

New Approaches to Heck Reaction Testing for Homogeneity–Heterogeneity

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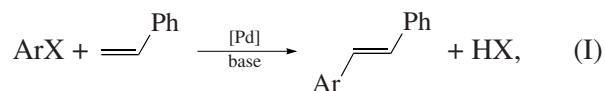
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Abstract—Modified catalytic reaction tests for homogeneity–heterogeneity are proposed. In these tests, the time dependence of a reaction response (conversion, product yield, or selectivity) to various manipulations used in traditional tests rather than the suppression or retention of catalytic activity (positive or negative test results) is of crucial importance. With the use of the Heck reaction as an example, it is demonstrated that the results of these modified and traditional tests can lead to opposing conclusions. In this case, the results of the modified tests are consistent with each other and with the results of studies on the kinetics and selectivity of the reaction, as well as with a great body of other experimental data published in the past five to seven years, which are indicative of the true homogeneous character of the Heck reaction.

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INTRODUCTION

The reaction of alkene arylation by aryl halides, which was discovered in 1971–1972 by Heck and Nolley [1] and Mizoroki et al. [2], is currently one of the most intensively studied catalytic processes (see reviews [3–9]):



where X = I or Br.

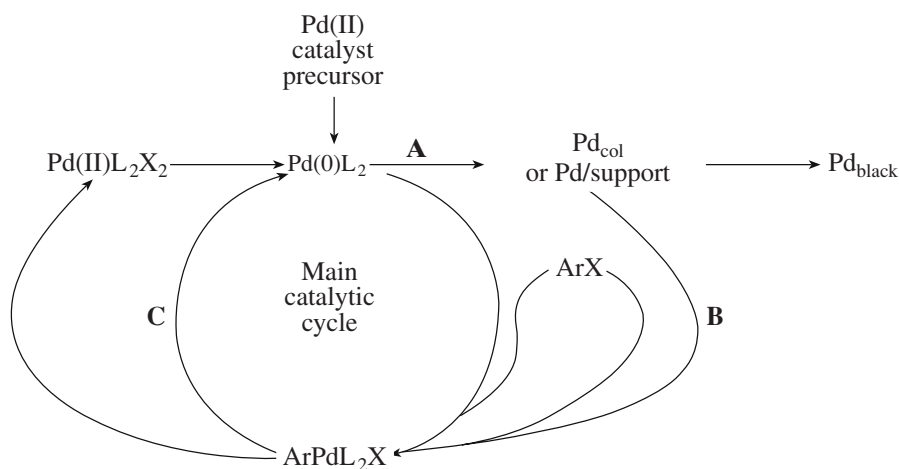
The nature of catalysis in this reaction has been actively discussed in the literature [5–13]. Since 1996 [14], data have been obtained to provide support for homogeneous catalysis in this reaction [13, 15–23]. However, there is also an opposite point of view, which assumes the occurrence of the Heck reaction as a heterogeneous catalytic reaction on palladium metal (colloidal and/or supported). This hypothesis is based on the positive results of a number of standard catalytic reaction tests for heterogeneity (Widegren and Finke [24] gave a survey of these tests).

However, the traditional interpretation of standard tests is quite ambiguous because of the specific transformations of palladium outside the main catalytic cycle of the reaction. The results of long-term studies published in 2006 [8, 9, 25] suggest that heterogeneous and colloidal palladium is a catalytically inactive catalyst species in the Heck reaction, and the agglomeration and dissolution of palladium in the course of the catalytic reaction should be considered as catalyst deactivation and regeneration processes, respectively (an analogous point of view has also been published [13, 14, 26–30]). The mechanistic schemes proposed [8, 9, 25]

(Scheme 1 is analogous to that presented in our review [9]) contain the same catalyst species in the course of the Heck reaction (the molecular complexes of Pd(0) and Pd(II) in solution and the colloidal and heterogeneous forms of palladium metal). All of the authors believed that these catalyst species continuously converted into one another to provide a classical example of kinetically coupled (including cyclic) reaction paths.

A number of tests [7, 24] are based on the principle of catalyst poisoning. In this case, the search for an appropriate reagent capable of selectively suppressing the activity of a homogeneous, heterogeneous, or colloidal catalyst has been mainly discussed [10]. However, in our opinion, the search for a selectively acting reagent is less important than the problems of interpreting the results of this testing. A positive result of this test for reactions in which homogeneous, colloidal, and heterogeneous catalyst species are continuously converted into each other can only provide support for the occurrence of interconversion processes involving various catalyst species; however, it cannot answer the question concerning the contributions of these species to the conversion of a substrate.

