Effect of macrokinetic factors on the ligand-free Heck reaction with non-activated bromoarenes

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Abstract

Styrene phenylation by non-activated bromobenzene (Heck reaction) in the presence of ligand-free catalytic systems based on $PdCl_2$ proceeds under diffusional controlled regime. It was experimentally found that an increase in the agitation speed leads to an increase in the reaction rate, a substantial decrease of the time for attaining a product complete yield and gives rise to the extra high TOF ($150,000\,h^{-1}$ in 50 min at 780 rpm).
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Keywords: Heck reaction; Ligand-free condition; Macrokinetic factors; Palladium

1. Introduction

The Heck reaction is a perspective synthetic route to substituted alkenes [1–5]. Recent attention of chemists has been focused on a search for catalytic systems capable of activating the more accessible but less reactive chloro- and bromoarenes (see review [2,4,5] and references cited therein). This would make the Heck reaction much more acceptable for industrial use. In this field significant progress was made when phosphine-containing catalysts were used [6–10]. In this connection, catalytic systems without ligands are of special interest [11–16]. Nowadays, detailed kinetic studies of catalytic reactions [17], in particular Heck catalysis [5], are rather occasional, though the subtle trend toward understanding the reaction mechanism and a search for an effective catalytic system is impossible without it. Kinetics of the Heck reaction with aryl iodides has been studied earlier; a concept of the reaction mechanism has been developed and the trends of catalyst transformation outside the catalytic cycle have been clarified (Scheme 1).

The Pd(II) reduction to Pd(0) (Scheme 1, A) proceeding as an autocatalytic reaction was found to be necessary not only at the reaction starting but throughout the overall process due to side reductive conversions of aryl halides into Ar–Ar (Scheme 1, B)

[18,19]. However, that problem might be solved by the addition of reducing agent small amounts (for example, sodium formate) [15,20]. The second undesirable process is an agglomeration of catalytically active Pd(0) complexes (Scheme 1, C and D), an acceleration of which is favored by a lowering of ArX reactivity, i.e. a decrease of the catalytic cycle rate (Scheme 1, F) [19]. In Scheme 1 the agglomeration is presented via the intermediate formation of Pd colloidal particles ($Pd_{col.}$) established unequivocally earlier [21]. The partial return of the aggregated Pd in the catalytic cycle is possible (Scheme 1, E) through its interaction with aryl halide [18,19,21–24]. Formally, in this case (see supplementary data) a succession of the stages E, G, C (Scheme 1) should be defined as one more catalytic cycle (catalytic cycle II).

Using less reactive arylating agents (ArBr and ArCl) more intensive Pd(0) agglomeration (Scheme 1, C and D) and, consequently, a more considerable effect on reaction kinetics should be expected. Note that according to obtained data [18] the agglomeration has been more of the second order kinetics in Pd(0) concentration. Taking into account the reaction mechanism presented in Scheme 1, one can assume that catalytic activity should increase with an increase in arylating agent and reductant concentrations and a decrease in total Pd concentration. These factors lead to the more successful competition of the catalytic cycle I (Scheme 1, F) and catalytic cycle II (Scheme 1, E) with both agglomeration (Scheme 1, C and D) and oxidation of palladium (Scheme 1, F, B and E, B). The given concept has been

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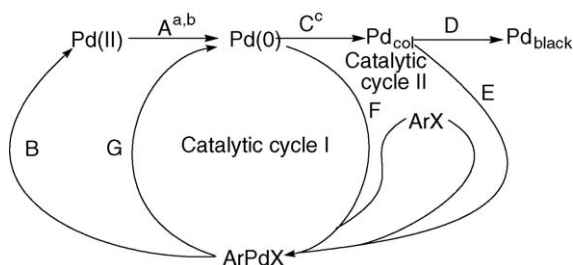
Scheme 1. The key processes of the Heck reaction. [a]autocatalytic reaction [19]; [b]using PdCl$_2$ as a precursor process includes the stage of its previous dissolution; [c]more than second order kinetics in Pd(0) concentration [18].

corroborated by several works [11–15,25–27]. Moreover, with an increase in ArBr concentration the reaction rate increases not so much as product yield, which is indicative of a longer catalyst life-time [15,27]. Besides, the reaction has been of the negative order kinetics in Pd [25,26] (the same conclusion can be made from experimental data presented in reference [11]).

