Gas–liquid–liquid reaction engineering: the Koch synthesis of pivalic acid from iso- and tert-butanol; Reaction kinetics and the effect of a dispersed second-liquid phase

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Abstract

In gas–liquid–liquid reaction systems with fast parallel and consecutive reactions the effects of mass transfer and mixing on the product yield can be significant. The Koch synthesis of pivalic acid, using sulfuric acid as catalyst, was chosen to study these effects. Reaction kinetics and the effect of the catalyst-phase composition have been investigated by using isobutanol as reactant. For studying the effect of an immiscible liquid phase on the reaction products obtained, the more reactive tert-butanol was used. Pivalic acid can be produced from isobutanol using sulfuric acid as a catalyst solution with 2-methylbutanoic acid as main byproduct, if gas–liquid mass transfer limitations are excluded. The selectivity towards 2-methylbutanoic acid is generally less than 20% and decreases strongly with decreasing acidity. The reaction is first order in isobutanol and dehydration is likely to be rate determining. The presence of pivalic acid and isobutanol strongly reduces the apparent reaction rate constant by decreasing the solution acidity (Ho). For the industrially applied backmixed reactors in the Koch synthesis, this may imply that these operate at much lower values for Ho. On addition of an immiscible heptane phase, the reaction products are extracted to some extent and this adds to maintaining a high catalyst solution acidity. Using tert-butanol, the yield and pivalic acid selectivity was found to depend strongly on CO transport to the reaction zone through gas–liquid mass transfer and mixing. The presence of an immiscible heptane phase increased the product yield and selectivity towards pivalic acid significantly. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Gas–liquid–liquid reaction systems may be encountered in several important fields of application as e.g. hydroformylation, alkylation, carboxylation, polymerization, hydrometallurgy, biochemical processes and fine chemicals manufacturing. However, the reaction engineering aspects of these systems have only been considered occasionally. For reaction systems with very slow reaction kinetics this is not surprising, as the three phases will be at physical equilibrium. In reaction systems with fast parallel and consecutive reactions the effects of mass transfer and mixing on the product yield can be significant. A fascinating example of such a reaction system is the Koch synthesis of pivalic acid. In this work this reaction system was chosen as model system to study these effects.

In 1955 Herbert Koch published a pioneering study on the synthesis of tertiary carboxylic acids from olefins, carbon monoxide and water (Koch, 1955). Generally, the reaction is thus operated as gas–liquid–liquid reaction system since the reactants originate from different phases; carbon monoxide as gas phase reactant, the alkene is introduced as organic liquid phase and water and the catalyst are present within the aqueous catalyst phase. Depending on the process operating conditions, the Koch acids produced will be transferred to the organic phase. Due to parallel-consecutive reaction routes with fast, chemical reactions in combination with mass transfer phenomena the reaction product distribution is very sensitive to the process operating conditions, resulting in a substantial potential for selectivity improvements of the overall process. Several Brønsted acids and Lewis acids have been applied as catalyst, but especially mixtures of BF3 and a Brønsted acid are attractive for industrial application, since these acid mixtures can be separated from the reaction products by phase settling and no re-concentration
step before recycling of the catalyst solution is required. In this work sulfuric acid is chosen as catalyst system in order to be able to operate the system as gas–liquid system and as gas–liquid–liquid system for studying the effect of a dispersed second liquid phase on the product yield and selectivity obtained.

For allowing a more detailed analysis of these effects of mass transfer and mixing, first the reaction kinetics will be considered. By choosing the smallest Koch acid, pivalic acid, as the model compound the number of possible isomers is minimized and the effect of different reactants, as isobutene, iso- and tert-butanol, all leading to the same product can be studied. Although isobutene (and -oligomers) is the commercially preferred feedstock for pivalic acid production, initially isobutanol was taken as reactant since isobutanol is expected to be less reactive and therefore the effects of catalyst composition can be studied more easily. Scouting experiments for the effect of an immiscible heptane phase on the product yield have been performed using the more reactive tert-butanol as reactant.

