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State of Palladium in Ligandless Catalytic Systems for the Heck Reaction of Nonactivated Bromobenzene

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Abstract—In the Heck reaction of bromobenzene catalyzed by the palladium salts (PdX_2) without phosphine ligands, a considerable amount of palladium (up to 70%) is not involved in the catalytic cycle and exists as the catalytically inactive anionic complex $[PdX_4]^{2-}$.

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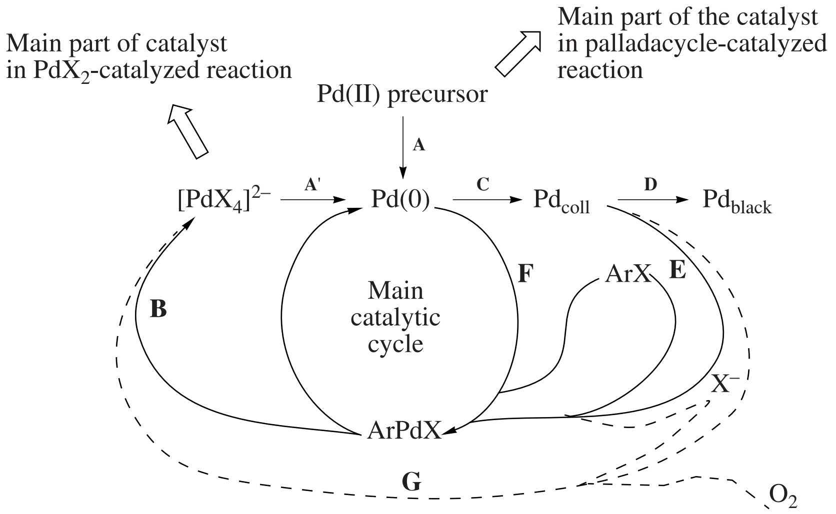
INTRODUCTION

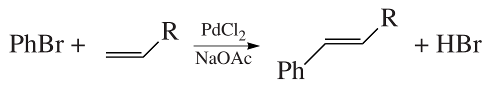
In the early 1970s, the discovery of the reaction of aryl halides with alkenes in the presence of palladium compounds [1, 2] served as the starting point for the further development of the catalytic methods for the synthesis of compounds with new C–C bonds [3–8]. This process was named the Heck reaction, and later a variety of palladium-catalyzed coupling reactions of aryl halides were discovered (Suzuki [9–11], Sonogashira [12], Stille [13], and Buchwald–Hartwig [14–16] reactions). It was found rather long ago, while studying the "ligandless" Heck reaction between ethylene and iodobenzene in the presence of NaOAc as a base using UV spectroscopy, that the catalytically inactive anionic complex $[PdI_4]^{2-}$ forms rapidly under relatively mild conditions [17]. Moreover, almost all palladium is converted into this species. Based on these and later data [8, 18, 19], the authors proposed a scheme of palladium transformations during the Heck reaction (scheme) including the formation of complexes of the $[PdX_4]^{2-}$ type, which are not involved in the main catalytic cycle.

The formation of anionic palladium complexes in the reactions with aryl iodides was also observed [20–24]. No direct evidence has been obtained so far for the appearance of these complexes under the conditions of the real catalytic process involving less reactive aryl bromides. The $[PdBr_4]^{2-}$ complexes were observed only in the interaction between colloidal palladium [25], Pd/Al_2O_3 [26], and Pd/C [8] with aryl bromides in experiments modeling the catalytic process. Thus, no quantitative data are available that could allow us to estimate what fraction of palladium in the form of



Scheme.

$[PdBr_4]^{2-}$ is involved in the catalytic reaction with aryl bromides:



(I)

R = Ph, COOBu.

