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Reaction from Dimethyl Carbonate (DMC) to Diphenyl Carbonate (DPC). 2. Kinetics of the Reactions from DMC via Methyl Phenyl Carbonate to DPC

J. Haubrock,^{*,†} W. Wermink,[†] G. F. Versteeg,^{†,‡} H. A. Kooijman,[‡] R. Taylor,[‡] M. van Sint Annaland,[†] and J. A. Hogendoorn[†]

Department of Science and Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands, and Department of Chemical and Biomolecular Engineering, Clarkson University, Potsdam, New York 13699-5705

The kinetics of the reaction of dimethyl carbonate (DMC) and phenol to methyl phenyl carbonate (MPC) and the subsequent disproportion and transesterification reaction of methyl phenyl carbonate (MPC) to diphenyl carbonate (DPC) have been studied. Experiments were carried out in a closed batch reactor in the temperature range from 160 to 200 °C for initial reactant ratios of DMC/phenol from 0.25 to 3 and varying catalyst (titanium-*n*-butoxide) concentrations. The concept of a closed, ideally stirred, isothermal batch reactor incorporating an activity based reaction rate model has been used to fit kinetic parameters to the experimental data taking into account the catalyst concentration, the initial reactant ratio DMC/phenol and the temperature.

1. Introduction

Diphenyl carbonate is a precursor in the production of polycarbonate (PC) which is widely employed as an engineering plastic in various applications basic to the modern lifestyle: in electronic appliances, office equipment, and automobiles, for example. About 2.7 million tons of PC are produced annually, a figure that is expected to increase by 5–7% yearly up to at least 2010.¹

Traditionally, PC is produced using phosgene as an intermediate. This process suffers from a number of drawbacks: a 4 ton portion of phosgene is needed for the production of 10 tons of PC; phosgene is very toxic, and when it is used, the formation of undesired salts cannot be avoided; and the process uses 10 times as much solvent (on a weight basis) as PC produced. The solvent, methylene chloride, is suspected to be carcinogenic, and it is soluble in water. This results in a large amount of wastewater that has to be treated prior to discharge.²

Many attempts have been made to overcome the disadvantages of the phosgene-based process.³ The main focus has been a route that produces diphenyl carbonate (DPC) via dimethyl carbonate (DMC), which then reacts further with bisphenol-A to form PC. The critical step in this route is the synthesis of DPC from DMC that takes place via a transesterification reaction to methyl phenyl carbonate (MPC), usually followed by a disproportionation and/or transesterification step to DPC. However, in a batch reactor with an equimolar feed, an equilibrium conversion to MPC of only about 3% can be expected. Therefore, creative process engineering is required to successfully carry out the reaction of DMC to DPC on a commercial scale.

To make viable the process from DMC to DPC, the conversion of DMC to the intermediate MPC has to be substantially increased. As one of the reaction products, methanol in this case, is the most volatile component in the mixture, it might be attractive to use reactive distillation to remove methanol directly from the reaction zone to enhance

the conversion of DMC toward MPC. A reactive distillation process to produce DPC would need to be operated as close to chemical equilibrium as possible in order to achieve the highest possible conversion of the reactants toward DPC. This, in turn, requires the reactions to proceed sufficiently fast. To assess whether reactive distillation is an attractive process alternative to improve the conversion of DMC toward MPC, it is essential to know how fast chemical equilibrium can be achieved, as this determines the required residence time in the reaction zone and, hence, also the dimensions of the equipment.

In this paper, we present reaction rate data for the conversion of DMC to DPC at different initial molar ratios of DMC/phenol in the temperature range between 160 and 200 °C. In addition, an activity-based reaction rate model is employed to model the experimental data, with the reaction rate constants being the actual fit parameters. The required activity coefficients as applied in the reaction rate model are estimated with the UNIFAC group contribution method.⁴

2. Reactions

The synthesis of diphenyl carbonate (DPC) from dimethyl carbonate (DMC) and phenol takes place through the formation of methyl phenyl carbonate (MPC) and can be catalyzed either by homogeneous or heterogeneous catalysts. The reaction of DMC to DPC is a two-step reaction. The first step is the transesterification of DMC with phenol to the intermediate MPC and methanol (see Scheme 1).^{2,5}

For the second step two possible routes exist: the transesterification of MPC with phenol (see Scheme 2) and the disproportionation of two molecules of MPC yielding DPC and DMC (Scheme 3).

According to Ono,² side reactions also may occur (see Scheme 4). For this kind of reaction system, anisole is the main byproduct, which can be formed from DMC and phenol through methylation.

3. Catalysts

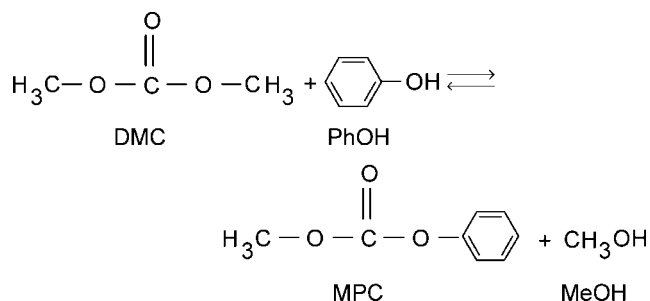
Numerous catalysts are known to promote common transesterification reactions. Nevertheless, many of these catalysts are not suitable for the transesterification of DMC to DPC as they

* To whom correspondence should be addressed. Phone: +49-2365-49-2261. Fax: +49-2365-49-802261. E-mail: j.haubrock@alumnus.utwente.nl.

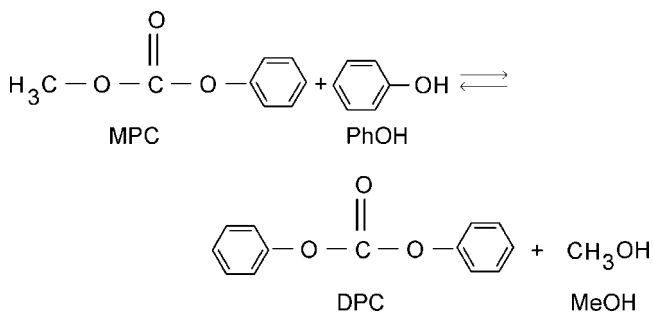
[†] University of Twente.

[‡] Clarkson University.

Scheme 1. Transesterification 1



Scheme 2. Transesterification 2



also catalyze the decarboxylation to anisole.² First, it has to be decided whether a heterogeneous or homogeneous catalyst is preferred.

In industrial use, heterogeneous catalysts usually are considered to be more desirable than homogeneous catalysts because of the ease of separation and regeneration of the catalyst.⁶ Most of these catalysts are supported metal oxides, such as MoO₃ on silica. Ono² investigated different types of heterogeneous catalysts and showed that the selectivity of these catalysts for the reaction toward anisole is much higher than that of homogeneous catalysts where only traces of anisole were detected. As anisole formation should be avoided if at all possible, it was decided to adopt a homogeneous catalyst in this study.

