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Approach to the determination of kinetic order of catalyst deactivation: observation of unusual kinetics in the Suzuki–Miyaura reaction

Elizaveta V. Larina, Anna A. Kurokhtina and Alexander F. Schmidt

Deduction of the yield equations in the cases of different orders of catalyst deactivation process

1. If catalytic reaction exhibits overall first-order kinetics and deactivation of active catalyst (transformation of *Pd* catalyst to less active $Pd^{/}$ catalyst) proceeds as the zero-order reaction, the behavior of the catalytic reaction is described by the system of equations (1):

$$\begin{cases} \dfrac{d[P]}{dt} = k_{cat}[Pd] + k'_{cat}[Pd'] \\ \dfrac{d[Pd]}{dt} = -k_{deact} \end{cases} \qquad (1)$$

The first equation of the system describes the rate of product formation as an operation result of two catalysts (*Pd* and $Pd^{/}$) with different activity (k_{cat} and $k^{/}_{cat}$) on assumption of pseudo-zero order kinetics in substrate. The second equation describes the rate of *Pd* catalyst transformation to less active $Pd^{/}$ catalyst. Assuming $[Pd]_0 = [Pd] + [Pd']$, where $[Pd]_0$ is concentration of loaded catalyst, integration of the second equation of the system (1) give the following equation:

$$[Pd] = [Pd]_0 - k_{deact}t \qquad (2)$$

So the rate of the product concentration increase is given by equation (3):

$$\frac{d[P]}{dt} = k_{cat}([Pd]_0 - k_{deact}t) + k'_{cat}([Pd]_0 - [Pd]_0 + k_{deact}t) \qquad (3)$$

Integral equation will be written as:

$$[P] = k_{cat}[Pd]_0 t + k_{deact}(k'_{cat} - k_{cat})t^2/2 \qquad (4)$$

Integral equation for product yield *vs*. time in this case is as follows:

$$\frac{[P]}{[S]_0} \times 100 = \left(\frac{k_{cat}[Pd]_0 t}{[S]_0} + \frac{k_{deact}(k'_{cat} - k_{cat})t^2}{2[S]_0} \right) \times 100 \qquad (5)$$

If the reaction mixture is diluted with the solvent (**1:α** dilution), product yield equation will be modified:

$$\frac{[P]}{[S]_0} \times 100 = \left(\frac{\alpha k_{cat}[Pd]_0 t}{\alpha [S]_0} + \frac{\alpha k_{deact}(k'_{cat} - k_{cat})t^2}{2[S]_0} \right) \times 100 \qquad (6)$$

After simplification this equation will be written as:

$$\frac{[P]}{[S]_0} \times 100 = \left(\frac{k_{cat}[Pd]_0 t}{[S]_0} + \frac{\alpha k_{deact}(k'_{cat} - k_{cat})t^2}{2[S]_0} \right) \times 100 \qquad (7)$$

It is obvious from (7) that in the case of zero-order kinetics of catalyst deactivation the product yield *vs*. time curves *should depend* on a dilution degree of reaction mixture.

2. If catalytic reaction and deactivation of active catalyst exhibit overall first-order kinetics the behavior of the catalytic reaction is described by the system of equations (8):

$$\begin{cases} \dfrac{d[P]}{dt} = k_{cat}[Pd] + k'_{cat}[Pd'] \\ \dfrac{d[Pd]}{dt} = -k_{deact}[Pd] \end{cases} \tag{8}$$

Assuming $[Pd]_0 = [Pd] + [Pd']$, integration of the second equation of the system (8) give the following equation:

$$[Pd] = [Pd]_0 e^{-k_{deact}t} \tag{9}$$

So the rate of the product concentration increase is given by equation (10):

$$\frac{d[P]}{dt} = k_{cat}[Pd]_0 e^{-k_{deact}t} + k'_{cat}\left([Pd]_0 - [Pd]_0 e^{-k_{deact}t}\right) \tag{10}$$

Integral equation will be written as:

$$[P] = [Pd]_0 \left(\frac{k_{cat}}{k_{deact}}(1 - e^{-k_{deact}t}) - \frac{k'_{cat}}{k_{deact}}(1 - e^{-k_{deact}t}) + k'_{cat}\, t \right) \tag{11}$$

Equation for product yield *vs*. time in this case is as follows:

$$\frac{[P]}{[S]_0} \times 100 = \frac{[Pd]_0}{[S]_0} \left(\frac{k_{cat}}{k_{deact}}(1 - e^{-k_{deact}t}) - \frac{k'_{cat}}{k_{deact}}(1 - e^{-k_{deact}t}) + k'_{cat}\, t \right) \times 100 \tag{12}$$

If the reaction mixture is diluted with the solvent (**1:α** dilution), product yield equation will be modified:

$$\frac{[P]}{[S]_0} \times 100 = \frac{\boldsymbol{\alpha}[Pd]_0}{\boldsymbol{\alpha}[S]_0} \left(\frac{k_{cat}}{k_{deact}}(1 - e^{-k_{deact}t}) - \frac{k'_{cat}}{k_{deact}}(1 - e^{-k_{deact}t}) + k'_{cat}\, t \right) \times 100 \tag{13}$$