The results of further kinetic researches of the styrene reaction with bromobenzene as typical non-activated arylbromides (Scheme 2) are presented in this paper. The most active catalytic system including available PdCl$_2$ as a precatalyst, sodium formate as a reductant and arylbromide excess is the subject of this research [15,27].

2. Experimental

2.1. General remarks

All reactions were carried out under an air atmosphere. All solvents and reagents were of analytical or chemical grade. DMF, bromobenzene and styrene were purified by standard methods [28]. 5%-Pd/C, Pd(PhCN)$_2$Cl$_2$ and Pd(acac)$_2$ were purchased from Sigma–Aldrich and used as received. The gas–liquid chromatograms were recorded on a chromatograph HP-4890 series equipped with a FID detector and a HP-5 column (cross-linked methyl, phenylsiloxane, 15 m × 0.53 mm × 1.5 μm film thickness). Products were identified by comparison with authentic samples. The reaction rate was calculated by a graphical differentiation of the time-conversion curves. Total yield of PhH + Ph–Ph was up to 1.5% with respect to ArX. The stylbene:1,1-diphenylethylene ratio (96:4) was unchanged in all experiments.

2.2. Catalytic runs

Bromobenzene (30 mmol), styrene (5 mmol), sodium acetate(5.6 mmol), sodium formate (0.9 mmol), naphthalene (1 mmol) as internal standard for GC analysis, DMF (5 mL) as
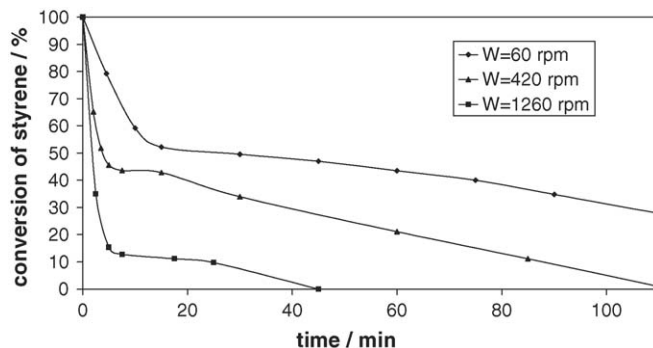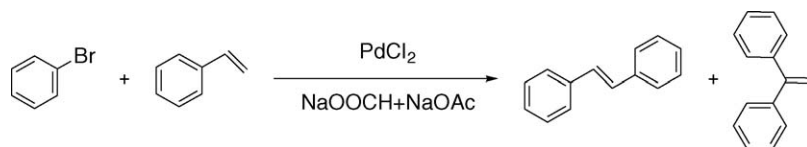

Fig. 1. Selected conversion vs. reaction time diagrams of the reaction (Scheme 2) at various agitation speed (W) with the tube as a reactor. Reaction conditions: bromobenzene (30 mmol), styrene (5 mmol), sodium acetate (5.6 mmol), sodium formate (0.9 mmol), naphthalene (1 mmol) as internal standard, DMF (5 mL) as solvent and PdCl$_2$ (0.08 mmol), 140 °C.

solvent and PdCl$_2$ (0.08 mmol, i.e. 1.6 mol% with respect to styrene) were introduced in a glass reactor (tubes or flasks) fitted with a magnetic stirring bar and septum inlet. The reactor was placed into a pre-heated, 140 °C oil bath and the reaction mixture was stirred. The reaction was monitored by taking small samples for GC analysis. The same protocol was carried out with 5%-Pd/C (0.17 g) as a precatalyst. In experiments with Pd(acac)$_2$ as a catalyst precursor the freshly prepared solution of Pd(acac)$_2$ (0.08 mmol) in DMF (5 mL) was used instead of solid PdCl$_2$. In low Pd-loading experiments (Fig. 5) the necessary volume of a solution of Pd(PhCN)$_2$Cl$_2$ in DMF (0.032 mol/L) was used as the precatalyst. In the experiment with a catalyst added successively (Fig. 7) freshly prepared Pd(acac)$_2$ solution (0.032 mol/L) was injected in the reactor (each portion 0.25 mL).

