Kinetics and Mechanism of the Reaction of Benzyl Bromide with Copper in Hexamethylphosphoramide

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ABSTRACT: The reaction of copper with benzyl bromides in hexamethylphosphoramide has been studied. The kinetic and thermodynamic parameters of the reaction have been obtained. Hammett plots of log (k/k°) vs the substituent constant σ gave good correlations ($\rho = 0.15$, $S_{\rho} = 0.02$, $r = 0.954$). The structure of the organic group has little effect on the rate of reaction of benzyl bromide with copper. In the absence of atmospheric oxygen, the oxidative dissolution of copper occurred by the mechanism of single-electron transfer with the formation of 1,2-diphenylethane and copper(I) complexes. The stereochemistry and intermediates compound was also investigated.

The reaction mechanism is discussed. © 2005 Wiley Periodicals, Inc. Int J Chem Kinet 37: 296–305, 2005

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 coordinating solvent, which occurs under mild conditions, is one of the methods for the synthesis of these compounds [1].

Being a destroyer of ozone, carbon tetrachloride is prohibited for use in chemical industry, and this is why its substitutes are being sought.

For the development of optimum conditions for the target-oriented synthesis of the complex compounds of copper halides with organic ligands, the kinetics and mechanism of the reaction of copper with benzyl bromide in the presence of hexamethylphosphoramide (HMPA) were studied in details. This work provides sufficient evidence to exclude many of the transition states conceivable for the rate-limiting step for reaction of benzyl bromide 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

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as internal standard. The accuracy of chemical shifts was ±0.01 ppm.

The ESR spectra were recorded at 77 K on a Radiopan radiospectrometer in films of copper co-condensates with benzyl bromide and HMPA (1:50:50) according to the literature [2,3] at 9 GHz frequency in the absence of saturation and amplitude broadening. The copper was evaporated from the corundum crucible at 1400–1440 K during continuous evacuation (10^{-4} mmHg).

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

The purity of starting substances was monitored, and the quantitative analysis of organic reaction products was performed using gas chromatography (GC). The conditions of GC analysis were described previously [4].

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

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

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

Inorganic reaction products (copper 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 an elutriator. 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 (GOST 7262-54 Russia, Cu content of 99.99%) 0.05 mm in diameter was held in HMPA 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 then HMPA.

All organic compounds were obtained from commercial sources.

The purity of 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 GLC. Compounds that contained toluene or were less than 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.

4-Methoxybenzyl bromide and 4-chlorobenzyl bromide were prepared by known methods. The purities of the products were checked by elemental analysis and comparison of physical properties with those reported in the literature [5].

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 [6]. Yield 74%. B.p. = 86–87°/11 mmHg, $[\alpha]_D^{25}$ +73.3° ($l = 1$) (lit. [6] b.p. = 86–87°/11 mmHg, $[\alpha]_D^{25}$ +96.3° ($l = 1$, 100%)). ^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 in accordance with [7,8]. Yield 55%. B.p. = 94–95°/14 mmHg, $[\alpha]_D^{25}$ −37.65° ($l = 1$) (lit. [7,8] b.p. = 94–95°/14 mmHg, $[\alpha]_D^{25}$ −44.2° ($l = 1$)). ^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 [9] b.p. = 144.0°C; $n_D^{20} = 1.5068$).

All solvents were purified according to standard procedures [10]. 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

A 1-g portion of Cu powder was dissolved in 10 mL of HMPA and 5 mL of benzyl bromide in an argon atmosphere at 50°C. After 5 h, the formed white precipitate (which rapidly became green in air) was filtered off in an atmosphere of argon freed from oxygen. The recrystallization from 3-MePy afforded 5.26 g (80%) of yellow crystals, which were stable in air [11]. Analysis: $C_{18}H_{21}N_3CuBr$ (422.01) calculated: 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 products of reaction were extracted with diethyl ether (20 mL). The residues of benzyl bromide and HMPA, as well as 1,2-diphenylethane and 4,4′-ditolyl, were detected in the ether solution. The isolated yield of 1,2-diphenylethane was 1.37 g (96%). m.p. = 51–52°C (lit [12] 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′-Ditolyl MS (EI, 70 eV): calculated $m/z = 182.11$ (M), found $m/z = 182$ $[M]^+$ (100), 167 $[M-CH_3]^+$ (56), 152 $[M-2CH_3]^+$ (15).

