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

Anatoly M. Egorov[1], **Svetlana A. Matyukhova**[2] **and Alexander V. Anisimov**[2]*

[1]Tula State University, 92 Prospekt Lenina, 300600 Tula, Russia
[2]Department of Chemistry, Moscow State University, 1 Leninskie Gory, 119899 Moscow, Russia

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The reaction of copper metal with various substituted benzyl bromides in dimethylformamide has been studied and the kinetic and thermodynamic parameters of the reaction have been obtained. Hammett plots of $\log(k/k^\circ)$ vs the substituent constant σ gave good correlations ($\rho = 0.24$, $S_\rho = 0.03$, $r = 0.951$). The structure of the organic group has little effect on the rate of reaction of substituted benzyl bromides with copper. In the absence of atmospheric oxygen, oxidative dissolution of copper occurred by the mechanism of single-electron transfer with the formation of 1,2-diphenylethanes and copper(I) complexes. The stereochemistry and intermediate compound were also studied and the reaction mechanism is discussed. Copyright © 2005 John Wiley & Sons, Ltd.

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

INTRODUCTION

The coordination compounds of copper are in considerable industrial use as selective catalysts in various chemical processes. The direct oxidative dissolution of copper metal in systems containing carbon tetrachloride and dipolar aprotic solvent, which occurs under mild conditions, is one of the methods for the synthesis of these compounds.[1] However, carbon tetrachloride is toxic. Being a destroyer of ozone, carbon tetrachloride generally is prohibited for use in the chemical industry and this is why substitutes are being sought.

For elaboration of optimal conditions for the target-oriented synthesis of coordination compounds of copper halides with organic ligands, the kinetics and mechanism of the reaction of copper with substituted benzyl bromides in the presence of dimethylformamide (DMF) were studied in detail. This work provides sufficient evidence to exclude many of the transition states conceivable for the rate-limiting step for reaction of substituted benzyl bromides 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 $CDCl_3$. Chemical shifts are given in ppm relative to tetramethylsilane as internal standard. The accuracy of chemical shifts was ±0.01 ppm.

The electron spin resonance (ESR) spectra were recorded at 77 K on a Radiopan radiospectrometer in films of copper co-condensates with benzyl bromide and DMF (1 : 50 : 50) according to the literature[2] at 9 GHz frequency in the absence of saturation and amplitude broadening.

The low-frequency infrared spectra were measured on a Perkin-Elmer 325 spectrophotometer; the samples were prepared as suspensions in mineral (Vaseline) oil.

The purity of the starting substances was monitored and quantitative analysis of the organic reaction products was performed using gas chromatography. The conditions of for gas chromatographic analysis were described previously.[3]

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

Organic reaction products were analyzed on a Hewlett-Packard gas chromatography–mass spectrometry instrument

*Correspondence to: Alexander V. Anisimov, Department of Chemistry, Moscow State University, 1 Leninskie Gory, 119899 Moscow, Russia.
E-mail: silver_sun@inbox.ru
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(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 and the heating rate was 30 °C min^{-1}. Helium was the 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.

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 with the use of 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 eluent and the rate of elution was 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 an atmosphere of argon free of oxygen.

A copper wire covered with varnish film (GOST 7262-54 Russia, Cu content of 99.99%) 0.05 mm in diameter was held in DMF for 24 h. Just before the experiment, the sample was purified mechanically to remove the swollen insulating film, exposed to concentrated nitric acid for 5–10 s and washed with water, acetone and then DMF. All operations were carried out in an atmosphere of argon free of oxygen.

All organic compounds were obtained from commercial sources. The purity of the commercial samples (Aldrich Chemicals Co. Ltd) of benzyl bromide, 3-methylbenzyl bromide, 4-methylbenzyl bromide, 3-methoxybenzyl bromide, 4-fluorobenzyl bromide, 3-fluorobenzyl bromide and 3-chlorobenzyl bromide was checked by gas chromatography. Compounds that contained toluene or were <99% purity 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.

4-Methoxybenzyl bromide and 4-chlorobenzyl bromide were prepared according to the literature.[4] The purities of the products were checked by elemental analysis and comparison of physical properties with those reported in the literature.[4]

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. Yield 74%, b.p. = 86–87 °C/11 mmHg, $[\alpha]_D^{25} + 94.0°$ ($l = 1$). Lit. data: b.p. = 86–87 °C/11 mmHg, $[\alpha]_D^{25} + 125.4°$ ($l = 1$, 100%).[5] ^1H 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 according to the literature.[6,7] 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, $[\alpha]_D^{25} - 44.2°$ ($l = 1$).[6] ^1H 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).

