ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 9, pp. 1667–1675. © Pleiades Publishing, Ltd., 2014.
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Kinetics and Mechanism of the Reaction of Benzyl Bromide with Copper in Dimethylacetamide in the Presence of Oxygen

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Received February 24, 2014

Abstract—The reaction of copper metal with benzyl bromide in dimethylacetamide in the presence of oxygen has been studied. Oxidative dissolution of copper follows the single-electron transfer mechanism with formation of benzaldehyde, benzyl alcohols, and copper(II) coordination compounds. The kinetic and thermodynamic parameters of the process have been determined by resistometry. Intermediately formed species have been identified and quantitated, and the reaction stereochemistry has been studied. The reaction mechanism is discussed.

Keywords: benzyl bromide, oxidative dissolution of copper, kinetics, reaction mechanism, dimethylacetamide

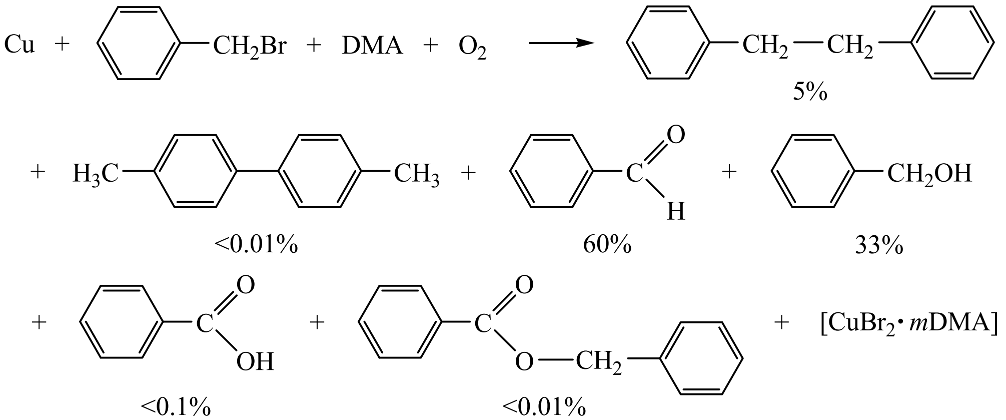
DOI: 10.1134/S1070363214090047

Oxidative dissolution of metals in organic media is a promising field of chemistry and chemical technology, which includes problems related to catalysis, corrosion, metal refining, analysis of metals and alloys, extraction, and preparation of various catalytic systems and coordination compounds. The use of organic solvents offers broad variation of donor–acceptor properties and allows oxidative dissolution to be accomplished under mild conditions both in the absence and in the presence of oxygen [1].

Unlike processes occurring in organic media in an inert atmosphere, oxidative dissolution of metals in the presence of oxygen has been studied relatively poorly, mechanisms of such processes generally have not been studied, and kinetic parameters have not been determined; therefore, these reactions cannot be performed on a large scale.

In the present work we studied the kinetics and mechanism of the reaction of benzyl bromide with copper in *N*,*N*-dimethylacetamide (DMA) in the presence of oxygen. Oxidative dissolution of copper in the system benzylbromide–DMA–oxygen leads to the formation of benzaldehyde and benzyl alcohol at a ratio of 2 : 1 and copper(II) coordination compounds (Scheme 1).

Scheme 1.



m = 2, 3.

Table 1. Parameters of the ESR s[ectra of 2,2,6,6-tetramethylpiperidine 1-oxyl

g factor	a_N, G	a_H, G	ΔH, G	Solvent
2.0055±0.0002	16.6±0.1	0.2±0.2	1.5±0.3	Benzyl bromide–dimethylacetamide[a]
2.0055	15.4±0.1	0.2±0.2	1.5±0.2	Benzene [4]
2.0055	16.2±0.1	0.2±0.2	1.5±0.2	Diethylene glycol [4]
2.0055	16.4±0.1	0.2±0.2	1.5±0.2	Formamide [4]

[a] Molar ratio 5 : 8. Data of this work.

Table 2. Reaction of benzyl bromide with copper in dimethylacetamide in the absence and in the presence of dicyclohexyldeuterophosphine (DCPD)

DCPD[a]/Cu, mol	Yield, mol %			
	$PhCH_2D$[b]	$PhCH_2CH_2Ph$	PhCHO	$PhCH_2OH$
0[c]	0	5±1	60±1	33±1
3	68±1	2±1	19±1	11±1
5	97±1	0	2±1	1±1

[a] Dicyclohexyldeuterophosphine contained 1% of dicyclohexylphosphine as impurity. [b] Toluene, 1%. [c] Benzoic acid (<0.1%) and benzyl benzoate (<0.01%) were also detected.

The observed benzaldehyde-to-benzyl alcohol ratio, as well as the presence of 1,2-diphenylethane and traces of 4,4'-dimethylbiphenyl, suggest radical mechanism of the reaction.

In order to analyze the reaction stereochemistry we synthesized (–)-(*R*)-1-bromo-1-phenylethane which was brought into reaction with copper in DMA. Organic products were isolated by preparative liquid chromatography and were optically inactive; their molar ratios were as follows: (*RS*)-1-phenylethanol, 2 : 1; (*RS*)- and (*RR*)/(*SS*)-2,3-diphenylbutanes, 1.03 : 1; styrene–ethylbenzene, 1 : 1. These ratios are very consistent with published data on the oxidation (with oxygen), recombination, and disproportionation of 1-phenylethyl radical in solution [2].