3. Results

It has been established that the reaction kinetics of the styrene phenylation by bromobenzene (ratio 1:6) in the presence of the catalytic system PdCl$_2$ + NaOOCH + NaOAc depends on the reactor type. Using a flask as a reactor the maximum reaction rate was higher and a complete product yield was reached for a shorter time than in the experiments performed in the tubes. Note that the distinction between the experiments in flasks and tubes has recently been noticed in the Sonogashira cross-coupling reaction [29], which is similar to the Heck reaction.

One of the possible reasons for the observed trends might be a different stirring efficiency when the some reaction stages proceed under a diffusional controlled regime. To check this assumption the experiments at various speeds of agitation were performed. A number of obtained time resolved reaction profiles for styrene conversion are presented in Fig. 1 (tubes) and Fig. 2

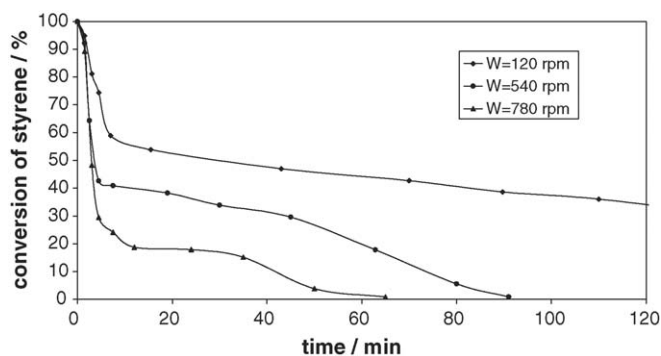Scheme 2. The Heck reaction of styrene with bromobenzene.

Fig. 2. Selected conversion vs. reaction time diagrams of the reaction (Scheme 2) at various agitation speed (*W*) with the flask as a reactor. Reaction conditions: bromobenzene (30 mmol), styrene (5 mmol), sodium acetate (5.6 mmol), sodium formate (0.9 mmol), naphthalene (1 mmol) as internal standard, DMF (5 mL) as solvent and PdCl$_2$ (0.08 mmol), 140 °C.

(flasks). In those concentration versus reaction time diagrams one might see at least two reaction periods of time (Period I and Period II below). Period I (the first 5–7 reaction minutes) is characterized by high rate. The reaction rate at Period II lasts till the complete styrene conversion is significantly lower. At Period II a rate acceleration effect is sometimes distinctly discerned.

An effect of the agitation speed on the maximum reaction rate at Period I is shown in Fig. 3. The type of dependencies indicates that even at the maximum possible agitation speed with a magnetic stirrer the reaction in both reactors remains under diffusional controlled regime. The stilbene yield at the fast Period I (the other reaction parameter) exhibits an even higher sensitivity to the agitation speed of reaction solution (Fig. 4) varying from 45% to 85%. The same pertains to the time of complete styrene conversion (Figs. 1 and 2).

Thus, the obtained results indicate that at least one or several stages of reaction (Scheme 2) proceeds under diffusional controlled regime using ligand-free catalytic systems. Appreciation of this fact and the employment of vigorous stirring make possible the attainment of extremely high turnover frequency (Fig. 5). The best turnover numbers in 50 min have reached 125,000 mol product per mol catalyst, which corresponds to an average TOF 150,000 h^{-1} (initial TOF 341,000 h^{-1}). Note the TOF for ligand-free catalytic system based on Pd(OAc)$_2$ [11]
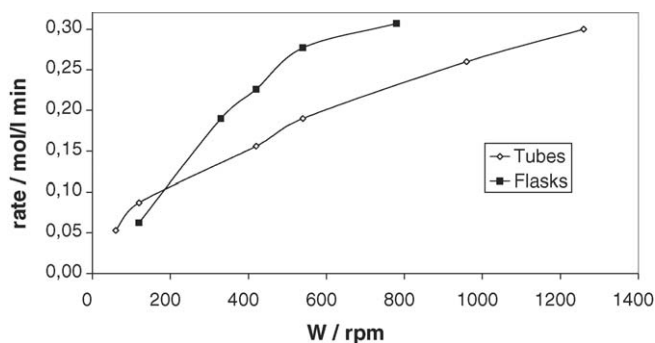

