



Verkade super base-catalysed transesterification of propylene carbonate with methanol to co-produce dimethyl carbonate and propylene glycol

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ABSTRACT

The co-generation of dimethyl carbonate (potential fuels additive, environmentally friendly replacement for more toxic methylating agents, etc.) and propylene glycol via the transesterification reaction of propylene carbonate and methanol was studied using base catalysis. Verkade super bases (proazaphosphatranes) proved especially effective at low catalyst loadings (0.5%) for the rapid transesterification of propylene carbonate with methanol under mild conditions and with high product selectivity (typically >99.5%). These bases neatly avoid the use of alkoxide catalysts which generate by-products in their neutralisation. The kinetics of the reactions were studied using data obtained from *in situ* NMR reaction monitoring. The influences of several reaction optimisation parameters are also dealt with.

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1. Introduction

Dimethyl carbonate (DMC) is a key industrial commodity chemical of low toxicity [1] that is readily biodegradable into innocuous materials [2] and is overall viewed as an environmentally friendly compound. It is useful as a methylating agent (replacing dimethyl sulfate and methyl iodide) [3] and may be used in organic transformations [4], replacing toxic phosgene in carboxylation [5] and carbonylation reactions [6]. DMC also provides a viable alternative to oxygenated solvents such as acetates, ketones and esters in many applications [7]. It is also seen as a viable option in oxygenate fuel additives [1], amongst others for its physical properties such as high oxygen content and water miscibility.

Of the three major processes for the production of DMC, the first involves the oxidative carbonylation of methanol (ENIChem) in the presence of CuCl as a catalyst [8]. The second is the two-step UBE process [9] in which methanol reacts with oxygen and NO in the presence of PdCl₂ as catalyst to form methyl nitrite and water in the first step. The second step involves carbonylation of methyl nitrite to form DMC, regenerating NO in the process. The third approach, which is applicable to the present study, is also a two-step procedure involving the insertion of carbon dioxide into epoxides to form a cyclic carbonate (typically propylene carbonate or ethylene carbonate) [10] and subsequent transesterification with methanol

(Scheme 1) in the presence of basic or acidic catalysts to generate the desired DMC. Base catalysts have been shown to be more effective for the latter process [11], but Lewis acids are also known esterification mediators [12]. Chitosan-supported ammonium salts have also recently been applied to this transformation [13] with some success.

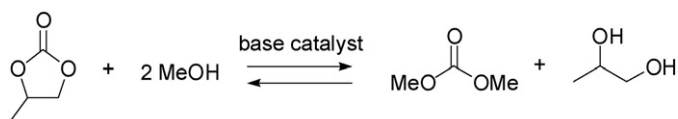
Recently developed advanced materials such as organic super bases have not been applied to the second transformation (cyclic carbonate + MeOH → DMC + glycol) in the CO₂-consuming epoxide-based route mentioned above. That route allows ready access to diol-derived carbonates and accordingly formed the basis of the present study, which has potentially important industrial applications. We report the use of commercially available non-ionic proazaphosphatranes super bases (Verkade bases) [14] (**1a–c**) as highly effective catalysts at low catalyst loadings (<1%) for the transesterification of propylene carbonate with methanol to yield DMC and propylene glycol (PG). Such bases have been previously used at high catalyst loadings (10–15%) to effect simple transesterification reactions with good results [15].

2. Experimental

Reagents were obtained from commercial sources and used as received. All samples were analysed using gas chromatography (GC), employing a computer loaded with Class-VP software for recording and processing of chromatograms. A free fatty acid (FFAP) analytical column (50 m, internal diameter 0.2 mm) was utilised together with a flame ionisation detector (FID). Nuclear magnetic

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Scheme 1. Transesterification of propylene carbonate into dimethylcarbonate.

resonance (NMR) spectroscopy using a Varian 400 MHz NMR spectrometer was applied to confirm the structures of the carbonates. The spectra were recorded in CDCl_3 at room temperature with TMS as internal standard. NMR-based reactions were performed in CD_3OD using a 600 MHz Unity Inova NMR instrument.

2.1. Catalysis and optimisation protocol

The base-catalysed reactions were carried out in a Parr 200 mL autoclave batch reactor. For example, propylene carbonate (44.39 g, 0.420 mol) and methanol (55.60 g, 1.73 mol) were weighed into the reactor vessel, after which the reactor was assembled and heated to the operating temperature with constant stirring (900 rpm). Upon reaching the reaction temperature, the catalyst, e.g. tri-*iso*-butyl proazaphosphatane base (3.596 g, 10.5 mmol), dissolved in methanol (10.0 mL) was added into the reaction mixture using a sample bomb pressurised with N_2 gas, this moment being set as time 0. Samples were taken at regular intervals for GC analysis. The reaction parameter optimisation studies were carried out in a similar manner, except that a glass reactor set-up was used, i.e. a 500 mL round bottom flask, fitted with a reflux condenser with the catalyst being introduced into the reactor using a syringe.