The radical mechanism of the oxidative dissolution of copper in $PhCH_2Br$–DMA was confirmed by the ESR study performed according to the known procedure [2, 3] at 293 K in the presence of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) as stable radical species; the molar ratio Cu–$PhCH_2Br$–DMA–TEMPO was 1 : 5 : 8 : 0.2. The ESR spectrum of the reaction mixture was a triplet with a width of 85 G, which corresponded to coupling of the unpaired electron with the nitroxyl nitrogen nucleus. The ESR parameters in combination with published data [4] are given in Table 1. These findings allowed us to attribute the observed ESR spectrum to nitroxyl radical.

The formation of radical species during the process follows from the disappearance of signals of TEMPO which is capable of reacting with radical intermediates. No TEMPO signal appeared after complete oxidation of copper and reduction of the reaction mixture with hydrogen peroxide under alkaline conditions [2, 3].

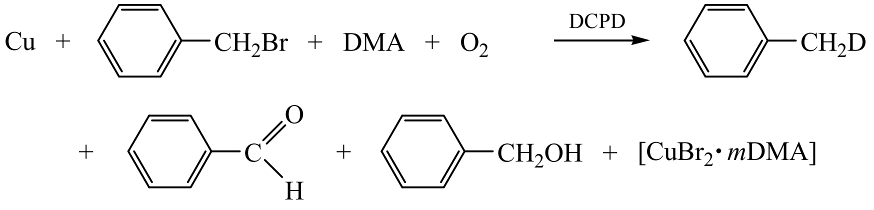
Radical intermediates were detected and identified using dicyclohexyldeuterophosphine (DCPD) which is known as an efficient trap for benzyl radical; also, the concentration of the latter in solution can be determined quantitatively in this way [2, 5]. The results are presented in Table 2.

The product composition in the dehalogenation of benzyl bromide with copper in DMA on exposure to air in the presence of DCPD depended on the Cu–DCPD molar ratio (Table 1). At a Cu–DCPD molar ratio of 1 : 5, the major product was α-deuterotoluene (97%), and small amounts of benzaldehyde (2%) and benzyl alcohol (1%) were detected (Scheme 2).

Analysis of the products formed in the reactions of copper with benzyl bromide in dipolar aprotic solvents in the presence and in the absence of DCPD indicated intermediate formation of benzyl radical (Table 2). In all cases, a green finely crystalline solid was isolated; it was a mixture of two coordination compounds of copper(II), which were difficult to separate. The copper compounds were identified as the complex with triphenylphosphine oxide (TPPO) $[CuBr_2(TPPO)_2]$, which was obtained by ligand exchange according to the following scheme:

$$CuBr_2\cdot m\text{DMA} + 2\text{TPPO} \rightarrow [CuBr_2(\text{TPPO})_2] + m\text{DMA}.$$

Scheme 2.



$m = 2, 3.$

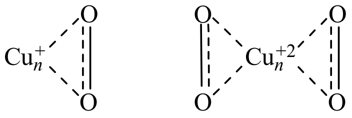
Analysis of the reaction mixture by ion chromatography showed the presence of copper(II) complexes and small amounts of copper(I) complexes, while no copper(III) compounds were detected. Copper(I) complexes could be formed via dehalogenation of benzyl halide with copper or as a result of reduction of copper(II) compounds with copper metal [3] or benzyl radical in dipolar aprotic solvents [6]. However, the process under anoxic conditions was very slow; therefore, the formation of large amounts of copper(I) coordination compounds in this way is hardly probable. When the reaction of copper with benzyl bromide was carried out in the presence of oxygen and anhydrous $CuCl_2$ ($Cu–CuCl_2$ molar ratio 1 : 1), the mixture contained 2% of benzyl chloride, indicating that benzyl radical partially reduces copper(II) compounds in solution to copper(I).

$$PhCH_2 + CuCl_2 \rightarrow PhCH_2Cl + CuCl.$$

We previously showed [7] that benzyl halides react with copper in dipolar aprotic solvents in an inert atmosphere under mild conditions and that the reaction occurs on the metal surface according to the radical mechanism. The products were 1,2-diphenylethane, traces of 4,4'-dimethylbiphenyl, and copper(I) coordination compounds. The reaction rate increases on exposure to atmospheric oxygen, and the product composition changes, indicating change of the reaction mechanism.

The kinetics of the oxidative dissolution of copper in the system $PhCH_2$–DMA–O_2 were studied by the resistometric method [8], which previously ensured high accuracy and reproducibility in kinetic studies of fast heterofeneous reactions. The reaction was carried out in benzene [donor number DN($SbCl_5$) = 0.42 kJ/mol] as inert solvent. Figure shows the dependences of the reaction rate on the concentrations of benzyl bromide and DMA. These dependences are typical of reactions following Langmuir–Hinshelwood or Eley–Rideal mechanism [2, 9].

Scheme 3.



Ia **Ib**

As shown in [10–12], oxygen adsorption on metallic copper is so rapid that its rate cannot be measured accurately. This means that the energy of activation of this process is very low. Presumably, adsorption of oxygen on the copper surface and formation of surface oxygen complexes like **Ia** and **Ib** [13] are the initial steps of the reaction. Complex **Ib** is more stable due to stabilization of copper(II) (Scheme 3).