The absence of catalytic activity from a filtrate obtained after terminating the reaction and separating the solid catalyst phase (the catalytic activity of the filtered-off solid phase was also occasionally tested [31]) is another argument frequently used by the advocates of the hypothesis of heterogeneous catalysis in the Heck reaction. It was found that only a portion of palladium loaded in a reactor rather than the entire palladium, which can almost completely return to the support surface at the end of the reaction, passed into solution [14, 15, 18, 20, 22, 23]. Therefore, the results of a test with



Scheme.

the filtration of the reaction mixture depend on the rates of dissolution and subsequent return of palladium to the surface (or agglomeration), as well as on the possible sensitivity of these processes to various operations (cooling, heating, filtration, and filtration time) and on the degree of conversion at which the catalytic reaction was terminated.

Thus, the positive results of the standard tests of the Heck reaction for heterogeneity, which were interpreted previously as evidence for heterogeneous catalysis in the Heck reaction, are really consistent with the mechanism shown in Scheme 1 [9]. The same conclusion has also been drawn based on other reaction schemes of catalyst conversion [7, 8, 25]. Note that the problems of testing the Heck reaction have been critically analyzed in most detail by Phan et al. [7] and Richardson and Jones [10].

Here, we report the results of tests for homogeneity–heterogeneity modified with consideration for the specific features of the Heck reaction. These tests use the filtration of a reaction mixture (split test), the addition of mercury metal (Hg(0) test), and the results of a comparative study of reaction selectivity with the use of homogeneous and heterogeneous catalyst precursors.

EXPERIMENTAL

The reactions were performed in *N,N*-dimethylformamide (DMF) solutions in a thermostated reaction vessel with a magnetic stirrer under aerobic conditions. Samples, taken at regular intervals, were analyzed on an HP 4890 gas–liquid chromatograph with a flame ionization detector and an HP 5 capillary column (Hewlett-Packard) 15 m in length (naphthalene was an internal standard) under conditions of programmed heating from 100 to 250°C. The rates of reactions were determined by the graphical differentiation of steady-state portions of kinetic straight lines. The solvents and

reagents were purified in accordance with standard procedures.

Test with the filtration of the reaction mixture.

The phenylation reaction of styrene with iodobenzene was performed at 80°C in a reactor shown in Fig. 1. In the first reactor, iodobenzene (10 mmol), styrene (10 mmol), tributylamine (13 mmol), and naphthalene (2 mmol) were dissolved in 10 ml of DMF and 4% Pd/C (0.16 mmol of palladium; fraction of 0.20–0.25 mm) was added. After 17-min reaction, the setup was turned upside-down and the reaction solution was filtered through glass filter No. 2 (pore size of 40–50 μm) using a low vacuum in the bottom reactor and an excess pressure of argon in the top reactor. After the filtration, the reaction was continued in the second reactor.

Hg(0) test. Styrene (5 mmol), iodobenzene or bromobenzene (30 mmol), HCOONa (0.98 mmol), NaOAc (5.6 mmol), naphthalene (2 mmol), and PdCl₂ (0.05 mmol) or a corresponding amount of 4% Pd/C were mixed in 5 ml of DMF. The reaction was performed at 140°C; 300 equiv of mercury on a palladium basis was added immediately before the onset of the reaction.

Study of the selectivity of competing reactions. To perform competitive arylation, two aryl iodides (10 mmol of each), styrene (10 mmol), HCOONa (1.8 mmol), NaOAc (11.2 mmol), naphthalene (2 mmol), and PdCl₂ (0.16 mmol) or a corresponding amount of 4% Pd/C were mixed in 10 ml of DMF. The reaction was performed at 140°C.

RESULTS AND DISCUSSION

The procedure proposed is based on the measurement of the time dependence of a reaction response (conversion, product yield, or selectivity) to various methods of the removal of a particular catalyst species from the reaction sphere (for example, filtration or the addition of poisoning compounds). Moreover, a classi-

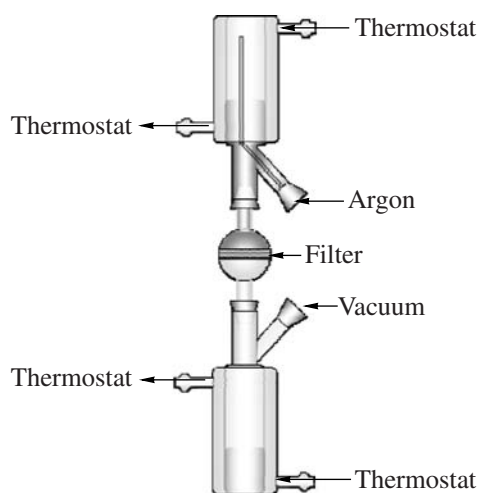


Fig. 1. System for rapid separation of the solid phase of a heterogeneous catalyst in the course of a catalytic process.

cal test that allows one to judge the constant nature of catalytically active complexes (or active sites on the surface) was not applied previously to the Heck reaction. The case in point is a comparative study of the selectivity of competing reactions with several substrates in the presence of homogeneous and heterogeneous catalyst precursors.