At the same time, it has been shown in many studies that most of the palladium remains in the form of the starting, catalytically inactive Pd(II) complex in the Heck reaction with poorly reactive aryl bromides and aryl chlorides in the presence of various palladacycles stable to reduction under severe conditions (140°C and higher) [27–31]. The formation of Pd(II) complexes of the $Pd(PPh_3)_2X_2$ type was also observed by NMR spectroscopy in the common phosphine-containing systems that catalyze the Heck reaction of benzoic anhydride [8]. Thus, as in the "ligandless" variant of the Heck reaction with aryl iodides [17, 20, 21], a considerable amount of palladium exists in the oxidized form, which is not involved in the catalytic cycle when the palladacycles and phosphine-containing catalytic systems are used (scheme).

On the other hand, several active "ligandless" catalytic systems based on the simple palladium salts ($Pd(OAc)_2$, $PdCl_2$), which can activate aryl bromides [20, 32–34] and aryl chlorides [8], are known. It was assumed that under the conditions of these reactions, unlike the reactions with the palladacycles not stabilized by ligands, the palladium salt is rapidly reduced and most of the metal during catalysis exists as colloidal particles or palladium black [20, 34, 35].

In the present work, we describe the results of experiments that made it possible to unambiguously determine the fraction of oxidized palladium existing as $[PdBr_4]^{2-}$ directly during the Heck reaction (I) of aryl bromides under comparatively severe conditions (compared to the reactions involving aryl iodides) in the absence of phosphine ligands in the catalytic system.

EXPERIMENTAL

Catalytic Experiments

All experiments were carried out in air without an inert atmosphere. Bromobenzene (30 mmol), styrene or butyl acrylate (5 mmol), NaOAc (5.6 mmol), HCOONa (0.9 mmol if any), NBu_4Br (0.48 or 1.6 mmol if any), naphthalene (1 mmol) as an internal standard for GLC, dimethylformamide (DMF, 5 ml) as a solvent, and $PdCl_2$ (0.08 or 0.04 mmol, i.e., 1.6 or 0.8 mol %, respectively) were mixed in a glass reactor. The reactor was placed in a temperature-controlled oil bath. The mixture was magnetically stirred. At intervals, the mixture was sampled through a rubber septum for analyses by GLC and UV spectroscopy. In selected experiments, a freshly prepared solution of Na_2PdBr_4 (0.08 mmol $PdBr_2$ + 0.8 mmol NaBr) in DMF (5 ml) was used instead of $PdCl_2$ as a catalyst precursor. The reaction rate was determined by the graphical differentiation of the steady-state regions in the kinetic curves.

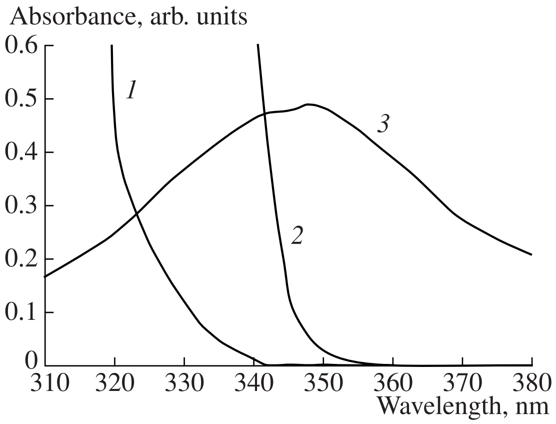


Fig. 1. UV spectra of solutions of (*1*) butyl cinnamate, (*2*) stilbene, and (*3*) $[PdBr_4]^{2-}$ at 60% yields of butyl cinnamate and stilbene and 40% yield of $[PdBr_4]^{2-}$.

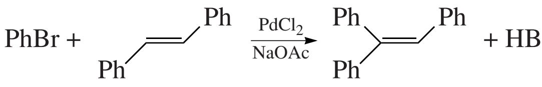
GLC Analysis

Samples of the reaction mixture were analyzed on an HP-4890 gas–liquid chromatograph equipped with a flame-ionization detector and an HP-5 capillary column 15 m in length with programmed heating from 100 to 250°C.