2. Reaction mechanism and — kinetics

The generally accepted mechanism for the Koch reaction includes four reversible reaction steps (Koch, 1955; Falbe, 1980). In Fig. 1 an alkene is used as reactant, but alcohols can be used as well. In this reaction system the acidic catalyst is indispensable and the acid strength of the catalyst solution, characterized by the well-known Hammett acidity function $H_0$, is an important factor. Although never a complete study on the detailed reaction kinetics of the complete Koch reaction system was published in literature, some of the reaction steps were used in studies on stabilized carbocations in superacidic media, see e.g. Hogeveen (1967a,b,c). Some results found in literature for the individual reaction steps are discussed below.

![Fig. 1. Basic reaction mechanism for the Koch synthesis.](image)

2.1. The carbocation formation

The carbocation formation by dehydration of iso-butanol or tert-butanol is in fact a two-step reaction involving a protonation of the alcohol followed by the release of a water molecule. Unfortunately, for the protonation and dehydration kinetics of iso- and tert-butanol in (strong) sulfuric acid solutions no data were found in literature. The protonation of olefins leading to the same $C_4$ carboxylations, has been studied more frequently in literature, see e.g. Brilman, Swaaij and Versteeg (1997) for a recent overview and update of data for isobutene and trans-2-butene. In these cases the protonation kinetics depend strongly on the acid strength of the catalyst solution and a log-linear relationship between the apparent first-order (in the alcohol or alkene concentration) reaction rate constant for the protonation reaction and the Hammett acidity function $H_0$ is found. Since the dehydration of isobutanol initially produces a primary carbocation, it is expected that the dehydration rate of isobutanol will be relatively slow. However, as isobutanol can also react directly with the sulfuric acid catalyst to an ester compound, a concerted dehydration mechanism may occur, possibly resulting in unexpected high dehydration rates, as e.g. is observed in the case of formic acid decomposition (Hogeveen, 1967b).

2.2. Carbonylation/decarbonylation

The decarbonylation reaction of the tert-butyl acylcation has been studied by Hogeveen, Baardman and Rooibeek (1970) and Hogeveen and Roobeek (1970) for HF/SbF$_5$ and FHSO$_3$/SbF$_5$ superacidic media. Since the acidic solvent seems not directly involved in the reaction mechanism the results may be similar to those for the sulfuric acid solutions used in this study. They found that the carbonylation reaction is first-order with respect to the carbocation and the carbon monoxide concentration and the second-order rate constant for this reaction was found to be approximately $10^3$ (l/mol s) for tertiary carbocations (293 K). The carbonylation equilibrium constant was found to be on the order of $10^3$–$10^4$ (l/mol) at 293 K. It is stressed again, that these results mentioned hold explicitly for the conditions used by Hogeveen and coworkers, and it is uncertain if these results also hold for the sulfuric acid catalyst system.

2.3. Hydration of the acylcarbocation and deprotonation of protonated carboxylic acids

For these reactions no kinetic rate data have been reported for sulfuric acid solutions. Deno et al. (1964b) studied these equilibria in sulfuric acid solutions for acetic acid, propionic acid and isobutyric acid. From these results it is likely that pivalic acid is protonated and only partly dehydrated in 80–96 wt% H$_2$SO$_4$ solutions.
This is supported by solubility measurements of pivalic acid in sulfuric acid solutions (Brilman, 1998).