Thus, assuming that the reaction follows the Langmuir–Hinshelwood pattern including adsorption of oxygen, benzyl bromide, and dimethylacetamide on different active sites of the surface, the process can be represented by the following scheme:

$$Cu_1 + O_2 \overset{K_1}{\rightleftarrows} Cu_1O_2, \tag{1.1}$$

$$Cu_1O_2 + O_2 \overset{K_2}{\rightleftarrows} O_2Cu_1O_2, \tag{1.2}$$

$$Cu_2 + \text{Solv} \overset{K_3}{\rightleftarrows} Cu_2(\text{Solv}), \tag{1.3}$$

$$Cu_3 + PhCH_2Hlg \overset{K_4}{\rightleftarrows} Cu_3(PhCH_2Hlg), \tag{1.4}$$

$$O_2Cu_1O_2 + Cu_2(\text{Solv}) \overset{K_5}{\rightleftarrows} \frac{\text{Solv}}{O_2Cu_1^{+}O\text{–}O^{-}} + Cu_2, \tag{1.5}$$

$$\frac{\text{Solv}}{O_2Cu_1^{+}O\text{–}O^{-}} + Cu_2(\text{Solv}) \overset{K_6}{\rightleftarrows} \frac{2\text{Solv}}{{}^{-}O\text{–}OCu_1^{2+}O\text{–}O^{-}} + Cu_2, \tag{1.6}$$

$$\frac{2\text{Solv}}{{}^{-}O\text{–}OCu_1^{2+}O\text{–}O^{-}} + Cu_3(PhCH_2Hlg) \xrightarrow{k_7} \text{Reaction products.} \tag{1.7}$$

Here, Cu_1, Cu_2, and Cu_3 are active sites on the copper surface, where oxygen is adsorbed; Solv stands for the solvent molecule (dimethylacetamide); K_1, K_2, K_3, and K_4 are the adsorption constants of oxygen, dimethylacetamide, and benzyl bromide on the copper surface; K_5 and K_6 are the equilibrium constants of electron transfer to oxygen; k_7 is the rate constant of the rate-determining step. Assuming that equilibria (1.1)–(1.6) are stationary, we obtain expression (1.8) for the overall reaction rate.

$$w = \frac{k_7 S_1 S_3 K_1 K_2 K_3^2 K_4 K_5 K_6 [\mathrm{PhCH_2Br}][\mathrm{Solv}]^2 P^2(\mathrm{O_2})}{(1 + K_4[\mathrm{PhCH_2Br}])\{1 + K_1 P^2(\mathrm{O_2}) + K_1 K_2 P^2(\mathrm{O_2}) + K_{1\gamma} K_2 K_3 K_5 P^2(\mathrm{O_2})[\mathrm{Solv}] + K_1 K_2 K_3^2 K_5 K_6 P^2(\mathrm{O_2})[\mathrm{Solv}]^2\}}. \quad (1.8)$$

Here, S_1 and S_3 are the surface areas of active sites Cu_1 and Cu_3, $P(O_2)$ is the oxygen pressure, and w is the reaction rate.

Taking into account that the constants K_1, K_2, and K_5 are very high ($K_1 > K_2$, $K_2 >> 1$, $K_5 >> 1$) [10–12], Eq. (1.8) is transformed into

$$w = \frac{k_7 S_1 S_3 K_3 K_4 K_6 [\mathrm{PhCH_2Br}][\mathrm{Solv}]}{(1 + K_4[\mathrm{PhCH_2Br}])(1 + K_3 K_6[\mathrm{Solv}])}. \quad (1.9)$$

If benzyl bromide and dipolar aprotic solvent molecules are adsorbed on the same sites, the reaction scheme is given by Eqs. (2.1)–(2.7).

$$\mathrm{Cu_1 + O_2} \overset{K_1}{\rightleftarrows} \mathrm{Cu_1O_2}, \quad (2.1)$$

$$\mathrm{Cu_1O_2 + O_2} \overset{K_2}{\rightleftarrows} \mathrm{O_2Cu_1O_2}, \quad (2.2)$$

$$\mathrm{Cu_2 + Solv} \overset{K_3}{\rightleftarrows} \mathrm{Cu_2(Solv)}, \quad (2.3)$$

$$\mathrm{Cu_2 + PhCH_2Hlg} \overset{K_4'}{\rightleftarrows} \mathrm{Cu_2(PhCH_2Hlg)}, \quad (2.4)$$

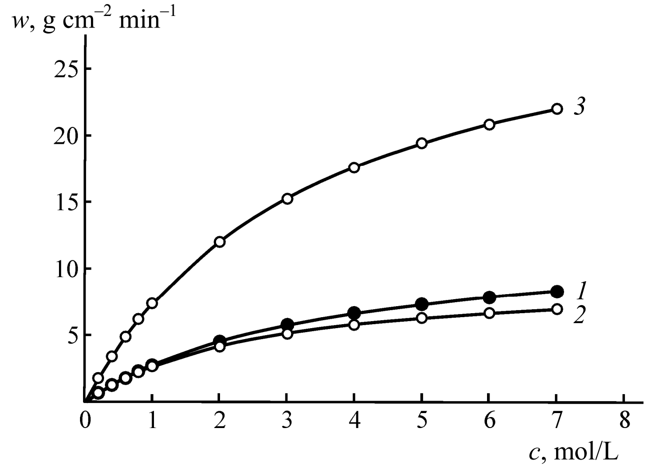
$$\mathrm{O_2Cu_1O_2 + Cu_2(Solv)} \overset{K_5}{\rightleftarrows} \frac{\mathrm{Solv}}{\mathrm{O_2Cu_1^{+}O{-}O^{-}}} + \mathrm{Cu_2}, \quad (2.5)$$

