System-theoretical Investigation of Possible Oscillatory States in the Hydroformylation Process in an Open Isothermal System

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The kinetic model for the hydroformylation process as given in a previous paper (SEELIG1) is extended in as far as the concentrations of all three substrates (olefin, H2, CO) are allowed to move freely, whilst in the first investigation this was the case only for CO, the concentrations of olefin and H2 being kept constant. So the derived hysteresis loop of \([\text{CO}]\) vs influx of CO is shifted back and forth by the varying \([\text{olefin}]\) and \([\text{H}_2]\), causing oscillations for particular combinations of the parameters. These oscillations are due to the substrate inhibition by CO and are not the result of instabilities of some external control circuit; so they would occur even in a perfectly isothermal open system.

Introduction

In a previous paper1, the hydroformylation or oxosynthesis

\[
\text{R-CH=CH-R'} + \text{CO} + \text{H}_2 \rightarrow \text{R-CH}_2\text{CH-R'}^* \quad \text{HC=O}
\]

was investigated in terms of system theory and stability theory. The scheme that took account of the various transition forms of the catalyst, essentially derivatives of Co-tri- and tetracarbonyls, but which neglected the appearance of isomers, consisted basically of two different cycles, a “3-cycle” of the especially active tricarbonyls, and a “4-cycle” of the much slower tetracarbonyls. The main feature was the substrate inhibition caused by CO, which by means of \(\text{HCo(CO)}_3 + \text{CO} \rightleftharpoons \text{HCo(CO)}_4\) transferred major parts of the sum concentration of the catalyst from the quick 3-cycle to the slow 4-cycle. The concentration of CO was allowed to move freely, being fed by a constant influx and being emptied by the oxo-synthesis and an overflow. The concentrations of olefin and H2 were assumed to be kept constant as pools. It was shown that the stationary concentrations of CO for different values of the influx, j, but constant values of all other parameters, formed a hysteresis loop to that in a certain range of j there were 3 steady states, one of which was unstable. So in this range, the actual state of the system depended on the initial conditions and discontinuous jumps of the steady state concentrations were characteristic for the system.

One autocatalytic step in the slower 4-cycle,

![Fig. 1. Model of the hydroformylation reaction](image-url)

3-hydro = Co-hydrotetraabonyl, HCo(CO)_4,
4-hydro = Co-hydrotetraabonyl, HCo(CO)_4,
3-alkyl = Co-alkyl-tricarbonvl, RCH_2CHRCo(CO)_3,
4-alkyl = Co-alkyl-tetracarbonvl, RCH_2CHRCo(CO)_4,
3-acyl = Co-acyl-tricarbonvl, RCH_2CHRCOCO(CO)_3,
4-acyl = Co-acyl-tetracarbonvl, RCH_2CHRCo(CO)_4.
together with the incomplete substrate inhibition, diminished the hysteresis effect. Consequences for the industrial application of the oxo-synthesis were briefly discussed.

It was clear from the beginning that the assumption of olefin- and H₂-pools was somewhat unrealistic, and was introduced only as a simplification of the rather complicated reaction scheme. In technological reality, all substrates are fed into the reactor simultaneously and unreacted materials are removed in the stream and recycled later on.

**General Open System Model**

The procedure of analysis is completely analogous to that of the previous paper, so that we can proceed quickly without major explanations.

The reaction scheme with the mentioned alterations is given in Fig. 1. We get the following equations for the rates of production of the various substances:

\[
\frac{d[\text{olefin}]}{dt} = j_{01} - k_{01}[\text{olefin}] - k_5[\text{olefin}][3\text{-hydro}] - k_6[\text{olefin}][4\text{-hydro}]
\]

\[
\frac{d[H_2]}{dt} = j_{H2} - k_{H3}[H_2] - k_5[H_2][3\text{-acyl}] - k_7[H_2][4\text{-hydro}][4\text{-acyl}]
\]

\[
\frac{d[\text{CO}]}{dt} = j_{co} - k_{co}[\text{CO}] - k_4[\text{CO}][3\text{-alkyl}] - k_5[\text{CO}][3\text{-hydro}] + k_5[4\text{-hydro}] - k_6[\text{CO}][3\text{-acyl}]
\]

\[
\frac{d[3\text{-hydro}]}{dt} = k_2[H_2][3\text{-acyl}] - k_9[\text{olefin}][3\text{-hydro}] - k_9[\text{CO}][3\text{-hydro}] + k_5[4\text{-hydro}]
\]