2.4. Other reactions

Next to the above described reactions the formation of oligomers, alkylsulfuric acids and esters of isobutanol and sulfuric acid may occur. Esters of isobutanol with sulfuric acid were found to disappear rapidly in excess sulfuric acid (Deno and Newman, 1950; Tian, 1950). Due to the excess sulfuric acid used, esterification is probably of minor importance. Since the reactions in the Koch reaction mechanism are reversible, a minor amount of olefinic components may be present in the acid solution (Deno, 1964b), leading to polymerization reactions. For the addition of butanols or isobutene to sulfuric acid solutions it is well known that oligomeric products (dimers, trimers and tetramers of isobutene) will be formed in 75–85 wt% sulfuric acid solutions. The dimers and higher oligomers thus formed will lead to higher molecular weight carboxylic acids via the basic reaction steps discussed above. It will be clear that C_9 and C_{13} isomeric acids are the primary products in this case. Isobutene trimer cations and higher (\( \geq C_{12} \)) can undergo additionally \( \beta \)-scission and other disproportionation reactions, leading to fragments other than C_4 and -oligomers. Under certain conditions (poor mixing, low-CO pressure, etc.) an impressive diversity of products can be obtained.

Deno, Boyd, Hodge, Pittman and Turner (1964a) identified the products formed by the \( \tau \)-butyl cation in 96 wt% sulfuric acid solutions in the absence of carbon monoxide. Under these conditions 50% of the reactant was converted to stable polyalkylcyclopentyl cations (PACP) and 50% to an immiscible alkane fraction. The reaction rate of the formation of the stable PACP cations was found to be second order in the tert-butyl cation concentration, and thus favored by high local concentration of the tert-butyl cations. For isobutene, trimethylpentenes and 1- and 2-butanol in 96 wt% acid solutions the same products were found. Other side reactions which may occur include alkyl sulfate formation, sulfonation (at higher temperatures and acidities) and carbonization of the hydrocarbons used. These side reactions will be more pronounced at higher acid concentrations and higher temperatures.

From the overview presented above, it can be concluded that the reaction kinetics for the systems considered are not uniquely determined and even the rate-determining step is not clear on beforehand. By varying process parameters as CO partial pressure, temperature and catalyst composition the reaction system will be analyzed.

3. Experimental work

The experimental set-up is shown schematically in Fig. 2. The high-pressure autoclave was usually operated semi-batch wise. The Büchi™ reactor (0.51 Hastelloy C-22 stainless steel) could be pressurized up to 60 bar and was equipped with a gas-inducing, 6-blade Rushton-type stirrer and a baffle mounted on the deckle. To minimize mass transfer limitations and inhomogeneities during the kinetic experiments with isobutanol the stirrer speed was chosen relatively high at 1800 rpm.

Prior to an experiment, the thermostated reactor was filled with 400 g of the sulfuric acid catalyst solution. The solution was degassed by applying vacuum while stirring. The injection vessel was filled with isobutanol. The reactor was pressurized via a pressure reducer at the desired
reaction pressure via the bypass line. The bypass line is closed (the reactor is now operated fully batch wise) and the gas inducing stirrer is started. From these physical absorption experiments the CO solubility as well as the volumetric gas–liquid mass transfer parameter, $k_{l,a}$, can be determined. After this, the reactor pressure was reduced by 1.5 bar to create a pressure drop over the injection vessel. Data acquisition and stirring is started again. Both valves of the injection vessel were opened and the carbon monoxide flow is used to inject the reactant. Injection of the reactant is usually accomplished within 4 s (for 8 g of isobutanol). Pressure is now maintained at the desired reactor pressure (± 0.01 bar) by a pressure regulating system. Temperature and pressure of both the reactor and the CO supply vessel are recorded continuously. If the CO consumption ends, data acquisition is stopped. From the pressurized reactor a sample of about 100 g from the reaction mixture is directly quenched on 200 g of icewater under vigorous stirring. After this, the reactor pressure is relieved, the reactor is emptied and cleaned several times with water, once with acetone, dried and closed under a nitrogen atmosphere.

For the tert-butanol experiments the feed rate was found to be important (Brilman, 1998). The experiments with the immiscible heptane phase were done using the injector for injection of the tert-butanol reactant at low feedrates where the product yield did not longer depend on the tert-butanol feed rate.