Advantages of the use of homogeneous catalysts when doing kinetic experiments are as follows:

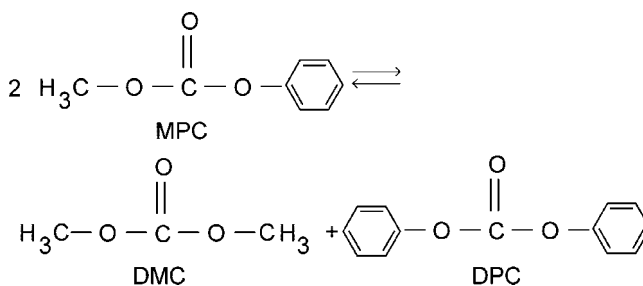
(1) Experimental results may be used directly to derive the kinetics. Mass transfer issues (e.g., diffusion limitations to/or inside the catalyst particles) might cloud the interpretation of experiments with heterogeneous catalysts.

(2) For the chemical system in this study, homogeneous catalysts are commercially available and hence no tailor-made manufacture of a supported heterogeneous catalyst is necessary.

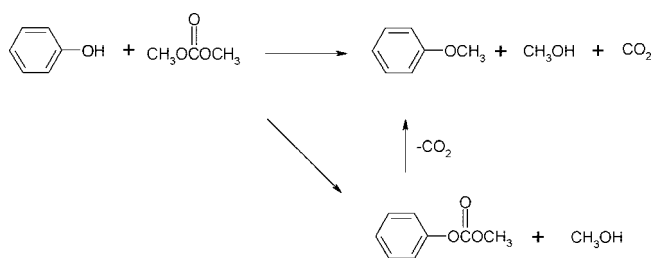
(3) The reproducibility of the kinetic experiments is better when utilizing a homogeneous, commercially available catalyst, as the grade of this kind of catalyst will change only marginally compared to tailor-made heterogeneous catalysts.

Shaikh and Sivaram⁷ studied the performance of various homogeneous catalysts for the reaction of DMC and phenol and the subsequent disproportionation of the intermediate MPC. The reaction was carried out under continuous removal of the methanol/DMC azeotrope, while the temperature of the reaction vessel was increased gradually from 120 to 180 °C. For the three tin-based catalysts, the authors reported yields of 41% and 44% for DPC and yields of MPC between 3% and 12% achieved in 24 h of reaction time. The two titanium-based catalysts exhibited yields between 27% and 33% for DPC and yields of 6% for MPC also achieved in 24 h reaction time.

Scheme 3. Disproportionation



Scheme 4. Side Reaction Forming Anisole, Methanol, and Carbon Dioxide



In another study, Fuming et al.⁸ presented a newly developed catalyst, namely Samarium-trifluoromethanesulfonate (STFMS) that was compared to a tin-based, a titanium-based, an aluminum-based and a zinc-based catalyst, respectively. The selectivity of the new STFMS catalyst toward DPC was between 2% (with respect to (wrt) the tin based catalysts) and 12% (wrt the zinc based catalyst) higher, respectively. The conversion that was achieved in 12 h with the new STFMS catalyst was 35%, which is close to the conversion that can be obtained with the zinc-based catalyst (37%) and the titanium-based catalyst (31%). The aluminum- and zinc-based catalysts exhibited conversions of DMC of less than 20% within 12 h of reaction time. It is worthwhile to mention that while employing the samarium-, aluminum-, and zinc-based catalysts, there was always a small amount of anisole formed which corresponded to roughly 1% of the converted DMC.⁸ Furthermore, it was reported that the DPC obtained when using the tin-based catalyst showed a grayish color due to the contamination with tin; this is undesirable if DPC is used as a precursor for polycarbonate production. All catalysts except the STFMS and the tin-based catalyst tend to hydrolyze in aqueous media. Thus, these catalysts cannot be utilized in aqueous environments and contact with air also should be avoided.

For this study, titanium-(*n*-butoxide) was used as catalyst. The selection for this catalyst is based on different considerations. A tin-based catalyst (*n*-Bu₂SnO) has been disregarded as the DPC made with this catalyst exhibits a grayish color,⁸ so that this catalyst does not seem suitable for the manufacture of polycarbonate without additional processing steps. AlCl₃ and ZnCl₂ have been disregarded as these catalysts are both susceptible toward water and thus tend to hydrolyze in the presence of aqueous media.⁸

To avoid the laboratory synthesis of a new catalyst and to eliminate the undesired formation of anisole, also the use of the samarium-trifluoromethanesulfonate (STFMS) has been rejected.⁸ The conversion rate of DMC as well as the selectivity toward MPC and DPC with the titanium-(*n*-butoxide) catalyst is close to that of the STFMS catalyst and the tin-based catalyst, and no noticeable anisole is formed.⁶ Therefore titanium-(*n*-butoxide) seems to be the most suitable catalyst to promote the reactions from DMC to DPC (see Schemes 1–3). All chemicals

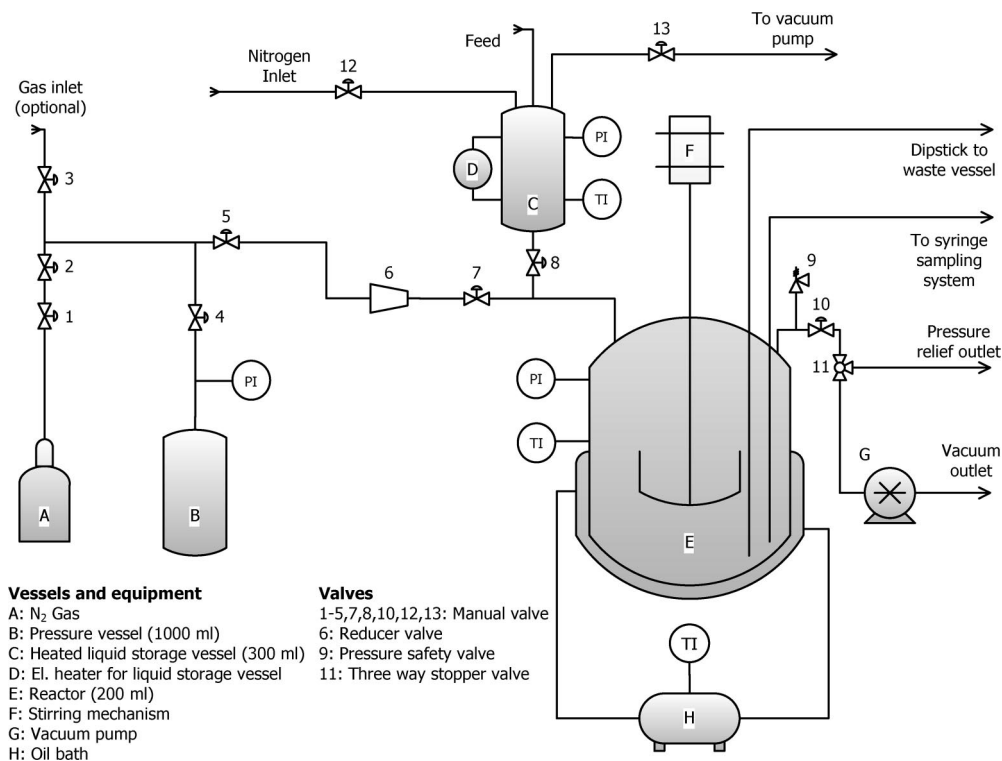


Figure 1. Experimental setup—closed batch reactor with supply vessel containing DMC.

used were either water free or contained only traces of water (e.g., phenol), which did not seem to affect the catalytic activity during the experiments.

