

Kinetics and mechanism of reaction of benzyl bromide with copper in dimethylacetamide

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ABSTRACT: The reaction of copper with various benzyl bromides in dimethylacetamide was studied. In the absence of atmospheric oxygen, oxidative dissolution of copper occurred by the mechanism of single electron transfer with the formation of 1,2-diphenylethane and copper(I) complexes. The kinetic and thermodynamic parameters of the reaction have been obtained and the reaction mechanism is discussed. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: benzyl bromide; dehalogenation; mechanism; ESR spectra; copper; kinetics; dimethylacetamide

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 method for the synthesis of these compounds.¹ Being a destroyer of ozone, carbon tetrachloride is prohibited for use in the chemical industry, which is why substitutes are being sought.

For the elaboration of optimal conditions for target-oriented synthesis of coordination compounds of copper halides with organic ligands, the kinetics and mechanism of the reaction of copper with benzyl bromide in the presence of dimethylacetamide (DMAA) were studied in detail.

EXPERIMENTAL

Equipment and analytical measurements

The ¹H NMR spectra were recorded on a Jeol LTD VEX-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.

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The ESR spectra were recorded on a Radiopan radio-spectrometer at 293 K according to a well-known procedure.^{2,3} 2,2,6,6-Tetramethyl-1-piperidinyloxy (TMPO) free radical was used as a radical trap. The ESR spectra were recorded at 77 K in films of copper co-condensates with 50–100-fold excess of benzyl bromide according to the literature^{4,5} at 9 GHz frequency in the absence of saturation and amplitude broadening. Benzyl bromide was evaporated at 0–35 °C and the copper was sublimated from the crucible at 1400–1440 K during continuous evacuation (10^{−4} mm Hg).

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

The purity of the starting substances was monitored and quantitative analysis of the organic reaction products was performed using gas chromatography (GC). The conditions of GC analysis were described previously.⁶

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 eluent. The rate of elution was 15 ml min^{−1} and the sample volume was 100 µl (after 1 : 1000 dilution with water).

Reaction products were analyzed on a Hewlett-Packard GC-MS instrument (USA) (HP 5972 mass-selective detector, HP 5890 chromatograph) using capillary column DB-1 (*l* = 30 m, *d* = 0.25 mm) and the column temperature was 50 °C. In 5 min the temperature of the column was increased to 280 °C at a heating rate of

10 °C min⁻¹. Helium was the carrier gas at (a flow rate of 1 ml min⁻¹). The injector temperature was 275 °C and the detector temperature was 290 °C. Components were identified by co-injection of authentic samples and GC-MS. Quantitative analyses were based on measured response factors using model mixtures.

Reagents

Copper powder of >99.99% purity was prepared by the reduction of CuSO₄ (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 DMAA 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 DMAA.

All organic compounds were obtained from commercial sources. Benzyl bromide (Aldrich) was dried with fused CaCl₂ and distilled: b.p. 83.5–84 °C/13 mmHg (lit⁷ b.p. 83.5–84 °C/13 mmHg). 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*_D²⁰ = 1.5067 (lit⁸ b.p. = 144.0 °C; *n*_D²⁰ = 1.5068). Dimethylacetamide was purified by slow double-vacuum distillation over a large amount of P₂O₅: ⁹b.p. = 83.5–84 °C/32 mmHg; *n*_D²⁰ = 1.4380 (lit⁸ b.p. = 84 °C/32 mmHg; *n*_D²⁰ = 1.4380).

Other solvents were purified according to standard procedures.¹⁰ 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 bromide with copper: general procedure

A 1-g portion of Cu powder was dissolved in 10 ml of DMAA 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. The recrystallization from 3-methylpyridine afforded 5.26 g (80%) of yellow crystals, which were stable in air¹¹. Analysis: C₁₈H₂₁N₃CuBr (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), ν = 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 DMAA, 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

Table 1. Product composition in the oxidative dissolution of copper in benzyl bromide–DMAA systems in the absence or presence of radical traps

DCPD ^a /Cu (mol/mol)	Yield (mol.%)	
	Ph—CH ₂ D ^b	Ph—CH ₂ —CH ₂ —Ph ^c
0	0	100
1	72	28
2	85	15
5	100	0

^a Admixture with 1% dicyclohexylphosphine.