3.1. Analysis of reaction products

The sample (≈ 100 g) of the reactor contents, quenched on icewater (≈ 200 g), was extracted in four steps with about 60 g of heptane (99.9%+, Merck, pro analyses). The organic layer was analyzed by gas chromatography using a Varian 3400 GC (FID detector, 250°C injection- and 300°C detection temperature, DB-FFAP column 30 m × 0.258 mm, 0.25 μm film, split injection (1:100), He or N$_2$ carrier gas). Column temperature was kept for 1 min at 120°C and then increased with 10°C/min–240°C, where it was maintained for about 20 min. The organic layer was titrated with a 0.01 M NaOH solution to determine the total concentration of weak acids. No sulfuric acid was found in this layer for the experiments using the 96 wt% H$_2$SO$_4$ catalyst, but some H$_2$SO$_4$ was found in experiments at 85 wt%. Further, a sample of the quenched product (before extraction) was titrated on total weak acids. The consumption of carbon monoxide during the reaction was recorded and used for the reaction kinetics as well as calculation of the total amount of CO containing products (acids) formed. The acid yield reported in this work refers to the molar ratio of the total amount of acids formed to the total amount of butanol injected.

4. Results

Apparent reaction kinetics for isobutanol were evaluated from the pressure–time ($P$–$t$) recordings as the CO consumption rate could be followed conveniently. In studying the effect of the carbon monoxide partial pressure and the reaction temperature the initial catalyst composition and amount of isobutanol injected was kept constant. The kinetic rate experiments were conducted at 278–320 K and at 5–60 bar carbon monoxide partial pressure. The reaction was found to be first-order in the isobutanol concentration. The absence of influence of CO pressure on the apparent first–order reaction rate constant suggests that CO is not involved in the rate-determining step. In two other series of experiments at 10 and 40 bar CO the reaction temperature was varied and from an Arrhenius plot an apparent activation energy of 85 (± 5) kJ/mol was obtained. In Fig. 3a the effect of the initial acid strength on the apparent first-order reaction rate constant $k_{\text{app}}$ is presented for experiments at constant temperature and CO pressure, but with varying acid concentration. From gas–liquid mass transfer experiments an apparent volumetric mass transfer coefficient of 0.2 (1/s) was obtained, indicating that gas–liquid mass transfer is not limiting in these experiments. The amount of CO dissolved physically in the catalyst solution (thus already present in the catalyst solution before isobutanol injection) is sufficient for approximately 10% conversion of the injected reactant at the standard set of conditions (8.3 g of isobutanol in 210 ml catalyst solution). For tert-butanol it was only possible to follow the CO consumption rate due to reaction at relatively low acid concentrations; 80–85 wt% H$_2$SO$_4$. At higher acid concentrations the rate of dehydration was too fast to be followed by CO consumption. The results are summarized in Fig. 3b.

The Ho value of the catalyst solution is rather sensitive to the water content of the solution, but when the reaction of isobutanol to pivalic acid is complete no net consumption or production of water occurs. However, also the reactant isobutanol and the product pivalic acid may influence the acidity of the catalyst solution. Therefore, experiments in which the amount of isobutanol was varied and experiments in which pivalic acid was initially present in the catalyst solution have been been conducted. In Fig. 4 the results of experiments with different amounts of pivalic acid present in an initially 96 wt% sulfuric acid solution are presented.

