## Kinetics and Mechanism of the Reaction of Benzyl Bromide with Titanium in Dimethylformamide

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**Abstract**—The reaction of titanium with benzyl bromide in dimethylformamide was studied. No reaction occurs in the presence of atmospheric oxygen. Under oxygen-free conditions, the oxidative dissolution of titanium occurs by the mechanism of one-electron transfer with the formation of 1,2-diphenylethane and Ti(IV) complexes. The kinetic and thermodynamic parameters of the process were determined. The reaction mechanism was discussed.

Titanium complexes are widely used in industry as selective catalysts of various chemical processes [1, 2]. One of the most promising methods of their preparation is direct oxidative dissolution of titanium metal in systems organic halide–coordinating solvent, which occurs under mild conditions [3].

To find optimal conditions for preparing complexes of titanium halides with organic ligands, we studied in detail the mechanism and kinetics of the reaction of titanium with benzyl bromide in the presence of dimethylformamide (DMF).

The reaction of titanium with benzyl bromide in DMF in an inert atmosphere yields a dark violet solution. Analysis of the reaction products showed that, in the absence of atmospheric oxygen (including oxygen adsorbed on the metal surface), dehalogenation of benzyl bromide with titanium in DMF follows the scheme



The complex  $[TiBr(L)_2]Br_2$  (I) subsequently reacts slowly with the benzyl bromide-dimethyl-formamide system to form a red-brown solution

containing bromopentakis(dimethylformamide)titanium(IV) tribromide (**II**).

$$\begin{array}{c} \swarrow -CH_2Br + [TiBr(L)_2]Br_2 + L \longrightarrow [TiBr(L)_5]Br_3 + \swarrow -CH_2 - CH_2 - \swarrow + H_3C - \swarrow -CH_3 \\ I I I L = DMF. \end{array}$$

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Rate of oxidative dissolution of titanium in the benzyl bromide–DMF system in the presence of an inert diluent (benzene) at 353 K as a function of the initial concentrations of the components: (1)  $C_{\text{RBr}}$  0.5 M, X = DMF; (2)  $C_{\text{DMF}}$  0.5 M, X = RBr; and (3)  $C_{\text{DMF}}$  2 M, X = RBr.

The structure of **II** was proved by an independent synthesis. The same complex is formed by dissolution of titanium in the dimethylformamide $-Br_2$  system [4]:

$$Ti + L + Br_2 \longrightarrow [TiBr(L)_5]Br_3$$
  
+ unidentified tarry product,  
$$L = DMF$$

However, this compound cannot be prepared by heating  $TiBr_4$  with DMF or with the reaction system under consideration.

Formation of 1,2-diphenylethane and 4,4'-ditolyl and the absence of 4-benzyltoluene in the reaction products indicate that the reaction occurs by the radical mechanism. In this case, the benzyl radicals can isomerize in a radical pair.

Polybenzyl, stilbene, tolan, and toluene, detected in the reaction products by GC–MS, may be decomposition products of organotitanium intermediates formed in small amounts [5–7]:

$$\bigcirc -CH_2 + [TiBr_2 \cdot nL \longrightarrow \bigcirc -CH_2TiBr_2 \cdot nL$$

$$L = DMF \quad n = 1 - 2$$

The IR spectrum of polybenzyl does not contain a characteristic band of 1,4-disubstituted aromatic compounds at 805 cm<sup>-1</sup>, which indicates that it has a nonlinear structure [8].

The kinetics of oxidative dissolution of titanium

in the benzyl bromide–DMF system was studied resistometrically, because this method allows monitoring of fast heterogeneous reactions and ensures high accuracy and reproducibility of the results [9, 10].

To determine the kinetic characteristics of the reaction, it was performed in an inert diluent, benzene  $[DN(SbCl_5) 0.42 \text{ kJ mol}^{-1}]$  [11].

In the presence of atmospheric oxygen, titanium is not oxidized with benzyl bromide in DMF, probably because of formation of an oxide film on the metal surface, and the equilibrium between  $TiO_2$  and  $TiBr_4$ 

$$\operatorname{TiO}_2 \xrightarrow[O]{[Br]} \operatorname{TiBr}_4.$$

is fully shifted toward formation of the Ti–O bond, since  $\Delta H_{298(Ti-O)}^0 < \Delta H_{298(Ti-Br)}^0$  [12, 13]; therefore, we thoroughly purified the inert gas (argon) to remove moisture and oxygen and exhaustively degassed the solvents and reagents.

