System-theoretical Investigation of Possible Hysteresis Effects in the Hydroformylation Process

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The complicated and partially controversial formulations of the various steps and branchings in the hydroformylation process are comprised in a reaction scheme that neglects the production of different isomers and isomerisations of olefins and is a compromise between the given complexity and a theoretical tractability. Special consideration is devoted to the inhibition of the process by one of its substrates, CO. In a first approximation complete inertness of the Co-tetracarbonyls is assumed and the existence of bistability and hysteresis for particular parameter combinations is proved. In the further treatment this approximation is again relaxed. Technological consequences of the analysis are discussed.

Introduction

The well-known hydroformylation or oxo-synthesis,

$$R-CH = CH-R' + CO + H_2 \rightarrow R-CH=CH-R'$$

which is catalyzed by the various transition forms of cobalt carbonyls is an important industrial production process leading in the first step to aldehydes and from there to various alcohols, amines, esters, carbonic acids etc. The kinetics of the complicated process has been the topic of various contributions and reviews 1-3. Nonetheless, the complicated complete reaction scheme is even nowadays partially controversial and quantitative data of the rate constants of the various reaction steps – ideally over a wide range of temperature – are nearly completely missing. But there are some general qualitative features that make just this process interesting for a system-theoretical investigation:

1) there is experimental evidence for inhibition of the process by one of its substrates, namely CO,

2) two steps, namely

$$\text{acyl-Co(CO)}_4 + \text{HCo(CO)}_4 \rightarrow \text{aldehyde} + \text{Co}_2(\text{CO})_8$$

$$\text{Co}_2(\text{CO})_8 + \text{H}_2 \rightarrow 2 \text{HCo(CO)}_4$$

form a rare autocatalytic subsystem with HCo(CO)_4 as the autocatalyst.

DUHIL and GAUBE 4 have shown that a controlled stirred-tank reactor can become unstable or show sustained oscillations, but this sort of instability is rather an instability of the control circuit together with the general autocatalysis of each exothermal process by heat than inherent to the special kinetics of the oxo-synthesis. Their oscillations cannot occur in a perfectly controlled, i.e. rigorously isothermal reactor. In contrast to those instabilities the ones treated here are purely chemical and occur even in perfectly isothermal systems.

The motivation to investigate just the oxo-synthesis under this aspect arose when the present author became aware of the close analogy of this reaction system to the phenomenon of substrate inhibition shown by many enzymes which together with the possibility of bistability and hysteresis was treated in some detail by SEELEG and DENZEL 5.

The basic features of possible instability and oscillations due to peculiarities of the reaction scheme of the oxo-synthesis were first given by the author at the “Colloquium on Automata Theory
and Chemical and Biological Systems” held in Paris, 1974, and some lectures at various places subsequently.

**Kinetic Scheme**

Aiming at a thorough system-theoretical analysis of the kinetic behavior of the hydroformylation process one is confronted with a scheme of a high complexity with various reactions in closed loops and many branchings, side chains that lead to by-products or isomers, and even some controversy about the importance or the relative weight of alternatives. Quantitative data are nearly unknown. If all single steps and branches were considered a tremendous number of substances and rate constants would arise, leading – in the theoretical formulation as differential equations – to a state space and a corresponding parameter space of high dimensions each. Analysis would be impossible, even a qualitative prediction of the behavior would be extremely impeded. So, unimportant side reactions must be discarded, several single steps must be “lumped”, partially in reaction steps of higher pseudo-order that must not be interpreted as real molecular events. In addition to the high internal complexity of the process under investigation there are different possibilities for the external realization in an open reaction system: the process can be led in such a way that the concentrations of all substrates are free to establish (as will be treated in a subsequent paper), or as another possibility, the arrangement can be such that some of them are kept fairly constant in well buffered pools with the pleasant effect that former state variables become adjustable parameters now, enhancing the flexibility of the system and the achievability of strange states considerably. So, as a compromise between rigour of treatment and tractability the reaction scheme as given in Fig. 1 is assumed to be a fairly correct model for the real process. Here only the substrate that causes inhibition, CO, is allowed to move freely in its concentration. The scheme can be characterized by several main features:

1) there are two reaction cycles, one involving tricarbonyls of cobalt, named “3-cycle”, and the other one containing different derivatives of cobalt tetracarbonyl, named “4-cycle”;

2) both cycles are connected by two common substances and one common reaction; in addition there is a cross-linking by the reaction \( \text{HCo(CO)}_5 + \text{CO} = \text{HCo(CO)}_4 \) which solely is formulated as a reversible reaction;

3) the 3-cycle is assumed to have far greater rate constants than the corresponding 4-cycle, nevertheless the normal steady state is such that the production of aldehydes runs strongly through the 4-cycle, because the CO-pressure is relatively high, so that the concentrations of the substances in the 3-cycle are rather low (CO-inhibited state with \(1/p_{CO}\) dependence of the turnover as found experimentally);

4) the slow 4-cycle is strongly favored in addition by the existence of autocatalysis in step 7, \( \text{HCo(CO)}_4 \) or “4-hydro” being the autocatalyst.