Study of the Reaction Kinetics

The reactions of copper with nine benzyl bromides in HMPA were studied by the resistometric method [13] according to a published procedure [14] in an atmosphere of water-free argon freed of oxygen.

Benzene was used as an neutral solvent for the determination of the kinetic characteristics of the reaction of copper with benzyl bromide in the presence of HMPA [15].

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. Tables I–III summarize the results of this study.

Studies of the Reaction of Active Copper with Benzyl Bromide and HMPA

Studies of the low-temperature reaction of active copper with benzyl bromide were carried out in vacuum apparatus analogous to that reported previously [16]. The reagents were evaporated in an evacuated (10^{-4} mmHg) reactor ($V = 10$ L) and condensed on the surface cooled with liquid N_2. Active copper was prepared by evaporating the purified metal from a corundum crucible at 1400–1440 K [17]. The rate of evaporation of Cu was 0.2 mmol min^{-1}. Benzyl bromide and HMPA was evaporated at 273–308 K (HMPA:$PhCH_2Br$:Cu = 0–10:10:1). The duration of co-condensation was 2–4 h.

After completion of co-condensation 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 1% solution of DCl in D_2O (99.5 atom.% D, Aldrich) at 298 K under an atmosphere of pure dry Ar. The liquid phase was analyzed by GLC. The reaction products were isolated by preparative liquid chromatography. The results are given in Table VI.

Studies of the Stereochemistry of the Reaction under Investigation

The reaction of (+)-R-1-bromo-1-phenylethane and HMPA with copper was studied analogously to the above procedure. Condensation of DCl at 77 K on the surface of the samples was carried out according to the below procedure.

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. DCl (50 g) was

Table I Kinetic and Thermodynamic Parameters of the Oxidative Dissolution of Copper in the Benzyl Bromide–HMPA System Calculated Using the Langmuir–Hinshelwood Mechanism from the Adsorption of the Reagent and the Solvent at Different 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	1.3 ± 0.1	0.936 ± 0.007	0.465 ± 0.006
	323	3.0 ± 0.1	0.664 ± 0.006	0.379 ± 0.005
	333	7.4 ± 0.1	0.510 ± 0.006	0.293 ± 0.005
	338	10.1 ± 0.2	0.428 ± 0.005	0.267 ± 0.005
	343	17.7 ± 0.2	0.370 ± 0.005	0.247 ± 0.005
	353	34.7 ± 0.3	0.295 ± 0.005	0.203 ± 0.005
r^a		0.998	0.999	0.998
E_A (kJ mol^{-1})		76.3 ± 4.7		
ΔH^o_{RBr} (kJ mol^{-1})			-26.7 ± 1.5	
ΔH^o_{HMPA} (kJ mol^{-1})				-19.2 ± 1.3

[a] Sample correlation coefficient.

Table II Relative Reactivities of Substituted Benzyl Bromides toward Copper in HMPA at 80°C

Substituent	$k \times 10^4$ ($\mathrm{g\ cm^{-2}\ min^{-1}}$)	σ	k/k°
m-Cl	3.92 ± 0.05	0.37	1.129
m-F	3.89 ± 0.04	0.34	1.121
p-Cl	3.97 ± 0.05	0.23	1.145
m-OMe	3.55 ± 0.04	0.12	1.023
p-F	3.65 ± 0.04	0.06	1.053
H	3.47 ± 0.03	0	1
m-Me	3.42 ± 0.03	−0.07	0.987
p-Me	3.34 ± 0.03	−0.17	0.968
p-OMe	3.13 ± 0.03	−0.27	0.902

condensed to their surfaces. Then evacuation was terminated, 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, and the composition of reaction products were isolated by preparative liquid chromatography. Yields are given in Table VII.