4. Experimental Work

The main ingredients of the equipment used for the experiments, shown schematically in Figure 1, were a stainless steel reactor of 200 mL and a storage vessel of 300 mL. For a detailed description of the setup and the operation procedure, the reader is referred to part 1 of this series.⁹

To determine the reaction rate constants k_1 – k_3 (see eqs 6–8) from the experimental measurements, the question arises which key components should be used as indicator of the progress of the reaction. As the equilibrium conversion of the reactants phenol and DMC is less than 3%, it was decided not to use the concentration of either to determine the reaction rate parameters as the relative error would be large. Instead, the concentrations of the products, methanol, MPC, and DPC, respectively, were initially chosen as the key components. Eventually the use of methanol as key component also has been omitted as GC analysis of the reactant DMC showed that it contained always a small amount (<1 wt %) of methanol. Apart from that, methanol is also the most volatile component and a small part of it might evaporate to the gas phase (5% of the overall amount at V–L equilibrium), which would require an additional correction of the GC results of the liquid samples. For these reasons, also methanol was disregarded as a key component and only MPC and DPC have been taken as the key components for the determination of the reaction rate parameters. Nevertheless, the initial amount of methanol introduced with the reactant DMC has been taken into account in the analysis of the experimental data.

Experiments were carried out at temperatures of 160, 180, and 200 °C at different catalyst concentrations and DMC/phenol reactant ratios. The catalyst mole fractions x_{cat} added in the experiments varied between 1.0×10^{-4} and 4.5×10^{-4} . The

time to achieve equilibrium typically varied between 60 min for the lowest catalyst amount and 15 min for the highest catalyst amount (chemical equilibrium was judged to be reached when a plot of the concentration profile as a function of time leveled off). Additional experiments with mole fractions x_{cat} of around 1.5×10^{-3} have been carried out, which demonstrated that chemical equilibrium could be achieved in less than 5 min. This already indicates that the reaction can be quite fast, using reasonable amounts of catalyst. Some prior studies^{10,11} have reported reaction times of up to 20 h, but from our present perspective, such long times do not seem to be required.

To ascertain that the initial level of mixing did not influence the measurements, experiments with two different stirrer speeds (800 and 1600 rpm) have been carried out, while otherwise maintaining the same experimental conditions. At both stirrer speeds the measured conversion rates were identical within experimental uncertainty. We conclude that it is safe to assume that mixing is sufficient to justify adopting an ideally mixed reactor in order to model this process (see below).

The catalyst, titanium-(*n*-butoxide), tends to hydrolyze in the presence of water. To study the occurrence of any unwanted hydrolysis of the catalyst, several experiments with varying amounts of catalyst were carried out, while maintaining the same conditions (180 °C, reactant ratio phenol/DMC = 1, nitrogen atmosphere). No detectable traces of degradation products in the GC diagram were found, which seems to indicate that catalyst degradation does not occur or, if it does, only to a negligible extent.

All chemicals employed in the experiments were used as received from the supplier. Dimethyl carbonate (purity: 99+%) was purchased from Aldrich, phenol (99+%) and tetra-(*n*-butyl orthotitanate) (98+%) were acquired from Merck. The catalyst was stored over molecular sieves (type 4a) to prevent degradation due to moisture from air.

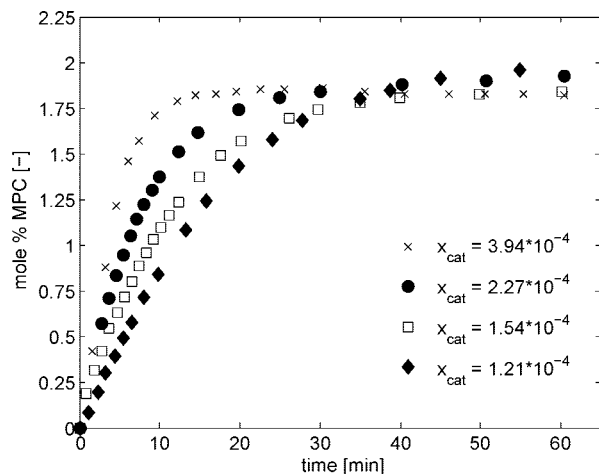


Figure 2. Dependence of the catalyst concentration on the temporal evolution of the MPC concentration ($T = 180\text{ }^{\circ}\text{C}$, molar ratio DMC/phenol = 1).

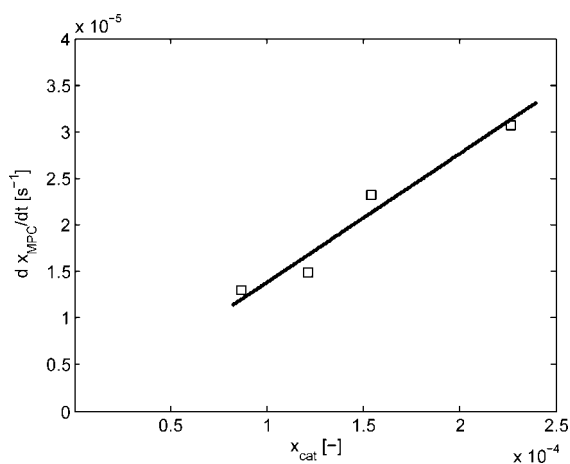


Figure 3. Dependence of the initial reaction rate of MPC on the catalyst mole fraction at $180\text{ }^{\circ}\text{C}$ and a DMC/phenol ratio of 1 (markers = initial slope of concentration vs time for MPC taken at low MPC yields; solid line = linear fit).

5. Effect of Catalyst Concentration

To investigate the extent to which the catalyst concentration influences the reaction rate, a series of experiments with relatively low catalyst mole fractions (1.0×10^{-4} and 2.5×10^{-4}) were carried out at identical initial concentrations of DMC and phenol and at the same temperature ($180\text{ }^{\circ}\text{C}$). The results of these experiments are shown in Figure 2, which suggest that the equilibrium concentration is reached in times that vary from around 15 min at the higher concentrations of catalyst to something just over an hour at the lower concentrations. It has also been confirmed by additional experiments at $180\text{ }^{\circ}\text{C}$ that in the absence of catalyst the MPC mole fraction reaches only 6% of the equilibrium mole fraction after 2 h.

