Simple Kinetic Method for Distinguishing between Homogeneous and Heterogeneous Mechanisms of Catalysis, Illustrated by the Example of "Ligand-Free" Suzuki and Heck Reactions of Aryl Iodides and Aryl Bromides

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Abstract—Using a simple method based on an analysis of the phase trajectories of competing reactions of several substrates, it has been established that the selectivity of catalytically active species in the Suzuki reaction of aryl bromides depends on the nature of the catalyst precursor. This indicates that there is a considerable contribution from heterogeneous catalysis. At the same time, in the reaction involving aryl iodides, when the catalyst concentration in the solution is much higher, the selectivity of the catalyst is precursor-independent, suggesting that homogeneous catalysis is dominant. In the Heck reaction of both aryl bromides and aryl iodides, pure homogeneous catalysis takes place.

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Among the numerous coupling reactions of aryl halides with various compounds (alkenes, alkynes, amines, organometallics), the Heck and Suzuki reactions ((I) and (II), respectively) are of greatest importance and are the focus of researchers' attention [1, 2]:

R = H, COMe, Me; Hal = Br, I

The nature of catalysis in the Heck reaction has been keenly discussed in the literature since the late 1990s. The authors of some reviews [3-6] have arrived at the conclusion that homogeneous catalysis in this reaction is more likely, irrespective of the nature of the catalyst precursor generating active species. All authors believe that the same catalytic species are involved in the reaction, namely, dissolved molecular complexes of Pd(0) and Pd(II), colloidal palladium

particles in solution and/or on the supports surface, and larger particles of palladium metal. The heterogeneous palladium species are only sources of catalytic, dissolved Pd(0) and Pd(II) complexes, the species that are directly involved in the catalytic cycle. It is believed that all active and inactive species generated by the catalyst precursor undergo interconversion during the catalytic reaction and the most important role in these conversions is played by the aryl halide (Scheme 1).



Palladium conversions outside the catalytic cycle of the Heck and Suzuki reactions

There is still no consensus to the nature of catalysis in the Suzuki reaction, unlike the Heck reaction. Some researchers hold to the hypothesis that the Suzuki reaction occurs via a homogeneous catalytic mechanism [7-16], while others believe that this reaction is heterogeneous catalytic and involves catalysis on the surface of palladium nanoparticles as well [17-24]. There is convincing evidence in favor of the homogeneous mechanism. For example, there are numerous proofs of palladium dissolution from insoluble catalyst precursors, including palladium nanoparticles [8, 9, 11, 14, 18, 25-27]. In addition, there is a correlation between catalytic activity and the amount of dissolved palladium [14, 25, 27]. The homogeneous character of catalysis in the Suzuki reaction is confirmed by the specific dependence of the turnover frequency (TOF) of the catalyst on its amount [7], by the effects of catalyst poisons [9], an by the changes in the particle size of the nanosized catalyst precursor during the reaction [15]. At the same time there is cogent evidence in favor of heterogeneous catalysis in the Suzuki reaction [24, 28]. This evidence was obtained using Operando spectroscopy.

The contradictoriness of the results obtained by different authors and of the conclusions following from these results, as well as the continuing discussion of the mechanism of the Heck reaction [3-6], demonstrates how difficult it is to ascertain whether homogeneous or heterogeneous catalysis takes place in coupling reactions, including the Suzuki reaction. In our opinion (see also [24, 28, 29]), this situation is mainly due to the continuous interconversion of species generated by the catalyst precursor. This circumstance is often disregarded in planning of experiments and in data interpretation. The existence of this interconversion makes the results of all conventional homogeneity/heterogeneity tests ambiguous (for a review of these tests, see [30]). This is mainly due to a "counterbalancing effect" occurring in the catalytic system (like Le Chatelier's principle in an equilibrium system): the system responds to removal of one of the

active species of the catalyst being tested (e.g., to withdrawal of the solid phase or introduction of a selective poison). The most complicated case in which both homogeneous and heterogeneous catalyses take place in the reaction also cannot be ruled out. This possibility for the Suzuki reaction was clearly formulated only in two reports [31, 32]. The relative contributions from homogeneous and heterogeneous catalyses to the overall substrate conversion may vary during the reaction, so test data interpretation may depend on many factors that are not usually controlled by researchers. In addition, when deducing, from experimental data, that catalysis is homogeneous in nature, researchers sometimes disregard the existence of "dissolved" palladium nanoparticles, on which the catalytic reaction can occur as well. The formation of nanoparticles in situ was observed not only when soluble precursors were used, but also in reactions involving common heterogeneous catalysts [29, 33, 34]. Thus, although there is extensive evidence in favor of the homogeneous catalytic mechanism of the Suzuki reaction, the possibility of this reaction proceeding simultaneously via the homogeneous and heterogeneous catalytic pathways cannot be unequivocally ruled out.