$$\frac{\mathrm{Solv}}{\mathrm{O_2Cu_1^{+}O{-}O^{-}}} + \mathrm{Cu_2(Solv)} \overset{K_6}{\rightleftarrows} \frac{\mathrm{Solv}}{\mathrm{{}^{-}O{-}OCu_1^{2+}O{-}O^{-}}} + \mathrm{Cu_2}, \quad (2.6)$$

$$\frac{\mathrm{2Solv}}{\mathrm{{}^{-}O{-}OCu_1^{2+}O{-}O^{-}}} + \mathrm{Cu_2(PhCH_2Hlg)} \xrightarrow{k_{o7}} \mathrm{Products}. \quad (2.7)$$

Here, K_4' is the adsorption constant of benzyl bromide on Cu_2, and k_{07} is the rate constant of the rate-determining step provided that benzyl bromide and dimethylacetamide are adsorbed on the same active sites. Application of the steady-state approximation yields Eq. (2.8) for the reaction rate.

$$w = \frac{k_{o7} S_1 S_3 K_1 K_2 K_3^2 K_4' K_5 K_6 [\mathrm{PhCH_2Br}][\mathrm{Solv}]^2 P^2(\mathrm{O_2})}{(1 + K_3[\mathrm{Solv}] + K_4'[\mathrm{PhCH_2Br}])\{1 + K_1 P_{\mathrm{O}_\gamma}^2 + K_1 K_2 P^2(\mathrm{O_2}) + K_1 K_2 K_3 K_5 P^2(\mathrm{O_2})[\mathrm{Solv}] + K_1 K_2 K_3^2 K_5 K_6 P^2(\mathrm{O_2})[\mathrm{Solv}]^2\}}. \quad (2.8)$$



Plots of the rate of oxidative dissolution of copper in the system benzyl bromide–dimethylacetamide–oxygen versus initial reactant concentrations at 353 K in benzene: (*1*) c_{RBr} = 0.5 M, c_{DMA} = 0–7 M; (*2*) c_{DMA} = 0.5 M, c_{RBr} = 0–7 M; (*3*) c_{DMA} = 2 M, c_{RBr} 0–7 M.

Here, S_1 and S_3 are the surface areas of active sites Cu_1 and Cu_3, respectively.

Using the same approximations as in the derivation of Eq. (1.9), we obtain Eq. (2.9).

$$w = \frac{k_{o7} S_1 S_3 K_3 K_4' K_6 [\mathrm{PhCH_2Br}][\mathrm{Solv}]}{(1 + K_3[\mathrm{Solv}] + K_4'[\mathrm{PhCH_2Br}])(1 + K_3 K_6[\mathrm{Solv}])}. \quad (2.9)$$

If dioxygen anion reacts with benzyl bromide supplied from the bulk solution, the following reaction scheme can be proposed:

$$\mathrm{Cu_1 + O_2} \overset{K_1}{\rightleftarrows} \mathrm{Cu_1O_2}, \quad (3.1)$$

$$\mathrm{Cu_1O_2 + O_2} \overset{K_2}{\rightleftarrows} \mathrm{O_2Cu_1O_2}, \quad (3.2)$$

$$\mathrm{Cu_2 + Solv} \overset{K_3}{\rightleftarrows} \mathrm{Cu_2(Solv)}, \quad (3.3)$$

$$\mathrm{O_2Cu_1O_2 + Cu_2(Solv)} \overset{K_5}{\rightleftarrows} \frac{\mathrm{Solv}}{\mathrm{O_2Cu_1^{+}O{-}O^{-}}} + \mathrm{Cu_2}, \quad (3.4)$$

$$\frac{\text{Solv}}{\text{O}_2\text{Cu}_1^{+}\text{O–O}^{-}} + \text{Cu}_2(\text{Solv}) \overset{K_6}{\rightleftarrows} \frac{2\text{Solv}}{{}^{-}\text{O–OCu}_1^{2+}\text{O–O}^{-}} + \text{Cu}_2, \tag{3.5}$$

$$\frac{2\text{Solv}}{{}^{-}\text{O–OCu}_1^{2+}\text{O–O}^{-}} + \text{PhCH}_2\text{Hlg} \xrightarrow{k_7'} \text{Reaction products.} \tag{3.6}$$

Here, k_7' is the rate constant of the rate-determining step assuming approach of benzyl bromide from the bulk solution. Using the steady-state approximation we arrive at Eq. (3.7).

$$w = \frac{k_7'S_1K_1K_2K_3^2K_4K_5K_6[\text{PhCH}_2\text{Br}][\text{Solv}]^2P^2(\text{O}_2)}{1 + K_1P^2(\text{O}_2) + K_1K_2P^2(\text{O}_2) + K_1K_2K_3K_5P^2(\text{O}_2)[\text{Solv}] + K_1K_2K_3^2K_5K_6P^2(\text{O}_2)[\text{Solv}]^2}. \tag{3.7}$$