3-Methylpyridine (Janssen) was dried with fused KOH and twice distilled over KOH in an inert gas atmosphere: b.p. = 143.7–144 °C; $n_D^{20} = 1.5067$ (lit.[8] b.p. = 144.0 °C; $n_D^{20} = 1.5068$).

All solvents were purified according to standard procedures.[9] They were freed from dissolved gases by repeatedly freezing and thawing at a reduced pressure and stored in ampoules in the absence of air.

Reaction of benzyl bromide with copper: general procedure

Copper powder (1g) was dissolved in 10 ml of DMF and 5 ml of benzyl bromide in an argon atmosphere at 50 °C. After 5 h, the white precipitate formed (which rapidly became green in air) was filtered off in an atmosphere of argon free from oxygen. Recrystallization from 3-methylpyridine afforded 5.26 g (80%) of yellow crystals of tris-3-methylpyridine copper(I) bromide $[Cu(3\text{-}MePy)_3Br]$, which were stable in air.[10] Anal. (calc.) for $C_{18}H_{21}N_3CuBr$ (422.01): Cu, 15.40; Br, 18.90 C, 51.10; H, 5.00; N, 9.53. Found Cu, 15.35; Br, 18.87 C, 51.00; H, 5.01; N, 9.77%. IR (mineral oil), $\nu = 480$ (m, Cu–N), 418 (w, Cu–N), 348 (s, Cu–N), 230 (vs, Cu–Br), 225 (s, Cu–N) cm^{-1}.

Organic reaction products were extracted with diethyl ether (20 ml). The residues of benzyl bromide and DMF, as well as 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.[11] m.p. = 51–52 °C). ^1H 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 $[M\text{-}CH_3]^+$ (56), 152 $[M\text{-}2CH_3]^+$ (15).

Study of the reaction kinetics

The reactions of copper with nine benzyl bromides in DMF were studied by the resistometric method[12] according to a published procedure[13] in an atmosphere of water-free argon free from oxygen.

To obtain kinetic and thermodynamic parameters of the process we carried out three series of experiments. The first one was carried out at initial $C_{RBr} = 0.5$ mol l^{-1} and the 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 the initial C_{RBr} was changed from 0.2 to 7 mol l^{-11} (Fig. 1, curve 2). We made the third series at initial $C_{DMF} = 2$ mol l^{-1} and changed the initial C_{RBr} from 0.2 to 7 mol l^{-11} (Fig. 1, curve 3).

Benzene was used as a neutral solvent for determination of the kinetic characteristics of the reaction of copper with benzyl bromide in the presence of DMF.[14] The reaction was

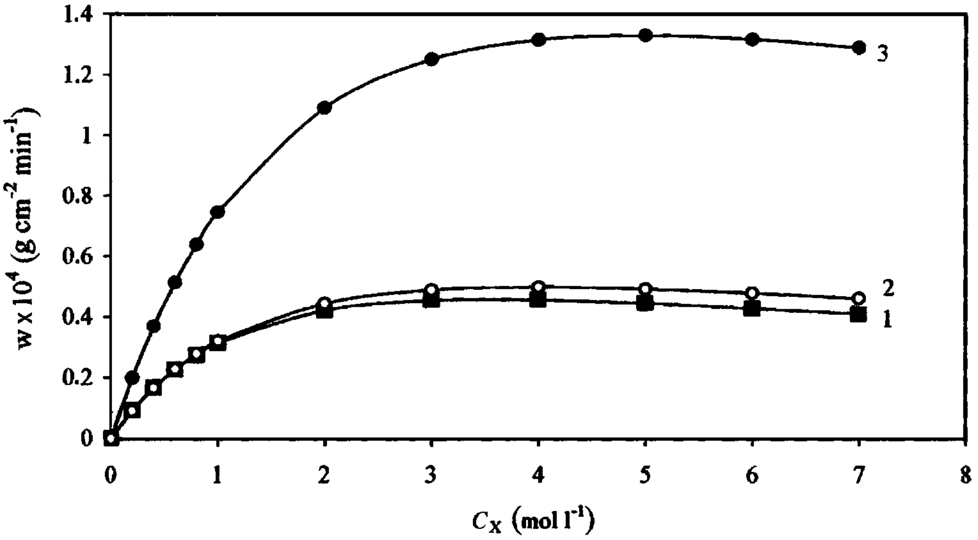


Figure 1. The dependence of the rate (*w*) of oxidative dissolution of copper in the benzyl bromide–DMF system on initial concentrations of mixture components in the presence of a neutral solvent (benzene) at 353 K: (1) $C_{RBr} = 0.5$ mol l^{-1}, X = DMF; (2) $C_{DMF} = 0.5$ mol l^{-1}, X = RBr; (3) $C_{DMF} = 2$ mol l^{-1}, X = RBr.