\[
\frac{d[4\text{-hydro}]}{dt} = k_2[\text{CO}][3\text{-hydro}] - k_5[4\text{-hydro}] + k_7[H_2][4\text{-hydro}][4\text{-acyl}] - k_6[\text{olefin}][4\text{-hydro}]
\]

\[
\frac{d[3\text{-alkyl}]}{dt} = k_5[\text{olefin}][3\text{-hydro}] - k_4[\text{CO}][3\text{-alkyl}]
\]

\[
\frac{d[3\text{-acyl}]}{dt} = k_3[\text{catalyst}] - [3\text{-hydro}] - [4\text{-hydro}]
\]

\[
- [3\text{-alkyl}] - [3\text{-acyl}] - [4\text{-acyl}]
\]

\[
- k_5[H_2][3\text{-acyl}] - k_6[\text{CO}][3\text{-acyl}]
\]

\[
\frac{d[4\text{-acyl}]}{dt} = k_4[\text{CO}][3\text{-acyl}] - k_7[H_2][4\text{-hydro}][4\text{-acyl}]
\]

Again, the redundancy of [4-alkyl] has been removed by using the condition that the sum of concentrations of all Co-compounds add up to the parameter [catalyst]. The original system is thus made up of 8 variables plus time and 16 parameters, of which 12 are rate constants.

Again, we introduce dimensionless variables and parameters, which reduces the number of parameters only slightly (from 16 to 14), but allows for a grouping of them into fixed and adjustable. We define – in part slightly different from the previous paper –:

\[
\tau = k_1 t 
\]

\[
a = k_5[\text{olefin}]/k_1 
\]

\[
\beta = k_2[H_2]/k_1 
\]

\[
\gamma = k_4[\text{CO}]/k_1 
\]

\[
\xi_3 = [3\text{-hydro}]/[\text{catalyst}] 
\]

\[
\xi_4 = [4\text{-hydro}]/[\text{catalyst}] 
\]

\[
\eta_3 = [3\text{-alkyl}]/[\text{catalyst}] 
\]

\[
\eta_4 = [4\text{-alkyl}]/[\text{catalyst}] 
\]

\[
\zeta_3 = [3\text{-acyl}]/[\text{catalyst}] 
\]

\[
\zeta_4 = [4\text{-acyl}]/[\text{catalyst}] 
\]

for the variables and for the parameters:

\[
\varphi_1 = k_5[\text{catalyst}]/k_1 
\]

\[
\varphi_2 = k_4[\text{catalyst}]/k_1 
\]

\[
\varphi_3 = k_4[\text{catalyst}]/k_1 
\]

\[
\varphi_1 = j_{01}/(k_2[\text{catalyst}]) 
\]

\[
\varphi_2 = j_{H2}/(k_3[\text{catalyst}]) 
\]

\[
\varphi_3 = j_{co}/(k_4[\text{catalyst}]) 
\]

\[
\mu_1 = k_3[\text{catalyst}]/k_5 
\]

\[
\mu_2 = k_4[\text{catalyst}]/k_7 
\]

\[
\mu_3 = k_6[\text{catalyst}]/k_8 
\]

\[
\chi_1 = k_5/k_4 
\]
To give a comprehensive interpretation of the arbitrary transformations: \( \tau, \alpha, \beta, \gamma \) represent dimensionless time and substrate concentrations in such a way that we get rid of \( k_1 \) through \( k_4 \). \( \xi_3 \) through \( \xi_4 \) represent the relative amounts of catalytic species compared to the total concentration. \( q_1, q_2, q_3 \) are fixed rate factors typical for olefin, \( \text{H}_2 \) and \( \text{CO} \), which are immaterial if only steady states are considered. Since the maximum flow in the catalytic cycles is \( k_1[\text{catalyst}] \) – equivalent to the case where all cobalt is in the form of \( \text{alkyltetracarbonyl} \equiv "4\text{-alkyl}" \) – the three \( \varphi \)'s are the relative influxes which should be equal for a stoichiometric reaction if there were neither side reactions nor overflow, and \( \mu_1 \alpha, \mu_2 \beta, \mu_3 \gamma \) are the relative effluxes of the substrates. These 6 parameters are adjustable by virtue of the \( j \)'s and \( k_{\text{substrate}} \)'s. The autocatalysis constant \( e \) is adjustable by \([\text{catalyst}]\), too. Only \( x_1 \) through \( x_4 \) are fixed parameters relevant for the position of the steady states; here \( x_1 \) and \( x_2 \) are typical for the substrate inhibition, whereas \( x_3 \) and \( x_4 \) indicate the disadvantage of a 4-cycle reaction compared to the corresponding 3-cycle reaction and should be \( \ll 1 \) each.