Our previous modified tests for homogeneity/heterogeneity led us to conclude that heterogeneous catalysis makes a large contribution to the Suzuki reaction of aryl bromides [29]. In this study, in order to verify this conclusion, we took another kinetic approach: we measured the ratio of the conversion rates of competing substrates in the Suzuki reaction and performed a comparative investigation of catalyst selectivities in the Suzuki reaction and in the wellunderstood Heck reaction.

EXPERIMENTAL

All experiments were carried out without using an inert atmosphere. The reaction mixture was sampled at intervals and was analyzed by GLC (HP-4890 chromatograph, flame-ionization detector, 15-m-long

HP-5 column, (5% phenyl)-methylpolysiloxane stationary phase, oven temperature of $100-250^{\circ}$ C). The bromobenzene conversion in the Suzuki reaction at different points in time was in good agreement with sum of the biphenyl and benzene yields, indicating that the contribution from side reactions such as the reductive homocoupling reaction of bromobenzene and the oxidative homocoupling of phenylboric acid is insignificant. In all runs, the product (ArH) yield in the side reaction of aryl halide reduction was 3-10%.

Catalyst Preparation

The Pd/C catalyst was prepared using $Pd(OAc)_2$, whose amount was set so that the catalyst contained 4 wt % palladium. The carbon support Sibunit (1 g, particle size of 0.2-0.25 mm) was placed in toluene (20 ml). Thereafter, Pd(OAc)₂ was added and the mixture was stirred for 30 min at 95°C. Next, formic acid (0.04 ml) was added and the mixture was stirred for another 20 min, until the solution became colorless. The resulting catalyst was collected on a filter, washed with acetone, and vacuum-dried. The Pd/Al₂O₃ and Pd/SiO₂ catalysts were prepared in a similar way, and Pd/MgO was obtained using $Pd(NO_3)_2$. In this case, an aqueous solution of NaOH (0.14 mol/l, 4 ml) was added to a suspension of MgO (3 g) in water (20 ml). The mixture was stirred for 10 min, and an aqueous solution of $Pd(NO_3)_2$ (0.028 mol/l, 40 ml) was then added at room temperature. After 20 min, the solution was centrifuged and decanted. The solid was washed five times with distilled water and acetone and was then vacuum-dried at 110°C for 3 h. The resulting catalyst was reduced with flowing hydrogen at 250°C.

Catalytic Tests

A glass reactor fitted with a rubber septum and a magnetic stirrer was charged with 4-bromoacetophenone and bromobenzene or, alternatively, 4-iodotoluene and iodobenzene (2.5 mmol of either reactant), a PdCl₂ or 4% Pd/support catalyst (0.08 mmol Pd), 5 mmol of PhB(OH)₂ (Suzuki reaction) or 5 mmol of styrene (Heck reaction), 1 mmol of naphthalene as the internal standard for GLC, 6.5 mmol of NaOAc as the base, and 5 ml of *N*,*N*-dimethylformamide. The reactions were conducted at 140°C under stirring. Each run was repeated three times to make sure that it is reproducible.

RESULTS AND DISCUSSION

When unequal differential selectivities are observed with different catalyst precursors, this is unambiguous evidence that these precursors generate different active species acting as true catalysts. This circumstance can be used to verify assumptions as to identical or different natures of catalytic species in reactions involving different catalyst precursors. For measuring differential selectivity in the Suzuki and Heck reactions, it is necessary to choose at least one pair of competing aryl halides with different substituents (Scheme 2).