Modified Test with the Filtration of a Reaction Mixture

In the filtration of a reaction mixture, it is technically difficult to perform the continuous measurement of catalytic activity without terminating the reaction, and special equipment should be used for this purpose [11]. However, rapid filtration with the retention of the other reaction conditions would minimize the possible effect of a relationship between the rates of dissolution, agglomeration, and/or deposition of palladium onto the support surface on the result of the test. For this testing, the reaction of styrene with iodobenzene was performed under mild conditions (80°C). In this case, the rate of arylation was not very high in the presence of Pd/C as a heterogeneous catalyst precursor, and this rate cannot be related to palladium traces in solution. The filtration time was considerably shortened (~1 min) because of the use of excess pressure (argon) in the first reactor and a low vacuum in the second reactor (Fig. 1). In this case, the total reaction time in a control experiment without filtration was longer than 2 h. This testing procedure is fundamentally different from well-known published analogs, when the reaction was simply terminated after an uncertain time or the palladium content of the liquid phase was determined after completion of the reaction [18, 29, 32–35].

As follows from Fig. 2, the catalytic activity remained almost unchanged for 15 min after filtration. Thereafter, the rate of reaction decreased and palladium black appeared in the solution. Thus, even with the retention of the reaction temperature and the concentra-

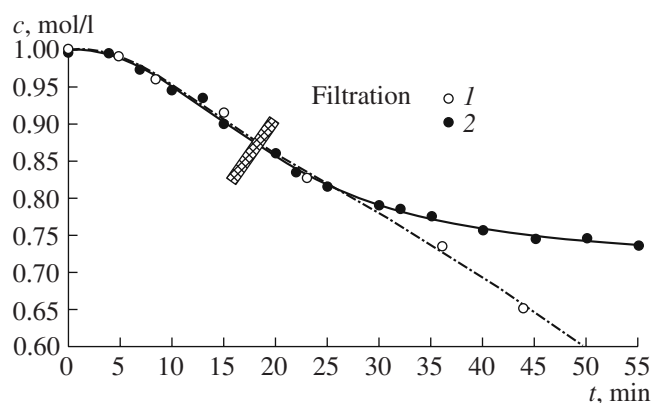


Fig. 2. Changes in the concentration of styrene in the course of the reaction with iodobenzene in the presence of Pd/C as a catalyst precursor: (1) ordinary experiment and (2) experiment with the filtration of the reaction mixture 17 min after the onset of reaction.

tions of reaction mixture components, if the filtration time were longer than 15 min, this test would lead to an erroneous conclusion on the absence of an active catalyst from the solution. The delayed determination of palladium in the liquid phase would also give incorrect results.

In the control experiment (without filtration), the steady-state catalytic activity (Fig. 2, dashed line) was retained until the almost complete consumption of the substrate. Consequently, the shape of kinetic curves with a clearly pronounced self-acceleration period at the beginning of the reaction and an extended portion of stable catalytic activity without filtration or a dramatic decrease in the activity 15 min after filtration can be explained by the dissolution of palladium from the catalyst surface (Scheme 1, B) and its steady-state distribution between liquid and solid phases. This explanation, which was proposed previously by Shmidt et al. [14, 36], is fully consistent with Scheme 1 with the use of palladium metal as a catalyst precursor. The violation of a steady-state distribution of palladium as a result of the removal of the solid phase (Fig. 2) leads to an additional transfer of a portion of Pd in the solution → solid phase direction and to a decrease in the reaction rate. The formation of palladium black in the course of the Heck reaction can be an autocatalytic process [9, 37]; this fact is responsible for the relative kinetic stability of dissolved palladium for 15 min.

Thus, the results of the above test allowed us to exclude a heterogeneous palladium species from those responsible for catalysis. However, it is clear that this test does not allow us to distinguish between the cases of catalysis by homogeneous and colloidal palladium species. A modified mercury test can give the answer to this question.