Fig. 3. Effect of agitation speeds (*W*) on maximum reaction rate at Period I. Reaction conditions: bromobenzene (30 mmol), styrene (5 mmol), sodium acetate (5.6 mmol), sodium formate (0.9 mmol), naphthalene (1 mmol) as internal standard, DMF (5 mL) as solvent and PdCl$_2$ (0.08 mmol), 140 °C.
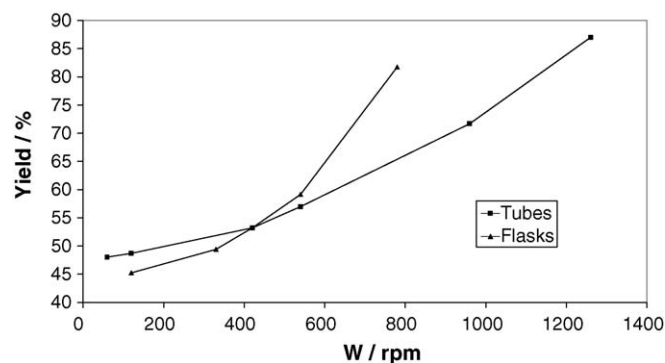

Fig. 4. Effect of agitation speeds (*W*) on the yield of the reaction (Scheme 2) at Period I (the first 5–7 reaction minutes in Figs. 1 and 2).
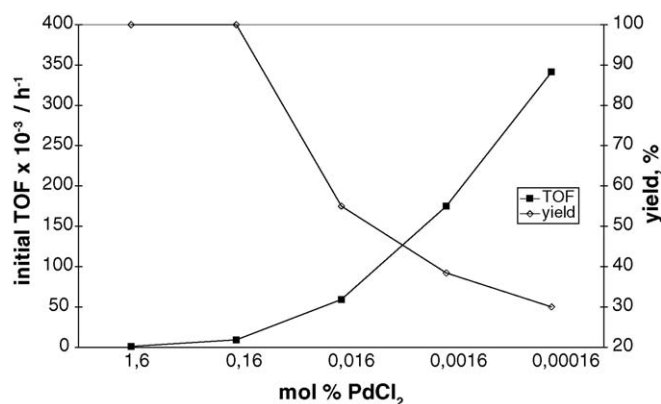

Fig. 5. Effect of the palladium/substrate ratio on the TOF and yield of the reaction (Scheme 2) with the flask as a reactor. Reaction conditions: bromobenzene (30 mmol), styrene (5 mmol), sodium acetate (5.6 mmol), sodium formate (0.9 mmol), naphthalene (1 mmol) as internal standard, DMF (5 mL) as solvent and PdCl$_2$ (0.00016–1.6 mol% with respect to styrene), 140 °C, 780 rpm magnetic stirring.

(reaction of bromobenzene with butyl acrylate) was 900 h^{-1}. The TOF for reaction with less reactive styrene was 132 h^{-1} (using data [11] we ourselves have calculated the TOF for this reaction). Although the usage of catalyst poor quantities (so-called low Pd-loading approach [11–13]) has lowered the reaction product yield, a separation of reagents remained in reaction mixture (styrene and bromobenzene excess) is performed easily by distillation, so their repeated use with a new portion of catalyst is quite possible.

4. Discussion

Substitution of bromobenzene with iodobenzene gave rise to the disappearance of reaction kinetic sensibility to the stirring rate already at 300 rpm (Table 1, runs 1–4). So, a diffusion influence on the stages of catalytic cycle I (Scheme 1) seem to be impossible. It is related to other processes in which arylhalogenide does not take part, including dissolution of an employed base (NaOAc). Considering the more significant effect of the catalyst transformations outside the catalytic cycle I on catalytic activity in the reaction with bromobenzene the reason for observed trends (Figs. 1–4) should be, indeed, hidden in those

Table 1
Effect of agitation speeds on maximum reaction rate (Scheme 2)