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

Parameter		$k \times 10^4$ (g cm^{-2} min^{-1})	K_1 (l mol^{-1})	K_2 (l mol^{-1})
T(K)	313	0.6 ± 0.1	1.03 ± 0.02	0.93 ± 0.02
	323	1.5 ± 0.1	0.73 ± 0.02	0.66 ± 0.01
	333	3.5 ± 0.1	0.55 ± 0.01	0.50 ± 0.01
	338	5.2 ± 0.1	0.46 ± 0.01	0.42 ± 0.01
	343	7.2 ± 0.1	0.39 ± 0.01	0.37 ± 0.01
	353	14.5 ± 0.1	0.32 ± 0.01	0.29 ± 0.01
Correlation coefficient r		0.999	0.998	0.999
E_A (kJ mol^{-1})		73.2 ± 2.9		
ΔH°_{RBr} (kJ mol^{-1})			−27.4 ± 2.2	
ΔH°_{DMF} (kJ mol^{-1})				−26.9 ± 1.2

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

Substituent	$k \times 10^3$	σ	k/k°
m-Cl	1.71 ± 0.01	0.37	1.18
m-F	1.70 ± 0.01	0.34	1.17
p-Cl	1.78 ± 0.02	0.23	1.23
m-OMe	1.49 ± 0.01	0.12	1.03
p-F	1.55 ± 0.01	0.06	1.07
H	1.45 ± 0.01	0.00	1.00
m-Me	1.38 ± 0.01	−0.07	0.95
p-Me	1.33 ± 0.01	−0.17	0.92
p-OMe	1.22 ± 0.01	−0.27	0.84

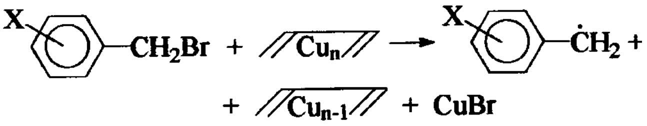
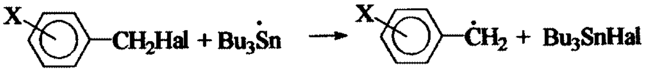
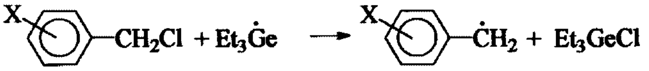
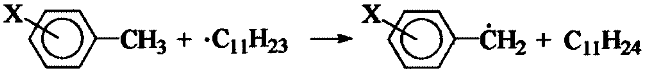
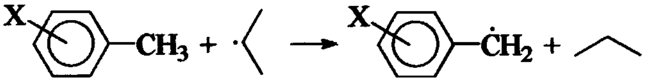
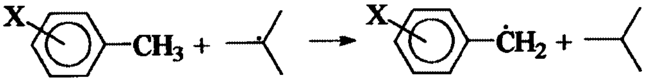
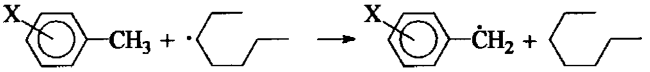
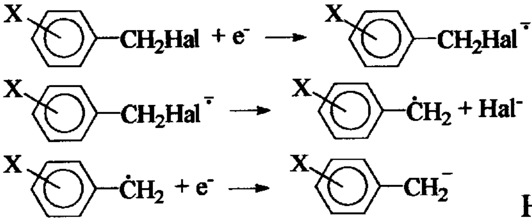
k° is the rate constant for reaction of copper with unsubstituted benzyl bromide in DMF; σ is the Hammett substituent constant. Data for substituted benzyl bromides was obtained from Langmuir-Hinshelwood scheme for different active centers.

studied in kinetic mode, as evidenced by the independence of the rate of copper dissolution in the test media from the rate of stirring. Tables 1–3 summarize the results of this study.

Studies of the reaction of copper with benzyl bromide and DMF at low temperature

Studies of the low-temperature reaction of copper with benzyl bromide were carried out in a vacuum apparatus analogous to that reported previously.[15] The reagents were evaporated in an evacuated (10^{-4} mmHg) reactor ($V = 10$ 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.[16] The rate of evaporation of copper was 0.2 mmol min^{-1}. Benzyl bromide and DMF were evaporated at 273–308 K (DMF : $PhCH_2Br$: Cu = 0–10 : 10 : 1). The duration of co-condensation was 2–4 h.