2.2. NMR-based reactions for kinetics studies

The NMR spectroscopy-analysed reactions catalysed by proazaphosphatanes and TBD were conducted in a 600 MHz Unity Inova NMR instrument in which temperature probe was set to, for example, 30 °C. TBD (0.21 g; 1.48 mmol) was dissolved in CD_3OD (10.68 g; 296.1 mmol) in a 10 mm NMR tube, whereafter propylene carbonate (PC) (0.41 g; 4.02 mmol) was added into the NMR tube. Spectra were recorded at 5 min intervals to monitor the depletion of PC and the formation of PG.

2.3. Modelling of kinetics studies

All modelling calculations were performed on a standard personal computer running Microsoft Excel Solver, using the following approach:

At time 0, $n_{\text{PG},0}$ = initial number of mols of propylene glycol.
 From the reaction and experimental data, at time x ,
 $\Delta n_{\text{PG}} = n_{\text{PG},x} - n_{\text{PG},0}$
 Thus, $n_{\text{MeOH},x} = n_{\text{MeOH},0} - 2 * \Delta n_{\text{PG}}$ and n_{PC} and $n_{\text{DMC}} = \Delta n_{\text{PG}}$
 Thus, for time $x + 1$, $\Delta n_{\text{PG},x+1} = n_{\text{PG},x+1} - n_{\text{PG},x}$

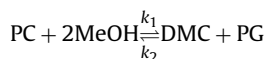
Accordingly, $n_{\text{MeOH},x+1} = n_{\text{MeOH},x} - 2 * \Delta n_{\text{PG},x+1}$ and $n_{\text{PC},x+1}$ and $n_{\text{DMC},x+1} = \Delta n_{\text{PG},x+1}$. Using n we can therefore calculate [PG] etc. for all time periods.

To determine k_1 and K_{eq} values, a k_1 -value was assumed and an initial estimate for K_{eq} calculated from the final experimental concentrations. Then using Eq. (2) and k_1 and K_{eq} , r was calculated and the concentrations predicted.

By using all experimental data and an iterative solution technique (Newton) [Excel Solver] a best-fit value for k_1 and K_{eq} could be found.

The kinetics of reactions catalysed by **1c** was determined making use of the NMR-derived data. The overall transesterification

reaction between propylene carbonate and methanol is a reversible reaction at each step, which can be represented overall as follows:



At equilibrium the rate of the forward reaction is equal to the rate of the reverse reaction and the equilibrium constant K_{eq} is defined by

$$K_{\text{eq}} = \frac{[\text{PG}][\text{DMC}]}{[\text{PC}][\text{MeOH}]^2} \quad (1)$$

Taking the elementary reactions into account, i.e. (1) PC to the half ester and (2) the half ester to DMC, the rate of formation of DMC can be represented by the equation:

$$r_{\text{DMC}} = k_1[\text{PC}][\text{MeOH}]^2 - k_2[\text{DMC}][\text{PG}]$$

and at equilibrium by

$$K_{\text{eq}} = \frac{[\text{PG}][\text{DMC}]}{[\text{PC}][\text{MeOH}]^2} = \frac{k_1}{k_2}$$

which reduces to

$$r_{\text{DMC}} = k_1 \left([\text{PC}][\text{MeOH}]^2 - \frac{1}{K_{\text{eq}}} [\text{DMC}][\text{PG}] \right) \quad (2)$$

The reaction is second order with respect to methanol and first order with respect to PC.

K_{eq} was calculated using the end of run concentrations. Since $[\text{DMC}] = [\text{PG}]$, Eq. (1) can be rewritten to give

$$K_{\text{eq}} = \frac{[\text{PG}]^2}{[\text{PC}][\text{MeOH}]^2} \quad (3)$$

Because each mole of DMC formed consumes two moles of MeOH, the molar concentration of MeOH was calculated using the initial molar concentration of CD_3OD added to the NMR tube together with the amount of DMC formed.

