

Performance of octene in fluoruous biphasic hydroformylation: octene distribution and reversible transfer between perfluoromethylcyclohexane and nonanal

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Abstract

During fluoruous biphasic hydroformylation 1-octene is transferred from the fluoruous into the organic product phase and then from the product layer back to the fluoruous layer again, due to the immiscibility of nonanal with PFMCH. The effect of the temperature and the total amount of octene on the above behaviour were also studied.

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1. Introduction

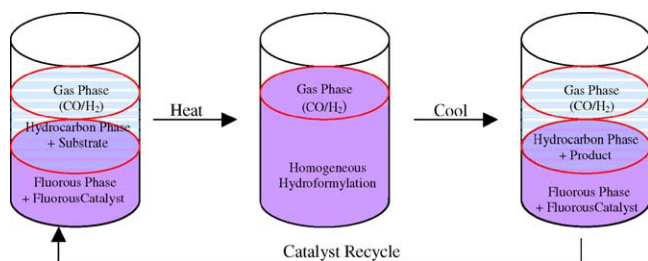
With production figures over 7 million tonnes of aldehyde per annum, hydroformylation has been one of the most important and powerful organochemical methods for the functionalisation of alkenes in the production of plasticisers, soaps and detergents [1–4]. In hydroformylation, usually a terminal alkene reacts with synthesis gas (CO/H₂) to produce a linear and/or branched aldehyde(s) without any by-products, so hydroformylation is also well known as a prototype of an ideal atom economic C/C-bond forming reaction [5,6]. In the field of homogeneously catalysed hydroformylation, soluble rhodium complex catalysts possess the highest activity and selectivity but they are expensive. In the production of lower aldehydes, the rhodium catalyst can be used efficiently and economically because it can be separated easily from the reaction mixture by product distillation. However, the much higher boiling point of long-chain aldehydes makes their separation by distillation impossible without decomposing the catalyst and therefore an alternative recycling process for the expensive catalysts is necessary for its industrialisation [7,8]. To tackle this disadvantage of homogeneous rhodium complex catalysts and apply them success-

fully on an industrial scale, development of novel approaches for facile catalyst recycling has become one of the most vigorously pursued research topics in the field of homogeneous transition metal catalysis [9], especially hydroformylation catalysed by rhodium–phosphine complexes [10].

So far, there have been two main techniques developed to deal with this inherent drawback of homogeneous hydroformylation catalysed by rhodium complexes. One technique is to immobilise complex catalysts over solid and insoluble supports [11,12]. Although this approach has been practised for many years, continuous loss of expensive catalyst as well as low reactivity hamper the commercialisation prospects of such catalytic system. We know of only one system where catalyst leaching has been reduced to acceptable levels [13]. The other technique is introducing a liquid/liquid biphasic system [1,14–18]. In this process, catalyst and ligands are designed to reside in one of the liquid phases used, while the organic product stays in the other. The product can then be separated by decantation. Liquid–liquid biphasic systems have attracted much attention during the last decade mainly for hydroformylation. This principle has been applied industrially in the Shell high olefins process (SHOP) [19,20] and in the Ruhrchemie/Rhone-Poulenc process [21,22]. In the former case, the Ni catalyst is dissolved in 1,4-butanediol, which is immiscible with the product alkenes, whilst in the latter, water is used as the immiscible phase containing complexes solubilised by sulphonated ligands [23]. Since then,

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Scheme 1. Process of fluorous biphasic hydroformylation.

several other catalyst systems have been investigated in the aqueous biphasic and some of them have been applied industrially [24,25].

However, aqueous biphasic processes can neither be applied to substrates, which might undergo undesired side reactions with water, nor to many organic reagents which react too slowly with water-confined catalysts due to their very low solubility in water and low mass transfer rates. Many further methods have been investigated to improve the rate of hydroformylation of higher alkenes and allow facile product separation [26–36]. A recently proposed alternative system is the so-called fluorous biphasic catalysis. In this case, a perfluorinated solvent, in which the catalyst is made soluble by functionalisation with suitable perfluoroalkyl chains, is used [15,37,38]. The fluorous solvent is miscible at the reaction temperature with the organic phase containing the dissolved reactants. However, on cooling to ambient temperature, separation of the two phases occurs rapidly [9]. This method can be summarised as shown in Scheme 1.