Table 3. Hammett ρ values for reactions involving cleavage of bonds or electron transfer with a benzyl moiety

Reaction	ρ	Solvent	Ref.
	0.24	DMF, benzene	This work
 Hal = Cl			22
Br	0.40	Benzene	
	0.22	Benzene	
I	1.05	Benzene	
	0.312	Benzene	23
	0.4	Benzene	24
	0.47		25
	0.5		26
	0.8		27
	1.0		28
	0.99		27
	0.7		29
	0.66		30
 Hal = Cl Br	1.45	DMF	31
	2.8	CH_3CN	32

After completion of co-condensation, evacuation was terminated and the reactor was filled with pure dry argon (760 mmHg). The samples were heated to 298 K, at which 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) at 298 K in pure dry argon. The liquid phase was analyzed by gas chromatography and the reaction products were isolated by preparative liquid chromatography. The results are given in Table 4.

Study of stereochemistry

The co-condensation of (+)-*R*-1-bromo-1-phenylethane and DMF with copper (10 : 10 : 1) was studied as with the above procedure for the low-temperature reaction. The co-condensation results in white films on the reactor surface. Condensation of DCl at 77 K on the surface of the samples was carried out according to the procedure below.

After completion of co-condensation the samples were heated to 160 K, kept at this temperature for 20 min and then cooled to 77 K, when DCl (50 g) was condensed onto their surfaces. Then evacuation was terminated and the reactor was filled with dry pure argon (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. Excess DCl was removed at 190–200 K (100 mmHg). The reaction mixtures were heated to 298 K and reaction products were

Table 4. Composition of reaction products produced by acidolysis of reaction mixtures

		Yield (%)	
Cu : $PhCH_2Br$: DMF	T (K)	$PhCH_2CH_2Ph$[a]	$PhCH_2D$[b]
1 : 10 : 0	160	98	2
1 : 10 : 0	298	99	1
1 : 10 : 5	160	94	6
1 : 10 : 5	298	98	2
1 : 10 : 10	160	93	7
1 : 10 : 10	298	98	2

[a] Impurity of 4,4′-dimethylbiphenyl <0.1%.

[b] Impurity of toluene = 1%.

Table 5. Yields of products **1–5** (%) by studying the stereochemistry of the reaction under investigation

	Yields of products (%)				
Acidolysis	1	2	3	4	5
1[a]	10	45.64	44.31	0.05	–
2[b]	2	47.69	46.31	2	2

[a] Acidolysis carried out at 160 K.

[b] Acidolysis carried out at 298 K.

isolated by preparative liquid chromatography. Yields are given in Table 5.

The reaction products were characterized as follows:

(+)-*S*-1-Phenylethane-1D (1). B.p. 135–136 °C, $n_D^{20} = 1.4954$, $[\alpha]_D^{20} + 0.05$ ($l = 0.1$). ^1H NMR ($CDCl_3$): $\delta = 1.23$ (d, 3H, CH_3), 2.62 (q, 1H, CH), 7.20 (m, 5H, -Ph.) ppm. Lit. data: b.p. 135–136 °C, $n_D^{20} = 1.4919$,[17] $[\alpha]_D^{20} + 0.81$ ($l = 0.1$).[18]

Mixture of *RS*-1-phenylethane-1D and phenylethane (**1** and **4**), 1 : 1. ^1H NMR ($CDCl_3$): $\delta = 1.20$ (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-Diphenylbuthane (**2**). B.p. 130–132 °C/7 mmHg, $n_D^{20} = 1.5557$. ^1H NMR ($CDCl_3$): $\delta = 1.17$ (d, 6H, $2CH_3$), 2.76 (m, 2H, CH–CH), 7.24 (m, 10H, 2Ph.) ppm. Lit. data: b.p. 130–132 °C/7 mmHg,[17] $n_D^{20} = 1.5557$.[18]

RS,RS-2,3-Diphenylbuthane (**3**). B.p. 144–149 °C/12 mm Hg, m.p. 126–127 °C. ^1H NMR ($CDCl_3$): $\delta = 1.03$ (d, 6H, $2CH_3$), 2.75 (m, 2H, CH–CH), 7.24 (m, 10H, 2Ph.) ppm. Lit. data: b.p. 144–149 °C/12 mmHg,[17] m.p. 126–127 °C.[18]

Identification of radical species in solution

The reaction in the presence of a radical trap was studied in a similar way to the general procedure. Dicyclohexyldeuterophosphine (DCPD) was used as the radical trap.[19]

The residues of benzyl bromide and DMF, as well as 1,2-diphenylethane and α-deuterotoluene, were detected in the diethyl ether solutions. Table 7 summarizes the yields of organic reaction products.

α-Deuterotoluene ^1H 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).