Run	Catalyst precursor	Arylating agent	Agitation speed (rpm)	Maximum reaction rate (mol/(L min)
1	PdCl$_2$	PhI	180	12×10^{-2}
2	PdCl$_2$	PhI	300	14×10^{-2}
3	PdCl$_2$	PhI	540	16×10^{-2}
4	PdCl$_2$	PhI	780	15×10^{-2}
5	Pd(acac)$_2$ solution	PhBr	180	10×10^{-2}
6	Pd(acac)$_2$ solution	PhBr	300	16×10^{-2}
7	Pd(acac)$_2$ solution	PhBr	540	25×10^{-2}
8	Pd(acac)$_2$ solution	PhBr	780	29×10^{-2}
9	5%-Pd(0)/C	PhBr	300	16×10^{-2}
10	5%-Pd(0)/C	PhBr	420	17×10^{-2}
11	5%-Pd(0)/C	PhBr	1020	16×10^{-2}

PhX (30 mmol), styrene (5 mmol), sodium acetate (5.6 mmol), sodium formate (0.9 mmol), naphthalene (1 mmol) as internal standard, DMF (5 mL) as solvent and catalyst precursor (1.6 mol% of Pd with respect to styrene), 140 °C.

processes (Scheme 1, A–E). To check some hypotheses of what stages are under diffusional controlled regime a number of precursor experiments have been performed.

First of all, it was necessary to verify an assumption of PdCl$_2$ dissolution under diffusional controlled regime since PdCl$_2$ used in previous experiments as a catalyst precursor, dissolved restrictedly in dimethylformamide (DMF). However, this hypothesis was not confirmed experimentally since the agitation speed continued to influence the reaction rate when palladium bis-acetylacetonate solution (Pd(acac)$_2$) prepared previously was used instead of solid PdCl$_2$ (Table 1, runs 5–8). On the other hand the PdCl$_2$ used as a precursor and iodobenzene used as an arylating agent have resulted in a disappearance of reaction sensibility to stirring speed (Table 1, runs 1–4).

Unlike the reaction with iodobenzene where the major deactivation process is Pd oxidation (Scheme 1, F and B) [18–20,30], in the reaction with bromobenzene the influence of agglomeration (Scheme 1, C and D) and Pd dissolution (Scheme 1, E) on catalytic activity was expected to be more significant (due to low reactivity of PhBr [11]). The agglomeration of metal atoms non-stabilized in the solution occurs at a great rate because of considerable energetic winning; this rate may potentially exceed the diffusion rate of both single atoms and growing aggregates in the solution. As a result, the process can progress under a diffusional controlled regime. The dissolution (Scheme 1, E) might also occur under diffusional limitation due to the possible difficulties of reagent access to the surface (ArX as oxidizing agent in this case) and the necessity of the intensive transfer of dissolving substances from dissolution area to a decrease of the solution saturation.

The TOF increase with a decrease of precursor amount (Fig. 5) may indicate that only a negligible part of loaded Pd truly acts in catalytic cycles [31]. The remainder of Pd is unlikely to exist in oxidated state (Pd(II) in Scheme 1) under relatively forcing conditions of the Heck reaction with aryl bromides [11] and, especially, in the reductant (HCOONa) presence. The fast Pd reduction followed by the formation of Pd$_{col.}$ and Pd$_{black}$ (Scheme 1) is more credible. This conclusion is in accordance

with the earlier developed concept [11,15,26] that the Pd main part transits into microheterogeneous and heterogeneous states (Pd$_{col.}$ and Pd$_{black}$) almost at the reaction starting. At first sight all of above seems to be indicative of the catalytic activity in reaction (Scheme 2) depends more on the rate of colloidal particle dissolution (Scheme 1, E) than on the rate of Pd(0) dissolved complex agglomeration (Scheme 1, C), i.e. the dissolution proceeds under diffusional controlled regime. However, the following facts and speculations below make it possible to come to another conclusion. We believe that the agglomeration rather than the dissolution progresses under diffusional controlled regime (vide infra).