UV Spectroscopy

The UV spectra of the reaction mixture were recorded on a Specord UV-VIS spectrophotometer in quartz cells (l = 0.01 cm). The $[PdBr_4]^{2-}$ concentration was measured as the absorbance at 350, 360, 370, and 380 nm. Calibration plots were constructed for these wavelengths using the spectra of standard solutions of $[PdBr_4]^{2-}$ obtained by the successive dilution of a solution containing 0.16 mmol $PdBr_2$ and 3.2 mmol NBu_4Br in 10 ml of DMF.

As can be seen from the data in Fig. 1, the absorption of stilbene and butyl cinnamate (products of reaction (I)) is not superimposed on the absorption of $[PdBr_4]^{2-}$ in the peak region or in the long-wavelength spectral region. The complex concentration was calculated as the average value obtained by measuring the absorption at 350, 360, 370, and 380 nm. A slight absorption of stilbene at 350 nm was taken into account using the data on its concentration obtained by GLC. Unfortunately, the absorption band of the product of styrene double arylation (triphenylethylene) formed in the reaction



(II)

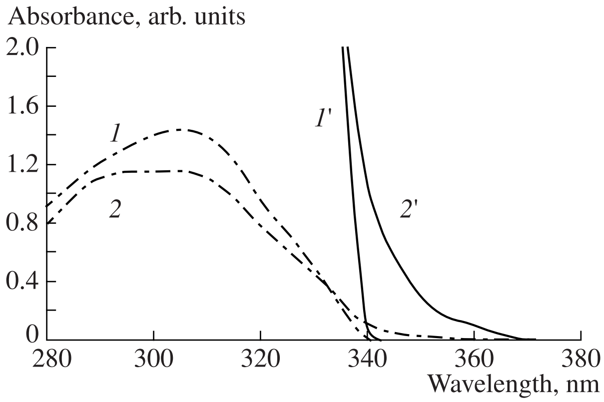


Fig. 2. UV spectra of solutions of (*1*, *1*') stilbene and (*2*, *2*') triphenylethylene at product yields of (dot-and-dash lines) 1% and (solid lines) 10%.

overlaps with the absorption band of $[PdBr_4]^{2-}$ even when the product yield is 10% (Fig. 2). However, as was found experimentally, styrene phenylation yielding stilbene occurs with nearly 100% selectivity. Triphenylethylene is not formed until styrene is completely consumed (Fig. 3). Thus, the $[PdBr_4]^{2-}$ concentration can quantitatively be determined directly during the catalytic experiment.

RESULTS AND DISCUSSION

It has been established above that the concentration of the $[PdBr_4]^{2-}$ complex during catalytic styrene and butyl acrylate phenylation with bromobenzene can be monitored by UV spectroscopy. The time dependences of the fraction of palladium in the $[PdBr_4]^{2-}$ form and substrate conversion are presented in Figs. 4–6. Contrary to earlier views [20, 34, 35], a considerable amount of palladium as $[PdBr_4]^{2-}$ (up to 70% in the reaction of styrene) appears within the first 7–20 min of the reaction in the $PdCl_2$-based catalytic system. Most of the substrate undergoes conversion within the same period of time. The addition of a reducing agent ($PdCl_2$ + 11HCOONa catalytic system) decreases the fraction of oxidized palladium and increases the catalytic reaction rate in the reactions of bromobenzene with both styrene (Fig. 4) and butyl acrylate (Fig. 5). This should be expected because at present it is doubtless that only compounds of reduced palladium are reactive in the coupling reactions of aryl halides, whereas the $[PdX_4]^{2-}$ complexes are an inactive form of the catalyst and are not involved in the catalytic cycle (scheme). Nevertheless, the almost complete cessation of the catalytic reaction in experiments with the reducing agent (approximately at the fifth minute of the reaction) cannot be caused by the conversion of palladium into $[PdBr_4]^{2-}$, because $[PdBr_4]^{2-}$ disappears from the reaction mixture simultaneously with the cessation of the reaction (Figs. 4, 5). This can be due to the accelerated formation of palladium black in the presence of the strong reducing agent (see the scheme, routes **A'**, **C**, and **D**). Palladium black is also inactive in the Heck reaction. Thus, the $[PdBr_4]^{2-}$ content correlates with the catalytic activity of the system, indicating the reversible character of the deactivation of the catalyst due to its oxidation. At the same time, the formation of palladium black results in an almost irreversible deactivation, which agrees with the scheme.