The given model is described mathematically by the following differential equations derived by application of the simple law of mass action (the abbreviations of the substances are defined in Fig. 1):

\[
\frac{d[\text{CO}]}{dt} = j - k_0[\text{CO}] - k_4[\text{CO}][3-\text{alkyl}] - k_5[\text{CO}][3-\text{acyl}] + k_5[3-\text{hydro}] + k_6[4-\text{hydro}] - (1)
\]

\[
\frac{d[3-\text{hydro}]}{dt} = k_5[3-\text{acyl}] - k_6*[3-\text{hydro}] - (2)
\]
\[
\begin{align*}
\frac{d[4\text{-hydro}]}{dt} &= k_5[\text{CO}][3\text{-hydro}]-k_5[4\text{-hydro}]+k_7[4\text{-acyl}][4\text{-hydro}]-k_8^*[4\text{-hydro}]
(3) \\
\frac{d[3\text{-alkyl}]}{dt} &= k_3^*[3\text{-hydro}]-k_4[\text{CO}][3\text{-alkyl}]
(4) \\
\frac{d[4\text{-alkyl}]}{dt} &= -k_1[4\text{-alkyl}]+k_2[4\text{-alkyl}]+k_3[4\text{-hydro}]
(5) \\
\frac{d[3\text{-acyl}]}{dt} &= k_4[4\text{-acyl}]-k_5[3\text{-acyl}]-k_6^*[3\text{-acyl}]
(6) \\
\frac{d[4\text{-acyl}]}{dt} &= k_7[3\text{acyl}][3\text{acyl}]-k_8[4\text{acyl}][4\text{acyl}]
(7)
\end{align*}
\]

Equations (2) through (7) are not linearly independent; they add up to zero, reflecting the fact that the sum of the concentrations of all catalytic intermediates, [catalyst], as measured by the sum concentration of cobalt, is constant. So we can replace one of these differential equations, say (5), by the algebraic equation

\[
[4\text{-alkyl}] = [\text{catalyst}] - [3\text{hydro}] - [4\text{hydro}] - [3\text{alkyl}] - [3\text{acyl}] - [4\text{acyl}]
(8)
\]

and replace [4-alkyl] in the rest.

Thus we are left with 6 state variables + time and 12 parameters, where the primed formal rate constants \(k'_2\) and \(k'_7\) contain the constant \([\text{H}_2]\) as a factor, whilst the starred ones \(k_3^*\) and \(k_8^*\) are attached to the constant [olefin] and are thus adjustable in a wide range though not independently. The same adjustability is available for the parameters \(j, k_0\) and [catalyst], only \(k_1, k_4, k_5, k_7\) and \(k_8\) being fixed for a given temperature.

Usually it is possible to get rid of some parameters by introducing dimensionless variables and parameters, a procedure which is quite exact, but not unique.

One possible transformation of the variables is

\[
\tau = k_1t
(9)
\]

\[
\gamma = \frac{k_4}{k_1}[\text{CO}]
(10)
\]

\[
\xi_3 = [3\text{hydro}]/[\text{catalyst}]
(11)
\]

\[
\xi_4 = [4\text{hydro}]/[\text{catalyst}]
(12)
\]

\[
\eta_3 = [3\text{alkyl}]/[\text{catalyst}]
(13)
\]

\[
\zeta_4 = [4\text{acyl}]/[\text{catalyst}]
(15)
\]

and for the parameters

\[
q = k_4/\text{catalyst} / k_1
(16)
\]

\[
\varphi = j/(k_1/\text{catalyst})
(17)
\]

\[
x_1 = k_0/(k_4/\text{catalyst})
(18)
\]

\[
x_2 = k_2/k_1
(19)
\]

\[
x_3 = k_3^*/k_1
(20)
\]

\[
x_4 = k_5/k_4
(21)
\]

\[
x_5 = k_5/k_1
(22)
\]

\[
x_6 = k_6/k_4
(23)
\]

\[
x_7 = k_7/[\text{catalyst}]/k_1
(24)
\]

\[
x_8 = k_8^*/k_1
(25)
\]