This equation can be simplified to (3.8) by applying the same approximations as for Eq. (1.9):

$$w = \frac{k_7'S_1K_3K_6[\text{PhCH}_2\text{Br}][\text{Solv}]}{1 + K_3K_6[\text{Solv}]}. \tag{3.8}$$

If the dioxygen molecular complex reacts with dimethylacetamide coming from the bulk solution, while the resulting dioxygen anion reacts with benzyl bromide adsorbed on the copper surface, the reaction scheme may be represented as follows:

$$\text{Cu}_1 + \text{O}_2 \overset{K_1}{\rightleftarrows} \text{Cu}_1\text{O}_2, \tag{4.1}$$

$$\text{Cu}_1\text{O}_2 + \text{O}_2 \overset{K_2}{\rightleftarrows} \text{O}_2\text{Cu}_1\text{O}_2, \tag{4.2}$$

$$\text{Cu}_3 + \text{PhCH}_2\text{Hlg} \overset{K_4}{\rightleftarrows} \text{Cu}_3(\text{PhCH}_2\text{Hlg}), \tag{4.3}$$

$$\text{O}_2\text{Cu}_1\text{O}_2 + \text{Solv} \overset{K_5'}{\rightleftarrows} \frac{\text{Solv}}{\text{O}_2\text{Cu}_1^{+}\text{O–O}^{-}} + \text{Cu}_2, \tag{4.4}$$

$$\frac{\text{Solv}}{\text{O}_2\text{Cu}_1^{+}\text{O–O}^{-}} + \text{Solv} \overset{K_6'}{\rightleftarrows} \frac{2\text{Solv}}{{}^{-}\text{O–OCu}_1^{2+}\text{O–O}^{-}}, \tag{4.5}$$

$$\frac{2\text{Solv}}{{}^{-}\text{O–OCu}_1^{2+}\text{O–O}^{-}} + \text{Cu}_3(\text{PhCH}_2\text{Hlg}) \xrightarrow{k_7} \text{Reaction products.} \tag{4.6}$$

Here, K_5' and K_6' are the equilibrium constants for electron transfer to oxygen from solvent molecules in the bulk solution. In this case, the rate of the process is given by Eq. (4.7) or (4.8) in terms of the steady-state approximation.

According to the Eley–Rideal mechanism, in the reactions of dioxygen molecular complex with dimethylacetamide and of dioxygen anion thus formed with benzyl bromide, the solvent and reagent molecules are supplied from the bulk solution.

$$\text{Cu}_1 + \text{O}_2 \overset{K_1}{\rightleftarrows} \text{Cu}_1\text{O}_2, \tag{5.1}$$

$$\text{Cu}_1\text{O}_2 + \text{O}_2 \overset{K_2}{\rightleftarrows} \text{O}_2\text{Cu}_1\text{O}_2, \tag{5.2}$$

$$\text{O}_2\text{Cu}_1\text{O}_2 + \text{Solv} \overset{K_5}{\rightleftarrows} \frac{\text{Solv}}{\text{O}_2\text{Cu}_1^{+}\text{O–O}^{-}}, \tag{5.3}$$

$$\frac{\text{Solv}}{\text{O}_2\text{Cu}_1^{+}\text{O–O}^{-}} + \text{Solv} \overset{K_6'}{\rightleftarrows} \frac{\text{Solv}}{{}^{-}\text{O–OCu}_1^{2+}\text{O–O}^{-}}, \tag{5.4}$$

$$\frac{2\text{Solv}}{{}^{-}\text{O–OCu}_1^{2+}\text{O–O}^{-}} + \text{PhCH}_2\text{Hlg} \xrightarrow{k_7'} \text{Reaction products.} \tag{5.5}$$

Steady-state approximation gives Eq. (5.6) for the reaction rate:

$$w = \frac{k_7'S_1K_1K_2K_5'K_6'[\text{PhCH}_2\text{Br}][\text{Solv}]^2P^2(\text{O}_2)}{1 + K_1P^2(\text{O}_2) + K_1K_2P^2(\text{O}_2) + K_1K_2K_5'PP^2(\text{O}_2)[\text{Solv}] + K_1K_2K_5'K_6'P^2(\text{O}_2)[\text{Solv}]^2}. \tag{5.6}$$

Assuming that $K_1 >> K_2$, $K_2 >> 1$, and $K_5' >> 1$ [9–12], this equation is simplified to Eq. (5.7).

$$w = \frac{k_7'S_1K_6'[\text{PhCH}_2\text{Br}][\text{Solv}]}{1 + K_6'[\text{Solv}]}. \tag{5.7}$$

All dependences of the reaction rate on the concentration of dimethylacetamide are smooth; the curve described by Eq. (2.9) passes through a maximum. Equations (3.8) and (5.7) are linear dependences of the reaction rate on the concentration of benzyl bromide. Therefore, reaction schemes (2.1)–(2.7), (3.1)–(3.6), and (5.1)–(5.5) can be ruled out.