It is known that trialkylammonium salts are often used as additives or reaction media (ionic liquids) in the Heck reaction and other coupling reactions of aryl halides. It is usually believed that the main cause of their positive effect on the catalytic activity is the stabilization of colloidal palladium species. Several other

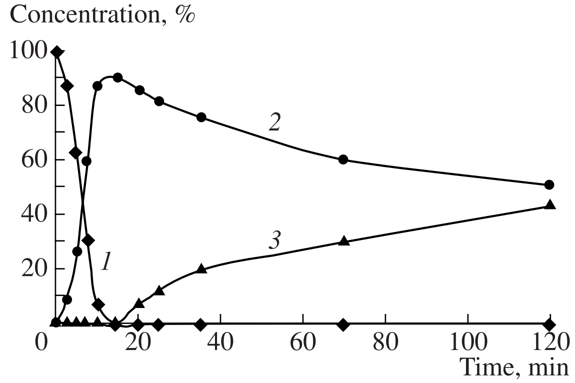


Fig. 3. Change in the concentrations of (*1*) styrene, (*2*) stilbene, and (*3*) triphenylethylene during the reaction of styrene with bromobenzene. The reaction temperature was 140°C, the $PdCl_2$ content was 0.08 mmol, no HCOONa was added, and the contents of other components are given in Experimental.

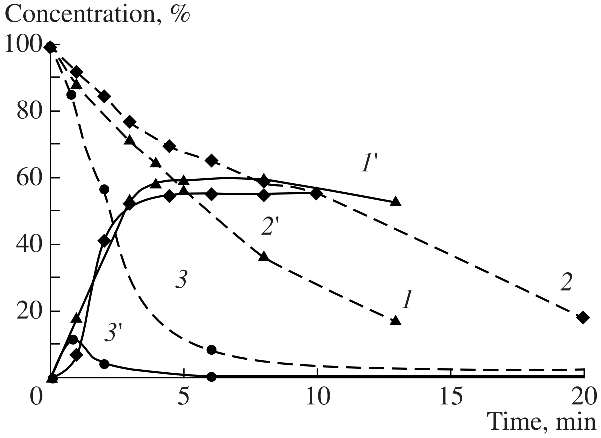


Fig. 4. Plots of the concentrations of (dashed lines) styrene and (solid lines) $[PdBr_4]^{2-}$ versus time of the reaction of styrene with bromobenzene occurring in the presence of the catalytic systems: (*1*, *1*') $PdCl_2$ (1.6 mol %), (*2*, *2*') $PdCl_2$ (0.8 mol %), and (*3*, *3*') $PdCl_2$ (1.6 mol %) + 11HCOONa. The reaction temperature was 140°C, and the contents of other components are given in Experimental.