Scheme 1 indicates that the long-chain alkene reagent should stay in the fluorous solvent together with the fluorous soluble catalyst through the whole process of hydroformylation. However, when we tested the phase behaviour of perfluoromethylcyclohexane/octene/nonanal system under the typical hydroformylation conditions, we found that the behaviour of 1-octene was more complex than illustrated in Scheme 1, largely because the product aldehyde is not fully miscible with the fluorous solvent even at the reaction temperature and the 1-octene partitions into the aldehyde phase. In this paper, we report the results of these studies on the reversible transfer of 1-octene between the solvent (perfluoromethylcyclohexane) and the product of hydroformylation (nonanal).

2. Experimental

2.1. General

Perfluoromethylcyclohexane (PFMCH, 90% pure), nonanal (95% pure) and 1-octene (98% pure) were all used as purchased from Aldrich without further purification. All liquid chemicals were deoxygenated using ultrasound prior to use in order to reduce oxidation of nonanal as much as possible.

All experiments were carried out in a pressured glass reactor under a nitrogen atmosphere. The reactor was kept in a temperature controlled water bath and all the liquids in the reactor were continuously stirred, so that perfect mixing could be assumed before settling of the phases took place. Samples were taken for analysis only after all liquids came to equilibrium with one another at one temperature after a few hours.

2.2. Analysis

The analysis of all samples was carried out using a gas chromatograph (PERKIN-ELMER 8410, split injection of 1:100) equipped with a J&W Scientific DB-Petro capillary column (100 m × 0.25 mm × 0.5 μm) and a flame ionisation detector (FID), using the following temperature programme: $T_1 = 40^\circ\text{C}$ for 8.0 min, then temperature increase of 10 K min^{-1} to $T_2 = 160^\circ\text{C}$ for 14 min and temperature increase of 20 K min^{-1} to $T_3 = 250^\circ\text{C}$, for 30 min. In order to make sure that samples from different phases did not contaminate each other, fluorous layer samples were taken from the bottom of the phase while product layer samples were taken from the top of the organic phase. Two series of calibration mixtures containing all components were used to calibrate the FID signal. One series containing small quantities of the organic components in PFMCH and a second series containing small quantities of PFMCH in 1-octene and/or nonanal.

The mass balance of 1-octene during partitioning between the two phases, top and the bottom, is obtained from the partition ratio (G), which is defined by the relationship:

$$G = \frac{\text{number of moles of octene in the top layer}}{\text{number of moles of octene in the bottom layer}}$$

The distribution of octene between the two bulk phases is characterised by the total percentage of octene in the top or bottom layer:

$$\begin{aligned} \text{distribution of octene in top layer} \\ = \frac{\text{octene in the top layer}}{\text{octene in the top layer} + \text{octene in the bottom layer}} \\ \times 100\% \end{aligned}$$

$$\begin{aligned} \text{distribution of octene in bottom layer} \\ = \frac{\text{octene in the bottom layer}}{\text{octene in the top layer} + \text{octene in the bottom layer}} \\ \times 100\% \end{aligned}$$

3. Results and discussion

3.1. Phase performance of PFMCH and nonanal in the absence of 1-octene

Horvath et al. [17] and Cole-Hamilton and co-workers [39] have reported that perfluoromethylcyclohexane/toluene/1-octene form a monophasic system under typical hydroformylation conditions. Cole-Hamilton and co-workers [39]

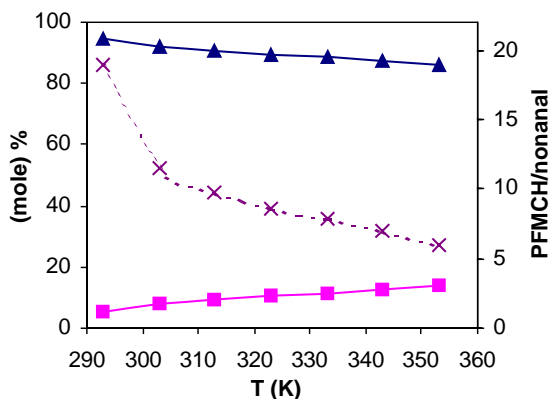


Fig. 1. Effect of temperature on the bottom layer without octene added: (■) nonanal; (▲) PFMCH; (×) molar ratio of PFMCH to nonanal.