A characteristic feature of the kinetic curves (see figure) is the presence of maxima; an increase in the DMF concentration from 0.5 to 2 M does not alter the shape of the dependence of the reaction rate W on the benzyl bromide concentration, which indicates that the reaction occurs by the Langmuir–Hinshelwood mechanism with adsorption of the halide and DMF on similar active centers of the metal surface [14]:

$$PhCH_2Br + S \xleftarrow{K_1} (PhCH_2Br)S, \qquad (1)$$

$$L + S \xleftarrow{\kappa_2} L(S), \qquad (2)$$

$$(PhCH_2Br)S + (L)S \xrightarrow{K} Products, \qquad (3)$$

where L is DMF;  $K_1$  and  $K_2$  are the equilibrium constants of adsorption of benzyl bromide and DMF, respectively; K is the rate constant of the chemical reaction; and S denotes active centers on which benzyl bromide and DMF are adsorbed.

In this case, the kinetic equation includes the degrees of the surface coverage with each component, obtained from the Langmuir adsorption isotherms, and the expression for W is as follows:

$$W = k \frac{K_1 K_2 [\text{PhCH}_2 \text{Br}] [\text{L}]}{\left(1 + K_1 [\text{PhCH}_2 \text{Br}] + K_2 [\text{L}]\right)^2},$$
 (4)

where  $k = KN^2$  and N is the number of active centers on the metal surface, responsible for the adsorption of benzyl bromide and DMF.

Treatment of the experimental data (see figure) using the system of Eqs. (1)-(3) allowed deter-

mination of the equilibrium constants of adsorption of benzyl bromide and DMF on the Ti surface ( $K_1$ ,  $K_2$ ) the rate constant k of the chemical process. From the kinetic data obtained at varied temperature, we determined the activation energy  $E_a$  of the chemical process and the enthalpies and entropies of adsorption of the reactants on the Ti surface (see table).

The Langmuir–Hinshelwood scheme of the process implies that the limiting step is the reaction of the adsorbed reactant molecules with the metal surface, i.e., a chemical reaction on the surface.

To identify the reaction intermediates, we examined the ESR spectra of films obtained by cocondensation of titanium with a 50-100-fold excess of benzyl bromide, or of benzyl bromide matrices condensed on the surface of the compact metal at 77 K according to [15].

Titanium is evaporated from a corundum crucible in a vacuum  $(10^{-2}-10^{-5} \text{ mm Hg})$  at  $1500-1700^{\circ}\text{C}$ very slowly [16]; therefore, we generated atomic Ti by evaporation of the metal in a low-voltage electric arc (12 V, 30 A) between two titanium electrodes.

The cocondensation of atomic Ti with benzyl bromide [ratio 1 : (50-100)] results in formation of black films stable at 77 K for no less than 24 h. The ESR spectrum of this cocondensate at 77 K was weak and ill-resolved and furnished no definite information. Condensation of excess benzyl bromide onto a film of compact Ti was accompanied by the growing loss of the UHF power in the sample due to an increase in its electrical conductivity, which further impaired the resolution of the ESR spectra. The resolution is not improved on warming the samples to the melting point. On melting the cocondensate (270 K), a dark violet solution is formed.

In the reaction mixtures obtained in the system benzyl bromide-compact or atomic Ti [(50-100):1], after disappearance of the compact metal film (150 K) and hydrolysis of the frozen (270 K) samples, we detected by GC-MS 1,2-diphenylethane (98–99%), 4,4'-ditolyl (<0.1%), toluene (<0.1%), and traces of stilbene and tolan (<0.01%). The absence of hydrogen in the gas phase indicates that the reaction of Ti with benzyl bromide was quantitative. When the hydrolysis temperature was increased from 270 to 298 K, the yield of the organic products remained virtually unchanged, but hydrogen evolution was observed. When the samples were hydrolyzed at 298 K after preliminary melting at 270 K, the yield of 1,2-diphenylethane decreased to 95–97%, and the content of toluene, stilbene, and tolan in the reaction mixture increased to 0.5, 0.06, and 0.04%, respectively; hydrogen was not detected in the gas phase.

Kinetic and thermodynamic parameters of oxidative dissolution of titanium in the benzyl bromide–DMF system, calculated within the framework of the Langmuir– Hinshelwood mechanism assuming adsorption of the reagent and solvent on similar active centers of the metal surface<sup>a</sup>

<i>Т</i> , К	$k \times 10^4$ , <sup>b</sup> g cm <sup>-2</sup> min <sup>-1</sup>	$K_1, \overset{c}{\operatorname{mol}^{-1}}$	$K_2$ , <sup>d</sup> l mol <sup>-1</sup>
313 323 333 338 343 353	$\begin{array}{c} 0.03 \pm 0.01 \\ 0.14 \pm 0.01 \\ 0.42 \pm 0.02 \\ 0.79 \pm 0.02 \\ 1.50 \pm 0.02 \\ 4.60 \pm 0.03 \end{array}$	$\begin{array}{c} 0.339 \pm 0.003 \\ 0.291 \pm 0.002 \\ 0.261 \pm 0.002 \\ 0.238 \pm 0.001 \\ 0.226 \pm 0.001 \\ 0.199 \pm 0.001 \end{array}$	$\begin{array}{c} 0.289 \pm 0.002 \\ 0.255 \pm 0.002 \\ 0.231 \pm 0.001 \\ 0.220 \pm 0.001 \\ 0.205 \pm 0.001 \\ 0.190 \pm 0.001 \end{array}$