Thus, the experimental kinetic curves can be described by Eqs. (1.9) and (4.8). Insofar as it was

Table 3. Kinetic and thermodynamic parameters of the oxidative dissolution of copper in the system benzyl bromide–dimethylacetamide according to schemes (1.1)–(1.7) and (4.1)–(4.6)[a]

T, K	$k \times 10^4$, g cm^{-2} min^{-1}	K_4, L/mol	K'_6	K_3[b], L/mol	K_6[c]
313	8.1±0.1	0.95±0.03	7.74±0.05	1.49±0.02	5.19±0.9
323	15.7±0.2	0.69±0.02	3.65±0.04	1.04±0.02	3.51±0.8
333	27.7±0.3	0.49±0.02	1.55±0.03	0.70±0.02	2.21±0.7
338	34.6±0.4	0.44±0.01	1.11±0.03	58±0.01	1.91±0.6
343	46.1±0.5	0.39±0.01	0.85±0.03	0.51±0.01	1.67±0.5
353	74.2±0.6	0.29±0.01	0.40±0.02	0.36±0.01	1.11±0.5

[a] E_a = 50.6±2.2, $\Delta H^0_{\mathrm{RBr}}$ = –27.0±1.5; $\Delta H^0_{\mathrm{DMA}}$ = –32.8±1.4; ΔH^0_6 = –35.2±2.6; $\Delta H^0_{6'}$ = –68.0±3.6 kJ/mol; 298 K: $\Delta S^0_{\mathrm{RBr}}$ = –86.8±0.8; $\Delta S^0_{\mathrm{DMA}}$ = –102±1; ΔS^0_6 = –200±7, $\Delta S^0_{6'}$ = –98.1±0.9 J mol^{-1} K^{-1}; sample correlation coefficients for the dependence ln $Y = f(1/T)$: R = 0.999 ($Y = k$), R = 0.995 ($Y = K_4$), R = 0.999 ($Y = K'_6$). [b] Data of [16]. [c] Calculated by the formula $K_6 = K'_6/K_3$.

impossible to distinguish reaction mechanisms corresponding to these equations, we calculated the kinetic and thermodynamic parameters of the process according to both schemes.

By linearization of the experimental curves in the $1/w$—$1/c$ coordinates, we calculated the values of $k = k_7\ S_1\ S_3$, K_4, and K'_6 using Eqs. (1.9) and (4.8) and determined the heat of adsorption of benzyl bromide ($\Delta H^0_{\mathrm{RBr}}$), change in the enthalpy of steps (1.6) (ΔH^0_6) and (4.6) ($\Delta H^0_{6'}$), and the energy of activation (E_a) for the rate-determining step.

As follows from Eqs. (1.9) and (4.8), $K'_6 = K_3K_6$. We showed in [14] that the oxidative dissolution of copper in the system carbon tetrachloride–dimethylacetamide follows the Langmuir–Hinshelwood mechanism involving independent adsorption of the components on different active sites on the metal surface. Comparison of the mechanism given by reactions (1.1)–(1.7) with the mechanism proposed in [14] indicated that steps (2) [14] and (1.4) refer to the same process; therefore, these steps should be characterized by similar thermodynamic parameters; i.e., the adsorption constant of dimethylacetamide on copper surface can be used to calculate K_6. The results are presented in Table 3.

Thus, the results of our present study and published data [7, 10–14] allowed us to propose the following steps of the oxidative dissolution of copper in the system benzyl bromide–dimethylacetamide under oxic conditions:

(1) Adsorption of oxygen on the copper surface.

$$\mathrm{Cu_1 + O_2 \overset{K_1}{\rightleftarrows} Cu_1O_2},$$

$$\mathrm{Cu_1O_2 + O_2 \overset{K_2}{\rightleftarrows} \underset{\textbf{IIa}}{O_2Cu_1O_2}}.$$

(2) Electron transfer from the metal surface to oxygen and simultaneous reaction of adsorbed species **IIa** with dimethylacetamide according to Langmuir–Hinshelwood or Elley–Rideal. In the first case, adsorbate **IIa** reacts with dimethylacetamide adsorbed on a different site of the metal surface.

$$\mathrm{Cu_2 + DMAc \overset{K_3}{\rightleftarrows} Cu_2(DMA)},$$

$$\mathrm{O_2Cu_1O_2 + Cu_2(DMA) \rightleftarrows \frac{DMA}{O_2Cu_1^{+}O{-}O^{-}} + Cu_2},$$

$$\mathrm{\frac{DMA}{O_2Cu_1^{+}O{-}O^{-}} + Cu_2(DMA) \overset{K_6}{\rightleftarrows} \underset{\textbf{IIb}}{\frac{DMA}{{}^{-}O{-}OCu_1^{2+}O{-}O^{-}}} + Cu_2}.$$

In keeping with the Eley–Rideal mechanism, adsorbate **IIa** reacts with dimethylacetamide arriving from the bulk solution.

$$\mathrm{\underset{\textbf{IIa}}{O_2Cu_1O_2} + DMA \overset{K_5}{\rightleftarrows} \frac{DMA}{O_2Cu_1^{+}O{-}O^{-}} + Cu_2},$$

$$\mathrm{\frac{DMA}{O_2Cu_1^{+}O{-}O^{-}} + DMA \overset{K_6'}{\rightleftarrows} \underset{\textbf{IIb}}{\frac{DMA}{{}^{-}O{-}OCu_1^{2+}O{-}O^{-}}}}.$$

These mechanisms are impossible to distinguish. Positive charge generated as a result of electron transfer is delocalized over a group of copper atoms, thus stabilizing superoxide anions. Coordination of dimethylacetamide to $\mathrm{Cu_1^{2+}}$ also favors stabilization of superoxide complexes **IIb**.