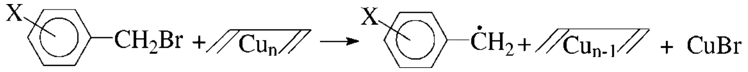
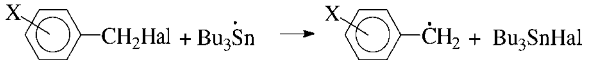
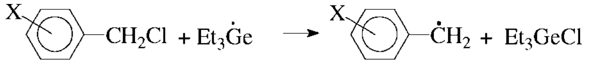
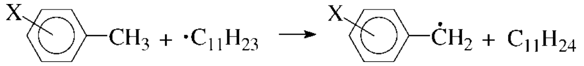
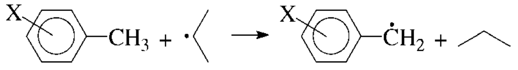
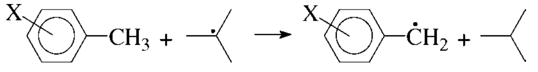
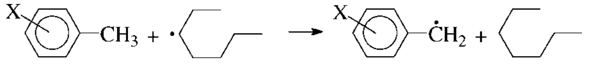
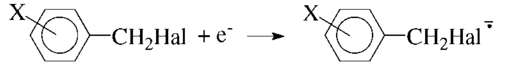
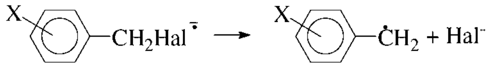
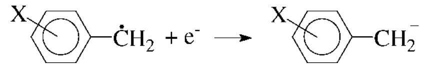
(+)-*S*-1-Phenylethane-1D (**1**). B.p. 135–136°C, $n_D^{20} = 1.4954$, $[\alpha]_D^{20}$ +0.05 ($l = 0.1$). ^{1}H NMR ($CDCl_3$): $\delta = 1.23$ (d, 3H, CH_3), 2.62 (q, 1H, CH), 7.20 (m, 5H, —Ph) ppm. Lit. data: b.p. 135–136°C, $n_D^{20} = 1.4919$ [18], $[\alpha]_D^{20}$ +0.81 ($l = 0.1$) [19].

Mixture of *RS*-1-phenylethane-1D and phenylethane (**1** and **4**), 1:1. ^{1}H 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, $n_D^{20} = 1.5557$. ^{1}H 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 [18], $n_D^{20} = 1.5557$ [19].

RS,*RS*-2,3-Diphenylbuthane (**3**). B.p. 144–149°C/12 mmHg, m.p. 126–127°C. ^{1}H NMR ($CDCl_3$):

Table III Hammett ρ Values for Reactions Involving Cleavage of Bonds to, or Electron Transfer with, an Benzyl Moiety

Reaction		ρ	Solvent	References
		0.15	Benzene + HMPA	This work
				[22]
Hal = Cl		0.40	Benzene	
Br		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		[27]
				[28]
		0.7		[29]
		0.66		[30]
	Hal = Cl	1.45	DMF	[31]
	Br	2.8	CH_3CN	[32]
				

$\delta = 1.03$ (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 [18], m.p. 126–127°C [19].

Identification of Radical Species in Solution

The reaction in the presence of a radical trap was studied analogously to the general procedures. Dicyclohexyldeuterophosphine (DCPD) was used as the radical trap [20].

The residues benzyl bromide and HMPA, as well as 1,2-diphenylethane and α-deuterotoluene, were detected in the diethyl ether solutions. Table V 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 $[M-C_2H_3]^+$ (9), 65 $[M-C_2H_2D]^+$ (11).

RESULTS AND DISCUSSION

The reaction kinetics of the oxidative dissolution of Cu in the benzyl bromide-HMPA 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 [13,21].

To determine the kinetic characteristics of the process, the reaction was performed in an indifferent solvent of benzene ($DN_{SbCl5} = 0.42$ kJ mol^{-1}) [15].

The Fig. 1 demonstrates the kinetic curves. An increase in the concentration of HMPA from 0.5 to 2 mol^{-1} L did not change the shape of curves for the dependence of the reaction rate on the concentration of benzyl bromide. These facts indicate that the process occurs by the Langmuir–Hinshelwood mechanism with the adsorption of the reagent and the solvent at different active centers of the metal surface [14]:

$$PhCH_2Br + S_1 \underset{}{\overset{K_1}{\rightleftharpoons}} (PhCH_2Br)S_1 \quad (1)$$

$$L + S_2 \overset{K_2}{\rightleftharpoons} (L)S_2 \quad (2)$$

$$(PhCH_2Br)S_1 + (L)S_2 \overset{K}{\rightleftharpoons} \text{Products} \quad (3)$$

where L is HMPA; K_1 and K_2 are the equilibrium constants of benzyl bromide and HMPA adsorption, respectively; K is the rate constant of the chemical process; S_1 and S_2 are the active centers at which the adsorption of benzyl bromide and HMPA, respectively, takes place.