Effect of the addition of mercury on the Heck reaction

Entry	ArX	Catalyst	Additive	Turnover number, (mol product)/(g-atom Pd)	Contribution from the main catalytic cycle*, %	Contribution of the second catalytic cycle*, %
1	PhB	Pd/C	—	100	—**	—**
2	PhB	Pd/C	Hg	0	0	0
3	PhI	Pd/C	—	100	—**	—**
4	PhI	Pd/C	Hg	0	0	0
5	PhB	PdCl ₂	—	100	97.8	2.2
6	PhB	PdCl ₂	Hg	45	100	0
7	PhI	PdCl ₂	—	100	83.3	16.7
8	PhI	PdCl ₂	Hg	5	100	0

*The contribution of the second catalytic cycle was taken equal to 100% in the experiments with the addition of Hg(0). In control experiments, the contributions of individual cycles were calculated based on this assumption (see comments in the text).

**The contributions of catalytic cycles cannot be determined because substrate conversion was entirely absent in the Pd/C + Hg(0) system.

Modified Hg(0) Test

An analysis of the coupled reaction mechanism of the Heck reaction (Scheme 1) allowed us to reach the formal conclusion that the dissolution of palladium metal under the action of an aryl halide with the formation of an intermediate (ArPdL₂X) in the main catalytic cycle resulted in the transformation of the sequence of steps **A**, **B**, and **C** into an additional catalytic cycle of the Heck reaction (henceforth, the second catalytic cycle). The ratio between the rates of agglomeration and dissolution (Scheme 1, **A** and **B**), which form a part of the second cycle, can have a determining effect on the amount of palladium in the main catalytic cycle. With consideration for this fact, it is of importance to determine the relative contributions of the two competing catalytic cycles to the overall substrate conversion.

In principle, the Hg(0) test is suitable for this purpose. If mercury is able to irreversibly block colloidal palladium and/or supported palladium metal formed in the course of catalysis, the second catalytic cycle ceases to operate. Nevertheless, in accordance with Scheme 1, the reaction will occur for a time after the introduction of a poison because of the retention of palladium in the main catalytic cycle. As a first approximation, the catalyst turnover number reached in the reaction before the complete suppression of catalytic activity in the presence of mercury additives can be related to the maximally possible turnover number of the catalyst in the main catalytic cycle before the removal of the catalyst from the cycle because of agglomeration. In this case, the ratio between the contributions of the two catalytic cycles to substrate conversion can be evaluated. As in the case of filtration, the fundamental difference between this and traditional reaction testing is that the duration and stability of catalyst operation rather than the fact of retaining or suppressing catalytic activity after the introduction of a catalyst poison becomes of crucial importance. It is desirable that the tested reactions should occur at comparable rates. Then, it is

believed that the ratio between the rates of reaction and catalyst deactivation remained approximately constant. In this case, it is assumed that mercury has no effect on other reaction intermediates; unfortunately, this effect cannot be completely excluded [24].

In all of the experiments (see the table), the substrate/palladium ratio was 100 : 1; that is, the maximally possible catalyst turnover number was 100. In control experiments with iodobenzene and bromobenzene (without the addition of Hg(0)), the use of PdCl₂ and Pd/C as catalyst precursors allowed us to reach the complete conversion of the substrate (table, experiments 1, 3, 5, 7). In this case, the rates of reactions with both of the aryl halides were comparable. In the presence of 300 equiv of Hg(0), the catalyst turnover numbers significantly decreased in the case of PdCl₂ (experiments 6, 8) or were equal to zero with the use of Pd/C (experiments 2, 4). This is consistent with published data [38–42], which were interpreted to demonstrate the occurrence of the reaction on the surface of dissolved nanosized palladium or supported palladium. However, as noted above, this behavior of catalytic systems is consistent with Scheme 1, which is based on the concepts of a homogeneous character of the main catalytic cycle.

With the use of Pd/C as a catalyst precursor in the reaction, in fact, palladium dissolution as a part of the second catalytic cycle plays the role of formation of a catalyst that participates in the main catalytic cycle. If the second catalytic cycle does not operate in the presence of Hg(0), the complete absence of conversion from reactions with Pd/C upon the addition of mercury is expected (table, experiments 2, 4). At the same time, with the use of homogeneous precursors, palladium dissolution plays the role of catalyst regeneration rather than formation with respect to the main catalytic cycle. Thus, palladium can participate in the main (homogeneous) catalytic reaction cycle. This is supported by an increase in the catalyst turnover number with the use of