<sup>a</sup>  $\Delta E_{a}$  114.2±5.6,  $\Delta H_{RBr}^{0}$  -12.1±0.8,  $\Delta H_{DMF}^{0}$  -9.7± 0.7 kJ mol<sup>-1</sup>; at 298 K,  $\Delta S_{RBr}^{0}$  -47.4±3.2,  $\Delta S_{DMF}^{0}$  -40.7± 2.8 J mol<sup>-1</sup> K<sup>-1</sup>. Estimated correlation coefficient for the dependence ln *Y* = *f*(1/*T*): <sup>b</sup> *R* 0.999 (*Y* = *k*), <sup>c</sup> *R* 0.998 (*Y* = *K*<sub>1</sub>), and <sup>d</sup> *R* 0.998 (*Y* = *K*<sub>2</sub>).

Analysis of the reaction products after the hydrolysis, taking into account known data on the reaction of Ti(II) compounds with water [17], shows that the reaction of benzyl bromide with titanium evaporated in a low-voltage electric arc yields  $TiBr_2$  even at 77 K; this compound rapidly reacts with benzyl bromide after melting of the matrix to form  $TiBr_3$ , as also indicated by the absorption maximum at 480 nm in the spectrum of the samples after melting of the matrices [18].

Our results suggest the radical mechanism of the reaction. To confirm this assumption, we studied the reaction by ESR at 298 K in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl, a stable radical reacting with radical intermediates. The disappearance of its ESR signal in the course of the reactions suggests the radical mechanism of the oxidative dissolution of Ti in the system benzyl bromide–DMF, since the ESR signals of 2,2,6,6-tetramethylpiperidine-1-oxyl do not appear after oxidation of titanium and reduction of the mixtures with KI in acetate buffer [19–21].

The radical species in solution were detected and identified using a radical scavenger. We chose dicyclohexyldeuterophosphine ( $Cy_2PD$ ), which was successfully used for these purposes previously and allows not only detection of radical intermediates, but also determination of their content in solution [22].

Dehalogenation of benzyl bromide with titanium in DMF yields 1,2-diphenylethane (98%), toluene (0.1%), stilbene (<0.01%), tolan (<0.01%), and poly-

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benzyl (0.1%). In the presence of  $Cy_2PD$ , the composition of the reaction products changes depending on the Ti :  $Cy_2PD$  molar ratio. At Ti :  $Cy_2PD = 1:5$ ,

1,2-diphenylethane, silbene, tolan, and polybenzyl are not formed; instead, an equivalent amount of  $\alpha$ -deuterotoluene and 1% toluene were detected.

$$4 \swarrow -CH_2 - Br + Ti + 5L \xrightarrow{Cy_2 PD} \swarrow -CH_2 D + [TiBr(L)_5]Br_3$$

L = DMF.

In the latter case, the formation of toluene is due to the presence of 1% Cy<sub>2</sub>PH in Cy<sub>2</sub>PD.

Analysis of the reaction products obtained in the presence of radical scavengers and in their absence shows that the reaction occurs by the radical mechanism via benzyl radical:



Our results show that dehalogenation of benzyl bromide on the Ti surface follows the radical pathway via benzyl radicals and occurs by the Langmuir– Hinshelwood mechanism with adsorption of the reagent and solvent on similar active centers of the metal surface:



The solvated radical TiBr reacts on the metal surface with a new benzyl bromide molecule by the Langmuir–Hinshelwood or Eley–Rideal mechanism to form the benzyl radical and solvated  $\text{TiBr}_2$  molecule which can escape into the solution:



In the solution,  $TiBr_2$  readily disproportionates into compound I and Ti metal [18] or reacts with a new benzyl bromide molecule:



The reaction of the solvated  $TiBr_2$  molecule with benzyl bromide is also possible on the metal surface, with the escape of the forming complex I into the solution.

In the solution, complex **I** slowly reacts with benzyl bromide to form compound **II** and benzyl radical:

$$[TiBr(L)_2]Br_2 + \swarrow - CH_2Br + 3L$$
$$\longrightarrow \swarrow - \dot{C}H_2 + [TiBr_2(L)_5]Br_3$$
$$L = DMF.$$

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Benzyl radicals in the solution either recombine

via a radical pair or return to the Ti surface:



## EXPERIMENTAL

The IR spectra were taken on a Nicolet Impact-400d spectrophotometer; samples were prepared as KBr pellets.