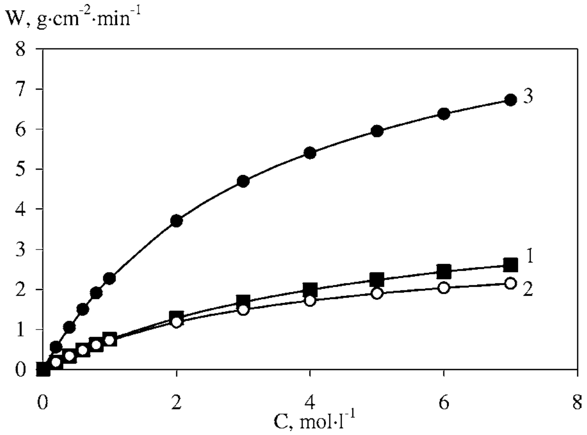


Figure 1 The dependence of the oxidative dissolution of copper in the benzyl bromide-HMPA system on the initial concentrations of mixture components in the presence of an indifferent solvent (benzene) at 353 K: 1—$C_{RBr} = 0.5$ mol l^{-1}, 2—$C_{HMPA} = 0.5$ mol l^{-1}, and 3—$C_{HMPA} = 2$ mol l^{-1}.

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

$$w = \frac{k \cdot K_1 \cdot K_2[PhCH_2Br][HMPA]}{1 + K_1[PhCH_2Br] + K_2[HMPA] + K_1K_2[PhCH_2Br][HMPA]} \quad (4)$$

where $k = K \cdot N_1N_2$; N_1 and N_2 are the numbers of active centers of the metal surface at which the adsorption of benzyl bromide and HMPA, respectively, takes place.

The treatment of the experimental relations (Fig. 1) using the set of Eqs. (1)–(3) allowed us to determine the equilibrium constants of benzyl bromide and HMPA 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 allowed us to find E_A of the chemical reaction and the enthalpies of adsorption of the reactants on the surface of copper. Table I summarizes the results.

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

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

Figure 2 shows a plot of the logarithm of the relative rates against the Hammett σ constants, and it will

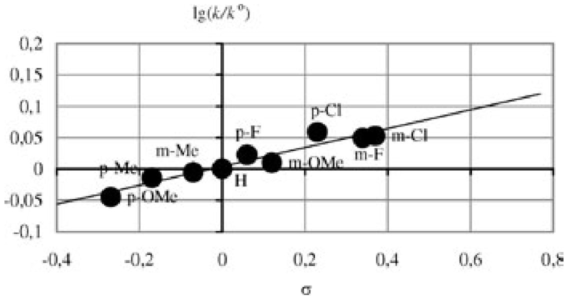


Figure 2 Hammett plots of log (k/k^{o}) vs the substituent constant σ obtained in this work.

be seen that there is a reasonably good linear relationship ($\rho = 0.15, r = 0.954, S_\rho = 0.02$). The ρ value obtained here is, however, considerably lower than the values associated with ionic reactions. This indicates that the polar effect on the abstraction of 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 similar to those reported by D.D. Tanner ($\rho = 0.22$, $r = 0.95$, $S_\rho = 0.03$) for the reaction of tri-n-butyl tin and benzyl bromide in benzene [22] (see Fig. 3).

The abstraction of bromine atom from a benzyl bromide by tri-butyltin radical is probably good model for atom abstraction by a metal surface. For comparison abstraction of chlorine atom from substituted benzyl chlorides by triethylgermyl radical has $\rho = 0.312$ [23].

The positive ρ values also have been obtained from the 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 III.