RESULTS AND DISCUSSION

Kinetic studies

The reaction kinetics of the oxidative dissolution of Cu in the benzyl bromide–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.[14,20] To determine the kinetic characteristics of the process, the reaction was performed in a neutral solvent of benzene ($DN_{SbCl_5} = 0.42$ kJ mol^{-1}).[15]

Figure 1 demonstrates the kinetic curves with their maxima. An increase in the concentration of DMF from 0.5 to 2 mol^{-1} did not change the shape of the curves because the reaction rate depends on the concentration of benzyl bromide. This fact indicates that the process occurs by the Langmuir–Hinshelwood mechanism, with adsorption of the reagent and solvent at identical active centers of the metal surface (Eqns (1)–(3)):[21]

$$PhCH_2Br + S \xrightleftharpoons{K_1} (PhCH_2Br)S \tag{1}$$

$$L + S \xrightleftharpoons{K_2} (L)S \tag{2}$$

$$(PhCH_2Br)S + (L)S \xrightarrow{K} \text{products} \tag{3}$$

where L is DMF; K_1 and K_2 are the equilibrium constants of benzyl bromide and DMF adsorption, respectively; K is the rate constant of the chemical process; and S is the active center at which the adsorption of benzyl bromide and DMF, respectively, takes place.

In this case, surface coverages derived from Langmuir isotherms for the adsorption of individual components appear in the rate equation, and an expression for rate of reaction (w) has the form:

$$w = \frac{k \cdot K_1 \cdot K_2[PhCH_2Br][DMF]}{(1 + K_1[PhCH_2Br] + K_2[DMF])^2} \tag{4}$$

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

Treatment of the experimental relations (Fig. 1) using Eqns (1)–(3) allowed us to determine the equilibrium constants of benzyl bromide and DMF adsorption on the surface of copper (K_1 and K_2, respectively) and the rate constant k of the chemical reaction. Study of the reaction kinetics at different temperatures allowed us to find E_A of the chemical reaction and the enthalpies and entropies of adsorption of the reactants on the surface of copper. Table 1 summarizes the results.

A comparison of the results with the published data[20] on oxidative dissolution of copper in the I_2–DMF system demonstrated that $\Delta H_{\text{ads DMF}}$ at the surface of copper remained almost unchanged (-26.9 ± 1.2 kJ mol^{-1}) when the iodine was replaced by $PhCH_2Br$, whereas the corresponding values for a organic halide changed considerably (from -70 ± 8 to -27.4 ± 2.2 kJ mol^{-1}). This fact is indicative of the selective adsorption of a dipolar aprotic solvent (which participates in the reaction) on the surface of copper.

The Langmuir–Hinshelwood scheme for the test process suggests that the interaction of adsorbed reactant molecules with the metal surface (i.e. a surface chemical reaction) is the rate-limiting step of the reaction.

Relative reactivities of nine substituted benzyl bromides were obtained from the kinetic experiments, as shown in Table 2. Figures 2 and 3 show plots of the logarithm of the relative rate vs the Hammett substituent constant σ and it will be seen that there is a reasonably good linear relationship ($\rho = 0.24$, $r = 0.951$, $S_\rho = 0.03$). The Hammett ρ value obtained here is, however, considerably lower than the values associated with ionic reactions. This indicates that the polar effect on abstraction of the bromine 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 quite similar to those reported by Tanner[22] ($\rho = 0.22$, $r = 0.95$, $S_\rho = 0.03$) for the reaction of tri-n-butyltin radical and benzyl bromide in benzene. The abstraction of a bromine atom from benzyl bromide by a tributyltin radical is probably a good model for atom abstraction by a metal surface. For comparison, abstraction of a chlorine atom from substituted benzyl chlorides by a triethylgermyl radical has $\rho = 0.312$.[23]

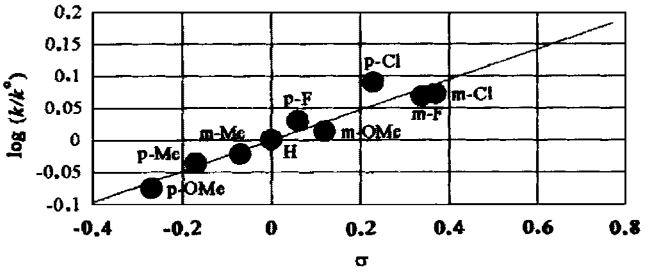


Figure 2. Hammett plots of log($k/k°$) vs substituent constant σ.

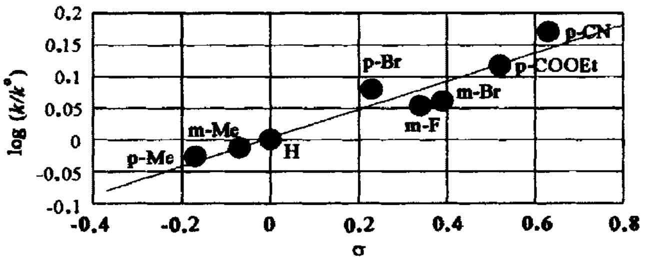


Figure 3. Hammett plots of log($k/k°$) vs substituent constant σ obtained for reaction of n-tributyltin radical with benzyl bromides.[22]

Positive ρ values have been obtained also from kinetic studies of a number of alkyl radicals generated in the presence of a series of substituted toluenes.[24–30] These data are listed in Table 3.

