

Supplementary materials

Suzuki reaction: mechanistic multiplicity versus exclusive homogeneous or exclusive heterogeneous catalysis

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Suzuki reaction time profile at 22°C

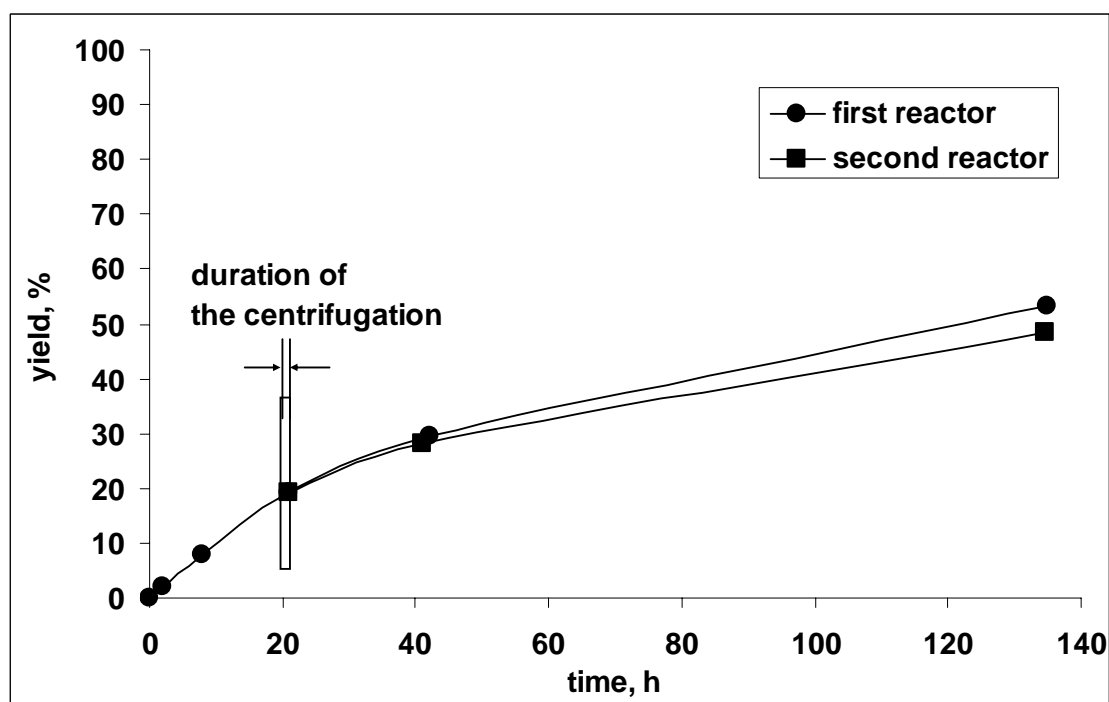


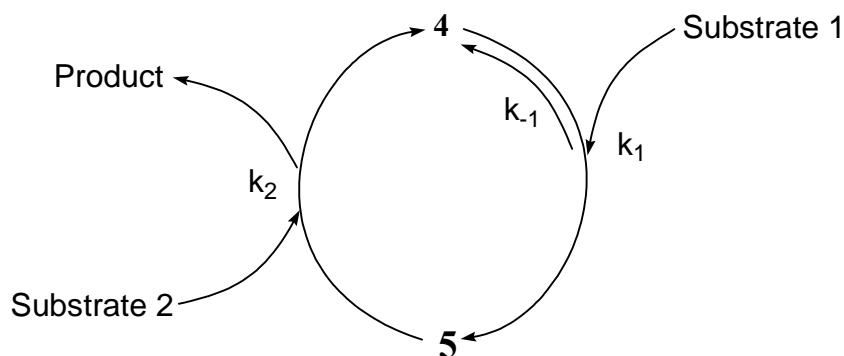
Figure S1. Suzuki reaction time profile at 22°C without (first reactor) and with (second reactor) centrifugation (the duration of centrifugation is indicated by the marked area). Reaction conditions: bromobenzene (5 mmol), PhB(OH)₂ (5 mmol), sodium acetate(6.5 mmol),

naphthalene (1 mmol) as internal standard, DMF-H₂O (5 mL) as solvent and 4%-Pd(0)/C (0.08mmol of Pd). Centrifugation was applied at 21 hours.

An influence of the substrate concentration on the selectivity estimation.

When two or more substrates are competing for common catalyst a ratio of the parallel reaction rates can be determined by the rates of stages irrespective of whatever these stages are rate-limiting (*R. W. Hoffmann, Aufklärung von Reaktionsmechanismen, Thieme, Stuttgart, 1976*). There are examples of such kinetic equations for two competitive substrates in the literature (*Shmidt A. F., et al. Kinetics and Catalysis, Vol. 42, No. 6, 2001, p. 800; Consorti C. S., et al. J. Am. Chem. Soc. 2005, 127, 12054; Schmidt A. F., et al. Kinetics and Catalysis, 2007, Vol. 48, No. 5, p. 716.*).