PdCl_2 (experiments 6, 8) in the presence of mercury, as compared with analogous experiments with Pd/C (experiments 2, 4). If the catalyst turnover number due to the main catalytic cycle in a reaction with bromobenzene in the presence of mercury is 5 (experiment 8), in terms of approximations made, each turnover in the second cycle can potentially induce five turnovers of the main catalytic cycle (a ratio of 1 : 5) in the absence of $\text{Hg}(0)$ (experiment 7). Thus, in the control experiment (experiment 7), one molecule (or 16.7%) of each six product molecules formed appears because of the operation of the second catalytic cycle, whereas five molecules (or 83.3%) result from the main catalytic cycle. In a reaction with iodobenzene in the presence of mercury (experiment 6), 45 catalyst turnovers were observed (a ratio of 1 : 45), which corresponds to 2.2% of the second and 97.8% of the main catalytic cycles of the reaction. Note that, although the turnover number and, consequently, the yield of the product (5% on a styrene basis) considerably decreased on the addition of mercury in an experiment with bromobenzene (experiment 8), the fraction of the product formed in the main catalytic cycle in the control experiment (experiment 7) was found to be sufficiently high (~83%). However, the above results are also clearly indicative of a strong effect of palladium aggregation–dissolution processes on catalytic activity even in the case of iodobenzene, which is more reactive. For iodobenzene, it is usually believed that aggregation has a negligible effect on the kinetics of the process. The use of iodobenzene will facilitate successful competition of the main catalytic cycle with the agglomeration of palladium. This is also consistent with our estimations of the contribution of the main catalytic cycle, which was higher than 97% in a reaction with iodobenzene (experiment 5). However, in this case, a considerable decrease in the yields of products was observed (from 100 to 45%) on the suppression of the second catalytic cycle by mercury (experiments 5, 6).

Comparative Selectivity Study

A study of the selectivity of a catalytic process cannot answer the question concerning the nature of catalytically active compounds. However, it allows us to determine whether the nature of compounds responsible for catalysis remains unchanged with the use of various catalyst precursors in the reaction. In particular, this approach can be used in a comparative study of homogeneous and heterogeneous catalyst precursors. It is very unlikely that the reaction selectivity is the same when the reaction occurs on the surface of palladium metal or under the action of molecular complexes in solution. Djakovitch et al. [21] studied the selectivity of several homogeneous and heterogeneous catalysts, which were used in reactions with the same substrate. The result of this test can be even more significant with the use of a few substrates rather than a single substrate under competitive reaction conditions. In the case of

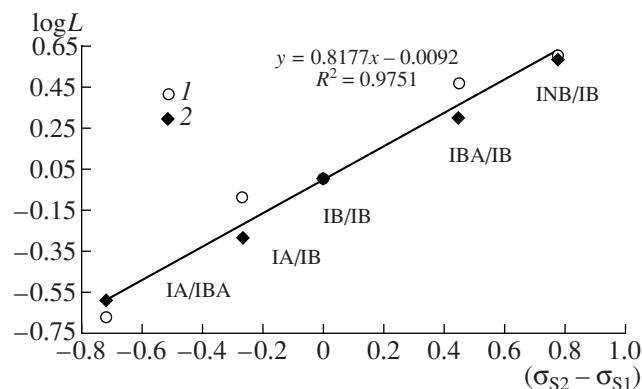


Fig. 3. Hammett plot for the reaction of styrene with various pair combinations of $\text{C}_6\text{H}_5\text{I}$ (IB), 4-(HOOC)- $\text{C}_6\text{H}_4\text{-I}$ (IBA), 4-(CH_3O)- $\text{C}_6\text{H}_4\text{-I}$ (IA), and 4-(O_2N)- $\text{C}_6\text{H}_4\text{-I}$ (INB) in the presence of (1) homogeneous PdCl_2 and (2) heterogeneous Pd/C .

the Heck reaction, this can be a set of aryl halides with different substituents at the *para* position of the benzene ring; this allows one to apply a Hammett equation formalism to the results of this study. Studies of this kind with the use of the Hammett equation have been performed for the Heck reaction only to compare various homogeneous catalyst precursors [43, 44].

Figure 3 shows the Hammett plot for the competing reactions of styrene with various aryl iodide pair combinations in the presence of homogeneous PdCl_2 and heterogeneous Pd/C . The experimental results are adequately described by a linear equation. This means that the selectivity of the competing Heck reaction remained unchanged on going from a homogeneous catalyst to a heterogeneous one. Moreover, selectivity changes were the same on varying substituents in aryl iodide for both catalyst types. On this basis, we can unambiguously conclude that the nature of catalytically active compounds that participate in catalytic cycle steps responsible for reaction selectivity was the same.

Taking into account the above test results, previously obtained data on palladium dissolution from the surface of heterogeneous and colloidal catalysis in the course of the Heck reaction, and the correlation of catalytic activity with the concentration of palladium in solution [7–9, 11–20], we can state that homogeneous catalysis in the Heck reaction is much more probable than heterogeneous catalysis.

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