3. Results and discussion

3.1. Organic- and super base-catalysed reactions: catalyst selection and reaction optimisation

At the outset, a number of catalysts (Fig. 1) were tested against each other (Table 1), including proazaphosphatanes **1a–c**, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 1,4-diazabicyclo[2.2.2]octane (DABCO) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Metal alkoxide bases such

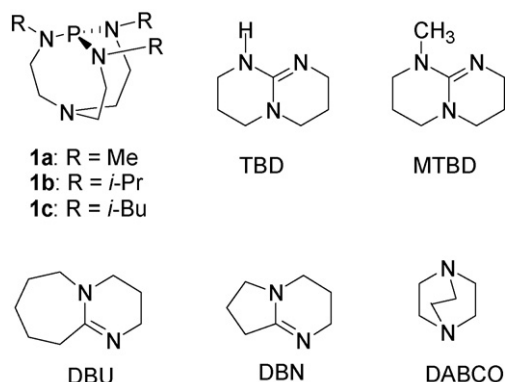


Fig. 1. Strong organic base catalysts.

Table 1
Propylene carbonate transesterification using basic catalysts (2 mol%).

Catalyst	T (°C)	Yield (%) ^a	TOF ^b	pK _a
DABCO	120	74	600	8.7 [17]
DBN	80	74	200	13.8 [18]
DBU	80	75	1800	14.3 [19]
NaOH	120	75	97	15.7 [20]
LiOMe	80	78	2400	17.0 [21]
MTBD	80	75	2100	17.9 [21]
TBD	80	77	2600	21.0 [19]
NaOMe	80	77	2500	22.1 [22]
1a	80	70	2000	32.90 [23]
1b	80	71	2200	33.63 [23]
1c	80	71	2500	33.53 [23]

^a The selectivity of all reactions was >99.5%, as determined by GC-FID analysis.

^b TOF is the turn over frequency as a measure of rate (mol prod/mol cat/h).

as LiOMe and NaOMe [16] were employed as benchmark base catalysts for comparative purposes. The reactions were performed in a 200 mL Parr batch reactor set-up, employing a methanol to propylene carbonate mole ratio of 15:1 and a catalyst loading of 2.0 mol% relative to PC.

Table 1 shows that the rate of the reaction somewhat follows the pK_a trend, but is not strictly linked to this characteristic, probably also being influenced by steric bulk of the base catalyst. It is immediately evident that the stronger nitrogen bases performed approximately as well (based on turn over frequency) as the more generally used, but corrosive, alkoxides. It is also clear that the reactions had all approximately reached equilibrium, the position of which would be determined primarily by the relative ratios of PC and MeOH. As a consequence, we investigated the influence of this ratio on the outcome of the reaction, in the process also investigating other parameters such as temperature and catalyst loading, the results of which are presented below, making use of Verkade base **1c** as catalyst.

While investigating to role of methanol/propylene carbonate ratio at 45 °C using a catalyst loading of 0.5 mol% (Fig. 2) it became clear (1) that the rate of the reaction is somewhat retarded at increasing MeOH/PC ratios, presumably by virtue of a dilution effect of PC and the catalyst and (2) that the position of the equilibrium reacts positively to increasing MeOH/PC ratios up to 15:1, whereafter any benefits of higher ratios become marginal. To counteract the diminished rate, a run at a MeOH/PC ratio of 20:1 was performed using 1 mol% of the catalyst **1c**, affording a much-improved reaction from the perspective of rate. Indeed, this particular reaction was complete within approximately 15 min (Fig. 2).

Temperature (45 °C and 100 °C) was found to substantially influence the rate of the reaction (MeOH/PC 15:1, 0.5 mol% catalyst) while having a minor influence on the equilibrium position (Fig. 3). Subsequent reactions were carried out at the higher of the two temperatures.

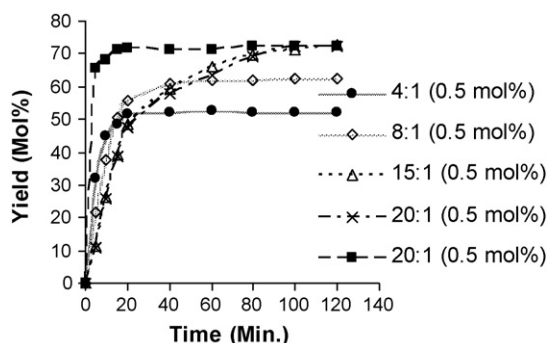


Fig. 2. Influence of MeOH/PC ratio at 45 °C (0.5 mol% **1c**).

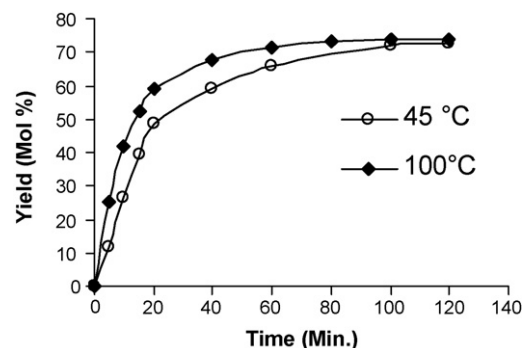


Fig. 3. Influence of temperature on reaction rate (MeOH/PC 15:1, 0.5 mol% **1c**).