Polarographic reductions of organic halides are well known to be irreversible[31,32] and the overall two-electron transfer process leads to a carbanion that is subsequently protonated:

$$\text{RHal} + e^- \longrightarrow \text{RHal}^{\bar{\bullet}} \tag{5}$$

$$\text{RHal}^{\bar{\bullet}} \longrightarrow \text{R}^\bullet + \text{Hal}^- \tag{6}$$

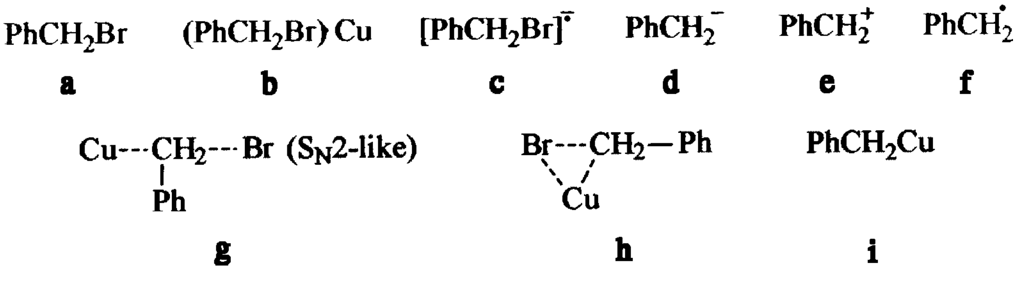
$$\text{R}^\bullet + e^- \longrightarrow \text{R}^- \tag{7}$$

Decomposition of the radical anion is very fast or even concerted in combination with electron transfer.

The ρ values calculated from least-squares slopes of $\Delta E_{1/2}$ vs σ^- plots were $\rho = 0.5$ for the series of benzyl chlorides and $\rho = 2.8$ for the series of benzyl bromides. There was no correlation between σ substituent constants ($r = 0.77$, $S_\rho = 0.28$, $r = 0.78$, $S_\rho = 0.14$).[32]

To determine the rate-limiting step we considered nine possible limiting transition states for the organic moiety, as summarized by **a**–**i** structures (Scheme 1),[33] where Cu represents the copper atom of a copper metal surface.

Because ρ has a significant positive value, the transition state cannot resemble the starting material and therefore structure **a** can be discarded. The magnitude of ρ seems too



Scheme 1.

large to be compatible with physisorption (structure **b**) and the sign of ρ is incompatible with the intermediate benzyl cation (structure **e**). Because the largest values of ρ observed are similar to those for tin hydride reduction and considerably smaller than that estimated for reactions generating benzyl anions ($\rho = 2.8$),[32] the magnitude of ρ seems to be too small for a fully formed benzyl anion (structure **d**). A rate-determining step involving an intermediate in which the carbon–copper bond is partially (structure **h**) or fully (structure **i**) formed is unlikely because such a transition state bears a large negative charge on carbon and would be expected to show a large value for ρ; also, cleavage of the carbon–bromine bond appears to be irreversible.

It is more difficult to differentiate between reactions leading to the three remaining limiting structures—electron transfer from copper to benzyl bromide to generate the radical anion (**c**) bromine abstraction by copper to form the benzyl radical (**f**) and insertion of copper directly into the carbon–bromine bond of the adsorbed benzyl bromide, (**g**)—on the basis of available evidence.

It is well known that ESR provides 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 bromide and DMF (1 : 50 : 50) at 77 K is a triplet of quartets with a full width of ~50 G and $g = 2.002$. The parameters of the ESR spectrum of the benzyl radical are presented in Table 6 and comparison shows that the ESR spectrum of co-condensates of copper with benzyl bromide and DMF coincides with that of the benzyl radical.

When the excess benzyl bromide and DMF (1 : 1) is condensed on the compact copper film (thickness of the film is $\sim 10^{-4}$ mm), losses of UHF power in the sample increase due to an increase in the electroconductivity, which results in considerable worsening of the resolution of the ESR spectra. Paramagnetic species that appeared in the benzyl bromide—DMF–atomic copper systems did not differ from those that formed with the compact copper film.