The initial forward rate of reaction 1 can be obtained by differentiation of the data in Figure 2. The resulting linear fit $dx_{\text{MPC}}/dt|_{t=0} = 0.138x_{\text{cat}} [\text{s}^{-1}]$ derived from the slope of the fitted straight line shown in Figure 3, suggests that the initial rate of reaction is directly proportional to the amount of catalyst and that the initial reaction rate can be expressed in the form: $dx_{\text{MPC}}/dt|_{t=0} = x_{\text{cat}} k x_{\text{DMC}}^{\text{initial}} x_{\text{phenol}}^{\text{initial}}$. This kinetic expression is equivalent to assuming that an elementary irreversible reaction (reaction 1) is taking place. At low yields of MPC ($<1\%$), the equilibrium yield of MPC is only around 2%—it can be assumed that the

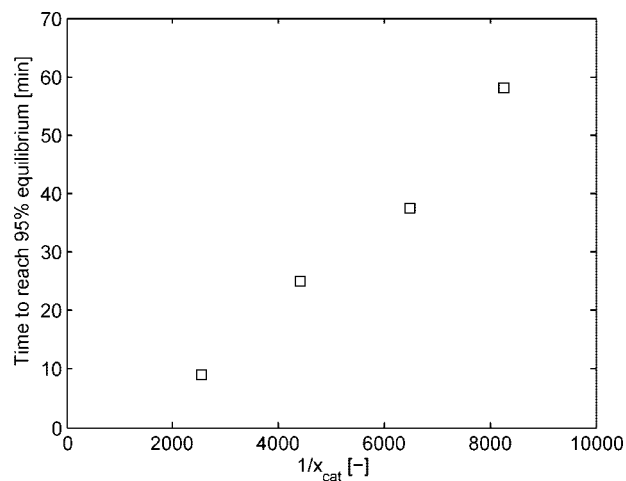


Figure 4. Time to reach 95% equilibrium versus the reciprocal catalyst mole fraction.

backward reaction rate of MPC with methanol is much lower than the forward reaction rate of DMC with phenol.

Figure 4 shows the time required to reach 95% of equilibrium as a function of the reciprocal amount of catalyst. At the highest catalyst mole fraction employed in the experiments (3.94×10^{-4}), the MPC mole fraction reached 95% of the mole fraction at chemical equilibrium after just 10 min (see Figure 4). This time increases to about 60 min for the lowest catalyst mole fraction (1.21×10^{-4}). This lends additional support to the notion that we can model this system with a linear dependence of the reaction rate on the catalyst mole fraction, not only for the initial phase of the conversion but over the entire time of these experiments where the backward reaction also becomes important.

6. Do Both Reactions, Transesterification 2 and the Disproportionation, Contribute to the DPC Formation?

To investigate whether or not the disproportionation reaction proceeds sufficiently fast, experiments were carried out with no reactive component other than MPC present. Solvents DMC and phenol were replaced by inert *n*-heptane. In the absence of phenol, MPC can only react to DPC via the disproportionation reaction and not at all via the transesterification reaction. Thus, if DPC is found within the usual time frame of an experiment, this should mean that the disproportionation reaction is able to proceed at an appreciable rate and must be considered in the analysis of the data. To determine the influence of *n*-heptane, an experiment with an equimolar ratio of DMC/PhOH, catalyst, and 50 mol% *n*-heptane was carried out. This experiment yielded the same results in terms of the chemical equilibrium constant and—corrected for the mole fractions of DMC and phenol—the same reaction rate as in the experiments without added solvent. We infer that it is likely that *n*-heptane does not influence the reaction rate in these experiments.

The results of the experiments with MPC dissolved in *n*-heptane indicate that DPC and DMC are formed at nearly the same rate (deviation $<10\%$). Furthermore, the amounts of DPC and DMC created are identical within experimental accuracy which supports the presumption that DPC and DMC are formed from MPC in equimolar amounts via the disproportionation reaction. Methanol is present only in trace amounts. This suggests that the formation of DPC is—under the present experimental conditions—not taking place via the transesterification of MPC and phenol.

7. Reaction Kinetics and Modeling

For a simple well-mixed batch reactor, the material balances for the five components in the liquid phase can be written as follows:

$$\frac{dx_{\text{MeOH}}}{dt} = R_1 + R_2 \quad (1)$$

$$\frac{dx_{\text{DMC}}}{dt} = R_3 - R_1 \quad (2)$$

$$\frac{dx_{\text{PhOH}}}{dt} = -R_1 - R_2 \quad (3)$$

$$\frac{dx_{\text{MPC}}}{dt} = R_1 - R_2 - R_3 \quad (4)$$

$$\frac{dx_{\text{DPC}}}{dt} = R_2 + R_3 \quad (5)$$

We propose that the rates of the three reactions (Schemes 1–3) can be expressed in the following form:

$$R_1 = k_1 x_{\text{cat}} \left(\gamma_{\text{PhOH}} x_{\text{PhOH}} \gamma_{\text{DMC}} x_{\text{DMC}} - \frac{1}{K_{a,1}} \gamma_{\text{MPC}} x_{\text{MPC}} \gamma_{\text{MeOH}} x_{\text{MeOH}} \right) \quad (6)$$

$$R_2 = k_2 x_{\text{cat}} \left(\gamma_{\text{PhOH}} x_{\text{PhOH}} \gamma_{\text{MPC}} x_{\text{MPC}} - \frac{1}{K_{a,2}} \gamma_{\text{DPC}} x_{\text{DPC}} \gamma_{\text{MeOH}} x_{\text{MeOH}} \right) \quad (7)$$

$$R_3 = k_3 x_{\text{cat}} \left(\gamma_{\text{MPC}}^2 x_{\text{MPC}}^2 - \frac{1}{K_{a,3}} \gamma_{\text{DMC}} x_{\text{DMC}} \gamma_{\text{DPC}} x_{\text{DPC}} \right) \quad (8)$$

In eqs 6–8, x_{cat} denotes the molar amount of catalyst, k_i the forward reaction rate constant of reaction i , x_j is the mole fraction of species j , γ_j the activity coefficient of species j , and $K_{a,i}$ is the corresponding activity based chemical equilibrium constant. A nearly identical approach has been applied by Steyer and Sundmacher¹² to describe the reaction rate of the esterification of cyclohexene with formic acid and subsequent splitting of the ester yielding cyclohexanol. As shown in Figure 2, the time taken to achieve chemical equilibrium depends strongly on the catalyst mole fraction used in the individual experiments; it seems therefore justified and necessary to account for the catalyst amount by the introduction of the catalyst mole fraction in the reaction rate equation. One should note that the results in Figure 2 do not imply that the catalyst activity coefficient can also be considered constant for all experiments (e.g., for different DMC/phenol ratios).

The activity based equilibrium constants of reactions 1–3 are given in eqs 9–11, with the overall chemical equilibrium coefficient defined by eq 12:

$$K_{a,1} = \frac{a_{\text{MPC}} a_{\text{MeOH}}}{a_{\text{DMC}} a_{\text{PhOH}}} \quad (9)$$

$$K_{a,2} = \frac{a_{\text{DPC}} a_{\text{MeOH}}}{a_{\text{MPC}} a_{\text{PhOH}}} \quad (10)$$

$$K_{a,3} = \frac{a_{\text{DPC}} a_{\text{DMC}}}{a_{\text{MPC}}^2} = \frac{K_{a,2}}{K_{a,1}} \quad (11)$$

$$K_{a,\text{ov}} = \frac{a_{\text{DPC}} a_{\text{MeOH}}^2}{a_{\text{DMC}} a_{\text{PhOH}}^2} = K_{a,1} K_{a,2} = (K_{a,1})^2 K_{a,3} \quad (12)$$

In the formulation of the reaction equilibrium equations, it has been assumed that reactions 1–3 represent elementary reaction steps. To justify this assumption, detailed knowledge

Table 1. Activity Based Equilibrium Constants of Reactions 1–3⁹

reaction	activity based equilibrium value $K_{a,i}$
1	$\ln K_{a,1} = -2702/T[K] + 0.175$
2	$\ln K_{a,2} = -2331/T[K] - 2.59$
3	$\ln K_{a,3} = \ln(K_{a,2}/K_{a,1})$

of the reaction mechanism is required that is not available in the open literature. On the basis of the satisfactory description of the chemical equilibrium found by Haubrock et al.⁹ by assuming elementary reactions, it seems reasonable to make the same assumption here. The relations for the activity based equilibrium values $K_{a,i}$ valid in the temperature range from 160–200 °C determined by Haubrock et al.⁹ are reproduced in Table 1.