Competing reactions used to estimate the selectivity of catalytic systems in the Suzuki and Heck reactions (the neutral nucleophile NuX in the Suzuki reaction is PhB(OH)₂, and that in the Heck reaction is styrene)



Note that a comparative study of catalytic activity rather than selectivity under "noncompetitive" conditions (when a series of experiments is performed for each aryl halide alone) may lead the researcher to wrong conclusions, because different catalyst precursors may generate different quantities of active species. Unlike catalytic activity, the ratio of the rates of competing reactions is independent of the quantity of active species [35] and is determined only by their nature. (If there only two such reactions, the ratio of their rates is an unambiguous measure of differential selectivity.)

The relative reactivity of two substrates is conventionally estimated using the simplest integral equation for competing reactions that are first-order with respect to the substrates [36, 37]. This equation does not take into account the conversions of the catalyst outside the catalytic cycle. Taking into consideration the kinetics of these conversions complicates the reaction rate equations and makes it impossible to derive integral equations for selectivity. At the same time, in order to obtain a qualitative estimate of the ratio of the rates of competing reactions and to see how this ratio varies during the process, one can use integral kinetic data on product accumulation. Variation of the rate ratio during the reaction can readily be detected by correlating the yield of the product of one competing reaction to the yield of the product of the other one at different points in time. The curves obtained in this way without any processing of primary experimental data are so-called phase trajectories of the reaction, since the coordinate system in which they are plotted involves no time axis. (If there are only two products, we have a phase surface.) The slope of the tangent to the phase trajectory at any of its points is the ratio of the product formation rates. The shape of the phase trajectory determined by the accumulation kinetics of the target products is a very specific and sensitive parameter depending on the nature of the catalytically active compounds.

Note that, even if the phase trajectories in a series of runs involving different catalyst precursors coincide totally, this is not ultimate evidence that the active species forming in situ in these runs are identical. The equality of the ratios of the rates of competing reactions may be due to the similarity of the rate constants of the interactions of the substrate with different active species. Another plausible explanation is that changing the catalyst precursor causes only insignificant changes in the proportions of catalytic species. Therefore, additional experimental data are required here for making better substantiated inferences. The noncoincidence of phase trajectories alone provides good reason to conclude that the species responsible for catalysis differ in their nature.

The competitive Suzuki reaction involving 4-bromoacetophenone and bromobenzene as the competing substrates and phenylboric acid as the common reactant was carried out in the presence of different insoluble catalyst precursors (Pd/C, Pd/MgO, Pd/SiO_2 , Pd/Al_2O_3) and a soluble one ($PdCl_2$). The plot of the 4-phenylacetophenone concentration versus the biphenyl concentration at different points in time in a competition run is a phase trajectory (Fig. 1). The noncoincidence of phase trajectories obtained with different catalysts is unambiguous evidence that the nature of the active species forming in the system depends on the catalyst precursor. It is a commonly accepted view that, in the "ligand-free" Suzuki and Heck reactions, molecular palladium complexes in the solution are represented by Pd(0) complexes ("naked Pd") [38] and Pd(II) σ -aryl complexes, which are likely stabilized by endogenic halide ions resulting from aryl halide conversion [4, 5, 39]. Therefore, the phase trajectories in the case of the reaction taking place only on dissolved palladium complexes should remain invariable, because the nature of the Pd(0) and Pd(II) complexes involved in the "homogeneous" catalytic cycle remain the same, irrespective of whether the catalyst precursor is soluble or insoluble in the reaction medium. This view is proved by the absolute coincidence of the phase trajectories for the Heck reaction in the presence of different catalysts (Fig. 2). As was mentioned above, the hypothesis that catalysis in this reaction is purely homogeneous is universally accepted. The fact that phase trajectories for the Suzuki reaction do not coincide with one another (Fig. 1) provides reason to revise the conclusion that catalytic species in this reaction differ in nature and



Fig. 1. Phase trajectories (4-phenylacetophenone yield versus biphenyl yield) for the Suzuki reaction of the competing substrates 4-bromoacetophenone and bromobenzene with phenylboric acid in the presence of different catalyst precursors: (*1*) Pd/C, (*2*) Pd/SiO₂, (*3*) Pd/MgO, (*4*) Pd/Al₂O₃, and (*5*) PdCl₂.