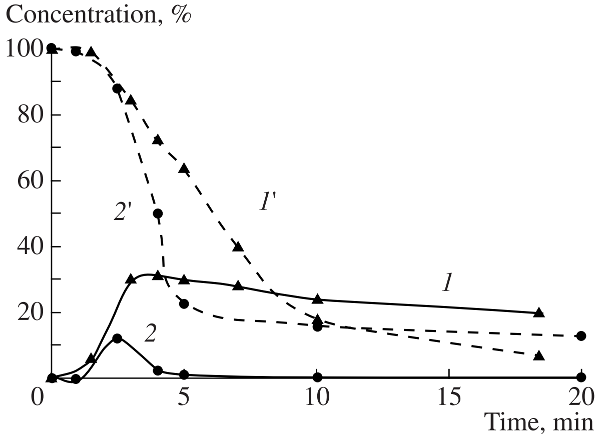


Fig. 5. Plots of the concentrations of (dashed lines) butyl acrylate and (solid lines) $[PdBr_4]^{2-}$ versus time of the reaction of butyl acrylate with bromobenzene occurring in the presence of the catalytic systems: (*1*, *1'*) $PdCl_2$ (1.6 mol %) and (*2*, *2'*) $PdCl_2$ (1.6 mol %) + 11HCOONa. The reaction temperature was 140°C, and the contents of other components are given in Experimental.

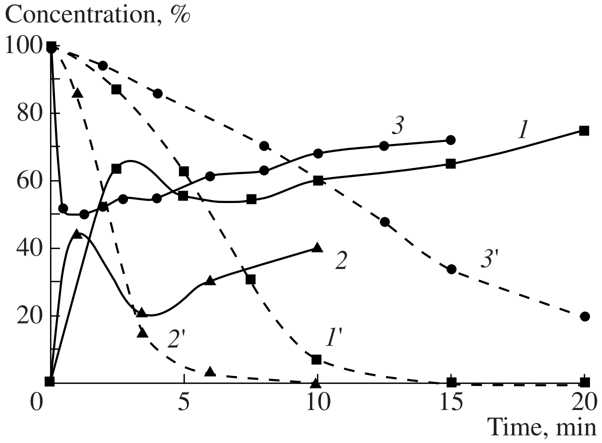


Fig. 6. Plots of the concentrations of (dashed lines) styrene and (solid lines) $[PdBr_4]^{2-}$ versus time of the reaction of styrene with bromobenzene occurring in the presence of the catalytic systems: (*1*, *1'*) $PdCl_2$ (1.6 mol %) + $20NBu_4Br$, (*2*, *2'*) $PdCl_2$ (1.6 mol %) + 11HCOONa + $20NBu_4Br$, and (*3*, *3'*) Na_2PdBr_4 (1.6 mol %). The reaction temperature was 140°C, and the contents of other components are given in Experimental.

factors are assumed to favor the increase in the lifetime and activity of the catalytic system upon the addition of ammonium salts. In particular, the presence of an ammonium salt was shown to substantially facilitate palladium dissolution (scheme, route **E**) [8, 18, 19, 25, 26, 36]. In our experiments, the ammonium salt ($PdCl_2$ + $20NBu_4Br$) exerted a comparatively weak effect on the $[PdBr_4]^{2-}$ concentration (Fig. 6). The addition of a reducing agent ($PdCl_2$ + 11HCOONa + $20NBu_4Br$) to this catalytic system decreased the amount of $[PdBr_4]^{2-}$; however, the effect was much weaker than that in the system containing no ammonium salt.

It was found previously [8, 34, 37] that two consecutive autocatalytic processes occur simultaneously in the system accelerating the Heck reaction: palladium reduction (scheme, routes **A** and **A**') and the formation of colloidal particles (scheme, route **C**). A theoretical analysis [37] showed that this mechanism can bring about complicated time dependences of the concentrations of the palladium-containing intermediates, including the appearance of oscillations of these concentrations. Therefore, the maxima and minima in the $[PdBr_4]^{2-}$ curves in the presence of the $PdCl_2$- and NBu_4Br-based catalytic systems (Fig. 6) are quite natural. At least, the theoretical calculation of the kinetic dependences using a simplified mathematical model [37] describing the autocatalytic reduction and agglomeration of palladium qualitatively confirmed the possibility of the appearance of maxima and minima in these curves.