In order to use $K_{a,i}$ values to predict the equilibrium composition, we need to know the activity coefficients, for which Haubrock et al.⁹ used the UNIFAC method. It proved to be necessary to introduce a new UNIFAC group, the carbonate group O–CO–O, which was not then part of the published UNIFAC database. The interaction parameters of this new OCOO group with other UNIFAC groups, which are of importance for the system presented here, were fitted to VLE data for phenol–DMC, methanol–DMC, methanol–diethyl carbonate (DEC), alkanes–DMC/DEC, alcohols–DMC/DEC, and toluene–DMC. For complete details, the reader is referred to the Ph.D. thesis of Haubrock.¹³

The temperature dependence of the reaction rate constants k_1 , k_2 , and k_3 is accounted for by using the Arrhenius equation (eq 13):

$$k_i = k_{0,i} \exp(-E_{A,i}/(R_{\text{gas}} T)) \quad (13)$$

There are, therefore, six parameters that need to be fitted to experimental data using eqs 1–13: the three pre-exponential factors $k_{0,i}$ and the three activation energies $E_{A,i}$. Our approach was to fit k_1 , k_2 , and k_3 for each temperature. An Arrhenius plot may then be employed to determine $k_{0,i}$ and $E_{A,i}$. The similarity of the reactions forming MPC and DPC by transesterification suggests that k_1 and k_2 will be in the same order of magnitude.

The influence of the catalyst amount on the reaction rate is accounted for via the catalyst mole fraction x_{cat} as a linear factor implemented in the reaction rate equations (eqs 6–8). However, this might not be sufficient as it is likely that not only the activity coefficients of the reactants and products change at different process conditions but also the activity coefficient of the catalyst (γ_{cat}). In eqs 6–8, it is implicitly assumed that the activity coefficient of the catalyst γ_{cat} is constant and, therefore, independent of the liquid phase composition. If this assumption is not justified, the rate constants (k_1 , k_2 , and k_3) will probably vary with composition as the influence of the “nonconstant” catalyst activity coefficient is in this case lumped into the optimized rate constants. Hence, in the interpretation of the experiments, k_1 , k_2 , and k_3 will be optimized for each experiment conducted at a specific DMC/phenol reactant ratio. The optimized values of k_1 , k_2 , and k_3 will subsequently be compared to the optimized results of experiments at other DMC/phenol reactant ratios.

The batch reactor model neglects mass transfer from the liquid phase (where the reaction takes place) to the gas phase; even for the most volatile component methanol, exploratory VLE calculations have indicated that at gas–liquid equilibrium about 95% of the amount of methanol formed will remain in the liquid phase (volume ratio liquid/gas phase = 3:1). For the less volatile components, this percentage is near 100%. It should be noted that in case of an open system, as for example in a reactive

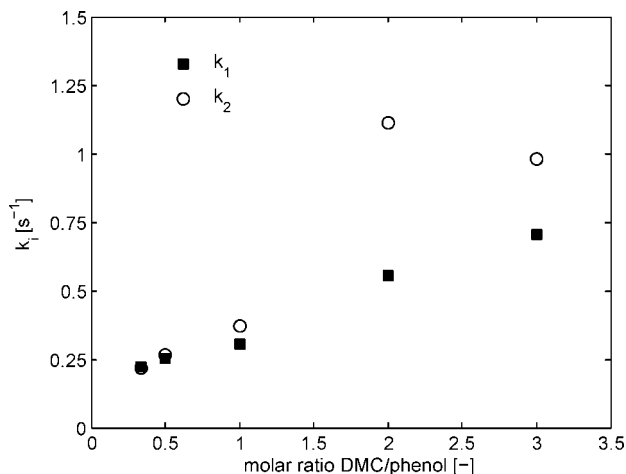


Figure 5. Reaction rate constants k_i as a function of the initial reactant ratio DMC/phenol ($T = 160\text{ }^\circ\text{C}$).

distillation column, especially methanol would steadily evaporate from the liquid phase and mass transfer to the gas phase should be taken into account.

8. Estimation of Rate Constants

Physically meaningful estimates as well as the likely range of values of the reaction rate constant k_1 were estimated from the initial slopes of the mole fraction-time curve of MPC applying the following equation $dx_{\text{MPC}}/dt|_{t=0} = x_{\text{cat}}kx_{\text{DMC}}^{\text{initial}}x_{\text{phenol}}^{\text{initial}}$. As already discussed, at low conversions (yield MPC $\sim 1\%$), the reverse reaction is not important and the estimation of k_1 is straightforward. The MPC mole fractions used for the estimation of k_1 were not corrected by the amount of DPC formed from MPC as the amount of MPC which reacts further to DPC is less than 2 mol % under the conditions investigated here.

The reaction rate constants of the first and second transesterification reaction k_1 and k_2 as well as the reaction rate constant of the disproportionation reaction k_3 have been optimized by fitting the theoretically predicted temporal evolution of the mole fractions of MPC and DPC (eqs 4 and 5). The actual fitting of the rate coefficients was carried out using the simulation environment gProms. The objective function minimized by gProms was

$$\Phi = \frac{N}{2} \ln(2\pi) + \frac{1}{2} \min \left\{ \sum_{k=1}^{N_E} \sum_{j=1}^{N_{V_k}} \sum_{m=1}^{N_{M_{kj}}} \left[\ln(\sigma_{kjm}^2) + \frac{(\tilde{\chi}_{kjm} - \chi_{kjm})^2}{\sigma_{kjm}^2} \right] \right\} \quad (14)$$

9. Effect of the Reactant Ratio DMC/Phenol

The results of the optimization are summarized for k_1 and k_2 in Figure 5 ($160\text{ }^\circ\text{C}$) and Figure 6 ($180\text{ }^\circ\text{C}$) and for k_3 in Figure 7 (160 and $180\text{ }^\circ\text{C}$). The average deviations between the experimental and predicted values of the mole fractions were less than 10% for MPC and less than 15% for DPC in the 95% confidence interval, respectively. In the case of very low experimental MPC and DPC mole fractions, usually observed at DMC/phenol reactant ratios larger than two, the deviation between a single experimental and predicted mole fraction can amount at most up to 15% for MPC and 30% for DPC, respectively.

