This file contains answers to selected questions from the book *Catalysis: Concepts and Green Applications*, ISBN 978-3-527-31824-7. Additional teaching material is available free of charge at *www.catalysisbook.org*

There has been quite a lot of feedback regarding the exercises and answers. Basically, colleagues express mixed feelings on the issue of placing the answers to exercises on the internet. After some discussion, I have decided to include answers to selected questions only. In some cases, I included also references to background material and further reading, where possible with links to free-access websites

Selected answers for Chapter 1

A1.1 Green chemistry principles relating to the Atom Economy and the E-factor:

- I Prevent waste instead of treating it.
- II Design atom-efficient synthetic methods.
- V Minimise the use of auxiliary reagents and solvents.
- VIII Avoid unnecessary derivatisation.
- IX Replace stoichiometric reagents with catalytic cycles.

Principles relating to the environmental quotient, Q:

- III Choose synthetic routes using non-toxic compounds where possible.
- IV Design new products that preserve functionality while reducing toxicity.
- VII Preferably use renewable raw materials.
- IX Replace stoichiometric reagents with catalytic cycles.
- X Design new products with biodegradable capabilities.
- XII Choose feedstocks and design processes that minimise the chance of accidents.

A1.2 Example 1:

$2C_6H_5I + Cu \rightarrow C_6H_5–C_6H_5 + CuI_2$ (100% yield)

Here no reactant is left over, since the conversion is 100%. Thus, for every mol of biphenyl product, we obtain one mol of CuI_2 waste. First, we calculate the number of moles in one kg of product:

$Mw_{biphenyl}$, or $C_{12}H_{10}$, = 154 gr/mol, so 1 kg biphenyl = 6.5 mol biphenyl. This means that every kg of biphenyl product will give us 6.5 mol of CuI_2, which is equivalent to 6.5 × 317.5 = 2063.75 gr CuI_2.

The overall E-factor is therefore: $E_{factor} = \frac{kg(waste)}{kg(product)} = \frac{2.064}{1.000} = 2.064$

Example 2:

$2C_6H_5Br + Cu \rightarrow C_6H_5–C_6H_5 + CuBr_2$ (85% yield)

Importantly, we see that this reaction does not give 100% conversion. Since the E-factor is simply the quotient kg_{waste}:$kg_{product}$, everything which is not "product" is defined as "waste".

Thus, even a reactant which is left over (as in this example, because of incomplete conversion) is "waste". In some cases, you can minimise this waste by feeding back your unused reactant into the reactor, but this is not always the case, since it is not always so easy to separate the reactants from the other byproducts (even assuming that you separate the product). Sometimes (often, in the case of pharmaceuticals and fine chemicals) the "waste reactant" is thrown away and a new reactant batch is used. An important point for the students' attention is that the E-factor uses *kg*, not *mol*. Chemistry students are sometimes so used to using moles, they forget that the real world uses kg, because also when you dispose of waste you pay for it by kg !!

Thus, for every two moles of C_6H_5Br and one mol of Cu, we obtain 0.85 moles of biphenyl and 0.85 moles of CuBr2. The overall reaction equation should be written as:

$2C_6H_5Br + Cu \rightarrow 0.85C_6H_5–C_6H_5 + 0.85CuBr_2 + 0.15C_6H_5Br + 0.15Cu$

Hopefully, we can recycle (part of) the surplus reagents. If not, we must count them as "waste". Thus, for every mol of biphenyl product, this reaction produces 1 mol of $CuBr_2$ + 0.18 mol of C_6H_5Br + 0.18 mol of Cu. Since $Mw_{biphenyl}$ = 154 gr/mol, every kg of biphenyl product will give us

6.5 mol $CuBr_2$ = 6.5 × (63.5+160) = 1452.75 gr $CuBr_2$,

1.17 mol C_6H_5Br = 1.17 × (72+5+80) = 183.69 gr C_6H_5Br

1.17 mol Cu = 1.17 × 63.5 = 74.29 gr Cu

Total: 1453 + 187 + 74 = 1714 gr waste.

The overall E-factor is therefore: $E_{factor} = \frac{kg(waste)}{kg(product)} = \frac{1.714}{1.000} = 1.714$

Note that this E-factor is lower than the one above, even though we "threw away" 15% of the reagents, because of the large difference in mass between iodine and bromine.