The differential equations are now:

\[
\frac{\text{d}a}{\text{d}\tau} = q_1(\varphi_1 - \mu_1 a - \alpha \xi_3 - x_1 a \xi_4) \tag{33}
\]
\[
\frac{\text{d}\beta}{\text{d}\tau} = q_2(\varphi_2 - \mu_2 \beta - \beta \xi_3 - e \beta \xi_4 \xi_4) \tag{34}
\]

\[
\xi_3 = \frac{1 - \xi_4}{1 + \frac{\alpha}{\gamma} + \gamma \frac{x_3 a + x_1 (\beta + x_3 \gamma)}{x_4 a \beta + x_2 (\beta + x_3 \gamma)} + \alpha \frac{x_2 + x_4 (a + x_1 \gamma)}{x_4 a \beta + x_3 (\beta + x_3 \gamma)} (1 + \beta + x_3 \gamma)} \tag{45}
\]

\[
\eta_3 = \frac{a}{\gamma} \xi_3 \tag{46}
\]
\[
\xi_3 = \frac{x_2 + x_4 (a + x_1 \gamma)}{x_4 a \beta + x_2 (\beta + x_3 \gamma)} \xi_3 \tag{47}
\]
\[
\xi_4 = \frac{x_3 a + x_1 (\beta + x_3 \gamma)}{x_4 a \beta + x_2 (\beta + x_3 \gamma)} \xi_3 \tag{48}
\]
\[
\eta_4 = (\beta + x_3 \gamma) \xi_3 = f(\alpha, \beta, \gamma) \tag{49}
\]

and eventually

\[
\frac{\text{d}a}{\text{d}\tau} = q_1(\varphi_1 - \mu_1 a - \eta_4) \tag{50}
\]
\[
\frac{\text{d}\beta}{\text{d}\tau} = q_2(\varphi_2 - \mu_2 \beta - \eta_4) \tag{51}
\]
\[
\frac{\text{d}\gamma}{\text{d}\tau} = q_3(\varphi_3 - \mu_3 \gamma - \eta_4) \tag{52}
\]

In computations, the complicated function \( \eta_4 = f(\alpha, \beta, \gamma) \) can be evaluated in the most time
saving manner by the continued substitution
\[ a = a + \kappa_1 \gamma, \quad b = \kappa_2 + \kappa_4 a, \quad c = \kappa_1 \beta + \kappa_3 a, \]
\[ \zeta_1 = \kappa_2 a b / (\kappa c), \quad d = a \gamma, \quad e = \beta + \kappa_3 \gamma, \]
\[ f = \kappa_2 e + \kappa_4 a \beta, \quad g = \gamma c / f, \quad h = a b / f, \quad \xi_5 = (1 - \xi_4) / (1 + d + g + h(1 + e)), \]
\[ \eta_4 = \text{ch} \xi_5. \]

We want to show that there exist limit cycle oscillations for some suitable set of the 14 parameters. Since we assume that the 4-cycle is relatively slow compared to the 3-cycle, leading to partial substrate inhibition, it can be expected that \( \kappa_3, \kappa_4 \ll 1 \), i.e., it will be much easier to neglect these parameters at the beginning and to consider their influence later on.

We get
\[ \eta_{4,0} = \lim_{\kappa_2 \rightarrow 0} \frac{a \beta \gamma}{\kappa_2 a + a \gamma + \beta \gamma + a \beta \gamma + \frac{\kappa_1}{\kappa_2} \beta \gamma^2} \]

(53)

where \( \frac{\kappa_1}{\kappa_2} \) is the reduced equilibrium constant for the formation of 4-hydro from 3-hydro and CO. The term \( \frac{\kappa_1}{\kappa_2} \beta \gamma^2 \) in the denominator of (53) is responsible for the substrate inhibition and dominates for great values of \( \gamma \). Since \( \lim_{\gamma \rightarrow \infty} \eta_{4,0} = \frac{\kappa_2 a}{\kappa_1 \gamma} \) is independent from \( \beta \), we expect that there is a strong influence of the slowly varying variable \( \alpha \) on the oscillation, but only a small one of \( \beta \).