This renders the kinetic equations in the form

\[
\frac{d\gamma}{d\tau} = q(\varphi - x_1\gamma - \gamma\zeta_3 - x_2\zeta_3 + x_3\zeta_4 - x_6\gamma\zeta_3)
(26)
\]

\[
\frac{d\xi_3}{d\tau} = x_2\zeta_3 - x_3\zeta_3 - x_4\gamma\zeta_3 - x_6\zeta_4
(27)
\]

\[
\frac{d\xi_4}{d\tau} = x_1\gamma\zeta_3 - x_3\zeta_4 + x_7\zeta_4 - x_6\zeta_4
(28)
\]

\[
\frac{d\eta_3}{d\tau} = x_3\zeta_3 - x_3\gamma\zeta_3
(29)
\]

\[
\frac{d\zeta_3}{d\tau} = 1 - \xi_3 - \eta_3 - \zeta_4 - \zeta_4 - \xi_3\zeta_3 - \xi_3\gamma\zeta_3
(30)
\]

\[
\frac{d\zeta_4}{d\tau} = x_6\gamma\zeta_3 - x_7\zeta_4 - x_4\zeta_4
(31)
\]

**Special Case: Complete Substrate Inhibition**

In spite of the various approximations in this reaction it is still too complicated to see some fundamental features. In a first step we shall reduce therefore the scheme even further neglecting the 4-cycle completely for a while, which is equivalent to the assumption of complete substrate inhibition by CO, and which means mathematically that we assume

\[
k_6 = k_8 = 0 \text{ and } [4\text{acyl}] = 0,
\]

or \(x_6 = x_8 = \zeta_4 = 0\).

An analysis of the possible steady states without investigation of their stability starts from the corresponding differential equations with the time
derivatives set equal to zero. With the special simplifications of this section mentioned above we then end up with

\[ \varphi - \xi_1 \gamma = 1 - \xi_3 - \xi_4 - \eta_3 - \xi_3 = 0 \]

or

\[ \xi_3 = \gamma \eta_3 \]  \hspace{1cm} (32)

and

\[ \gamma \eta_3 \xi_3 = \xi_3 \xi_4 \]  \hspace{1cm} (33)

where (32) denotes the production rate of aldehyde. By continued substitution all variables can be expressed in terms of one, say \( \gamma \), and we end up with one equation in \( \gamma \), which is a polynomial of degree 3:

\[ \xi_3 = \frac{\varphi - \xi_1 \gamma}{\xi_3} \]  \hspace{1cm} (34)

\[ \xi_4 = \frac{(\varphi - \xi_1 \gamma) \xi_4}{\xi_3 \xi_5} \]  \hspace{1cm} (35)

\[ \eta_3 = \frac{\varphi - \xi_1 \gamma}{\gamma} \]  \hspace{1cm} (36)

\[ \xi_3 = \frac{\varphi - \xi_1 \gamma}{\xi_2} \]  \hspace{1cm} (37)

\[ \varphi - \xi_1 \gamma = 1 - (\varphi - \xi_1 \gamma) \left( \frac{1}{\xi_3} + \frac{\xi_4 \gamma}{\xi_3 \xi_5} + \frac{1}{\gamma} + \frac{1}{\xi_2} \right) \]  \hspace{1cm} (38)

or

\[ \gamma^3 + \gamma^2 \left[ \frac{\xi_5}{\xi_4} \left( 1 + \xi_3 + \frac{\xi_3}{\xi_2} \right) - \frac{\varphi}{\xi_1} \right] + \frac{\xi_5}{\xi_4} \gamma \left[ \xi_3 \left( 1 + \frac{1}{\xi_1} \right) - \frac{\varphi}{\xi_1} \left( 1 + \xi_3 + \frac{\xi_3}{\xi_2} \right) \right] - \frac{\xi_5}{\xi_4} \frac{\varphi}{\xi_1} = 0. \]  \hspace{1cm} (39)

The necessary (but not sufficient) conditions for getting bistability, \( \text{i.e.} \) 3 positive real solutions of (39), two of which correspond to stable steady states, are comprised in

\[ \frac{\xi_5}{\xi_4} \left( 1 + \xi_3 + \frac{\xi_3}{\xi_2} \right) < \frac{\varphi}{\xi_1} < \frac{\xi_5 \left( 1 + \frac{1}{\xi_1} \right)}{1 + \frac{\xi_3}{\xi_2} + \frac{\xi_3}{\xi_2}} \]  \hspace{1cm} (40)

because the further condition that the \( \gamma \)-free term must be negative is fulfilled automatically.