The corresponding Q-factors in both cases are medium.

(c) Calculating the catalyst TON and TOF. In this case, since the catalyst is a macroporous solid, 5 wt% Pd/C, we can calculate the number of moles of Pd present in 100 mg catalyst (note: we can also refer directly to the metal weight (see also the discussion in Chapter 4 on surface catalysis). 100 mg catalyst contains 5 mg Pd, and since Mw_{Pd} = 106.4 gr/mol, we obtain 0.005/106.4 = 0.046 mmol Pd. If we assume that the substrate amount is 1 mol, then after 40 minutes of reaction $TON = \frac{980 mmol}{0.046 mmol} = 21304$.

The corresponding TOF is simply 21304/40 min = 532 min^{-1}.

Note that the TON is always a pure number, while the TOF has units of $time^{-1}$.

Background material on the web on E-factors and atom economy: The Green chemistry network run by the Royal Society of Chemistry has an excellent website for education with many links to good examples, see

http://www.chemsoc.org/networks/gcn/educate.htm

A1.5 (a) See the example of the analogous life-cycle diagram for milk cartons in Figure 1.25, p 33.

(b) One fluorescent bulb consumes in its lifetime of 5000 h a total of 55 kWh. The same 5000 h of operation require 5 incandescent bulbs, which in turn consume a total of 375 kWh, so the difference in favour of the fluorescent bulbs is 320 kWh. The thermal energy content of coal is roughly 6.1 kWh/kg. However, although coal fired power generators are very efficient, the amount of electricity generated per kg of coal is only 2.4 kWh. Thus, the extra 320 kWh require an extra 133 kg of coal. A 20 ppm content of mercury corresponds to 20 mg mercury per kg coal, giving a total of 2660 mg mercury, of 2.66 gr mercury. Since a typical fluorescent bulb contains less than 5 mg of mercury, fluorescent bulbs are much better for the environment than incandescent ones.

Background material and further reading: There are several online articles on the "dim threat" of mercury in fluorescent light bulbs, see for example the following investigation that appeared on June 11, 2007, in *Popular Mechanics*:

http://www.popularmechanics.com/blogs/home_journal_news/4217864.html

A1.7 (For the definitions of TON and TOF, see p.11;)

When using *p*-chloro acetophenone, (R = Cl), 99% conversion was reached after 78 h, at a substrate:catalyst ratio of 50 000 : 1. This means that each catalyst molecule is active on average for 0.99 × 50 000, or 49 500 cycles. Thus:

TON = 49 500,

and TOF = 49 500/78 h = 635 h^{-1}.

Similarly:

for R = CH_3O, TON = 0.92 × 20 000 = 18 400, and TOF = 18 400 h^{-1}.

and for R = F, TON = 1 × 500 = 500, and TOF = 500 h^{-1}.

Note that in all these cases, the high conversions do not necessarily imply a high selectivity to the desired product.

Selected answers for Chapter 2

A2.3 (a) Looking at the data in Table 2.2 (p. 71), we see that regardless of the starting concentration, all of Michael's reactions have reached 50% conversions after 120 min (measurement 7 is a bad experiment and should be ignored). This points to a first-order reaction. Moreover, the reaction is independent of the concentration of methane (since liquid methane is the solvent, and the reaction volume is very large compared to the amount of substrate). The corresponding rate equation is therefore: $v = d[\mathbf{A}]/dt = k[\mathbf{A}]$.

(b) From Table 2.2, we know that $t_{1/2} = \ln 2/k = 120$ min. Solving for k we obtain: $k = \ln 2/t_{1/2} = \ln 2/120$ min = 0.0057 min^{-1}.

(c) Abdelhafid used much less methane, so it is not justified to say that the concentration of methane does not change. A likely rate second-order rate equation that fits the results of Abdelhafid is: $v = d[\mathbf{A}]/dt = k[\mathbf{A}][CH_4]$.

(d) The fact that Abdelhafid and Michael worked at different temperatures and using different concentrations of methane accounts for the differences in their results. Michael

used liquid methane as the solvent, transforming the second-order rate law into a pseudo-first-order one. This means that the concentration of methane was so high that for all practical purposes it did not change during the reaction.