To illustrate a general character of approach suggested consider a deduction of kinetic equation for the catalytic system with three competing substrates. The reaction is supposed to require two reagents similar to the Suzuki reaction (aryl halide and arylboronic acid). Adopt a typical example of mechanism from D. Blackmond's review (*Angew. Chem. Int. Ed. 2005, 44, 4302*):

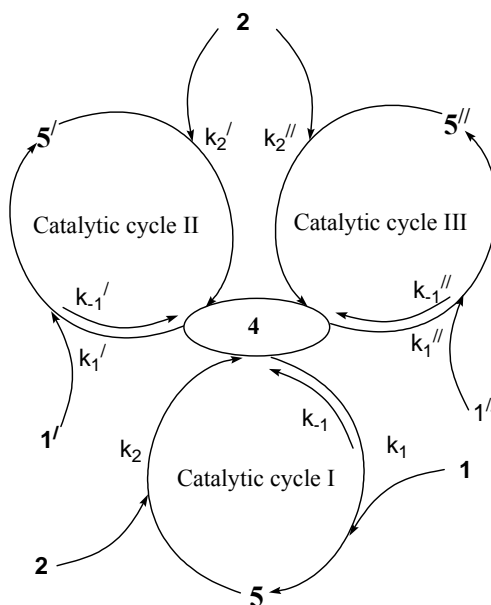


Using the steady-state approximation for the species **4** and **5**, the reaction rate equation can easily be found:

$$r = \frac{k_1 k_2 [1][2][Cat]_{\Sigma}}{k_{-1} + k_1[1] + k_2[2]}$$

where $[Cat]_{\Sigma} = [4] + [5]$ - catalyst total concentration

When three substrates **1**, **1'**, **1''** competing for common catalyst take part in the reaction there are three catalytic cycles of similar type:



In this case the kinetic equations of every competitive reaction become complicated:

$$r = \frac{k_1 k_2 [1][2][Cat]_{\Sigma} a' a''}{a a' a'' + k_1 [1] a' a'' + k_1' [1'] a a'' + k_1'' [1''] a a'}$$

$$r' = \frac{k_1' k_2' [1'][2][Cat]_{\Sigma} a a''}{a a' a'' + k_1 [1] a' a'' + k_1' [1'] a a'' + k_1'' [1''] a a'}$$

$$r'' = \frac{k_1'' k_2'' [1''][2][Cat]_{\Sigma} a a'}{a a' a'' + k_1 [1] a' a'' + k_1' [1'] a a'' + k_1'' [1''] a a'}$$

where $a = k_{-1} + k_2[2]$; $a' = k_{-1}' + k_2'[2]$; $a'' = k_{-1}'' + k_2''[2]$ and $[Cat]_{\Sigma} = [4] + [5] + [5'] + [5'']$ - catalyst total concentration.

Owing to the same denominators in the equations their ratios are simplified:

$$\frac{r'}{r} = \frac{k_1' k_2' [1'] a}{k_1 k_2 [1] a'} = \left(\frac{k_1' k_2'}{k_1 k_2} \right) \left(\frac{k_{-1} + k_2[2]}{k_{-1}' + k_2'[2]} \right) \frac{[1']}{[1]}$$

$$\frac{r''}{r} = \frac{k_1'' k_2'' [1''] a}{k_1 k_2 [1] a''} = \left(\frac{k_1'' k_2''}{k_1 k_2} \right) \left(\frac{k_{-1} + k_2[2]}{k_{-1}'' + k_2''[2]} \right) \frac{[1'']}{[1]}$$

These equations may be considered as the catalyst selectivity relative to chosen substrate **1**.

There are two limiting cases:

if $k_{-1} \gg k_2[2]$, $k_{-1}' \gg k_2'[2]$ and $k_{-1}'' \gg k_2''[2]$ then rate ratios are transformed as follows:

$$\frac{r'}{r} = \left(\frac{K_1' k_2'}{K_1 k_2} \right) \frac{[1']}{[1]} = Const'_{app} \frac{[1']}{[1]},$$

$$\frac{r''}{r} = \left(\frac{K_1'' k_2''}{K_1 k_2} \right) \frac{[1'']}{[1]} = Const''_{app} \frac{[1'']}{[1]},$$

where K_1 , K_1' и K_1'' – the equilibrium constants of the stages with participation of substrates **1**, **1'**, **1''**. Such a situation corresponds to the case of quasi-equilibrium of competitive stages.

if $k_{-1} \ll k_2[2]$, $k_{-1}' \ll k_2'[2]$ and $k_{-1}'' \ll k_2''[2]$ then ratios are described as follows:

$$\frac{r'}{r} = \left(\frac{k_1'}{k_1} \right) \frac{[1']}{[1]} = \text{Const}_{app}' \frac{[1']}{[1]};$$

$$\frac{r''}{r} = \left(\frac{k_1''}{k_1} \right) \frac{[1'']}{[1]} = \text{Const}_{app}'' \frac{[1'']}{[1]}$$

This situation is a case of the practically full irreversibility of the competitive stages.