(3) Electron transfer from dioxygen anion **IIb** to benzyl bromide adsorbed on a different active site of the metal surface.

$$Cu_3 + PhCH_2Hlg \overset{K_4}{\rightleftarrows} Cu_3(PhCH_2Hlg),$$

$$\frac{2DMAc}{{}^-O–OCu_1^{2+}O–O^-} + Cu_3(PhCH_2Hlg)$$

IIb

$$\xrightarrow{k_7} Ph\dot{C}H_2 + \frac{2DMAc}{BrCu_1^{+}O–O^-} + Cu_3 + O_2.$$

IIc

Transfer of one electron leads to decomposition of dioxygen anion with liberation of molecular oxygen and formation of adsorbed benzyl radical and superoxide anion **IIc**.

(4) Transfer of the second electron from superoxide **IIc** to benzyl bromide.

$$\frac{2DMA}{BrCu_1^{+}O–O^-} + Cu_3(PhCH_2Hlg)$$

IIc

$$\rightarrow Ph\dot{C}H_2 + CuBr_2(DMA)_2 + Cu_3 + Cu_1' + O_2.$$

In this case, the formation of radical ion pair is energetically less favorable than the formation of benzyl radical.

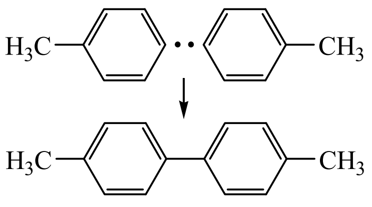
(5) Recombination and isomerization of benzyl radicals.

$$Ph\dot{C}H_2 + Ph\dot{C}H_2$$

$$\upharpoonleft\downharpoonright$$

$$PhH_2C{:}CH_2Ph \rightarrow PhCH_2CH_2Ph$$

$$\upharpoonleft\downharpoonright$$



The recombination and isomerization of two benzyl radicals in solution involves intermediate formation of the radical pair Ph–$H_2C\cdots CH_2$–Ph, which is directly confirmed by the detection of traces of 4,4'-dimethylbiphenyl.

(6) Oxidation of $PhCH_2$ radicals with atmospheric oxygen follows a radical chain mechanism [15, 16], which implies generation of $PhCH_2OO\cdot$ radicals and their disproportionation.

$$Ph–CH_2 + O_2 \rightarrow PhCH_2OO^{\cdot},$$

$$2PhCH_2OO\cdot \rightarrow PhCH_2OH + PhCHO + O_2.$$

(7) Reaction of $PhCH_2OO\cdot$ with copper(I) coordination compounds [16, 17].

$$Ph\dot{C}H_2OO\cdot + [CuBr(DMAc)_m]$$
$$\rightarrow PhCHO + [CuBr(OH)(DMAc)_m,$$

$$m = 1, 2.$$

(8) Formation of copper(II) coordination compounds.

$$CuBr_2(DMAc)_2] + m\text{-}2DMAc \rightarrow [CuBr_2(DMAc)_m],$$

$$m = 2–4.$$

Side reactions:

$$Cu + [CuBr_2(DMAc)_m] + n\text{-}mDMAc$$
$$\rightarrow 2[CuBr(DMAc)_n],$$

$$Ph\dot{C}H_2 + [CuBr_2(DMAc)_m]$$
$$\rightarrow PhCH_2Br + [CuBr(DMAc)_n] + n\text{-}mDMAc,$$

$$n = 2–4, m = 2–4.$$

EXPERIMENTAL

The ESR spectra of reaction mixtures were recorded on a Radiopan SE/X-2543 spectrometer (9400 MHz) at 293 K according to the procedure described in [2, 3] using 2,2,6,6-tetramethylpiperidine 1-oxyl [2, 14] as stable radical. The reaction mixtures were analyzed by GC/MS on a Hewlett Packard HP-5890 chromatograph coupled with an HP 5972 mass-selective detector (for conditions, see [14]). The ^1H NMR spectra were recorded on a Jeol LTD FX-90Q spectrometer with Fourier transform from 25–30% solutions in carbon tetrachloride or chloroform-*d*; the chemical shifts were determined with an accuracy of ±0.01 ppm relative to hexamethyldisiloxane as internal reference. The IR spectra were measured in the range from 400 to 4000 cm^{-1} on a Nicolet IMPACT 400d instrument from samples prepared as KBr pellets.

The purity of the initial reactants was checked, and the organic reaction products were quantitated, by GLC under the conditions described in [18].

Inorganic products (copper cations) were analyzed by ion chromatography on a Tsvet-3006 chromatograph as described in [14]. The elemental analyses were obtained on a Carlo Erba 1100 analyzer according to standard procedures. The composition of deuterium-containing compounds was determined according to the procedure reported in [19].

Copper powder with a purity of no less than 99.99% was prepared by reduction of $CuSO_4$ (analytical grade) with magnesium powder (MP-1) in water as described in [20]; the product was washed with acetone and dried under reduced pressure (10 mm). Yield 95%.

Copper wire (GOST 7262-54, 99.99%) with a diameter of 0.05 mm was kept for 24 h in dimethylformamide. Just before use, swelled insulation film was removed mechanically from a sample of copper wire, and the wire was kept for 5–10 s in concentrated nitric acid and washed with water, acetone, and dimethylacetamide.