(e) Both researchers would observe the deuterated lineatin as product. However, changes in the reaction rates would be observed if the use of the deuterated substrate would slow down one of the reaction steps so much so that it would become the new rate-determining step. The magnitude of this slowing down would depend on whether the C–D bond is broken in the rate-determining step or not. Such primary isotope effects are more likely in the case of Abdelhafid's experiments. Michael, on the other hand, may observe rate changes due to solvent isotope effects.

A2.4 This is a first-order reaction, for which $t_{1/2}$ = 20 min. Solving for k we obtain:

$k = \ln 2/t_{1/2} = \ln 2/20 \text{ min} = 0.0346 \text{ min}^{-1}$.

The dependence of the conversion on time for a first-order reaction is given by:

$-\ln(1 - \chi_A) = kt$

We then substitute $k = 0.0346 \text{ min}^{-1}$ and $\chi_A = 0.999$ (since we want the time at which the reaction will reach 99.9% conversion), and obtain:

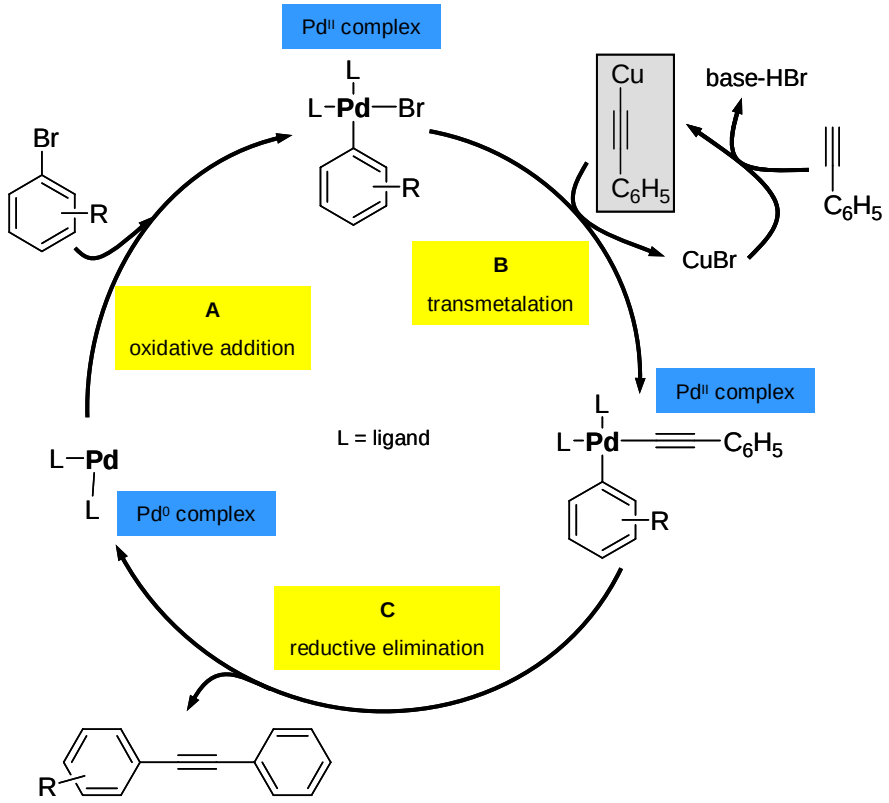
$-\ln(1 - 0.999) = 0.0346 \times t$

and therefore:

$t = -\ln(0.001)/0.0346 = 199.31 \text{ min} \sim 200 \text{ min}$, so (b) is the only correct answer.

Selected answers for Chapter 3

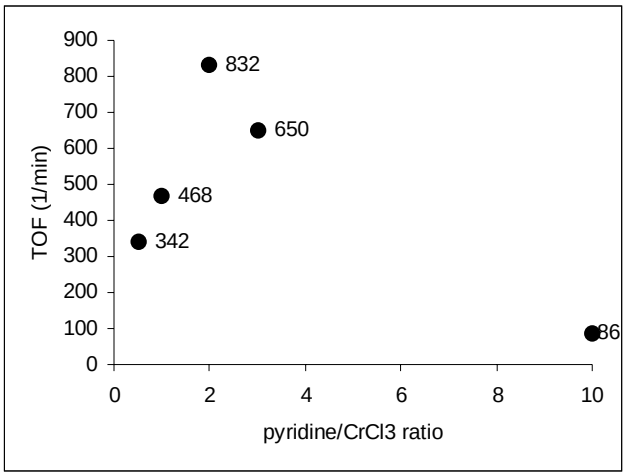
A3.2 (a,b) The figure below shows the completed catalytic cycle with the oxidation state of the Pd atom in the various catalytic intermediates.