^b Admixture with 1% toluene.

^c Admixture with <0.01% 4,4'-dimethylbiphenyl.

(96%), m.p. = 51–52 °C (lit¹² m.p. = 51–52 °C). ¹H NMR (CDCl₃): δ = 2.82 (s, 4H, —CH₂—), 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). Retention time 17.8 min.

4,4'-Dimethylbiphenyl MS (EI, 70 eV): calculated *m/z* = 182.11 (M); found *m/z* = 182 [M]⁺ (100), 167 [M—CH₃]⁺ (56), 152 [M—2CH₃]⁺ (15). Retention time 18.9 min.

Identification of radical species in solution

The reaction in the presence of a radical trap was studied analogously to the above procedures, with dicyclohexyldeuteriophosphine (DCPD) as the radical trap.¹³

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

α -Deuterotoluene ¹H NMR (CDCl₃): δ = 2.32 (m, 2H, —CH₂—), 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—C₂H₂]⁺ (9), 65 [M—C₂H₂D]⁺ (11).

Study of the reaction kinetics

The reactions of copper with benzyl bromide in DMAA were studied by the resistometric method¹⁴ according to a well-known procedure¹⁵ in an atmosphere of water-free argon free from oxygen.

Benzene was used as a neutral solvent for determination of the kinetic and thermodynamic characteristics of the reaction of copper with benzyl bromide in the presence of DMAA.¹⁶

The reaction was studied in kinetic mode, as evidenced by the independence of the rate of copper dissolution in the test media from the rate of stirring (Table 2 summarizes the results of this study).

Table 2. Kinetic and thermodynamic parameters of the oxidative dissolution of copper in the benzyl bromide–DMAA system calculated using the Langmuir–Hinshelwood mechanism from adsorption of the reagent and solvent at different active centers of the metal

Parameter		$k \times 10^4$	K_1	K_2
TK	313	0.9 ± 0.1	0.93 ± 0.02	1.49 ± 0.02
	323	2.2 ± 0.1	0.68 ± 0.01	1.04 ± 0.02
	333	4.4 ± 0.1	0.49 ± 0.01	0.70 ± 0.02
	338	6.8 ± 0.1	0.43 ± 0.01	0.58 ± 0.01
	343	9.4 ± 0.1	0.37 ± 0.01	0.51 ± 0.01
	353	20.8 ± 0.2	0.29 ± 0.01	0.36 ± 0.01
R^a		0.999	0.999	0.999
E_A (kJ mol ⁻¹)		71.0 ± 3.5		
$\Delta H^\circ_{\text{RBr}}$ (kJ mol ⁻¹)			-27.0 ± 0.9	
$\Delta H^\circ_{\text{DMAA}}$ (kJ mol ⁻¹)				-32.8 ± 1.4

^a Sample correlation coefficient.

RESULTS AND DISCUSSION

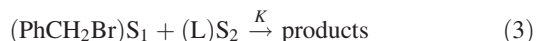
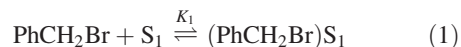
Kinetic studies

The reaction kinetics of the oxidative dissolution of Cu in the benzyl bromide–DMAA system has been studied using the resistometric method. This method provides an opportunity to study various kinetic features of fast heterogeneous reactions, characterized by high accuracy and reproducibility of results.^{14,15}

To determine the kinetic and thermodynamic characteristics of the process, the reaction was performed in a neutral solvent of benzene ($\text{DN}_{\text{SbCl}_5} = 0.4 \text{ kJ mol}^{-1}$).¹⁶

Figure 1 demonstrates the kinetic curves and an increase in the concentration of DMAA from 0.5 to

2 mol l^{-1} did not change the shape of the curves. This fact indicates that the process occurs by the Langmuir–Hinshelwood mechanism, with adsorption of the reagent and the solvent at different active centers of the metal surface¹⁷



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

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

$$W = \frac{kK_1K_2[\text{PhCH}_2\text{Br}][\text{DMAA}]}{1 + K_1[\text{PhCH}_2\text{Br}] + K_2[\text{DMAA}] + K_1K_2[\text{PhCH}_2\text{Br}][\text{DMAA}]} \quad (4)$$

where $k = KN_1N_2$ and N_1 and N_2 are the numbers of active centers of the metal surface at which adsorption of benzyl bromide and DMAA, respectively, takes place.