Investigators have always attempted to retard the Pd(0) agglomeration (e.g. the excellent low Pd-loading approach of de Vries and Reetz [11–13]). However, there is experimental evidence for the positive influence of intensive agglomeration on catalytic activity. For example, the presence of a small amount of reducing agent in the reaction with aryl bromides is always accompanied with an increase in catalytic activity [15,27]. High TOF obtained in our work (Fig. 5) indicates the same. The rate increase in Pd reduction (A) can lead to the agglomeration rate increase (C) and, therefore, to a decrease of Pd particle size [32,33]. From a speculative point of view the size of particles (or more precisely the part of their surface atoms) is able to play a crucial role in their capability to be dissolved (E). Actually, as was informed in [34], the usage of the more active reductants in the Heck reaction led to more active catalytic systems that were associated with a finer distribution of Pd particles. The positive relation between Pd-dispersion and the Heck reaction rate was also previously mentioned by several authors working with heterogeneous catalysts [35–39]. Hence, the positive correlation between the agglomeration rate and the efficiency of colloidal particle dissolution (consequently, catalytic activity) may well exist. In such a case fast Period I might be conditioned by the relatively high rate of the dissolution of finely dispersed palladium (Scheme 1, E) formed at the reaction starting due to fast stage C (Scheme 1). Retardation of stage C because of the Pd(0) concentration decrease in the solution along with the colloidal particle coagulation (Scheme 1, D) leads to both a decrease of the particle quantity and an increase of their size accompanied with a rate lowering of their dissolution. This was observed after 5–7 reaction minutes. Sensitivity of the Heck reaction to the stirring rate means that the rate-determining step should be under diffusion controlled regime. Taking into account our conclusion that the fast agglomeration (Scheme 1, C) is under diffusion-controlled regime, namely this step should be considered the rate-determining step. This seems contrary to the definition of rate determining step as the slowest reaction step, however, the agglomeration is not a conventional chemical reaction and its rate influences the size of formed Pd particles, i.e. on their capability to be dissolved (F).

If the high agglomeration rate was favorable for the catalytic activity the agglomeration would influence catalytic activity at both periods of reaction (Periods I and II). That hypothesis has been supported by the results of experiments where the agitation speed of reaction solution was changed after the first 6 min of the reaction (Table 2).

Table 2
Effect of agitation speeds on reaction rate at Periods I and II

Run	Agitation speed during first 6 reaction minutes (rpm)	Agitation speed after 6 min (rpm)	Reaction rate at Period II (after 6 min; mol/L min)
1	420	420	0.53×10^{-2}
2	540	420	1.10×10^{-2}
3	420	540	1.06×10^{-2}
4	540	540	1.35×10^{-2}

Bromobenzene (30 mmol), styrene (5 mmol), sodium acetate (5.6 mmol), sodium formate (0.9 mmol), naphthalene (1 mmol) as internal standard, DMF (5 mL) as solvent and PdCl$_2$ (0.08 mmol), 140 °C.

The experimental results (runs 1 and 2) indicate that the reaction rate at Period II depends on the agitation speed at Period I. At the same time, the rate is increasing as the agitation speed is being built up at Period II (runs 1 and 3) reaching maximum magnitude when the high agitation speed is attained at both periods (runs 1 and 4). Therefore, the catalyst activity at Period II depends on the agitation speed during both periods of the process. This type of trend can be explained if the high agglomeration rate is considered favorable to the dissolution efficiency of colloidal particles and, consequently, to the catalytic activity.

One more corroboration of the high probability that the agglomeration is responsible for the reaction sensitivity to agitation speed was obtained in experiments with Pd(0)/C as a catalyst precursor (Table 1, runs 9–11). These experiments point clearly to an absence of the macrokinetic factor influence on the catalysis. In terms of Scheme 1, one may accept that at the reaction starting palladium on the carbon surface exists in a metallic state close to Pd$_{col.}$ and Pd$_{black}$ (Scheme 1) rather than in Pd(II) compounds. Thus, at the reaction starting Pd dissolution from the surface plays a more important role than when PdCl$_2$ or Pd(acac)$_2$ is used as a precursor (see Pd dissolution from surface of heterogeneous catalysts in Heck reaction [19,21–23,35–41]). The absence of reaction sensibility to the agitation speed is indicative of the dissolution under a kinetic regime rather than under a diffusional controlled regime.