After simplification this equation will be written as:

$$\frac{[P]}{[S]_0} \times 100 = \frac{[Pd]_0}{[S]_0} \left(\frac{k_{cat}}{k_{deact}}(1 - e^{-k_{deact}t}) - \frac{k'_{cat}}{k_{deact}}(1 - e^{-k_{deact}t}) + k'_{cat}\, t \right) \times 100 \tag{14}$$

It is obvious from (14) that in the case of first-order kinetics of catalyst deactivation process and catalytic reaction the product yield *vs*. time curves *should not depend* on a dilution degree of reaction mixture.

3. If catalytic reaction exhibit overall first-order kinetics and deactivation of active catalyst proceeds as the second-order reaction, the behavior of the catalytic reaction is described by the system of equations (15):

$$\begin{cases} \dfrac{d[P]}{dt} = k_{cat}[Pd] + k'_{cat}[Pd'] \\ \dfrac{d[Pd]}{dt} = -k_{deact}[Pd]^2 \end{cases} \tag{15}$$

Assuming $[Pd]_0 = [Pd] + [Pd']$, integration of the second equation of the system (15) give the following equation:

$$[Pd] = \frac{[Pd]_0}{1+[Pd]_0 k_{deact} t} \tag{16}$$

So the rate of the product concentration increase is given by equation (17):

$$\frac{d[P]}{dt} = \frac{k_{cat}[Pd]_0}{1+[Pd]_0 k_{deact} t} + k'_{cat}\left([Pd]_0 - \frac{[Pd]_0}{1+[Pd]_0 k_{deact} t}\right) \tag{17}$$

Integral equation will be written as:

$$[P] = [Pd]_0 k'_{cat} t + \frac{k_{cat} - k'_{cat}}{k_{deact}} \lg\left([Pd]_0 k_{deact} t + 1\right) \tag{18}$$

Equation for product yield *vs*. time in this case is as follows:

$$\frac{[P]}{[S]_0} \times 100 = \frac{[Pd]_0 k'_{cat} t + \frac{k_{cat} - k'_{cat}}{k_{deact}} \lg\left([Pd]_0 k_{deact} t + 1\right)}{[S]_0} \times 100 \tag{19}$$

If the reaction mixture is diluted with the solvent (**1:α** dilution), product yield equation will be modified:

$$\frac{[P]}{[S]_0} \times 100 = \frac{\boldsymbol{\alpha}\left(\frac{[Pd]_0 k'_{cat} t}{\boldsymbol{\alpha}} + \frac{k_{cat} - k'_{cat}}{k_{deact}} \lg\left(\frac{[Pd]_0 k_{deact} t}{\boldsymbol{\alpha}} + 1\right)\right)}{[S]_0} \times 100 \tag{20}$$

After simplification this equation will be written as:

$$\frac{[P]}{[S]_0} \times 100 = \frac{[Pd]_0 k'_{cat} t + \frac{\boldsymbol{\alpha}(k_{cat} - k'_{cat})}{k_{deact}} \lg\left(\frac{[Pd]_0 k_{deact} t}{\boldsymbol{\alpha}} + 1\right)}{[S]_0} \times 100 \tag{21}$$

It is obvious from (21) that in the case of second-order kinetics of catalyst deactivation process the product yield *vs*. time curves *should depend* on a dilution degree of reaction mixture.
Thereby the independence of kinetic curves of product yield *vs*. time on dilution degree of reaction mixture is possible *only* in the case of first-order kinetics of catalyst deactivation and catalytic reaction.

Application of the approach to the Suzuki–Miyaura reaction between iodobenzene and PhB(OH)$_2$ and Heck reaction between bromobenzene and styrene

The Suzuki–Miyaura reaction using PhI and PhB(OH)$_2$ (22) has been carried out at different dilution degrees of reaction mixture. A glass reactor fitted with a rubber septum and a magnetic stirrer was charged with iodobenzene (5 mmol), PhB(OH)$_2$ (5 mmol), and naphthalene (1 mmol) as the internal standard for gas chromatography (GC); NaOAc (6.5 mmol) was used as the base, and PdCl$_2$ (0.08 mmol Pd) was used as the catalyst precursor; an *N,N*-dimethylformamide-water mixture (4/1, 5 ml) was used as the reaction medium. The reactions were conducted at 140 °C under stirring (477.5 rpm). To obtain the set of experiments with different dilution degrees of reaction mixture the amount of all reagents (except the solvent) were decreased in 5 and 10 times. The reaction was monitored by taking small samples for GC. The samples were analyzed by GC (HP-4890, FID, HP-5 15 m column).

$$\mathrm{PhB(OH)_2} + \mathrm{PhI} \xrightarrow[\mathrm{NaOAc}]{[\mathrm{Pd}]_{cat}} \mathrm{Ph\text{-}Ph} \tag{22}$$

The obtained kinetic curves are presented in Figure S1.