Oscillations for Special Sets of Parameters

Obviously, a complete discussion of the 14-dimensional parameter space is impossible. But since our goal is much more modest, namely to demonstrate only that for special sets of parameters oscillations do exist, our task will be simpler. In order to show that oscillatory states can not only be attained under very strange conditions, we adopt as many parameters as possible (from \( \kappa_3 \) to \( \epsilon \)) from the previous paper. The special sets chosen are given in Table I together with the equivalent designations of this and the previous paper. Note that in that paper, the concentrations of olefin and H₂ were constants because these substances were assumed to form pools. In consequence, what appear here as the variables \( a \) and \( \beta \) were there the corresponding parameters \( \kappa_3 \) and \( \kappa_2 \); also, no equivalents to the new parameters \( q_1, q_2, q_3, \mu_1, \mu_2 \) were needed there. Parameter sets I and II differ only in the values of \( \kappa_3, \kappa_4, \) and \( \epsilon \) and represent again a 100-fold and a 10-fold advantage of the faster 3-cycle over the slower 4-cycle, respectively.

The result of the simulation of parameter set I is depicted in Fig. 2: a) \( a, \beta, \gamma \) vs \( \tau \); b) production rate of aldehyde, \( \eta_4 \) vs \( \tau \); c) as a 2-dimensional projection of the 3-dimensional state space: \( \gamma \) vs \( \beta \). Set I yields undamped oscillations with a period of 2210 units of \( \tau \) and a limit cycle; it displays a fairly great non-linearity. Set II with only a slight disadvantage of the 4-cycle compared to the 3-cycle, i.e. a distinctly incomplete substrate inhibition shows weakly damped oscillations converging eventually to the stable steady state with \( a = \gamma = 14.571 \) and \( \beta = 7.2857 \), and the corresponding simulation is therefore not rendered here.

Table I. Parameter sets of the simulated oscillations and comparison of parameters and variables here with those in the previous paper.

<table>
<thead>
<tr>
<th>Parameter (p) or variable (v) in this paper</th>
<th>Set I</th>
<th>Set II</th>
<th>Parameter (p) or variable (v) in previous paper</th>
</tr>
</thead>
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<tr>
<td>( q_1 ) (p)</td>
<td>0.1</td>
<td>0.1</td>
<td>—</td>
</tr>
<tr>
<td>( q_2 ) (p)</td>
<td>0.1</td>
<td>0.1</td>
<td>—</td>
</tr>
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<td>1</td>
<td>( q ) (p)</td>
</tr>
<tr>
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<td>0.4</td>
<td>—</td>
</tr>
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<td>0.4</td>
<td>—</td>
</tr>
<tr>
<td>( q_6 ) (p)</td>
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<td>0.005</td>
<td>—</td>
</tr>
<tr>
<td>( q_7 ) (p)</td>
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<td>0.01</td>
<td>—</td>
</tr>
<tr>
<td>( q_8 ) (p)</td>
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<td>0.005</td>
<td>( x_1 ) (p)</td>
</tr>
<tr>
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<td>20</td>
<td>( x_4 ) (p)</td>
</tr>
<tr>
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<td>10</td>
<td>( x_3 ) (p)</td>
</tr>
<tr>
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<td>0.01</td>
<td>( x_6 ) (p)</td>
</tr>
<tr>
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<td>( x_8 ) (p)</td>
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<tr>
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<td>0.01</td>
<td>( x_7 ) (p)</td>
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<tr>
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<td>( x_4 ) (p)</td>
</tr>
<tr>
<td>( \kappa_4 ) (p)</td>
<td>10</td>
<td>10</td>
<td>( x_3 ) (p)</td>
</tr>
<tr>
<td>( \kappa_5 ) (p)</td>
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<td>0.01</td>
<td>( x_6 ) (p)</td>
</tr>
<tr>
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<td>0.005</td>
<td>( x_1 ) (p)</td>
</tr>
<tr>
<td>( \kappa_7 ) (p)</td>
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<td>0.01</td>
<td>( x_8 ) (p)</td>
</tr>
<tr>
<td>( \kappa_8 ) (p)</td>
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<td>0.005</td>
<td>( x_1 ) (p)</td>
</tr>
</tbody>
</table>

Relations of the Simplified Model to the Real System and to Technical Oxo-Plants

As was pointed out at the beginning, but might have been drowned out by the many formulas in the meantime, the model treated here contains some simplifications compared to chemical reality and is completely indistinct with respect to the very values of the parameters which are unknown. Some intermediates have been dropped or "lumped" in one species; so no difference has been made between
Fig. 2. Simulation of the oscillations for parameter set I of Table I. a) $\alpha$, $\beta$, $\gamma$ vs $\tau$, b) $\eta_4$ vs $\tau$, c) limit cycle $\gamma$ vs $\beta$.

