl according to the reaction:

$$PhCH_2Cu_n + DCl \rightarrow PhCH_2D + CuCl + Cu_{n-1}$$

Hence any organocopper present at the time of the quenching appears as reduced product, α-deuterotoluene. The compositions of the reaction products produced by acidolysis of organocopper compounds obtained by co-condensation of copper with benzyl chloride are given in Table 4.

As illustrated in Table 4, DMF stabilizes organocopper compounds and increases their amount. The slight stabilization of organocopper compounds takes place only at low temperatures. At 298 K the solvent does not exert any marked influence on the acidolysis products. The results obtained made it possible to conclude that a coordinating solvent stabilizes the formation of organocopper compounds. This conclusion agrees well with previous data.[45]

We studied the reaction of optically active $(+)$-(R)-1-chloro-1-phenylethane with copper in DMF, hoping to obtain experimental evidence for optical activity retention at the asymmetry center in the course of the formation of organocopper compounds. The main cause of

Table 4. Composition of reaction products obtained by acidolysis of the reaction mixtures

Cu:PhCH₂Cl:DMF	T (K)	Yield (%)	
		$PhCH_2CH_2Ph^a$	$PhCH_2D^b$
1:10:0	160[c]	97	3
1:10:0	298[d]	99	1
1:10:5	160[c]	92	8
1:10:5	298[d]	97	3
1:10:10	160[c]	90	10
1:10:10	298[d]	97	3

[a] Impurity of 4,4′-dimethylbiphenyl <0.1%.
[b] Impurity of toluene 1%.
[c] Gaseous DCl, condensation under vacuum conditions.
[d] 1% solution of DCl in D₂O in pure, dry Ar.

racemization of organocopper compounds is the stereochemical instability of the C—Cu bond which can arise just after the formation of organocopper. The configuration of organocopper reagents has to be fixed at the moment of their formation. This can be achieved by carrying out this reaction in the presence of deuterium chloride, which reacts very rapidly with organocopper compounds.

The co-condensation of copper vapor with $(+)$-(R)-1-chloro-1-phenylethane and DMF (1:10:10), which were precipitated in the molecular beam mode on the surface cooled with liquid N₂, produced white films. After thawing (273 K) and treatment of the samples with DCl, the optically inactive 1-phenylethane-1D (**10**) and four other unlabelled hydrocarbons, **11–14**, were detected in the reaction mixtures (Scheme 6).

It is well known that recombination of optically active 1-phenylethyl radicals proceeds within a solvent cage 15 times slower than inversion and leads to partial retention of configuration in the recombination products.[46]

The formation of optically inactive **11** and **12** with an **11**:**12** ratio of 1.03:1 along with **13** and **14** shows that the reaction occurs according to the radical mechanism and recombination and disproportination of 1-phenylethyl radical can proceed after they enter the solution.

The formation of racemic 1-phenylethane-1-D in the course of the reaction of $(+)$-(R)-1-chloro-1-phenylethane with copper strongly supports this theory. It can proceed by radical pair recombination at a lower rate than that of 1-phenylethyl radical inversion on the copper surface within the solvent cage.

Condensation of DCl at 77 K on the surface of the samples, which were prepared by heating co-condensates of copper with $(+)$-(R)-1-chloro-1-phenylethane and
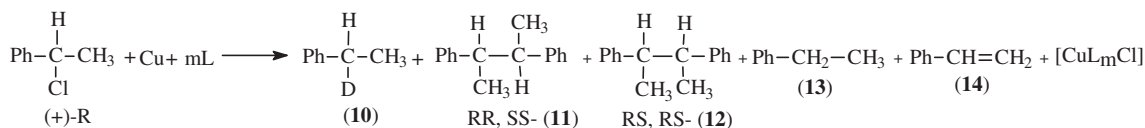
Scheme 6

Table 5. Yields of products **10–14** and stereochemistry of the reaction under investigation

No.	Yield (%)				
	10	**11**	**12**	**13**	**14**
1[a]	12	44.14	42.86	1	—
2[b]	3	46.17	44.83	3	3

[a] Acidolysis was carried out at 160 K.
[b] Acidolysis was carried out at 298 K.

DMF, produced white films. On completion of the DCl condensation, the samples were heated to 160 K (at this temperature films melted and were decolorized), kept at this temperature for 20 min and then heated to 298 K.

The compositions of the reaction products produced by acidolysis of the samples are given in Table 5.

The optical purity of 1-phenylethane-1D ($6 \pm 1\%$) does not exceed that for 1-phenylethane recombination within a solvent cage.

The results obtained suggest that the limiting step in the course of the reaction of $(+)$-(R)-1-chloro-1-phenyl-lethane with copper is a dissociative electron transfer to a copper surface.

CONCLUSIONS

The results of this work indicate that the dehalogenation process occurs at the surface of copper by a radical mechanism via formation of benzyl radicals, which undergo recombination and isomerization mainly in solution. The reaction occurs via a Langmuir–Hinshelwood mechanism (adsorption of reagent and solvent takes place at identical active centers of the metal surface) according to Scheme 7.

The limiting step of the reaction of benzyl chlorides with copper is a dissociative electron transfer to a metal surface. The yield of organocopper compounds depends on reaction conditions. It has been mentioned already that at temperatures above 273 K benzyl cuprates decompose as follows:[45]

$$PhCH_2Cu \rightarrow Ph\dot{C}H_2 + Cu$$
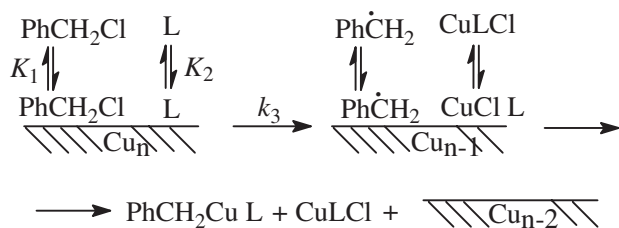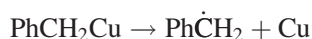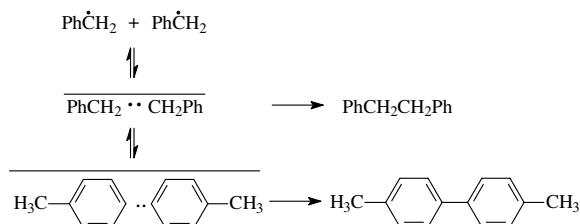
Scheme 7

At lower temperatures these organocopper compounds have higher stability but react quickly with benzyl chloride:[47]

$$PhCH_2Cu + PhCH_2Cl \rightarrow PhCH_2CH_2Ph + CuCl$$
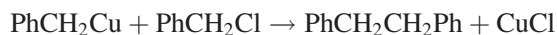
Recombination and isomerization of benzyl radicals proceed mainly in solution according to Scheme 8 (for X = H).

Scheme 8

The coordination compounds of copper(I) with organic ligands in solutions form di- or tetramers:[48]

$$CuLCl + Cu_{n-1}L_{n-1}Cl_{n-1} \longrightarrow Cu_nL_nCl_n$$
$$Cu_nL_nCl_n + (n-m)L \longrightarrow [Cu_nL_mCl_n] \downarrow$$
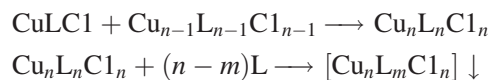
where L = DMF; $2 \leq n \leq 4$; $2 \leq m \leq 4$.

Acknowledgement

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