The possibility of bistability and hysteresis is easily verified for a special set of parameters, \( \text{e.g.} \)

\( x_1 = 0.005, x_2 = 100, x_3 = 10, x_4 = 20, x_5 = 10 \) (\( \varphi \) does not matter in this context!).

The corresponding hysteresis loop \( \gamma \text{ vs } \varphi \) is shown in Fig. 2. For \( \varphi = 0.4 \text{ e.g.} \) there are three solutions for \( \gamma \), 0.7963, 7.606 and 66.05, the second of which corresponds to an unstable steady state. Since the net production of aldehyde is \( \varphi - \xi_1 \gamma \) or the relative yield \( 1 - \xi_1 \gamma/\varphi \), the first steady state would give a relative yield of 99%, whilst the second “normal” one (\( \text{i.e.} \) \( \gamma = 66.05 \)) would give only 17.4%!

As can be seen from Fig. 2 there are three solutions \( \gamma \) of (39) in the interval of ambiguity \( a < \varphi < b \); a stability analysis would reveal the general result that the branch A-B represents unstable states which cannot be attained experimentally. Coming from small values of \( \varphi \) the system remains in the lower branch up to \( \varphi = b \), coming from high values it stays in the upper one down to \( \varphi = a \). Both separate branches are “connected” by discontinuous transitions.

**General Case: Partial Substrate Inhibition**

After a basic understanding of the phenomenon of bistability and hysteresis in the simpler special case of complete substrate inhibition and complete neglect of the 4-cycle we return to the more realistic general case as depicted in Fig. 1 and formulated by (26) through (31). The steady states are now characterized by

\[ \varphi - \xi_1 \gamma = 1 - \xi_3 - \xi_4 - \eta_3 - \xi_3 - \xi_4 = 0 \]

\[ = \xi_3 \xi_4 + \xi_3 \eta_3 \xi_3 = 0 \]

\[ \xi_5 \xi_4 = 0 \]

\[ \eta_3 \xi_3 = 0 \]

\[
\begin{align*}
\xi_3 & = \frac{\varphi - \xi_1 \gamma}{\xi_3} \\
\xi_4 & = \frac{(\varphi - \xi_1 \gamma) \xi_4}{\xi_3 \xi_5} \\
\eta_3 & = \frac{\varphi - \xi_1 \gamma}{\gamma} \\
\xi_3 & = \frac{\varphi - \xi_1 \gamma}{\xi_2} \\
\varphi - \xi_1 \gamma & = 1 - (\varphi - \xi_1 \gamma) \left( \frac{1}{\xi_3} + \frac{\xi_4 \gamma}{\xi_3 \xi_5} + \frac{1}{\gamma} + \frac{1}{\xi_2} \right) \\
\gamma^3 + \gamma^2 \left[ \frac{\xi_5}{\xi_4} \left( 1 + \xi_3 + \frac{\xi_3}{\xi_2} \right) - \frac{\varphi}{\xi_1} \right] + \frac{\xi_5}{\xi_4} \gamma \left[ \xi_3 \left( 1 + \frac{1}{\xi_1} \right) - \frac{\varphi}{\xi_1} \left( 1 + \xi_3 + \frac{\xi_3}{\xi_2} \right) \right] - \frac{\xi_5}{\xi_4} \frac{\varphi}{\xi_1} & = 0.
\end{align*}
\]
\[ x_2 \xi_3 = x_3 \xi_3 + x_4 y \xi_3 - x_5 \xi_4 \]  
(44)

where (41) represents the production of aldehyde, (42) and (43) the flow in the 3- and 4-cycle, respectively, and (44) a branching condition.