The ESR spectra were recorded on a Radiopan SE/X-2543 spectrometer at 293 K by the known procedure [19, 20]. As radical scavenger we used 2,2,6,6-tetramethylpiperidine-1-oxyl.

The ESR spectra at 77 K were recorded in films of cocondensates of Ti with a 50–100-fold excess of benzyl bromide, following the procedure from [15]. Titanium was evaporated in a low-voltage electric arc (12 V, 20 A) between two titanium electrodes.

The <sup>1</sup>H NMR spectra were recorded on a Jeol FX-90Q NMR Fourier spectrometer from 25–30% solutions of samples in CCl<sub>4</sub> or CDCl<sub>3</sub>, with HMDS as internal reference. The chemical shifts were determined with an accuracy of  $\pm 0.01$  ppm. The  $\delta$  scale was used.

Ti(III) and Ti(IV) were detected with a Beckman Instruments DU-520 spectrophotometer at 480 and 300 nm, respectively [18].

To check the purity of the reactants and quantitatively analyze the organic reaction products, we used GLC; the conditions were described in [23].

Gaseous reaction products were analyzed by gas chromatoghraphy with a Tsvet-162 chromatograph equipped with a thermal conductivity detector; a  $2000 \times 3$ -mm steel column was packed with 4 Å molecular sieves (0.25-mm fraction). The column temperature was 50°C; the carrier gas was Ar (flow rate 100 ml min<sup>-1</sup>).

The GC–MS analysis of the reaction products was

performed with a Hewlett–Packard device (the United States; HP-5972 mass detector and HP-5890 chromatograph). A  $30\,000 \times 0.25$ -mm HP-5 capillary chromatographic; column temperature  $40-250^{\circ}$ C; heating rate 30 deg min<sup>-1</sup>; carrier gas He (flow rate 1 ml min<sup>-1</sup>); injector temperature  $250^{\circ}$ C; detector temperature  $280^{\circ}$ C.

We used VT-2 grade titanium powder (REAKhIM, Russia) of >99.99% purity, fraction 0.2 mm. Titanium wire [GOST (State Standard) 17746-96, Ti content 99.74%] 0.2 mm in diameter was kept for 5-10 s in 20% sulfuric acid and washed with water, acetone, and then DMF (all manipulations were performed in an inert gas atmosphere). All the organic compounds were commercial chemicals. Benzyl bromide (Aldrich) was dried over melted CaCl<sub>2</sub> and distilled; bp 83.5–84°C (32 mm Hg),  $n_D^{20}$  1.4380 {published data: bp 83.5–84°C (32 mm Hg),  $n_D^{20}$  1.4380 [24]}. DMF was purified by double slow distillation in a vacuum from a large amount of P<sub>2</sub>O<sub>5</sub> [25]. Acetone, diethyl ether, and other solvents were purified by standard procedures [26]. Benzyl bromide and all the solvents were degassed by repeated freeze-pump-thaw cycles and were stored in ampules without air access.

Titanium complexes were prepared by the following procedures. To 0.2 g of titanium powder we added 8 ml of DMF and 8 ml of benzyl bromide. The reaction was performed in an inert gas atmosphere at 70°C for 6 h, after which the resulting red-brown solution was diluted with a 1 : 1 (by volume) diethyl ether–acetone mixture until a red-brown precipitate of [TiBr(DMF)<sub>5</sub>]Br<sub>3</sub> formed. This product was washed with acetone and diethyl ether and dried. Yield 1.37 g (53%). Red substance. The physicochemical properties of the complex agree with published data [4].

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A GC–MS analysis of the mother liquor after the precipitation of the complex revealed unchanged DMF and benzyl bromide, and also 1,2-diphenylethane and 4,4'-ditolyl. The yields of organic products were given above.

The reaction in the presence of a radical scavenger  $(Cy_2PD)$  was performed similarly.

The GC–MS analysis of the mother liquor after the precipitation of the complex revealed unchanged DMF and benzyl bromide, and also  $\alpha$ -deuterotoluene. The yields of organic products were given above.

The kinetics of the reaction of titanium with benzyl bromide in DMF was studied resistometrically [9] following the procedure from [27] in an atmosphere of dry deoxygenated argon. The stirrer rotation rate was 2500 rpm. At the rates exceeding 2000 rpm, the rate of titanium dissolution was independent of the stirring rate, i.e., the reaction was kinetically controlled.

In the kinetic study of the reaction of titanium with benzyl bromide in the presence of DMF, we used benzene as inert diluent [11].

The results are given in the table.

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