This clearly shows that the experimental set of data can be used reliably to determine k_1 whereas the k_2 and k_3 values

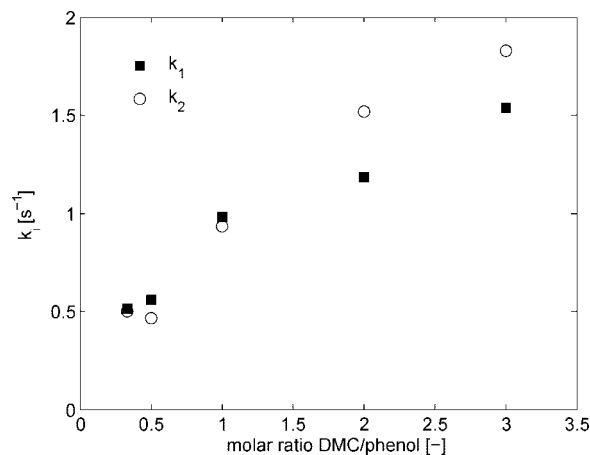


Figure 6. Reaction rate constants k_i as a function of the initial reactant ratio DMC/phenol ($T = 180\text{ }^\circ\text{C}$).

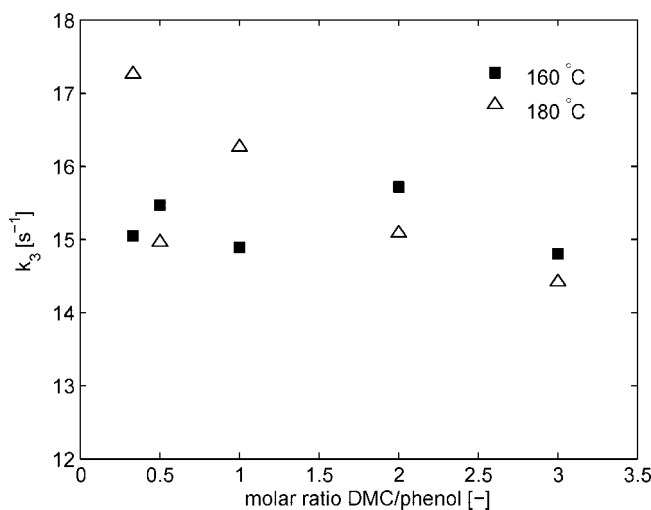


Figure 7. Reaction rate constants k_3 as a function of the initial reactant ratio DMC/phenol.

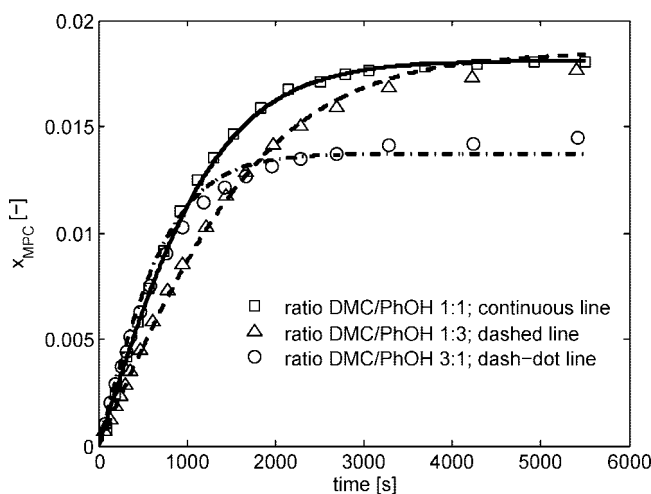


Figure 8. MPC mole fraction as function of time for different initial DMC/phenol reactant ratios ($T = 180\text{ }^\circ\text{C}$): markers experimental data; continuous line, model.

determined with the same experiments exhibit a somewhat larger deviation between the experimental and model predicted values of the mole fractions. However, the description of the experimental mole fractions of DPC is still good (see Figure 9) and the larger uncertainty in k_2 and k_3 does not yield a very large

scatter when the individually determined values of k_2 and k_3 are plotted against the DMC/phenol ratio (see Figures 5–7). The larger uncertainty in k_2 and k_3 is probably due to the very low amounts of DPC formed in our experiments.

To obtain even more accurate data for k_2 and k_3 , it would be necessary to carry out experiments under continuous removal of methanol. Exploratory experiments with MPC as starting component have shown that significantly larger amounts of DPC can be achieved; the absence of methanol means that the backward reaction of DPC with methanol to MPC is suppressed. The setup used in this study (Figure 1) does not allow for a “reactive-distillation-like” mode where methanol is evaporated at a specified pressure or temperature, respectively. Moreover, a mass transfer model would be needed, to interpret this kind of experiments and that would require physical property data (e.g., k_L values, diffusion coefficients, etc.) that are not known. For these reasons, experiments under continuous removal of methanol were not included within the scope of this study. The values of k_2 and k_3 determined in this study should, therefore, be handled with some care, if used for completely different conditions.

Figures 5 and 6 suggest that a linear relationship between the initial reactant ratio DMC/phenol and the reaction rate coefficients k_1 and k_2 , respectively, can be deduced. The reaction rate constant k_3 of the disproportionation reaction is not influenced by the DMC/phenol ratio (Figure 7), and this might be attributed to different reaction mechanisms of the disproportionation reaction and the transesterification reactions. The scatter of the k_3 values is around $\pm 10\%$ (see Figure 7), which corresponds to the experimental uncertainty of the DPC mole fractions used for the fitting of the reaction constant k_3 .

Figure 6 shows that the fitted reaction rate constants k_1 and k_2 (180 °C) have nearly the same value (within $\pm 15\%$ on average). The deviation between the k_1 and k_2 (160 °C) values shown in Figure 5 is larger—on average $\pm 35\%$ —which is mainly due to the comparatively large k_2 value at a DMC/phenol ratio of 2. From Figures 5 and 6, it can be concluded that the values of the kinetic constants k_1 and k_2 are similar and—for DMC/phenol ratios < 1 —nearly identical. Considering the very similar reactions, it could have been expected that also the reaction mechanism is identical and the kinetic rate similar which is supported by the nearly identical reaction rate constants.

In view of the fact that activity coefficients of all reactants and products were included in the model, we would hope that “nearly” constant values of the reaction rate constants might have been expected on purely fundamental grounds. This is obviously not the case for k_1 and k_2 (see Figures 5 and 6). There seem to be two possible reasons: it might be that either one or more of the activity coefficients are inaccurate or that the catalyst activity changes with the DMC/phenol ratio. A previous study on the equilibria of reactions 1–3 has shown that the activity coefficient of DMC, important in the proper determination of k_1 , might be prone to error because the equilibrium value of the first transesterification reaction showed some variation ($\pm 20\%$) with the DMC/phenol ratio. As depicted in Figures 5 and 6, k_1 changes by approximately a factor of 3 and it does not seem likely that an inaccuracy in the activity coefficient can be held responsible for the shifting value of k_1 .