From these relations we get

\[ \xi_3 = \frac{\varphi - x_1 y}{x_2 + x_5 y}, \quad \frac{x_2 x_5 + x_3 x_8 + x_4 x_5 y}{x_3 x_5 + x_3 x_8 + x_4 x_5 y} \]  
(45)

\[ \xi_4 = \frac{\varphi - x_1 y}{x_2 + x_5 y}, \quad \frac{x_2 x_4 + x_3 x_8 + x_4 x_5 y}{x_3 x_4 + x_3 x_8 + x_4 x_5 y} \]  
(46)

\[ \eta_3 = \frac{\varphi - x_1 y}{x_3 + x_5 y}, \quad \frac{x_3 x_5 + x_3 x_8 + x_3 x_8 y}{x_3 x_5 + x_3 x_8 + x_3 x_8 y} \]  
(47)

\[ \xi_3 = \frac{\varphi - x_1 y}{x_2 + x_5 y}, \quad \frac{x_6 x_5 + x_3 x_8 + x_4 x_5 y}{x_7 x_4 + x_3 x_6 + x_4 x_5 y} \]  
(48)

\[ \xi_4 = \frac{\varphi - x_1 y}{x_2 + x_5 y}, \quad \frac{x_6 x_5 + x_3 x_8 + x_4 x_5 y}{x_7 x_4 + x_3 x_6 + x_4 x_5 y} \]  
(49)

Substitution of (45) through (49) in

\[ \varphi = x_1 y + 1 - \xi_3 - \xi_4 - \eta_3 - \xi_3 - \xi_4 \]  
(50)

yields an explicit equation \( \varphi = f(\gamma) \), which, inversely, corresponds to a polynomial of order 5 in \( \gamma \).

The hysteresis loop (50) for the same parameters as in Fig. 2, but in addition \( x_6 = 0.01, x_7 = 1, x_8 = 0.1 \), is shown in Fig. 3a, showing that there are again 3 solutions \( \gamma \) in a certain range of \( \varphi \). This set of parameters means a 100-fold advantage of the 3-cycle over the 4-cycle with respect to the corresponding rate constants (i.e. a situation close to complete substrate inhibition); if, however, this advantage is only 10-fold \( (x_6 = 0.1, x_7 = 10, x_8 = 1) \), there is still a small hysteresis effect, as shown in Fig. 3b, which could grow again stronger for other values of the first group of parameters \((x_1, \ldots, x_5)\).

So far it has only been shown that there exists hysteresis for a few sets of parameters even in the most general case. A more interesting, but much more difficult question is, which is the limiting hypersurface in the high dimensional parameter space that encloses a region of the same qualitative behavior, namely hysteresis. There do exist methods and computer programs to solve this problem, but the gained results cannot be given in an analytical formula nor depicted in full detail. Only contour mappings in two dimensional subspaces can be given. If the fixed parameters of the actual oxo-process would be known, border lines for the adjustable parameters with respect to hysteresis would be interesting and could guide an optimal design of the technological process – optimal with respect to maximal turnover and yield of aldehydes.

![Fig. 3. Hysteresis loop \( \gamma \) vs \( \varphi \) for the case of only partial inhibition by CO. Parameters \( x_1 \) through \( x_4 \) as in Fig. 1. In addition:

a) \( x_6 = 0.01, x_7 = 1, x_8 = 0.1 \);

b) \( x_6 = 0.1, x_7 = 10, x_8 = 1 \).

Technological Consequences

Under normal technical conditions the oxo-process is strongly inhibited by CO as is stated by DUBIL and GAUBE (I.E.) that means that the reaction system is held on the upper branch of the hysteresis loop. Indeed, starting from (50) one can realize easily that for \( x_6 = x_8 = 0 \) in the limit \( \gamma \to \infty \) the net production, \( \varphi - x_1 y \), approaches \( x_3 x_5 / (x_4 y) \) in agreement with the Natta equation as cited by Falbe\(^8\) save its independence from \( H_2 \), whilst for \( x_6, x_8 \neq 0 \) the limit is \( (x_7 - x_8)(x_8/x_7) / 1 + x_8 \). Anyhow the production rate is unfavorable.

If the production rate is inversely proportional to the partial pressure or concentration of CO it is trivial that the rate can be increased by lowering that concentration; but what cannot be foreseen without a thorough analysis is that there may be a discontinuous jump by virtue of the existence of the hysteresis loop and that therefore the actual
state depends on the initial conditions. So, knowledge of the very process parameters, especially the fixed constants $x_4, x_5, x_6$ could lead to an optimal design of the process by a suitable choice of the adjustable parameters and a favorable initiation of the process.

There is still another hint to the possibility of a sudden increase of throughput: the author was informed about an explosion accident in an oxo plant in the Netherlands which could not yet be elucidated satisfactorily. It could be possible that the dynamical state of the plant got onto the lower branch of the hysteresis loop quite by chance. But since the turnover is highly increased in this state and since the process is exothermal it could be that the heat exchanger designed for the conventional state could not manage the higher rate so that the plant together with the temperature control circuit became unstable. But it is not claimed that these considerations explain that accident completely.

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