(+)-*R*-1-Bromo-1-phenylethane was synthesized by reaction of (–)-(*S*)-1-phenylethanol with $POBr_3$ in the presence of pyridine in pentane [21]. Yield 74%, bp 86–87°C (11 mm), $\alpha_D^{25} = +73.3°$ (neat); published data [21]: $\alpha_D^{25} = +96.3°$ (neat, *ee* = 100%) [21].

Triphenylphosphine oxide was synthesized by oxidation of triphenylphosphine (Aldrich) with potassium permanganate in acetone according to [22]. Yield 80%, mp 156–158°C [22].

All other organic reagents used were commercial products. *N*,*N*-Dimethylacetamide [2] and other organic solvents were purified according to standard procedures [23]. All solvents were degassed by repeated freezing and thawing under reduced pressure and were stored in air-tight ampules.

Copper coordination compounds. A mixture of 1 g of copper powder, 10 mL of dimethylacetamide, and 10 mL of benzyl bromide was heated at 70°C on exposure to air. After 2 h, the mixture was treated with 20 mL of diethyl ether. The diethyl ether layer was separated, and the residue was dissolved in 20 mL of acetone–hexane (1 : 1). After 24 h, green crystals separated, which were an intractable mixture of two copper(II) coordination compounds. The crystals were dissolved in 20 mL of dimethylacetamide, 11 g of Ph_3PO was added, and the mixture was heated for 10 min at 70°C. After cooling, dark brown $[CuBr_2(TPPO)_2]$ complex separated and was isolated by conventinal methods. Yield 8.7 g (70%), mp 299–299.5°C [24]. IR spectrum, ν, cm^{-1}: 3030 (C–H), 1600 (C–C), 1580 (C–C), 1500 (C–C), 1449 (C–C), 1150 (P=O), 1115 (C–H), 1080 (C–H), 730 (C–H), 755 (C–P), 695 (δ C–H), 539 (P=O). Found, %: C 55.45; H 3.80; Br 20.51; Cu8.17; P 7.96. $C_{36}H_{30}Br_2CuO_2P_2$. Calculated, %: C 55.46; H 3.85; Br 20.50; Cu 8.15; P 7.94.

The diethyl ether solution contained unreacted benzyl bromide and dimethylacetamide, 1,2-diphenylethane, benzyl alcohol, benzaldehyde, and traces of benzoic acid and benzyl benzoate, which were identified by ^1H NMR and GC/MS; their yields are given in Table 2.

The stereochemistry of the reaction was studied following the procedure described above for the synthesis of copper coordination compounds. (+)-(*R*)-1-Bromo-1-phenylethane was used as benzyl halide. After precipitation of solid product, the ether solution contained (according to the GC/MS data) acetophenone, (*RS*)-1-phenylethanol, (*RS*,*RS*)-2,3-diphenylbutane, (*RR*/*SS*)-2,3-diphenylbutane, ethylbenzene, styrene, and unreacted (+)-(*R*)-1-bromo-1-phenylethane and dimethylacetamide. All organic products were isolated by preparative liquid chromatography, and the physical constants of the isolated (*RS*,*RS*)-2,3-diphenylbutane, (*RR*/*SS*)-2,3-diphenylbutane, ethylbenzene, and styrene were consistent with published data [2, 25].

The reaction in the presence of radical scavenger was carried out by analogy with the above described procedures using dicyclohexyldeuterophosphine. The ether solution contained unreacted benzyl bromide and dimethylacetamide, as well as benzyl alcohol, benzaldehyde, and α-deuterotoluene. The yields are given in Table 2.

***α*-Deuterotoluene.** ^1H NMR spectrum, δ, ppm: 2.32 m (2H, CH_2), 7.15 m (5H, H_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): 93 (100) $[M]^+$, 92 (93) $[M-H]^+$, 91 (46) $[M-D]^+$, 66 (9) $[M-C_2H_3]^+$, 65 (11) $[M-C_2H_2D]^+$. Found, %: C 90.35; H 7.52; D 2.13. C_7H_7D. Calculated, %: C 90.27; H 7.56; D 2.17.

Copper coordination compounds were synthesized in the presence of anhydrous copper(II) chloride according to the procedure described above at a Cu-to-$CuCl_2$ molar ratio of 1 : 1. The ether solution contained unreacted benzyl bromide and dimethylacetamide, as well as 1,2-diphenylethane, benzyl alcohol, benzaldehyde, and benzyl chloride (2%).

Kinetic study. The kinetics of the reaction of copper with benzyl bromide in dimethylacetamide in the presence of oxygen were studied by resistometry in benzene on exposure to air [9]. Three series of experiments were carried out. In the first series, the concentration of dimethylacetamide was $c_{DMA} = 0.5$ M, and the initial concentration of benzyl bromide c_{RBr} was varied from 0 to 7 M; in the second series, the initial concentration of benzyl bromide was $c_{RBr} = 0.5$ M, and c_{DMA} was varied from 0 to 7 M; in the third series, the initial concentration of DMA was $c_{DMA} = 2$ M, and c_{RBr} was varied from 0 to 7 M. The results are presented in figure and Table 3. As followed from the dependence of the rate of dissolution of copper on the stirring speed, the reaction course conformed to the kinetic mode.

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