\( \sigma \)- and \( \pi \)-alkyl-Co-carbonyls; the appearance of different isomers has been ignored. The reversibility of the individual reaction steps was explicitly formulated in only one reaction where it was essential for the mechanism, namely

\[ \text{HCo(CO)}_3 + \text{CO} \rightarrow \text{HCo(CO)}_4; \]

for all other steps it was assumed that the dynamical state of the total system was so far from equilibrium that the reverse reactions could be neglected. Technically important modifications of the original oxo process, like the partial substitution of CO by triphenylphosphine, were not treated. Especially in the former publication, it was pointed out that smaller values of the CO-partial pressure would lead to a jump to the lower branch of the hysteresis curve which is connected with a much higher production rate of product. No account was taken of the fact that under a small CO pressure the carbonyls tend to dissociate, yielding in part metallic cobalt and thus decreasing the total amount of the catalyst. Nor was mentioned the experience that under those conditions that are at first glance more profitable, the relative amount of wanted \( n \)-aldehyde decreases in favor of the unwanted \( i \)-aldehyde. On the other side, the formulation of the substrates olefin, \( \text{H}_2 \), and CO as being fed by constant influxes and being depleted - save by the oxo reaction itself - by effluxes proportional to the concentrations of the substrates, is valid under the conditions of a reactor with ideal mixing. In this case, if \( v \) is the turnover expressed in volume per time, \( V \) is the volume of the reactor, \( x_0 \) is the constant initial value of the concentration of some substrate at the entrance and \( x(t) \) the corresponding homogeneous concentration inside the reactor and at its exit, and finally \( r \) the reaction rate leading to products, we get

\[
\frac{dx}{dt} = -x - r.
\]

So, in (1), (2), (3) each \( j_i \) is equal to the corresponding constant \( (v/V) x_0 \) and each \( k_i \) is equal to the overflow parameter \( v/V \) with \( i = \text{ol.}, \text{H}_2, \) and CO. The efflux parameters would thus be mutually equal if there were no parasitic side reactions as hydrogenation of olefin, hydrogenation of aldehyde, formation of \( \text{CH}_4, \text{CH}_3\text{OH} \) and higher alkyl derivatives from CO and \( \text{H}_2 \). So \( k_{\text{ol.}} , k_{\text{H}_2} \), and \( k_{\text{CO}} \) are primarily identical to \( v/V \) and are jointly adjustable by the turnover, but are modified by side reactions which need not be of first order in reality. Since the initial concentrations can be varied in a wide range, the \( j_i \)'s and thus the \( g \)'s are flexible parameters, too, and so is the total concentration of catalyst, although in homogeneous catalysis this is continuously fed into the reactor together with the substrates; however, since it is only distributed among the various forms of Co-carbonyls, but not varied in its sum, and since it is finally ejected at the same rate together with the products and the unreacted substrates, the
constancy of catalyst is warranted under technical conditions.

Of the 14 constants in the dimensionless system, many are adjustable: $\varphi_1$, $\varphi_2$, $\varphi_3$ fully, and $\mu_1$, $\mu_2$, $\mu_3$ partially. $\varphi_1$, $\varphi_2$, $\varphi_3$ are irrelevant for the position of the steady state, but influence its stability. $\kappa_3$, $\kappa_4 \ll 1$ and can be neglected, if substrate inhibition is nearly complete, i.e., if the 4-cycle is extremely slow compared to the 3-cycle. Especially important are the fixed constants $x_1$ and $x_2$, the ratio of which represents the equilibrium constant of $\text{HCo(CO)}_3 + \text{CO} \rightleftharpoons \text{HCo(CO)}_4$. Thus it should be possible to estimate at least, if not measure, from experiments the fixed parameters which were guessed arbitrarily in this treatment.

One other important point that influences the technical stability strongly is the heat production, which even alone can lead to oscillations, as shown by Dubil and Gaube$^3$, and is thus a source of further instability.

Computations and plots were performed on the Calculator HP 9820 with peripherals.

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1 F. F. Seelig, Z. Naturforsch. 31b, 336 [1976]; further references there.