Fig. 2. Phase trajectories (4-acetylstilbene yield versus stilbene yield) for the Heck reaction of the competing substrates 4-bromoacetophenone and bromobenzene with styrene in the presence of different catalyst precursors: (1) Pd/SiO₂, (2) Pd/Al₂O₃, and (3) PdCl₂.

hypothesize that catalysis is purely heterogeneous. Heterogeneous catalysis is also possible with dissolved $PdCl_2$ as the precursor, since visually observable palladium black precipitates instantaneously when this precursor is used in reactions involving aryl bromides. However, a more careful analysis of experimental data taking into account the interconversions of palladium species (Scheme 1) unambiguously indicates a significant contribution from heterogeneous catalysis, it



Fig. 3. Phase trajectories (4-iodotolune conversion versus iodobenzene conversion) for the Suzuki reaction involving phenylboric acid and for the Heck reaction involving styrene in the presence of different catalyst precursors: (1) Pd/C (Suzuki reaction), (2) Pd/Al₂O₃ (Suzuki reaction), (3) PdCl₂ (Suzuki reaction), and (4) PdCl₂ (Heck reaction).

cannot be ruled out that the Suzuki reaction proceeds partially via a homogeneous catalytic mechanism.

The point is that the noncoincidence of phase trajectories can theoretically be due not only to different natures of the catalysts, but also to the difference between the catalytic contributions from few actives species differing in their selectivity toward the competing substrates. It is for the Suzuki and Heck reactions that palladium distribution between the homogeneous species (molecular complexes) and the heterogeneous species (palladium on the surface of a support and "dissolved" palladium nanoparticles) can depend on the nature of the catalyst precursor (Scheme 1). For example, the variation of the palladium dissolution rate from one support to another (Scheme 1, conversions d, e) has an effect on the proportions of palladium as molecular complexes, palladium as "dissolved" nanoparticles, and supported palladium, because, kinetically, palladium dissolution is connected with aggregation (Scheme 1, conversions b, c), oxidation (Scheme 1, conversion f), and palladium reduction (Scheme 1, conversion a). Thus, if all of the palladium species or some of them are catalytically active, palladium redistribution among them can affect the selectivity and, accordingly, the phase trajectory of the reaction (Fig. 1). Passing from insoluble catalyst precursors to soluble ones (e.g., PdCl₂) also changes palladium distribution owing to the mutual effects of the processes presented in Scheme 1. In particular, use of soluble precursors sharply increases the proportion of palladium in the form of soluble molecular complexes (at least at the early stages of the reaction). In turn, this exerts an effect on the formation rate and subsequent aggregation of nanoparticles,

their size distribution [30], and, accordingly, their capacity to dissolve under the action of an aryl halide. However, it can be claimed with confidence that, as was noted above, the nature of the homogeneous active species accelerating the Heck and Suzuki reactions is precursor-independent.

Thus, the dependence of the phase trajectories of the Suzuki reaction on the nature of the catalyst precursor is evidence of a contribution made by heterogeneous catalysis, which can at least affect the observed ratio of the rates of the competing reactions. The operating heterogeneous catalyst in this case may be "dissolved" palladium particles of various sizes forming in the solution and palladium on the support surface.

In order to demonstrate the sensitivity of our approach to fine details of the mechanisms of complicated catalytic processes, we carried out similar experiments for the Heck reaction. In these experiments, phenylboric acid as a coupling partner was replaced with styrene (Scheme 2). The catalyst precursors included Pd/SiO₂ and PdCl₂, which differ most greatly in their selectivity in the Suzuki reaction, was used. The absolute coincidence of phase trajectories (Fig. 2) indicates that the ratio of the rates of the competing reactions is the sme at all stages of the process. Therefore, in the Heck reaction involving aryl bromides, different catalyst precursors yield the same type of catalytic species. As was mentioned above, the nature of dissolved palladium complexes should not depend on the precursor, so it can be concluded that only homogeneous catalysis takes place in this case, in full agreement with the universally accepted view.