Accordingly, the linear increase of k_1 most probably has to be attributed to a change in the activity of the catalyst. In which case, it is also likely that k_2 will be affected in the same way as k_1 ; the two transesterification reactions are similar and we would expect that both reactions should be affected to a comparable extent by a change in the catalyst activity. Although the linear

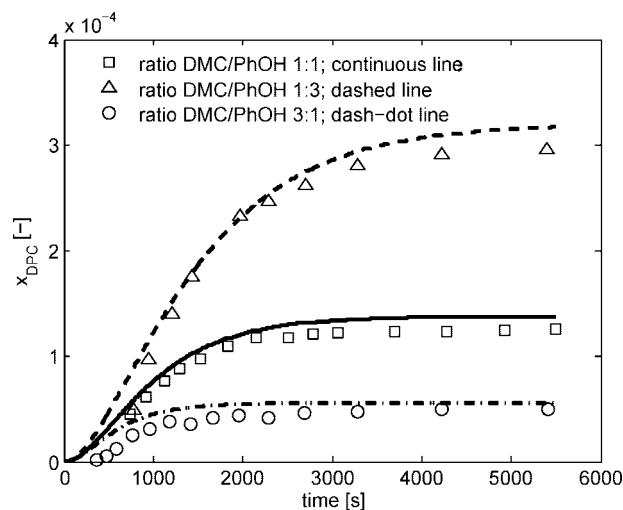


Figure 9. DPC mole fraction as function of time for different initial DMC/phenol reactant ratios ($T = 180$ °C): markers, experimental data; continuous line, model.

relationship of k_2 on the DMC/phenol ratio seems to suggest this fact, it cannot be concluded beyond a reasonable doubt because of the larger uncertainty in the individual k_2 values.

Nevertheless, a possible change of the catalyst activity with a change of the DMC/phenol ratio is not unlikely, considering the interaction of the in situ formed Ti-catalyst with the reactant phenol. Assuming that one or more of the four butoxide ligands of the titanium-(*n*-butoxide) catalyst have been substituted by phenol,¹⁴ the in situ formed titanium(phenoxide) catalyst is likely to show a substantial interaction with phenol. As the activity coefficient of phenol changes with a change of the DMC/phenol ratio, the activity of the catalyst is likely to change accordingly. There is no detailed information in the literature on the activity of the titanium(phenoxide) catalyst as a function of the composition of the mixture, and the present experiments also do not provide enough information to unambiguously establish any such dependence; thus, the influence of the reactant ratio of DMC/phenol on the catalyst activity can only be hypothesized. In order to establish the activity of the catalyst as a function of composition, an extensive study including various vapor–liquid–equilibrium (VLE) experiments with changing DMC/phenol ratios and catalyst concentrations would have to be carried out to determine the interactions between the catalyst and the various species in the system. Moreover, the interpretation of this kind of experiments is complicated by the fact that the species in the system are chemically reacting.

Looking again at Figures 5–7 and comparing the values of k_3 to those of k_1 and k_2 , it can be seen that the reaction rate constant k_3 is 1 order of magnitude larger than the values for k_1 and k_2 . This indicates that the disproportionation reaction is intrinsically faster than the two transesterification reactions; this is in agreement with the literature.¹⁵ Since there is normally an excess of phenol in these experiments, the formation rates of DPC by the second transesterification and the disproportionation reaction, respectively, are of the same order of magnitude. However, in industrial processes and at high reactant conversions, the concentration of phenol might be much lower and MPC much higher than in this study, so that the disproportionation reaction may be the main route of MPC to DPC; this should be kept in mind when scaling up the process.

Typical results of some experiments at different reactant ratios together with the accompanying theoretical predictions are given in Figures 8 and 9 using the individual fitted reaction rate

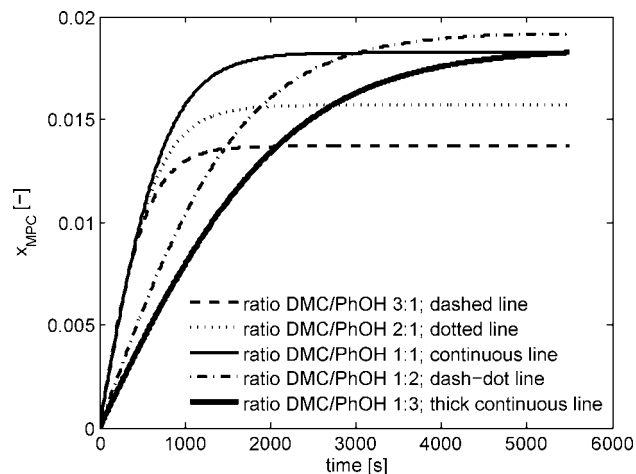


Figure 10. Model prediction: MPC mole fraction as a function of time for different initial reactant ratios of DMC/phenol at 180 °C ($x_{\text{cat}} = 1.50 \times 10^{-4}$).

constants k_1 , k_2 , and k_3 (Figures 5–7) and activity based equilibrium constants $K_{a,i}$ at nearly identical catalyst amounts ($8.4 \times 10^{-5} < x_{\text{cat}} < 1.7 \times 10^{-5}$). It can be seen that the experimental MPC and DPC mole fractions are well in line with the model predictions when using the individual fitted reaction rate constants k_1 , k_2 , and k_3 for the appropriate reactant ratio DMC/phenol. This suggests that the proposed reaction rate model is well suited to reproduce the experimental results.

Since the experiments as depicted in Figures 8–9 were carried out at slightly varying catalyst mole fractions ($8.4 \times 10^{-5} < x_{\text{cat}} < 1.7 \times 10^{-5}$), the reaction rates determined from the individual experiments cannot directly be compared to each other. However, the individually fitted k_1 , k_2 , and k_3 values as given in Figures 5–7 can be used with the batch reactor model to simulate the concentration–time profiles scaled to the same catalyst mole fraction (eqs 4 and 5) thereby excluding the effect of the catalyst amount on the reaction rate and making it possible to investigate the corresponding reaction rates at various DMC/phenol ratios. In Figure 10, the course of the MPC mole fraction versus time for different DMC/phenol ratios using a catalyst amount of $x_{\text{cat}} = 1.50 \times 10^{-4}$ is shown and it can be seen that DMC rich reactant mixtures (DMC/phenol ratio > 1) have only a slight influence on the formation rate of MPC, whereas in phenol rich reactant mixtures (DMC/phenol ratios < 1), the reaction rate of MPC slows down considerably. The time to reach equilibrium roughly doubles for phenol rich reactant mixtures.

As the same amount of catalyst is used in the simulations shown in Figure 10, the different reaction rates can either be attributed to changing activity coefficients of the involved species or to a varying catalyst activity. The product of the activity coefficients of DMC and phenol, $\gamma_{\text{DMC}}\gamma_{\text{PhOH}}$, changes only about 10% over the entire range of employed DMC/phenol ratios and can, therefore, not be held responsible for the slower reaction rates observed for reactant ratios less than 1. This supports the hypothesis that a varying catalyst activity is indeed responsible for the change in the reaction rate.

10. Effect of Temperature

An Arrhenius plot (Figures 11 and 12) may be used to determine the pre-exponential factor $k_{0,i}$ and the activation energy $E_{A,i}$ of the three reactions (see eq 13) from linear regression. The results of such a calculation are summarized in Table 2.