Treatment of the experimental relations (Fig. 1) using the set of Eqns (1)–(3) allowed us to determine the equilibrium constants of benzyl bromide and DMAA 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 the activation energy E_A of the chemical reaction and the enthalpies of adsorption of the reactants on the surface of copper. Table 2 summarizes the results.

A comparison of the results with the published data¹⁷ on the oxidative dissolution of copper in the CCl_4 –DMAA system demonstrated that $\Delta H_{\text{ads DMAA}}$ at the surface of copper remained almost unchanged ($\sim 33 \text{ kJ mol}^{-1}$) on replacing CCl_4 by PhCH_2Br , whereas the corresponding values for an organic halide changed considerably (from -4 to -27 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 interaction of adsorbed reactant molecules with the metal surface (i.e. a surface chemical reaction) is the rate-limiting step of the reaction.

A detailed study of the mechanism of any chemical reaction is a challenge. It has been established that the

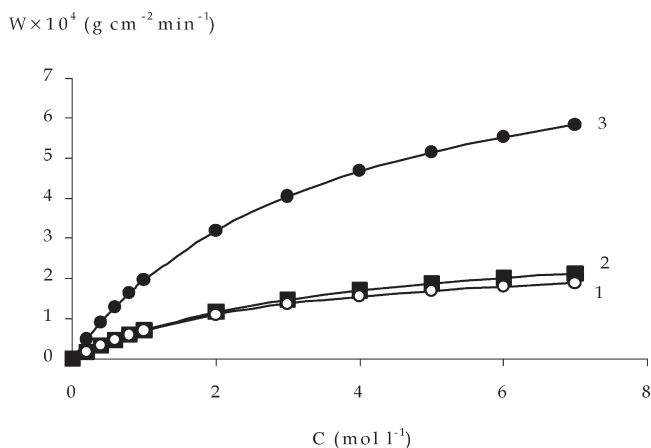
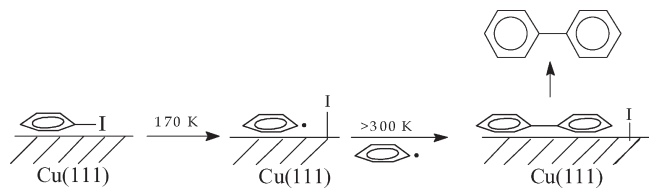


Figure 1. The dependence of the rate (W) of oxidative dissolution of copper in the benzyl bromide–DMAA system on the initial concentrations of mixture components in the presence of an indifferent solvent (benzene) at 313 K: (1) $C_{\text{RBr}} = 0.5 \text{ mol l}^{-1}$; (2) $C_{\text{DMAA}} = 0.5 \text{ mol l}^{-1}$; (3) $C_{\text{DMAA}} = 2 \text{ mol l}^{-1}$



Scheme 1

reactions of various reagents with metals in dipolar aprotic solvents occur by radical,¹⁸ radical-ion^{13,18} or carbanion¹⁹ and other mechanisms, the ratio between which depends on the nature of the metal, the reagent and the solvent.^{18,20}

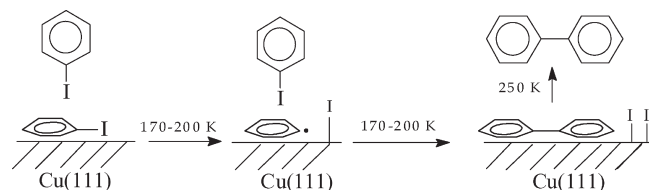
In a previous paper we showed that the mechanism of the reaction of benzyl halides with magnesium depends on the carbon–halogen bond strength.⁶ It is well known that the carbon–halogen bond strength in allyl and benzyl halides is weaker than in alkyl and aryl halides. The bond energy in benzyl bromide approaches that found in alkyl (aryl) iodides rather than the corresponding bromides²¹ and so the reaction of iodobenzene with copper is probably a good model for the reaction of benzyl bromide with copper.