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

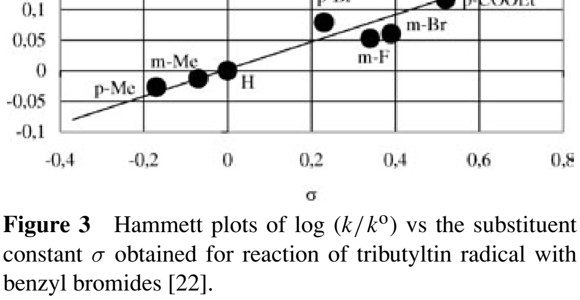


Figure 3 Hammett plots of log (k/k^{o}) vs the substituent constant σ obtained for reaction of tributyltin radical with benzyl bromides [22].

$$\mathrm{RHal} + e^- \rightarrow \mathrm{RHal}^{\bullet-}$$

$$\mathrm{RHal}^{\bullet-} \rightarrow \mathrm{R}^{\bullet} + \mathrm{RHal}^-$$

$$\mathrm{R}^{\bullet} + e^- \rightarrow \mathrm{R}^-$$

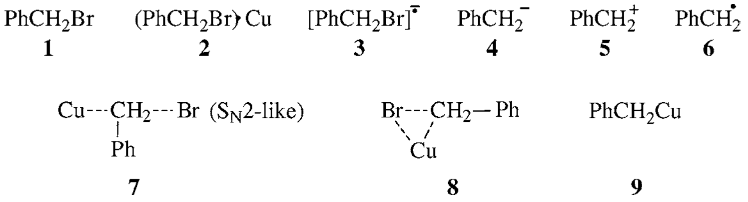
The decomposition of the radical anion is very fast or even concerted in combination with electron transfer.

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

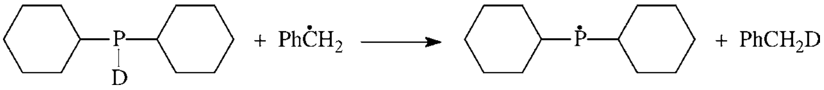
We have considered nine limiting transition states for the organic moiety summarized by structures **1**–**9** (Scheme 1) [33]. Here Cu represents a copper atom of a copper metal surface.

1: The unperturbed organic halide would represent the transition state if the overall rate of reaction was limited by the rate of encounter of this organic halide, either with the copper surface or with some other reactive species in solution.
2: The organic halide might adsorb at the metal surface in the rate-limiting step.
3: Electron transfer from the copper to the organic halide, either close to or adsorbed at the copper surface might be rate limiting.
4–6: The carbon—halogen bond might be broken in the transition state.
7–8: A copper atom at the metal surface (or possibly in solution) might displace halide from carbon in a $\mathrm{S_N2}$-like reaction or insert into the carbon—halogen bond in concerted process.
9: The rate-limiting step might involve a species with a covalent carbon—copper bond, for example, the rate of detachment of an organocopper species from the copper surface might be rate determining.

Since ρ has a significant 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 physical absorption, **2**. The sign of the ρ is incompatible with an intermediate benzyl cation, **5**. Since the largest values ρ observed are similar to those for the tin hydride reduction, and considerably smaller than that estimated for reactions generating benzyl anions ($\rho = 2.8$). The magnitude of ρ seems too small for a fully formed benzyl anion, **4**. A rate-determining step involving an intermediate in which the carbon—copper bond is partially or fully formed



Scheme 1



Scheme 2

(**9**) is unlikely, both because this transition state bears a large negative charge on carbon and would be expected to show a large value for ρ and because cleavage of 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 generating the radical anion **3**, bromine abstraction by copper forming an benzyl radical **6**, and insertion of copper directly in to the carbon—bromine bond of the adsorbed benzyl bromide **7**—on the basis of available evidence.

It is well known that ESR study of organic reaction is the most reliable evidence for the existence of paramagnetic particles as intermediates and 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 HMPA (1:50:50) at 77 K is a triplet of quartets with whole width about 50 G and g-factor of 2.002. The parameters of the ESR spectrum of benzyl radical are presented in Table IV.

A comparison shows that the ESR spectrum of the co-condensates of copper with benzyl bromide and HMPA coincides with that of benzyl radical.

When excess of benzyl bromide and HMPA (1:1) is condensed on the compact copper film (the thickness of the film is about 10^{-4} mm), losses of UHF power in the sample increase due to an increase in the electric conductivity, which results in considerable worsening of the resolution of the ESR spectra. Paramagnetic species that appeared in the benzyl bromide–HMPA atomic copper systems do not differ from those formed when the compact copper film is formed.