have also reported that 1-octene is fully miscible with perfluoromethylcyclohexane at temperatures above 60 °C and nonanal is visually separated even at 80 °C. This immiscibility of nonanal with perfluoromethylcyclohexane is very efficient for catalyst recycling and reuse as nonanal removal would shift the equilibrium of hydroformylation towards products and reach higher conversion. In order to have more accurate information on the phase behaviour of perfluoromethylcyclohexane and nonanal, we have investigated the partitioning of PFMCH and nonanal quantitatively in the biphasic system firstly in the absence of octene.

Although perfluoromethylcyclohexane and nonanal are immiscible even at 80 °C as shown in Figs. 1 and 2, the mole fractions of each component in the other phase, nonanal content in PFMCH and PFMCH content in nonanal, increase linearly with temperature. However, the amounts of PFMCH and nonanal in the other phase are kept below certain limits. Nonanal in PFMCH is ≤ 12.5 mol% even at 80 °C and PFMCH in nonanal is ≤ 3.8 mol%. In the bottom fluorous layer, the molar ratio of PFMCH/nonanal was 6.0 while in the top nonanal layer the molar ratio of nonanal/PFMCH was 21. These results indicate that, at the typical hydroformylation temperature (70 °C) even during the process of nonanal formation, the hydroformylation product nonanal is mostly separated from the fluorous phase, so that separation might be affected even under reaction conditions.

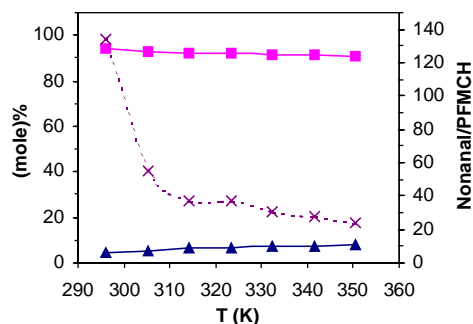


Fig. 2. Effect of temperature on the top layer without octene added: (■) nonanal; (▲) PFMCH; (×) molar ratio of nonanal to PFMCH.

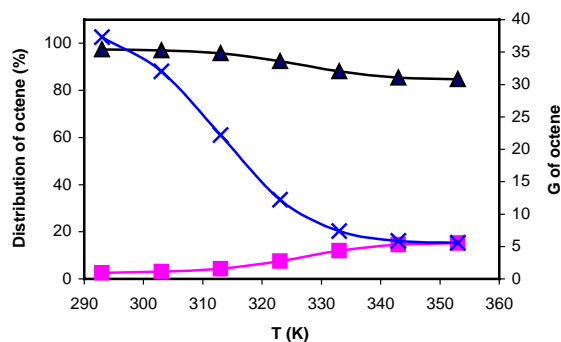


Fig. 3. Effect of temperature on the partitioning of octene in PFMCH/nonanal: (▲) in the top layer; (■) in the bottom layer; (×) G of octene.

3.2. Effect of temperature on 1-octene distribution in the PFMCH/nonanal biphasic system

Because of its immiscibility with perfluoromethylcyclohexane, nonanal should form another immiscible phase in the hydroformylation reaction system just after it is formed from 1-octene in the original single phase containing catalysts, 1-octene and PFMCH. Because of the miscibility of 1-octene and nonanal, some octene will be drawn out of the fluorous phase by nonanal. Due to the decrease of the concentration of 1-octene in the fluorous phase where the catalyst is retained, the hydroformylation rate might be reduced. In order to understand the hydroformylation process better, we have studied the distribution of 1-octene in the fluorous biphasic system ($V_{\text{PFMCH}}/V_{\text{nonanal}} = 1.0$). In all these experimental runs, the volume ratio of nonanal to octene was kept at 5.0 corresponding to a conversion of ca. 80%.