Note that on the time resolved reaction profile for styrene conversion in the reaction with Pd(0)/C as a precursor the acceleration period (about 2.5 min) was observed (Fig. 6). The feature of that period is an attainment of the maximum reaction rate at very low conversions of educts. According to developed theoretic approach [42], such an experimental reaction profile for substrate conversion is conditioned by autocatalytic kinetics of the catalyst formation from the precursor. It follows that the dissolution is able to demonstrate autocatalytic kinetics under the Heck reaction conditions, since only the Pd dissolution is responsible for catalytic species formation using Pd(0)/C. That conclusion is of fundamental importance offering a satisfactory explanation for the reaction autoacceleration at Period II, observed at a high agitation speed with PdCl$_2$ as a precursor (Figs. 1 and 2). The reasons for autocatalytic kinetics of dissolution are a real challenge, but they can be connected with a change of the saturation extent of particle surface relative to the most thermodynamically stable saturation shell ("magic" particles) [26].
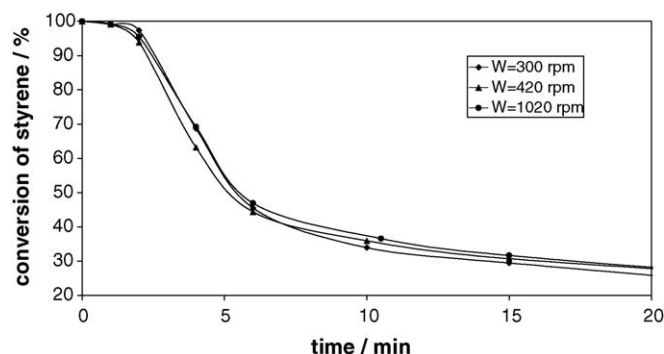

Fig. 6. Conversion vs. reaction time diagrams of the Heck reaction (Scheme 2) with 5%-Pd(0)/C as catalyst precursor at various agitation speeds (W) in flask as a reactor. Reaction conditions: bromobenzene (30 mmol), styrene (5 mmol), sodium acetate (5.6 mmol), sodium formate (0.9 mmol), naphthalene (1 mmol) as internal standard, DMF (5 mL) as solvent and 5%-Pd(0)/C (1.6 mol% of Pd with respect to styrene), 140 °C.

Noteworthy, as has been shown in a number of independent researches, several stages of the Heck reaction demonstrate autocatalytic kinetics. For instance, Pd reduction in the course of the Heck reaction (Scheme 1, A) was found to be an autocatalytic process [18,19,42]. Examples of similar dissolution kinetics are given above. Besides, the formation of colloidal particles (Scheme 1, C) might be a autocatalytic reaction [32,33]. In our mechanistic studies we have first received convincing indications for the autocatalytic agglomeration mechanism directly in the course of the Heck reaction.

The effect of successive addition of the catalyst precursor small portions into the reactor reduced with each subsequent portion (Fig. 7). It is consistent with the assumption of the Pd autocatalytic agglomeration since otherwise each catalyst additive would lead to practically equal styrene conversion. Interestingly, the addition of the fourth catalyst portion does not induce the system change at all. This may be related to the very intensive agglomeration being accelerated by Pd solid phase resulting from the addition of previous portions. That is why Pd does
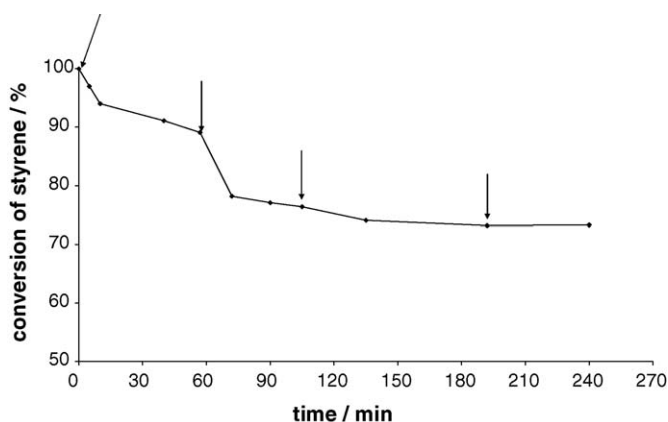