According to the scheme, the formation of $[PdBr_4]^{2-}$ includes the intermediate reduction of the starting palladium complex (route **A**). However, the formation of $[PdBr_4]^{2-}$ can also be a result of simple ligand exchange in $PdCl_2$, which was chosen as the catalyst precursor. The source of bromide anions can be both HBr formed in the Heck reaction (I) itself and NBu_4Br if the latter is a component of the catalytic system. To exclude completely the formation of $[PdBr_4]^{2-}$ due to possible ligand exchange, we carried out a special experiment in which a Na_2PdBr_4 solution prepared beforehand served as the catalyst precursor instead of $PdCl_2$ (Fig. 6). The minimum in the $[PdBr_4]^{2-}$ curve in this experiment unambiguously proves the formation of this complex directly during the catalytic reaction. This completely corresponds to the proposed scheme [8, 18], according to which the formation of $[PdBr_4]^{2-}$ is a consequence of the oxidation of catalytically active Pd(0) (routes **F** and **B**) and dissolution of colloidal palladium (Pd_{coll}) through intermediate oxidation (routes **E**, **B**, and **G**) rather than ligand exchange.

Therefore, the earlier ignored additional possibility of $[PdBr_4]^{2-}$ formation in the Heck reaction from palladium metal in the presence of NBu_4Br and air oxygen (scheme, route **G**) should be taken into account. Palladium metal was dissolved in the presence of oxygen and KI to form $[PdI_4]^{2-}$ [38, 39]. We compared the reactions of the reduced Pd/C catalyst with NBu_4I in an argon atmosphere and in air (Fig. 7). As can be seen from the data in Fig. 7, palladium is dissolved to a considerable extent in air. Under argon, the dissolution was observed only at the beginning of the reaction, after which the $[PdI_4]^{2-}$ concentration decreased. The dissolution of palladium in an inert atmosphere can be induced by the presence of the oxidized metal on the Pd/C surface (the catalyst samples were stored in air). The addition of excess oxygen (~5 equivalents with respect to palladium) substantially increased the intensity of the absorption band of $[PdI_4]^{2-}$ in both argon and

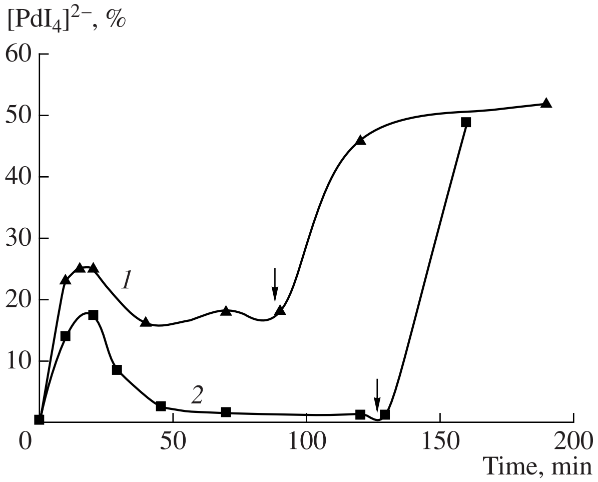


Fig. 7. Change in the $[PdI_4]^{2-}$ concentration in a solution using the 5% Pd/C + NBu_4I system in (*1*) air and (*2*) argon atmosphere. Reaction conditions: temperature 140°C, palladium content in the catalyst 0.08 mmol, and 1.6 mmol NBu_4I added. The moments of introduction of excess oxygen are marked by arrows.