As shown in Fig. 3, the concentration of 1-octene in the fluorous phase increases with temperature while it decreases in the organic phase. The distribution of 1-octene between the two layers changes dramatically up to 343 K above which it levels off. These results suggest that 1-octene has its most favourable distribution in PFMCH in a hydroformylation reaction mixture at 343 K (70 °C) or above. They confirm that 343 K is an ideal temperature for this fluorous biphasic system [17,39]. However, even under these conditions, the majority of the 1-octene (>82%) resides in the organic phase, so that reaction rates can be expected to be lower than if a monophasic system existed within the reactor. The problem is even more pronounced at lower temperatures, so that unreacted 1-octene will be removed with the aldehyde rather than recycled with the fluorous phase.

3.3. Effect of overall octene on its partitioning with equal volumes of PFMCH and nonanal, $V_{\text{PFMCH}}/V_{\text{nonanal}} = 1.0$

Due to the miscibility of 1-octene with both nonanal and perfluoromethylcyclohexane under the hydroformylation conditions (usually 343 K), it can be inferred that the total amount of octene in the PFMCH/nonanal biphasic system would affect the distribution of 1-octene in this system.

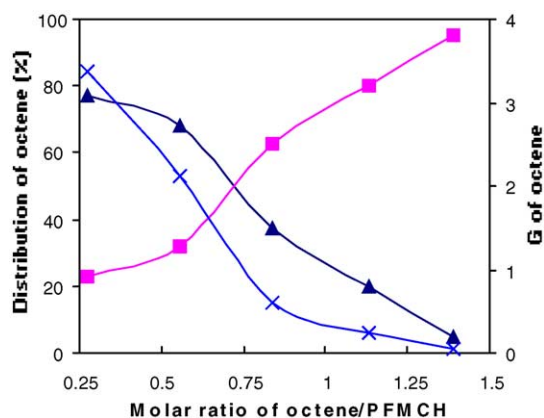


Fig. 4. Effect of octene/PFMCH on the partitioning of octene at 343 K: (▲) in the top layer; (■) in the bottom layer; (×) *G* of octene.

As shown in Fig. 4 which is obtained at 343 K, the distribution of 1-octene into PFMCH increases with the increase of the molar ratio of 1-octene/PFMCH from 0 to 1.4. However, the concentration of 1-octene in nonanal decreases dramatically above a molar ratio of 1-octene:PFMCH of 0.56.

3.4. Effect of conversion on partition of octene at systems with equal volumes of PFMCH and organic components, $V_{PFMCH}/(V_{nonanal} + V_{octene}) = 1.0$

Although our experimental runs were in the absence of an active catalyst, they enable us to investigate the effect of conversion of octene on its partitioning during hydroformy-