Considering the strong influence of the Hammet acidity function (Fig. 3a) and of the presence of pivalic acid on the CO consumption rate (Fig. 4), it was speculated that the addition of pivalic acid may cause a significant drop in the acidity of the catalyst solution. This was confirmed by the experimental results of UV experiments determining the Hammet acidity function for aqueous sulfuric acid solutions with and without the addition of pivalic
acid. With these measurements it was shown that the addition of pivalic acid reduced the Hammett acidity of the catalyst solution more strongly than an equimolar amount of water (Brilman, 1998). For the range of acid strengths investigated (70–90 wt%) the change in Hammett acidity could be related to the pivalic acid content according to:

\[ \Delta \text{Ho} \approx 0.08 \cdot (\text{wt\% pivalic acid}). \] (1)

A further validation of this was obtained by performing a set of kinetic experiments with a fixed amount of isobutanol at different initial acid concentrations and with different amounts of pivalic acid initially present. For the catalyst solutions loaded with initially present pivalic acid the Ho value of these solutions was calculated using Eq. (1), leading to the results in Fig. 5.

In Fig. 5 also a single data point is included in which another tertiary carboxylic acid, 2,2 dimethyl butanoic acid (C₆ acid), is used instead of pivalic acid, showing that the effect observed seems not to be restricted to pivalic acid only. The effect of the isobutanol concentration on the (apparent) Ho value was studied by performing experiments with different amounts of catalyst solution and
isobutanol. At molar ratios $\text{H}_2\text{SO}_4$: isobutanol $> 25$ the apparent reaction rate constant was no longer dependent on this ratio. This condition was satisfied for the kinetic experiments described above.

Apparently, the acidity of the catalyst solution is the main parameter determining the overall reaction kinetics for the Koch synthesis of pivalic acid, but this acidity is rather sensitive to the catalyst solution composition.

4.1. Reaction products

For the experiments with isobutanol a relatively clean reaction product was obtained, consisting of, primarily, pivalic acid and 2-methylbutanoic acid (less than 20% at 96 wt% to almost none at 82 wt% as main byproduct). In general, the selectivity to pivalic acid increases with decreasing acidity, increasing CO pressure and lower temperatures. In one experiment samples were taken...
during reaction and they showed that the 2-methylbutanoic acid content increased, thus suggesting that this component is produced slowly e.g. at the hydrolysis of butanol–sulfuric acid esters. On analysing ‘the reaction products’ after adding pivalic acid to sulfuric acid under CO pressure, no other components than pivalic acid were found. The amount of byproducts may increase significantly if (local) CO depletion can occur. This was illustrated by a single experiment in which the stirrer was started 25 s after isobutanol injection. In that case a wide variety of acids and cracking products was obtained.

With tert-butanol the product composition was found to depend on operating conditions, especially at high acid concentrations. Next to pivalic acid, especially C_9 acids stemming from the isobutene dimer, but also C_6–C_8 acids ( > C_9) were found. The amount of byproducts may increase significantly if (local) CO depletion can occur. This was illustrated by a single experiment in which the stirrer was started 25 s after isobutanol injection. In that case a wide variety of acids and cracking products was obtained.

4.2. Effect of a second liquid phase

With tert-butanol experiments were conducted with a 96 wt% H_2SO_4 catalyst solution. Under these conditions the dehydration is much faster than gas–liquid mass transfer and local CO depletion near the reactant inlet may occur. Since the product distribution obtained was found to depend strongly on CO pressure, stirring rate and reactant injection rate (Brilman, 1998), it can be concluded that the carbonylation reaction and the oligomerisation reactions are fast. The initial dehydration step may be still rate determining in this case, but the availability of CO in the reaction zone near the inlet of tert-butanol will then determine the selectivity obtained.

The experiments were performed at low injection rates where the acid yield is no longer a function of the injection rate. It can be seen in Fig. 6 that in this case the acid yield increases with increasing heptane fraction. Experimental checks on the inertness of heptane in this system have been carried out. It was therefore concluded that the heptane phase will probably enhance the product yield by increasing the local CO concentration in the reaction zone. This can be done either by transport of CO to the reaction zone near the feed inlet or, alternatively, by picking up reactant at the feed inlet and redistributing this throughout the whole vessel. An alternative explanation, assuming an increase of the local turbulence in the liquid–liquid dispersion, is not very likely (Brilman et al., 1999).