Xi and Bent have shown that the reaction of iodobenzene with copper occurs on a metal surface.²² Adsorbed iodobenzene dissociates on Cu(111) to form iodine atoms and adsorbed phenyl radicals. The authors suggest two pathways for the reaction mechanism: a low-coverage, high-temperature pathway forming adsorbed and subsequently coupled phenyl groups (Scheme 1);²² and a high-coverage, low-temperature coupling reaction between adsorbed phenyl radicals and molecular iodobenzene (Scheme 2).²²

The reaction of organic halides with copper is more complicated in the presence of dipolar aprotic solvent.

Nechaev *et al.*^{23,24} Brodskii and Urbakh²⁵ and Nechaev²⁶ have shown that adsorption of organic compounds on a metal surface depends on the ionization potential of the organic compounds, which is why the benzyl radical can leave the copper surface and enter solution.

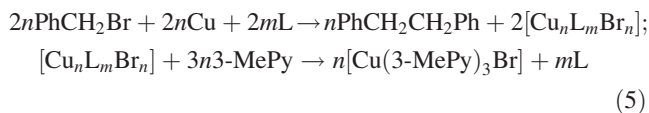
Recombination and isomerization of the benzyl radicals can proceed both on a copper surface (model A) and in solution (model D). The ratio between these models depends on the ionization potential of the reagents and free radicals.



Scheme 2

Study of reaction products

Analysis of the reaction products demonstrated that, in the absence of atmospheric oxygen (including oxygen adsorbed on the metal surface), dehalogenation of benzyl bromide with copper in DMAA occurred with the formation of 1,2-diphenylethane and the Cu(I) complex tris(3-methylpyridine)copper(I) bromide [Cu(3-MePy)₃Br]¹¹



where L = DMAA and 3-MePy is 3-methylpyridine; $1 \leq n \leq 4$ and $1 \leq m \leq 4$.

With the use of ion chromatography, we found that only copper(I) complexes were formed in the course of the process. These complexes were oxidized very readily when the reaction products were isolated in air.

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 radicals occurs only in the radical pair.

Determination of radical intermediates by ESR at 77 K

The ESR spectrum of copper co-condensate with benzyl bromide at 77 K in a solid matrix is a triplet of quartets with a whole width of 50 G and a *g* factor of 2.002. The spectrum is similar to the same spectrum of a co-condensate of magnesium with benzyl bromide.⁶ The parameters of the spectrum obtained and the literature data for the benzyl radical spectrum are listed in Table 3.

There is a triplet of quartets with a whole width of about 50 G in the spectrum of the benzyl radical in a solid matrix at 77–100 K,^{5,27,28} which can be explained by broadening of the lines.

Comparison of the parameters of the typical ESR spectrum obtained in this work with those of the benzyl radicals in solid matrices allows assignment of the signals of this spectrum to the benzyl radical. The total amount of paramagnetic particles at 77 K in the samples was 7%.

Table 3. Parameters of ESR spectra for benzyl radical in solid matrices

<i>g</i> -factor	a_{CH}^{H} (G)	a_o^{H} (G)	a_m^{H} (G)	a_p^{H} (G)	Ref.
2.002 ± 0.001	16.4 ± 0.5	5.5 ± 0.5	—	5.5 ± 0.5	*
2.002 ± 0.001	16.5 ± 0.5	5.5 ± 0.5	—	5.5 ± 0.5	6
2.002 ± 0.001	16.5 ± 0.5	5.5 ± 0.5	—	5.5 ± 0.5	27
2.0026	16.34	5.13	1.77	6.17	28

*Data obtained in this study.

Co-condensation of a copper vapor with benzyl bromide (which was precipitated in the molecular beam mode on the surface cooled with liquid N₂) afforded white films. These films are stable at 77 K for no less than 24 h. At the melting temperatures of the samples, these films were decolorized. The melts obtained contained small amounts of solid white inclusions.