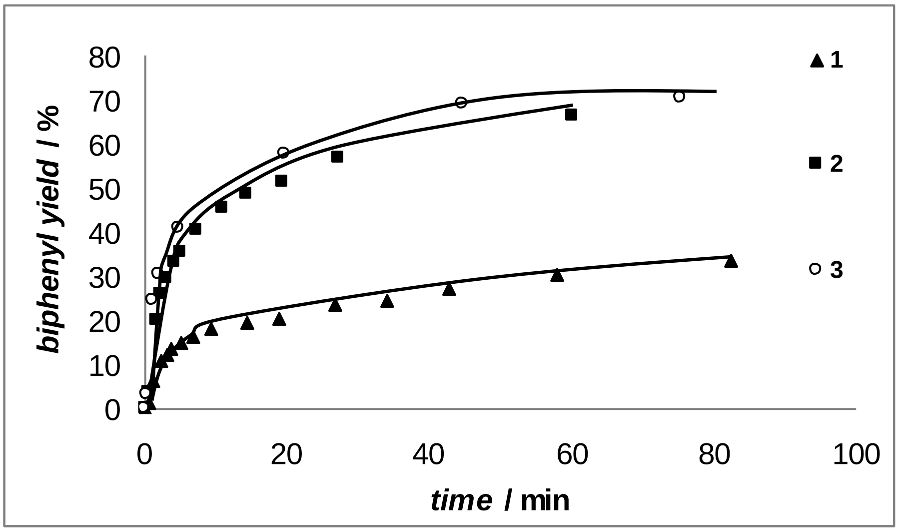
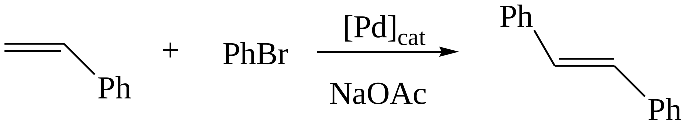


Figure S1 Biphenyl yield *vs*. time in Suzuki-Miyaura reaction with PhI at 140 °C at different degrees of reaction mixture dilution with the solvent: 1 – standard experiment (without dilution); 2 – 1:5 dilution; 3 – 1:10 dilution.

The Heck reaction using styrene and bromobenzene (23) has been carried out at different dilution degrees of reaction mixture. A glass reactor fitted with a rubber septum and a magnetic stirrer was charged with bromobenzene (5 mmol), styrene (5 mmol), 1 mmol of naphthalene as the internal standard for GC, 6.5 mmol of NaOAc as the base, $PdCl_2$ (0.08 mmol Pd), and 5 ml of *N*,*N*-dimethylformamide. The reactions were conducted at 140°C under stirring (477.5 rpm). To obtain the set of experiments with different dilution degrees of reaction mixture the amount of all reagents (except the solvent) were decreased in 10, 20 and 30 times. The reaction was monitored by taking small samples for GC. The samples were analyzed by GC (HP-4890, FID, HP-5 15 m column).



(23)

The obtained kinetic curves are presented in Figure S2.

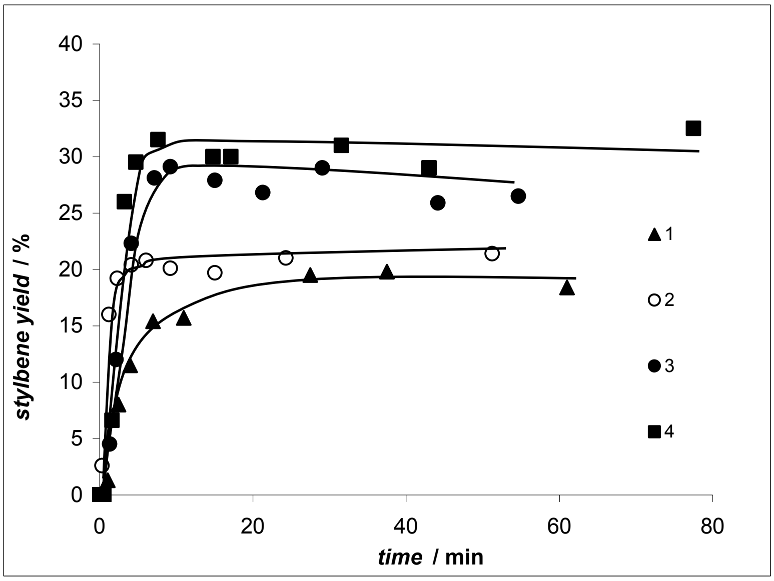


Figure S2 Stylbene yield *vs*. time in Heck reaction at 140 °C at different degrees of reaction mixture dilution with the solvent: 1 – standard experiment (without dilution); 2 – 1:10 dilution; 3 – 1:20 dilution; 4 – 1:30 dilution.