Table 7. Product composition in the oxidative dissolution of copper in benzyl bromide–DMF systems in the presence (and absence) of radical traps

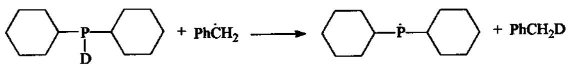
DCPD[a]/Cu (mol/mol)	Yield (mol. %)	
	$\mathrm{Ph{-}CH_2D}$[b]	$\mathrm{Ph{-}CH_2{-}CH_2{-}Ph}$[c]
0	0	100
1	63 ± 7	37 ± 7
2	78 ± 5	22 ± 5
5	98 ± 2	2 ± 2

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

Dicyclohexyldeuterophosphine (DCPD) provides an opportunity not only to detect radical intermediates but also to determine their concentration is solution.[19] In the dehalogenation of benzyl bromide with copper in DMF in the presence of DCPD, the composition of the reaction products changed according to the copper : DCPD molar ratio (Table 7). When the copper: DCPD molar ratio was 1 : 5 the formation of 1,2-diphenylethane was not observed (Table 7), but an equivalent amount of α-deuterotoluene was detected instead:

$$n\mathrm{PhCH_2Br} + n\mathrm{Cu} + m\mathrm{L} \xrightarrow{\mathrm{DCPD}} [\mathrm{Cu}_n\mathrm{L}_m\mathrm{Br}_n] + \mathrm{PhCH_2D} \tag{8}$$

where L = DMF. Analysis of reaction products in the presence (and absence) of radical traps indicates that the process occurs by a radical mechanism via the preliminary formation of a benzyl radical:



(9)

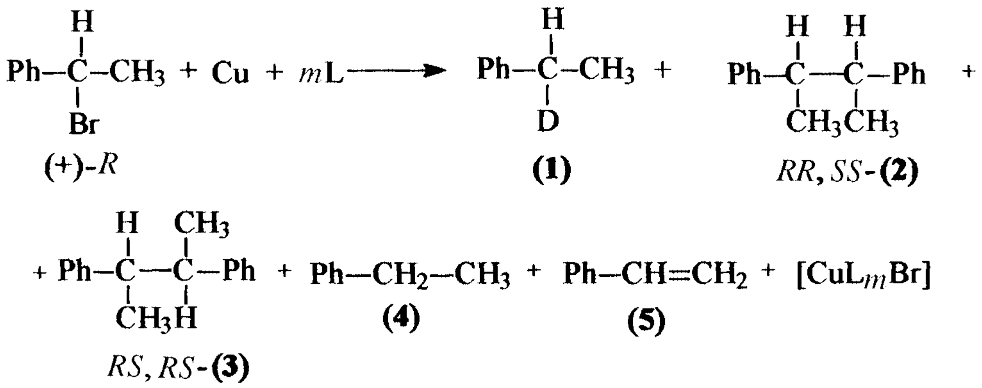
The results of this work indicate that the dehalogenation process occurs at the surface of copper by a radical mechanism via the formation of benzyl radicals, which undergo recombination and isomerization mainly in solution.

At temperatures above 273 K benzyl cuprates are known to be thermally unstable, giving the respective homocoupled products in good yield.[36] At lower temperatures these organocopper compounds have greater stability but react quickly with benzyl bromide to form the corresponding coupled products.[36] The low melting point of HCl made it possible to detect the reaction products both before (159 K) and after (298 K) defrosting of the sample and to observe unstable organocopper compounds at 298 K reacting with DCl according to:

$$\mathrm{PhCH_2Cu}_n + \mathrm{DCl} \longrightarrow \mathrm{PhCH_2D} + \mathrm{CuCl} + \mathrm{Cu}_{n-1}$$

Table 6. Parameters of the ESR spectrum for benzyl radical in solid matrices

g	$a^H_{CH_2}$ (G)	a^H_o (G)	a^H_m (G)	a^H_p (G)	Ref.
2.002 ± 0.001	16.4 ± 0.8	5.5 ± 0.5	–	5.5 ± 0.5	This work
2.002 ± 0.001	16.4 ± 0.5	5.5 ± 0.5	–	5.5 ± 0.5	33
–	16.5	6	–	6	34
–	16.5 ± 1	5.5 ± 0.5	–	5.5 ± 0.5	35



Scheme 2.

The composition of reaction products produced by acidolysis of organocopper compounds obtained by the co-condensation of copper with benzyl bromide is given in Table 4.

The results obtained allow us to conclude that coordinating solvent stabilizes the formation of organocopper compounds. This conclusion agrees well with previous data.[36]

We have studied the reaction of optically active (+)-*R*-1-bromo-1-phenylethane with copper in DMF, hoping to obtain experimental evidence of optical activity retention at the asymmetry center in the course of formation of organocopper compounds. The main cause of racemisation of organocopper compounds is the stereochemical instability of the C–Cu bond and this can arise just after organocopper formation. The configuration of organocopper reagents has to be fixed at the moment of its formation by carrying out the reaction in the presence of deuterium chloride, which reacts vary rapidly with organocopper compounds. The co-condensation of a copper vapor with (+)-*R*-1-bromo-1-phenylethane and DMF (1 : 10 : 10), which were precipitated in molecular beam mode on the surface cooled with liquid N_2, afforded white films. After thawing (273 K) and treatment of the samples with DCl, the optically inactive 1-phenylethane-1D (**1**) and four other unlabeled hydrocarbons **2**, **3**, **4** and **5** were detected in the reaction mixtures (Scheme 2).