Examination of the ESR spectra recorded at different temperatures provides data on the stability and conversions of reaction intermediates. The intensity of the ESR signal gradually decreases as the co-condensates of copper with benzyl bromide are heated to 100 K. At temperatures higher than 130–150 K the resolution of the ESR spectra is substantially impaired, apparently due to overlap of the signals of benzyl and 4-tolyl radicals, as well as the signals of the corresponding radical pairs.

The fact that only benzyl radical was detected at 77 K, and the intensity of its signal gradually decreases as the temperature increases, indicates that the formation of radical pairs $\text{Ph}\dot{\text{C}}\text{H}_2 \cdot \dot{\text{C}}\text{H}_2\text{Ph}$ occurs at $T > 77$ K, whereas their recombination and isomerization occur at $T > 130$ –150 K.

After thawing and decomposition of the samples with 20% HCl, 4,4'-dimethylbiphenyl (<0.01%) and toluene ($\leq 2\%$) were detected in the Cu–PhCH₂Br systems along with 1,2-diphenylethane (97–98%).

Analysis of solid white inclusions, which were detected upon thawing of samples, demonstrated that the samples contained Cu⁺ cations and bromide anions whose ratio corresponded to the formula CuBr.

Although excess benzyl bromide settles on the copper film surface (the thickness of the film is 10^{-4} mm), the UHF power dissipation increases. The consequent decrease of ESR spectrum resolution can be attributed to increase in the copper film electroconductivity. The paramagnetic particles appearing in benzyl bromide–compact copper systems are identical to the particles formed when atomic copper films are used; the ESR spectrum has poor resolution and low intensity in the latter case.

The formation of toluene in the reaction mixtures obtained after thawing and hydrolysis can occur due to decomposition of organocopper compounds with 20% HCl.²⁹

Determination of radical species in solution

The radical species in solutions were detected and identified with the use of radical traps.

The disappearance of the ESR signals of the added TMPO radical, which can react with radical intermedi-

ates, suggests a radical nature for the mechanism of oxidative copper dissolution in the benzyl bromide–DMAA systems because the ESR signals of TMPO did not appear after the oxidation of copper and reduction of the mixtures by KI in an acetate buffer solution.^{2,3}

We used DCPD as a chemical trap for the radicals, and this previously showed good performance. It provides an opportunity not only to detect radical intermediates but also to determine their concentration in solution.¹³

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



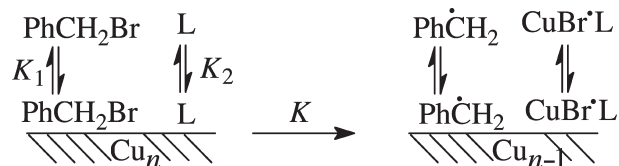
where L = DMAA.

The analysis of reaction products in the presence of a radical trap (or in the absence of it) indicates that the process occurs by a radical mechanism via the preliminary formation of benzyl radical (Scheme 3).



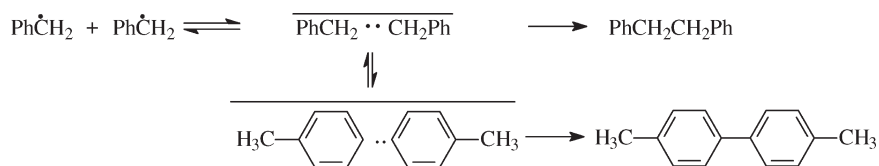
Scheme 3

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 both in solution and on a copper surface. The adsorption of the reagent and the solvent occurs by the Langmuir-Hinshelwood mechanism at different active centers of the metal surface according to Scheme 4.



Scheme 4

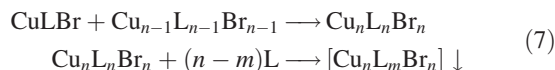
Recombination and isomerization of the benzyl radicals can proceed both in solution (model D) and on a metal surface (model A) according to Scheme 5.



Scheme 5

The ratio between these models depends on the ionization potential of the reagents and free radicals.

The coordination compounds of copper(I) with organic ligands in solution form di- or tetramers:³⁰



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

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