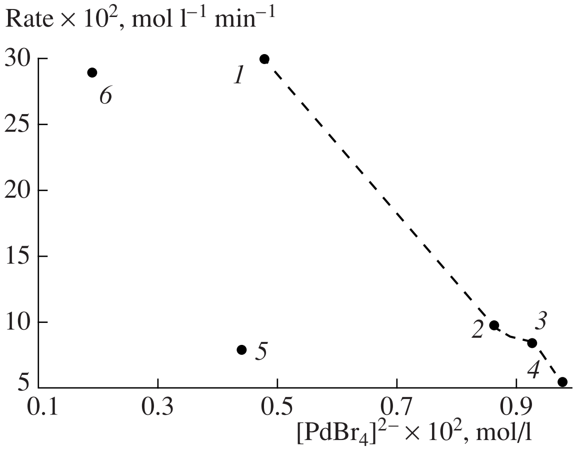


Fig. 8. Plots of the reaction rate of styrene with bromobenzene versus $[PdBr_4]^{2-}$ concentration in the presence of the catalytic systems: (*1*) $PdCl_2$ (1.6 mol %) + 11HCOONa + $20NBu_4Br$, (*2*) $PdCl_2$ (1.6 mol %) + $20NBu_4Br$, (*3*) $PdCl_2$ (1.6 mol %), (*4*) $PdCl_2$ (1.6 mol %) + $6NBu_4Br$, (*5*) $PdCl_2$ (0.8 mol %), and (*6*) $PdCl_2$ (1.6 mol %) + 11HCOONa.

air (Fig. 7), which unambiguously confirms the participation of oxygen in the dissolution process (scheme, route **G**). Note that the presence of oxygen or air along with NBu_4Br was a necessary condition for the successful Heck reaction with nonactivated aryl chlorides on the Pd/NaY catalyst [40, 41] or on the catalyst obtained from $PdCl_2$ as a precursor [8].

If $[PdBr_4]^{2-}$ were the single inactive form of palladium in the Heck reaction, a negative linear dependence would be observed between the reaction rate and the $[PdBr_4]^{2-}$ concentration in various catalytic systems. However, as already mentioned, the catalytic system includes other palladium species, which are not involved in the main catalytic cycle (colloidal palladium and palladium black), along with $[PdBr_4]^{2-}$. Nevertheless, the expected decrease in the reaction rate was observed with an increase in the $[PdBr_4]^{2-}$ concentration in the presence of catalytic systems *1–4* and *6* (Fig. 8) with the same starting palladium content. However, this dependence cannot confidently be considered to be linear ($R^2 = 0.8913$). The reason is probably the substantial increase in the fraction of aggregated palladium (Pd_{coll}, Pd_{black}) in catalytic system *6*, which contains a reducing agent admixture. The matter is that the Pd(0) concentration has a much stronger effect on the aggregation rate than on the catalytic conversion rate [8, 20, 33, 34]. When comparing system *6* and system *1* also containing an additive of HCOONa, in the first system reduced palladium is more prone to aggregation due to the absence of the stabilizing effect of NBu_4Br.

The point corresponding to catalytic system *5* (Fig. 8) falls out from the general dependence because of the lower total content of palladium in this system. However, a characteristic feature of the “ligandless” catalytic systems used in the Heck reaction appears in system *5*: in the presence of such systems, the reaction order with respect to the catalyst is substantially below unity [34]. This phenomenon is often called “homoeopathic” catalysis [4, 20]. As follows from the data in Fig. 8, the twofold decrease in the palladium content in the catalytic system exerts no effect on the reaction rate (compare systems *3* and *5*). This is explained by the lower Pd(0) concentration, which, contrary to system *6*, should exert a positive effect on the fraction of palladium involved in the catalytic cycle.

Thus, in the Heck reaction with bromobenzene in the presence of the “ligandless” catalytic systems, a considerable amount of palladium (up to 70% of total amount of the metal) is converted into the oxidized form $[PdBr_4]^{2-}$, which is inactive and does not participate in the main catalytic cycle. Taking into account our earlier data on similar reactions of aryl iodides and data for catalytic systems of other types (palladacycles, phosphine palladium complexes), we believe that the oxidation of palladium with the formation of catalytically inactive complexes of the PdL_2X_2 type (L is halogen or phosphine) is a general feature of the Heck reaction and, perhaps, other reactions of aryl halide coupling.

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