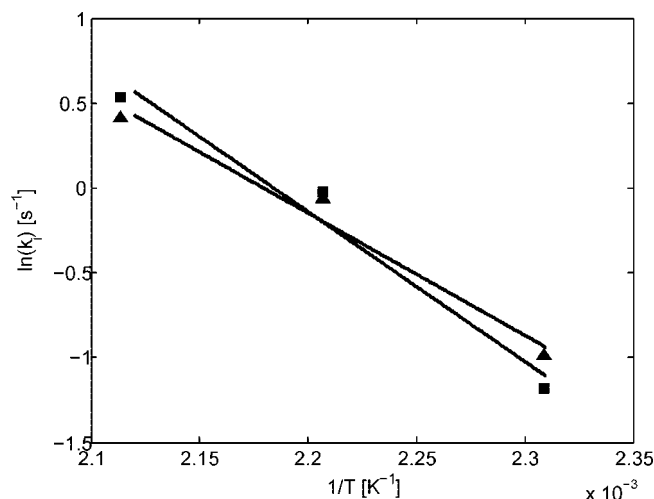


Figure 11. Arrhenius plot. Markers indicate fitted k_i values derived from kinetic experiments ($T = 160\text{--}200$ °C; 1:1 DMC/phenol ratio): transesterification 1 (squares) and transesterification 2 (triangles).

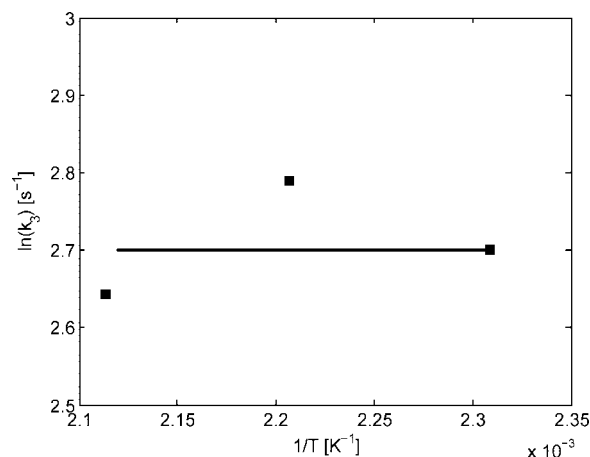


Figure 12. Arrhenius plot. Markers indicate fitted k_3 values from kinetic experiments ($T = 160\text{--}200$ °C; 1:1 DMC/phenol ratio).

Table 2. Values of the Pre-exponential Factor $k_{0,i}$ and the Activation Energy $E_{A,i}$ (Derived from Regression Lines in Figures 11 and 12, Respectively)

reaction	$k_{0,i}$ [s^{-1}]	$E_{A,i}$ [kJ mol^{-1}]
trans 1 ($i = 1$)	2.42×10^8	73.5
trans 2 ($i = 2$)	6.61×10^6	59.9
disprop ($i = 3$)	14.88	

In Figure 11, the Arrhenius plots of k_1 and k_2 and the corresponding fitted k_i values in the temperature range between 160 and 200 °C are shown. As already mentioned earlier, the two transesterification reactions seem to have the same reaction mechanism and the numerical values of the reaction rate constants derived from the experiments are similar. Hence, it could be expected that the temperature dependence of the two reaction rate constants k_1 and k_2 (Figure 11) would yield similar activation energies. The Arrhenius plot of k_3 and the corresponding fitted k_3 values in the temperature range between 160 and 200 °C are depicted in Figure 12. The disproportion reaction exhibits no significant temperature dependence—the scatter shown in Figure 12 is within the experimental error margin.

11. Conclusion

In this study, the reaction rate constants of the transesterification reaction of DMC with phenol yielding the intermediate

MPC, the reaction rate constants of the consecutive transesterification reaction of MPC with phenol, and the reaction rate constants of the disproportionation of MPC have been experimentally determined in a batch reactor.

The influence of the catalyst concentration (titanium-(*n*-butoxide)) and the temperature on the reaction rate constants in the temperature range between 160 and 200 °C has been investigated as well as the influence of the initial reactant ratio of DMC/phenol. The concept of a closed, ideally stirred, isothermal batch reactor incorporating an activity based reaction rate model, has been used to fit the values of the three reaction rate constants k_1 , k_2 , and k_3 to the experimental data.

The numerical values of the fitted reaction rate constants k_1 and k_2 are found to be similar whereas the numerical value of k_3 , belonging to the disproportionation reaction, is about 1 order of magnitude larger. Moreover, it was shown that the reaction rate constants of the two transesterification reactions (k_1 and k_2) are strongly influenced by the initial reactant ratio of DMC/phenol which was attributed to inaccuracies in the activity coefficients and to a changing catalyst activity. Nevertheless, the change of the reaction rate constants over the initial reactant ratio of DMC/phenol by a factor of 3 is too large to be caused only by flawed activity coefficients. Therefore, it is likely that the activity coefficient of the catalyst changes over the initial reactant ratio of DMC/phenol. However, at the moment this can only be regarded as a hypothesis as no detailed information of the catalyst activity is available. Additional VLE experiments should be carried out to determine the interactions between the catalyst and the other involved species yielding the activity coefficient of the catalyst to confirm the aforementioned hypothesis.

Experiments have shown that it seems necessary to remove methanol from the reaction mixture for two reasons: First, the removal of methanol increases the conversion of DMC and phenol thereby promoting the formation of the intermediate MPC via transesterification 1. Second, in the absence of methanol the disproportionation of MPC will contribute to the overall conversion of MPC to DPC as the backward reactions of transesterification 1 and 2, respectively, are suppressed. Therefore, the removal of methanol is important to achieve a selectivity toward DPC that is viable for industrial processes.

Reactive distillation might be used on an industrial scale not only to allow for higher conversions of the reactants but also for a higher selectivity toward the desired product DPC. It is expected that the correlations presented in this paper could be used in the modeling of reactive distillation processes for the industrial relevant system presented in this work.

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Notation

a_j = activity of component j (–)
 $E_{A,i}$ = activation energy of reaction i (kJ mol⁻¹)
 $k_{0,i}$ = pre-exponential factor of reaction i (s⁻¹)
 $K_{a,i}$ = activity based equilibrium coefficient of reaction i (–)
 k_i = reaction rate constant of reaction i (s⁻¹)
 N = total number of measurements taken during all experiments (–)

N_E = number of experiments performed (–)
 $N_{M_{k,j}}$ = number of measurements in the j th mole fraction in the k th experiment (–)
 N_{V_k} = number of variables measured in the k th experiment (–)
 R_{gas} = ideal gas constant (kJ mol⁻¹ K⁻¹)
 R_i = reaction rate of reaction i (s⁻¹)
 T = temperature (K)
 t = time (min or s)
 x_j = mole fraction of component j (–)
 $\tilde{x}_{k,j,m}$ = m th measured value of mole fraction j in experiment k (–)
 $x_{k,j,m}$ = m th predicted value of mole fraction j in experiment k (–)
 γ_j = activity coefficient of component j
 $\sigma_{k,j,m}^2$ = variance of the m th measurement of mole fraction j in experiment k (–)

Indices
 cat = catalyst (–)
 i = reaction i (–)
 j = component j (–)
 k = experiment k (–)
 m = measurement m (–)

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