DCPD provides an opportunity not only to detect radical intermediates but also to determine their concentration in solution [20].

In the dehalogenation of benzyl bromide with copper in HMPA in the presence of DCPD, the composition of reaction products changed depending on the copper:DCPD molar ratio (Table V). At the copper : DCPD molar ratio equal to 1:5, the formation of 1,2-diphenylethane was not observed (Table V), but an equivalent amount of α-deuterotoluene was detected instead:

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

where L = HMPA.

The analysis of reaction products in the presence of radical traps and in their absence indicates that the process occurs by a radical mechanism via the formation of the benzyl radical (Scheme 2).

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 in solution.

Table IV Parameter of Spectra ESR for Benzyl Radical in Solid Matrices (a, G)

g-factor	$a^{\mathrm{H}}_{\mathrm{CH_2}}$ (G)	a^{H}_{o} (G)	a^{H}_{m} (G)	a^{H}_{p} (G)	References
2.002 ± 0.001	16.4 ± 0.9	5.5 ± 0.6	–	5.5 ± 0.6	This work
2.002 ± 0.001	16.4 ± 0.5	5.5 ± 0.5	–	5.5 ± 0.5	[4]
–	16.5	6	–	6	[34]
–	16.5 ± 1	5.5 ± 0.5	–	5.5 ± 0.5	[35]

Table V Product Composition in the Oxidative Dissolution of Copper in Benzyl Bromide-HMPA Systems in the Absence and in the Presence of Radical Traps

Entry	DCPD[a]/Cu (mol/mol)	Yield (mol%)	
		Ph—CH_2D[b]	Ph—CH_2—CH_2—Ph[c]
1	0	0	100
2	1	69	31
3	2	81	19
4	5	99	1

[a] Admixture of dicyclohexylphospine 1%.

[b] Admixture of toluene 1%.

[c] Admixture of 4,4′-ditolyl < 0.1%.

Table VI The Composition of Reaction Products being Produced by Acidolyses of Organocopper Compounds

Cu:$PhCH_2Br$:HMPA	T (K)	Yields of $PhCH_2CH_2Ph$[a] (%)	Yields of $PhCH_2D$[b] (%)
1:10:0	160	98	2
1:10:0	298	99	1
1:10:5	160	93	7
1:10:5	298	97	3
1:10:10	160	91	9
1:10:10	298	96	4

[a] Admixture of 4,4′-ditolyl < 0.01%.

[b] Admixture of toluene 2%.

At temperatures above 273 K, benzyl cuprates are known to thermally decompose to give their respective homocoupled products in good yield along the elemental copper [36]. At lower temperatures, these organocopper compounds have greater stability but will react quickly with benzyl bromide present to produce 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 at 298 K copper organic compounds whose acidolysis proceeds via the equation:

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

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

The result obtained leads us to conclude that coordinating solvent stabilizes the formation of organocopper compounds. This conclusion agrees well with data in work [36].

We have investigated the reaction of optically active (+)-*R*-1-bromo-1-phenylethane with copper in HMPA to seek experimental evidence of optical activity retention at the asymmetry center in the course of formation of organocopper compounds.

The main cause of racemization of organocopper compounds is stereochemical instability of C—Cu bond and can arise just after organocopper formation. The configuration of organocopper reagents must be fixed at the moment of its formation. It can be achieved by carrying out this reaction in the presence of deuterium chloride that reacts vary rapidly with organocopper compounds.

The co-condensation of a copper vapor with (+)-*R*-1-bromo-1-phenyletane and HMPA (1:10:10) that were precipitated in the 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, optically inactive 1-phenylethane-1D (**1**) and four other unlabeled hydrocarbons **2, 3, 4**, and **5** were detected in the reaction mixtures (Scheme 3).

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 partial retention configuration of the recombination products [37].

The formation of optical inactive **2, 3** with the ratio of **2:3** equals 1.03 along with **4** and **5** both shows that the reaction occurs according to the radical mechanism, and recombination and disproportionation of 1-phenylethyl radical can proceed after they enter 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 HMPA, 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 being produced by acidolyses of samples obtained is listed in Table VII.