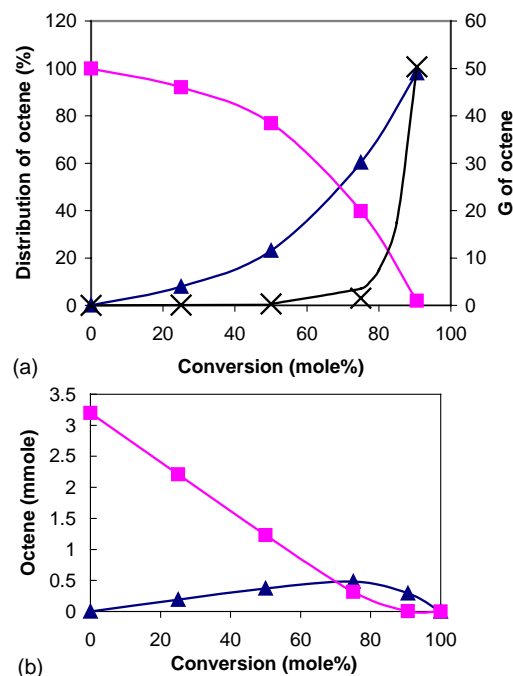
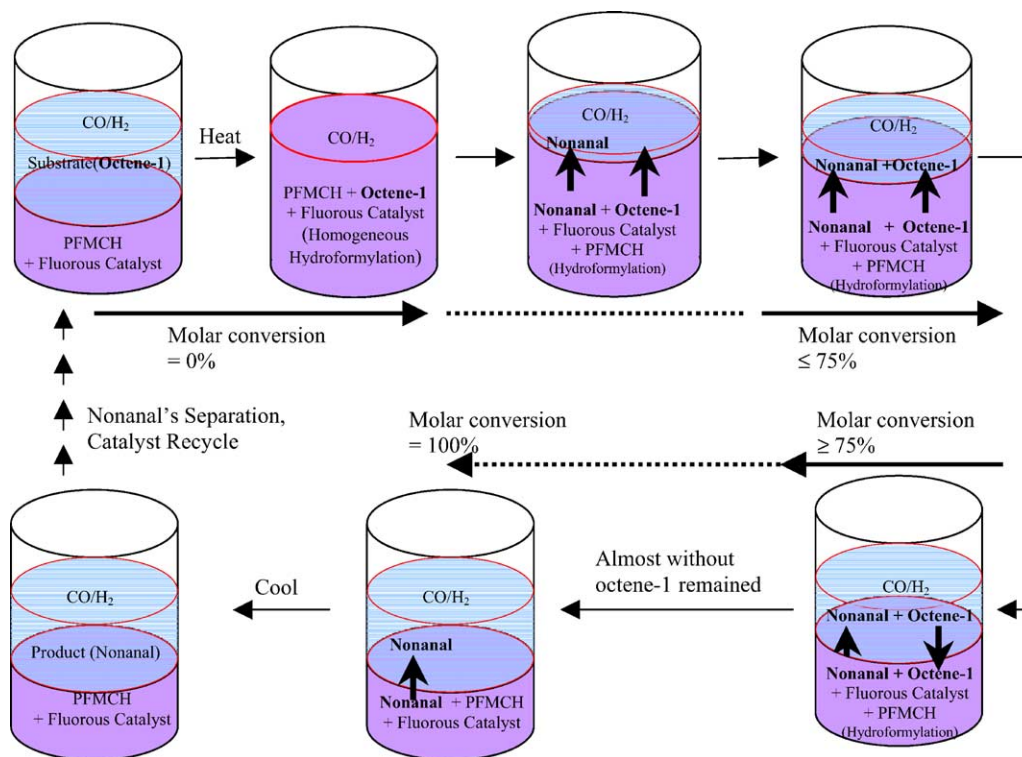


Fig. 5. Effect of total octene in product on the partitioning of octene at 343 K: (▲) octene in the top layer; (■) octene in the bottom layer; (×) *G* of octene.

lation in a fluorine biphasic system for the case where $V_{PFMCH}/(V_{nonanal} + V_{octene}) = 1$. In a hydroformylation system, conversion is equal to the mole fraction of nonanal amongst the organic components, nonanal and 1-octene.



Scheme 2. Octene's phase behaviour through the whole hydroformylation.

Each composition of the organic components corresponds to a reaction mixture of a specific conversion value. As shown in Fig. 5a, under the hydroformylation conditions (343 K), distribution of 1-octene in the fluoruous phase would decrease and that in the organic phase would increase with conversion until 1-octene has been converted completely into nonanal. Up to a conversion value of about 70%, the majority of the 1-octene is dissolved in PFMCH. The picture is reversed above this point.

However, as shown in Fig. 5b, the absolute amount of 1-octene in the organic phase increases until 1-octene conversion reaches about 75% (not 70% as for its distribution) and then decreases to zero because there is no 1-octene remaining in the system when the conversion is 100%. Initially, there is a high concentration of 1-octene in the fluoruous phase, which also contains the catalyst, but it is removed by reaction and partitioning into the growing nonanal phase as the reaction proceeds.

4. Conclusions

The above results clearly show that, because of the immiscibilities of nonanal and PFMCH, the phase behaviour of 1-octene during hydroformylation reactions is more complicated than if a single phase existed throughout the reaction (Scheme 1). The phase behaviour of 1-octene is affected dramatically by the system temperature, by the ratio of 1-octene:PFMCH and by the conversion of 1-octene during hydroformylation. We can summarise the phase behaviour of 1-octene under typical conditions (343 K) of fluoruous biphasic hydroformylation as in Scheme 2. During the hydroformylation process, 1-octene is first transferred from the fluoruous phase into the product phase and then from the product layer back to the fluoruous layer again. These non-linear effects on the concentration of 1-octene in the fluoruous phase will undoubtedly affect the reaction kinetics, which in many cases are more complex than the first order dependence on substrate concentration that is commonly found for hydroformylation reactions [39].

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