The effect of the presence of a heptane phase in the reactor was also studied for sulfuric acid solutions of 85 wt% loaded with 12 wt% of pivalic acid. For these catalyst solutions and using tert-butanol as reactant an apparent rate constant k_0 of 4.3 × 10^{-4} (1/s) was found. The addition of 33 vol% of heptane (based on the total liquid phase mixture) increased the k_0 value to 6.6 × 10^{-4} (1/s). The extraction of pivalic acid to the organic phase therefore adds to maintaining a high catalyst activity. This effect will be even stronger for higher molecular weight carboxylic acids which are more easily extracted from the catalyst solution.

5. Discussion

In determining the reaction kinetics for the synthesis using isobutanol as reactant it was found that especially the catalyst solution acidity determines the CO consumption rate. The presence of isobutanol and pivalic acid influence the solution acidity considerably and it is important in determining the reaction kinetics to recognize these influences on the apparent reaction kinetics. Since the reaction kinetics depend strongly on the Hammett acidity function for the catalyst solution, the effect of temperature on the solution acidity should be considered. Using the results of Johnson, Katritzky and Shapiro (1969) an apparent activation energy of −36 kJ/mol is obtained, due to the temperature dependence of −Ho only, thus implying that the activation energy for the intrinsic first-order reaction (in isobutanol) is approximately 120 kJ/mol.

Since in the kinetic experiments both the reactant, isobutanol, and the main reaction product, pivalic acid, affect the (apparent) Hammett acidity of the catalyst solution, the solution acidity is changed marginally during the course of the reaction in the kinetic experiments. It can be estimated that the net effect on the overall reaction rate constant for CO consumption is not more than 20% for experiments in this work. Since it appears that CO is not involved in the rate-determining step, the dehydration of isobutanol or the hydrolysis of intermediate alkylsulfuric acids are the main options for the rate-determining step in the reaction mechanism. When the results obtained in this study are compared to those
presented in literature, see Fig. 3b, it is obvious that the slope of the \( \log k_{ov} - \text{Ho} \) line differs from those obtained in the other studies, which may indicate that the reaction occurs via another reaction mechanism. The slope of the \( 10^\log(k_{ov}) - \text{Ho} \) plot (\( \approx 0.75 \)) agrees with the results of Deno and Newman (1950) for the rate of sulfation of 1- and 2-butanol, where a corresponding value of 0.8 is found. Although it is uncertain if the same slope should be expected for the hydrolysis of alkylsulfates.

6. Conclusions

Pivalic acid can be produced from isobutanol using sulfuric acid as a catalyst solution without many byproducts. The major byproduct is 2-methylbutanoic acid, if gas–liquid mass transfer limitations are excluded. The selectivity towards 2-methylbutanoic acid is generally less than 20% and decreases strongly with decreasing acidity. The reaction is first order in isobutanol and dehydration is likely to be rate determining. The presence of pivalic acid and isobutanol strongly reduces the apparent reaction rate constant by decreasing the solution acidity. For the industrially applied backmixed reactors in the Koch synthesis, this may imply that these operate at much lower values for Ho.

Preliminary work in studying the effects of mass transfer and mixing in the Koch synthesis of pivalic acid using tert-butanol has been performed. It was found that the presence of an immiscible heptane phase does not help to maintain a high catalyst activity by extracting carboxylic acids from the catalyst solution, but also improves the product yield, presumably by facilitating CO transport to the reaction zone. Additional work is, however, required.

Notation

- **Ho**: Hammett acidity function
- **\( k_{ov} \)**: overall first-order reaction rate constant, 1/s
- **\( k_La \)**: volumetric gas–liquid mass transfer coefficient, 1/s
- **\( \phi \)**: volume fraction heptane in the liquid–liquid dispersion (Fig. 6), dimensionless

7. For further reading

The following references are also of interest to the reader: Boyd et al. (1960), Chwang et al. (1977) and Deno et al. (1965).

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