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

Table VII Yield of Products (%) for Studying Stereochemistry of Reaction under Investigation

Yields (%)				
1	**2**	**3**	**4**	**5**
	Acidolysis was carried out at 160 K			
–	43.3	41.7	6.0	9.0
	Acidolysis was carried out at 298 K			
2	48.4	46.6	1.5	1.5

The results obtained suggest that the limiting step in the course of the reaction (+)-*R*-1-bromo-1-phenylethane with copper is the 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 [38–40] via the formation of benzyl radicals, which undergo recombination and isomerization in solution. The adsorption of the reagent and the solvent occurs by the Langmuir–Hinshelwood mechanism at different active centers of the metal surface in accordance with the Scheme 4. The limiting step of the reaction of benzyl bromides with copper is the dissociative electron transfer on a metal surface.

The yield of organocopper compounds depends on reaction conditions.

At temperatures above 273 K, benzyl cuprates are known to thermally decompose to give their respective homocoupled products [36]:

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

At lower temperatures, these organocopper compounds have greater stability but will react quickly with benzyl bromide [41]:

$$\mathrm{PhCH_2Cu} + \mathrm{PhCH_2Br} \rightarrow \mathrm{PhCH_2CH_2Ph} + \mathrm{CuBr}$$

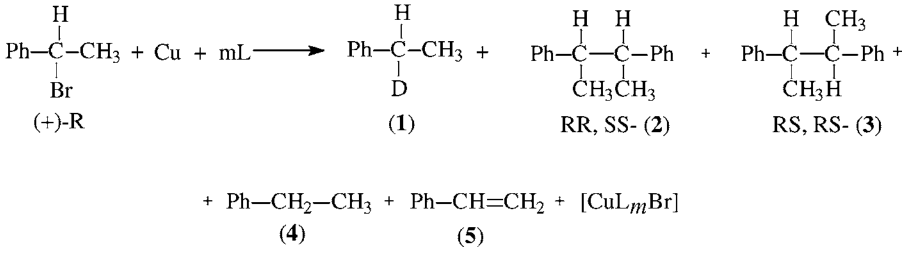
Recombination and isomerization of the benzyl radicals proceed in solution according to the Scheme 5 (for X = H).

The complex compounds of copper(I) with organic ligands in solutions form di- or tetramers [42]:

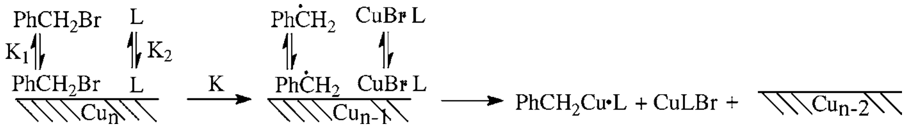
$$\mathrm{CuLBr} + \mathrm{Cu}_{n-1}\mathrm{L}_{n-1}\mathrm{Br}_{n-1} \rightarrow \mathrm{Cu}_n\mathrm{L}_n\mathrm{Br}_n$$

$$\mathrm{Cu}_n\mathrm{L}_n\mathrm{Br}_n + (n - m)\mathrm{L} \rightarrow [\mathrm{Cu}_n\mathrm{L}_m\mathrm{Br}_n]\downarrow$$

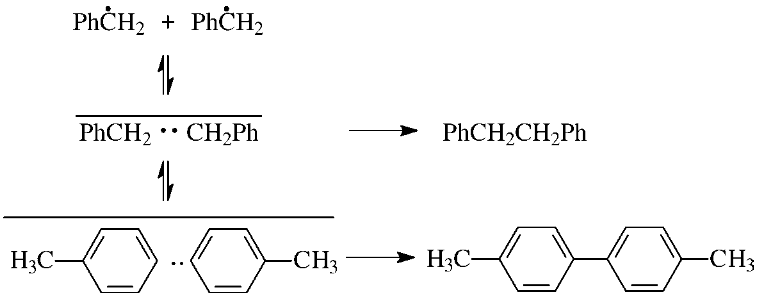
where L = HMPA; $2 \leq n \leq 4$; $2 \leq m \leq 4$.



Scheme 3



Scheme 4



Scheme 5

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