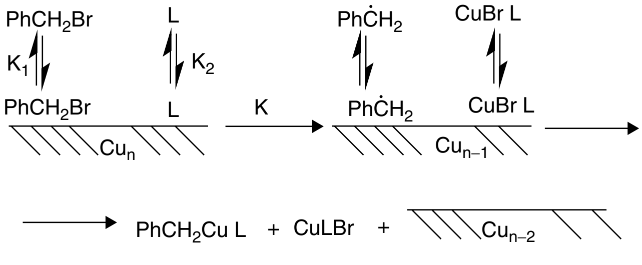
It is well known that recombination of optically active 1-phenylethyl radicals proceeds within a solvent cage 15 times more slowly than inversion and leads to the partial retention configuration of the recombination products.[37] The formation of optically inactive **2** and **3** (**2**:**3** = 1.03 : 1) along with **4** and **5** shows that the reaction occurs according to the radical mechanism and that recombination and disproportionation of the 1-phenylethyl radical can proceed after they enter the solution. The formation of racemic 1-phenylethane-1-D in the course of reaction of (+)-*R*-1-bromo-1-phenylethane with copper is reliable evidence for this suggestion and may proceed by radical pair recombination at a slower 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-bromo-1-phenylethane and DMF, afforded white films. After completion of condensation of DCl 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 composition of the reaction products produced by acidolysis of the samples is listed in Table 5. The optical purity of 1-phenylethane-1D (6 ± 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 reaction of (+)-*R*-1-bromo-1-phenylethane with copper is dissociative electron transfer on a copper surface.

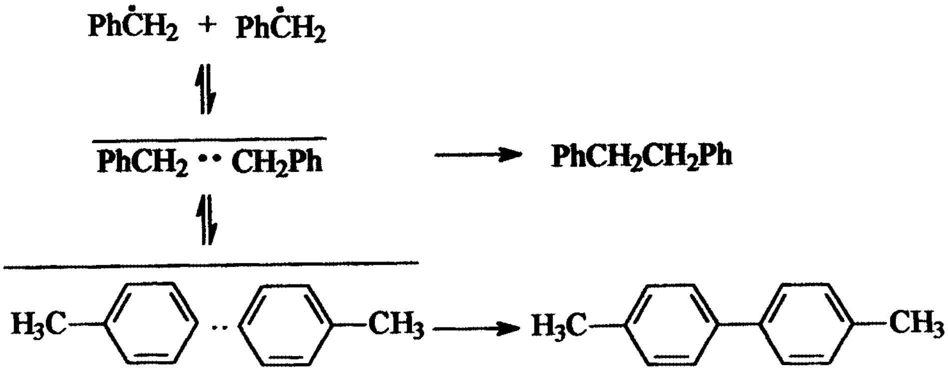
The results of this work indicate that the dehalogenation process occurs at the surface of copper by a radical mechanism via the formation of benzyl radicals, which undergo recombination and isomerization mainly in solution. Reaction occurs by the Langmuir–Hinshelwood mechanism at identical active centers of the metal surface according to Scheme 3. The limiting step of the reaction of benzyl bromides with copper is dissociative electron transfer on a metal surface. The yield of organocopper compounds depends on the reaction conditions.

We have mentioned already that at temperatures above 273 K benzyl cuprates decompose according to:[36]

$$PhCH_2Cu \longrightarrow Ph\dot{C}H_2 + Cu \qquad (11)$$



Scheme 3.



Scheme 4.

At lower temperatures these organocopper compounds have higher stability but react quickly with benzyl bromide:[38]

$$PhCH_2Cu + PhCH_2Br \longrightarrow PhCH_2CH_2Ph + CuBr \qquad (12)$$

Recombination and isomerization of benzyl radicals proceed mainly in solution according to Scheme 4 (for X = H). The coordination compounds of copper(I) with organic ligands in solution form dimers or tetramers:[39]

$$CuLBr + Cu_{n-1}L_{n-1}Br_{n-1} \longrightarrow Cu_nL_nBr_n \qquad (13)$$

$$Cu_nL_nBr_n + (n\text{-}m)L \longrightarrow [Cu_nL_mBr_n] \downarrow \qquad (14)$$

where L = DMF; $2 \leq n \leq 4$; $2 \leq m \leq 4$.

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