The proportions of homogeneous and heterogeneous catalytic species in the Heck reaction depend significantly on the nature of aryl halide, because the latter is responsible for the oxidation and subsequent dissolution of palladium metal (Scheme 1, conversions d, e). In particular, on replacing any bromides with aryl iodides, which are more reactive compounds, no palladium black precipitate is visually observable in the Suzuki and Heck reactions occurring in the presence of a soluble catalyst precursor. Thus, use of arvl iodides should increase the contribution from the "homogeneous mechanism" to the overall substrate conversion in the Suzuki reaction. If this were the case, the dependence of the ratio of the rates of competing reactions on the nature of the catalyst precursor would weaken or disappear entirely. In order to verify this assumption, we conducted the Suzuki reaction involving 4-iodotoluene and iodobenzene as the competing substrates. The phase trajectories obtained for this reaction in the presence of different catalyst precursors coincide totally. Therefore, a single type of catalytic species contributing most greatly to catalysis forms in the Suzuki reaction of highly reactive aryl iodides, irrespective of what is the catalyst precursor. As in the case of the Heck reaction of aryl bromides, these species may be dissolved molecular complexes of palladium.

Note that, in the commonly accepted mechanisms of the Suzuki and Heck reactions, the selectivity of the catalyst toward the competing aryl halides is determined by the same reaction stage, specifically, aryl halide oxidative addition to the Pd(0) compound. Therefore, if a catalytic system shows different selectivities toward the same pair of aryl halides in the Suzuki and Heck reactions, this seems to be evidence that the catalysts involved in these reactions are of different natures. Since the Heck reaction is known to occur via a homogeneous catalytic mechanism, the difference between the rate ratios observed in Heck and Suzuki reactions proves the above assumption that heterogeneous catalysis makes a considerable contribution to the Suzuki reaction of aryl bromides. The phase trajectories of the Heck and Suzuki reactions involving the same catalyst precursor and the same pair of aryl bromides indeed do not coincide (Figs. 1, 2). Significant deviations were also observed for pairs of aryl halides of which at least one is a bromide (e.g., 4-bromoacetophenone-iodobenzene and bromobenzene and iodobenzene). Note, however, that the selectivity of the catalyst in the Heck and Suzuki reactions may be determined not only by the oxidative addition stage, but also by other stages of the catalytic cycle, which are quite different in these reactions. This situation is possible if the oxidative addition stage is essentially reversible. It cannot also be ruled out that the components specific to these two reactions (phenylboric acid in the Suzuki reactions and styrene in the check reaction) exert a direct effect on the nature of the forming catalytic species. For this reason, we carried out additional experiments in which we fixed a pair of competing aryl bromides and varied the nature and concentrations of the other components of the Heck and Suzuki reactions (base, alkene, and arylboric acid). The results of these experiments led us to the unambiguous conclusion that the phase trajectory is independent of these parameters for both reactions. Thus, the different selectivities of catalytic systems in these reactions can indeed be due to the different natures of the active species involved in oxidative addition to the competing aryl bromides.

In our opinion, the inference that the Heck and Suzuki reactions of aryl bromides are catalyzed by different active species, which is based on a direct comparison of the ratios of the rates of the competing reactions, is conclusively corroborated by experiments on aryl iodide pairs. It was demonstrated above that use of highly reactive aryl iodides in the Suzuki reaction leads to the domination of homogeneous catalysis. It was, therefore, expected that the Heck and Suzuki reactions involving competing aryl iodides would take place on the same type of homogeneous species and, if the oxidative addition stage indeed determines the selectivity of the catalyst, the phase trajectories of this reactions would be identical. The phase trajectories of the Heck and Suzuki reactions involving 4-iodotoluene and iodobenzene as the competing aryl halides

were actually found to coincide closely (Fig. 3), unlike those of the same reactions involving competing aryl bromides.

Thus, both of the conceptions discussed in the literature—purely homogeneous catalysis and purely heterogeneous catalysis in the Suzuki reaction—are not consistent with the observed dependence of the phase trajectories of competing reactions on the nature of the catalyst precursor. Most likely, the Suzuki reaction involving aryl bromides proceeds simultaneously via homogeneous catalytic and heterogeneous catalytic mechanisms. There is direct evidence that the contribution from heterogeneous catalysis is sufficiently large to affect at least the selectivity of the catalyst toward the competing substrates. At the same time, the reaction involving aryl iodides most likely occurs via pure homogeneous catalytic mechanism. Our results point to the incorrectness of the widespread view that catalysis in the Suzuki reaction of aryl bromides is purely homogeneous. This should be taken into account in development of new catalytic systems for the Suzuki reaction. In particular, as distinct from the Heck reaction, which cannot be effected over a heterogeneous catalyst, for Suzuki reactions can be found a truly heterogeneous catalyst systems.

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