(c) In general, changing the concentration and/or type of reagent or catalytic intermediate that participates in the rate-determining step will affect the reaction kinetics. Thus, to determine, for example, if the oxidative addition step is rate-determining, you can perform a series of reactions using different starting concentrations of aryl bromide and compare their reaction profiles. Additionally, you can compare the reaction profiles of aryl halides that differ only in their halide leaving group, such as {*p*-F-$C_6H_4CH_3$, *p*-Cl-$C_6H_4CH_3$, *p*-Br-$C_6H_4CH_3$, and *p*-I-$C_6H_4CH_3$}.

Background material on the web: Check out Rob Toreki's well presented organometallic hypertextbook, see
http://www.ilpi.com/organomet/

A3.4 (a) Looking at the graph below, we can see that there is a maximum of activity at a 2:1 pyridine:Cr ratio. This indicates the involvement of a complex containing one Cr atom and two pyridine molecules (ligands) in the rate-determining step.



(c) A possible mechanism involving free-radical intermediates is a chain reaction mechanism with carene-oxo and carene-peroxo radicals carrying the chain. Since the initiation step is largely independent of the organic residue of the hydroperoxide, and since *tert*-butyl and carene have similar physical properties (*e.g.,* their solubility in the reaction medium is probably very similar) we can expect that adding 1 mol% of *tert*-butyl hydroperoxide would give the same effect.

A3.6 Tolman's cone angle is the base angle of a cone that encompasses the ligand, with the metal centre in its apex and the ligating P atom (the cone angle is defined for Phosphorous ligands, but can be in principle adapted to other ligating atoms) at a distance of 2.28 angstroms from it. The ligand bulk radius is the distance between the metal atom and the bulkiest cross-section of the ligand. The ligand solid angle is the solid angle at this cross-section.

In general, the cone angle is a good descriptor for C_3-symmetric ligands, such as PPh_3 and $P(o\text{-tolyl})_3$, while the other two descriptors are useful in cases of asymmetric ligands and ones with a centre of mass far from the ligating atoms. The best approach, however, is to calculate all three parameters and then examine their correlation with the predicted and/or experimental catalyst performance. For more details, see the discussion on catalyst descriptors in Chapter 6, pp. 241–248.

Selected answers for Chapter 4

A4.1 (a) $(CH_3)_2CH{=}CH_2 + H_2O \xrightarrow{Nafion} (CH_3)_3COH$

(c) The excess of *tert*-butanol is added to enhance the solubility of isobutylene in the reaction medium. In this case, adding *n*-pentanol would have a similar effect, since the two alcohols have similar structures and solubility parameters.

A4.5 (a) This is a type IV isotherm, which corresponds to a mesoporous solid, so it cannot be **B**, **C**, **D**, or **G** (for a discussion of isotherm types, see pp. 146–148). Neither the enzyme **E** nor the polystyrene support **F** would survive the calcination (the enzyme would be denatured even earlier, as the reaction temperature is 130 ºC). Catalyst **A** (Pt on mesoporous silica) is the only correct answer.

(b) The surface area is the same before and after the 1st reaction (look at the first part of the isotherm). However, the pore volume is smaller, so something must be 'stuck' in the pores, for example oligomer/polymer molecules formed by side-reactions. Nothing drastic has happened to the catalyst (*i.e.* the pores have not collapsed) as it evidently regained its activity following the calcination.

(c) Looking just at the surface area would show no change, so it is a bad move to try and save money in this case.

Background material on the web on adsorption isotherms: Wikipedia has a rather good article that explains and gives examples of the isotherms of different materials. See

http://en.wikipedia.org/wiki/Adsorption