Fig. 7. Conversion vs. reaction time diagrams of the Heck reaction (Scheme 2) on successive addition of Pd(acac)$_2$ (the addition time is marked by arrows). Reaction conditions: bromobenzene (30 mmol), styrene (5 mmol), sodium acetate (5.6 mmol), sodium formate (0.9 mmol), naphthalene (1 mmol) as internal standard, DMF (5 mL) as solvent and Pd(acac)$_2$ (0.16 mol% with respect to styrene in each portion), 140 °C, 420 rpm magnetic stirring.
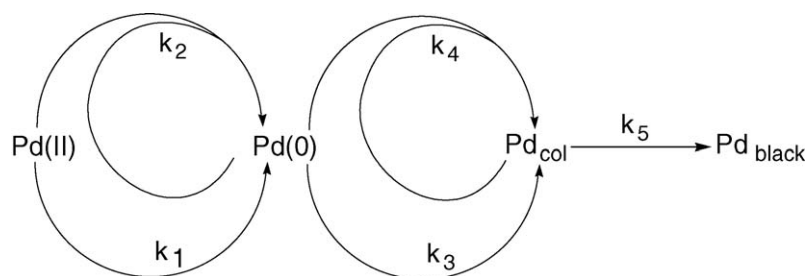
Scheme 3. Simplified reaction scheme of the catalyst transformation without the catalytic cycle. k_3 – rate constant of homogeneous nucleation k_4 – rate constant of autocatalytic growth of particles according to [32].

not take part in the Heck reaction being withdrawn irreversibly from the catalytic cycles to give catalytically inactive Pd_{black} (Scheme 1). de Vries et al. [11] have offered the explanation for the phenomenon of a TOF decrease with an increase of the total Pd concentration being due to an equilibrium shift between the palladium present in the colloid particles and Pd(0) that is taking part in catalytic cycle I. It is true only for the TOF, but this explanation was not supported for a reaction rate decrease (negative order kinetics in Pd) observed in our experiment (Fig. 7) (see supplementary data for more detailed information).

Based on autocatalytic kinetics of Pd reduction, agglomeration and dissolution the fundamental conclusion can be made: implementation of the complicated non-linear kinetic effects that can result in non-linear dynamics and kinetic oscillation is possible in the catalytic system of the Heck reaction.

For an example, analysis of the equation system (1) in the terms of qualitative theory of differential equations demonstrates the possibility of an appearance of dying oscillations of Pd(0) and Pd_{col} concentrations (see supplementary data). The equation system (1) corresponds to a simplified reaction scheme of the catalyst transformation outside the catalytic cycle (Scheme 3) and uses pseudo-chemical description (as in [32]) of autocatalytic process of the colloidal particle formation. An absence of catalytic cycles with Pd(0) or Pd_{col} in Scheme 3 implies their insignificant influence on Pd conversions outside the catalytic cycles. That may well be possible since steps F and E (Scheme 1) in the reaction with aryl bromides are the rate determining steps in catalytic cycles I and II, respectively.

$$
\begin{cases}
\dfrac{d[Pd(0)]}{dt} = k_1[Pd(II)] + k_2[Pd(II)][Pd(0)] \\
\qquad\qquad - k_3[Pd(0)] - k_4[Pd(0)][Pd_{col}] \\
\dfrac{d[Pd_{col}]}{dt} = k_3[Pd(0)] + k_4[Pd(0)][Pd_{col}] - k_4[Pd_{col}]
\end{cases}
\tag{1}
$$

5. Conclusions

It has first been established that styrene phenylation by bromobenzene in ligand-free catalysis proceeds under a diffusional controlled regime. An increase in the agitation speed increases the reaction rate, substantially decreases the time for quantitative yield attainment and causes the extra high TOF. Evidence is provided that the Pd agglomeration proceeds under a diffusional controlled regime and the major part of Pd loaded exists in Pd_{col}

and Pd_{black} forms practically at the reaction starting. Indications have first been obtained that Pd agglomeration and dissolution in the course of the Heck reaction are autocatalyzed. The last observation along with data obtained earlier on autocatalysis of Pd reduction in the Heck reaction allows one to expect non-linear dynamics and kinetic oscillations of the Heck reaction.

Acknowledgment

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at 10.1016/j.molcata.2006.01.051.

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