Note in this work the selectivities were measured only for the first 20 min of the reaction until full conversion of the most active substrate was achieved. The conversion of the reagent **2** common for all competitive reactions (phenylboronic acid in Suzuki reaction) was less than 25%. Thus even when the Suzuki reaction kinetics do not correspond to two limiting cases the ratios $\left(\frac{k_{-1} + k_2[2]}{k_{-1}' + k_2'[2]} \right)$ and $\left(\frac{k_{-1} + k_2[2]}{k_{-1}'' + k_2''[2]} \right)$ should not essentially change. Therefore we may use values of Const_{app}' and Const_{app}'' to estimate the selectivity. For this purpose the reaction rates measured over certain period of time are necessary to divide into corresponding concentrations of the substrate:

$$\frac{r'}{r} \frac{[1]}{[1']} = \text{Const}_{app}'$$

$$\frac{r''}{r} \frac{[1]}{[1'']} = \text{Const}_{app}''$$

In the presented work the consumption rates of different aryl halides are estimated according to their conversion over certain period of time ($t_{n+1} - t_n$):

$$r_n^{\text{ArBr}} = \frac{(C_n^{\text{ArBr}} - C_{n+1}^{\text{ArBr}})}{(t_{n+1} - t_n)}$$

Hence ratio of the consumption rates of competitive substrates is as follows:

$$\frac{r_n^{\text{ArBr}}}{r_n^{\text{PhBr}}} = \left(\frac{(C_n^{\text{ArBr}} - C_{n+1}^{\text{ArBr}})}{(t_{n+1} - t_n)} \right) \bigg/ \left(\frac{(C_n^{\text{PhBr}} - C_{n+1}^{\text{PhBr}})}{(t_{n+1} - t_n)} \right) = \frac{(C_n^{\text{ArBr}} - C_{n+1}^{\text{ArBr}})}{(C_n^{\text{PhBr}} - C_{n+1}^{\text{PhBr}})}$$

And the selectivity constants (like Const_{app}' and Const_{app}'' in the example above) in the certain time instance are calculated in such a way:

$$S_n^{\text{ArBr}} = \frac{(C_n^{\text{ArBr}} - C_{n+1}^{\text{ArBr}})}{C_n^{\text{ArBr}}} \frac{C_n^{\text{PhBr}}}{(C_n^{\text{PhBr}} - C_{n+1}^{\text{PhBr}})}$$

p Parameters of the Suzuki reaction

In accordance with above the values of the selectivities in general case depend on both the rate constants of the stages with participation of **1**, **1'**, **1''** substrates (the first stages of catalytic cycles) and the rate of the stages with participation of reagent **2** (the second stages of catalytic cycles):

$$\frac{r'}{r} = \frac{k'_1 k'_2 [1'] a}{k_1 k_2 [1] a'} = \left(\frac{k'_1 k'_2}{k_1 k_2} \right) \left(\frac{k_{-1} + k_2 [2]}{k'_{-1} + k'_2 [2]} \right) \frac{[1']}{[1]}$$

$$\frac{r''}{r} = \frac{k''_1 k''_2 [1''] a}{k_1 k_2 [1] a''} = \left(\frac{k''_1 k''_2}{k_1 k_2} \right) \left(\frac{k_{-1} + k_2 [2]}{k''_{-1} + k''_2 [2]} \right) \frac{[1'']}{[1]}$$

when it is considered that **1**, **1'**, **1''** substrates represent three competitive aryl halides and reagent **2** is arylboronic acid (Suzuki reaction) or alkene (Heck reaction) the selectivity of the Suzuki and Heck reactions in general case should differ due to different k_2, k'_2, k''_2 values.

But the selectivities of the reactions do not depend on the nature of the reagent **2** at all in one of the limiting cases where the first stages of catalytic cycles (reactions of **1**, **1'**, **1''** with **4**) are practically irreversible:

$$\frac{r'}{r} = \left(\frac{k'_1}{k_1} \right) \frac{[1']}{[1]} = Const'_{app} \frac{[1']}{[1]};$$

$$\frac{r''}{r} = \left(\frac{k''_1}{k_1} \right) \frac{[1'']}{[1]} = Const''_{app} \frac{[1'']}{[1]}$$

Therefore when the nature of the catalysts **4** is the same and the first stages of the catalytic cycles are irreversible ($k_{-1} \pi \pi k_2 [2]$, $k'_{-1} \pi \pi k'_2 [2]$, $k''_{-1} \pi \pi k''_2 [2]$) the selectivities of both the Suzuki and Heck reactions are expected to be entirely the same.