Catalyst loadings greater than 0.5 mol% led to extremely rapid reactions (MeOH/PC ratio of 15:1, 100 °C, Fig. 4). For example, the reaction was complete with 10 min at a catalyst loading of 2 mol%, and within 15 min at catalyst loadings of 1.5 mol% or 1 mol%. In all cases, selectivity for the desired products was >99.5% as determined by GC-FID. These findings indicate this chemistry to be potentially useful for rapid batch-type transesterification reactions using **1c** as a catalyst (1–2 mol% loading), at 100 °C reaction temperature and using a MeOH/PC ratio of 15:1. It is quite possible that this reaction would be applicable to immobilised versions of **1c** and its analogues [24], which have shown great success and very high activity as recyclable transesterification catalysts in the generation of biodiesel from soybean oil, and of TBD (see Table 1), allowing access to a continuous reactor set-up.

3.2. NMR studies and kinetics

NMR spectroscopy was used to provide *in situ* analytical data with the view to obtaining useful kinetics information for reactions performed in an NMR tube. For this purpose, **1c** and TBD (found to be active catalysts during the autoclave studies, see Table 1) were used to promote the reaction in deuterated methanol (CD₃OD) as solvent. This solvent was used to simplify the spectra and facilitate accurate interpretation of the data. Accordingly, the only species visible in the ¹H NMR spectra were PC (substrate) and PG (by-product); the depletion of the PC and the formation of PG were monitored over time. The relative amounts of methanol and DMC were calculated using stoichiometric ratios.

The autoclave reactor experiments showed that high DMC yields and PC conversions could be obtained when the reaction was carried out 100 °C, with a catalyst loading of 0.5–1.0 mol% and employing a MeOH/PC ratio of 15:1. The NMR-based reactions could

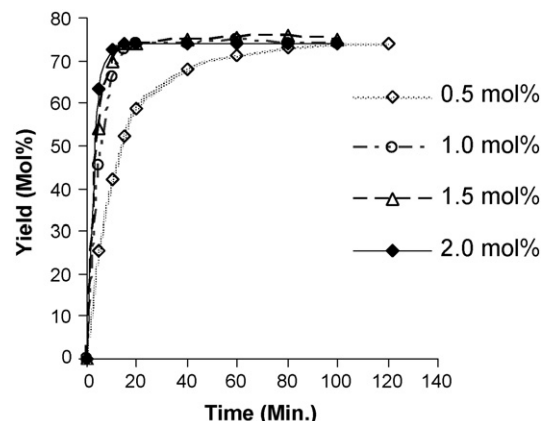


Fig. 4. Influence of catalyst **1c** loading (MeOH/PC 15:1, 100 °C).

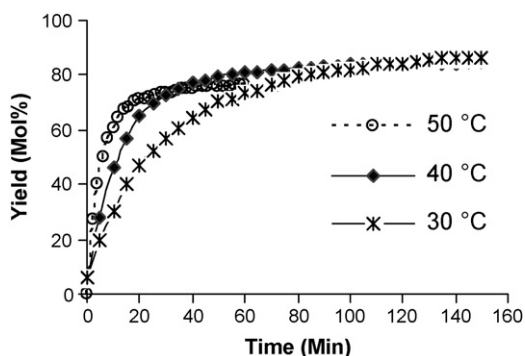


Fig. 5. NMR data for reactions catalysed by **1c** (0.5 mol% **1c**, MeOH/PC 15:1).

not be performed at temperatures above 60 °C, due to the high rate of the reaction and the relatively slow data acquisition speed with NMR spectroscopy. Therefore, these reactions were performed at 30 °C, 40 °C and 50 °C instead in the presence of only 0.5 mol% catalyst in order to provide sufficiently slow reactions suitable to monitoring by NMR spectroscopy (Fig. 5).

A clear increase in the rate of reaction with increasing temperature was noted (Fig. 5), as anticipated, with no significant change in equilibrium conversion, correlating well with the autoclave studies (Fig. 4 versus Fig. 5). The results from both techniques showed equilibrium yields of 70–80 mol% under similar reaction conditions (MeOH/PC 15:1, 0.5 mol% catalyst). The NMR data indicated a slight temperature dependence by the equilibrium conversion, lower temperatures favouring slightly higher yields at equilibrium.

With TBD as catalyst (MeOH/PC 15:1, 0.16 mol% loading, Fig. 6) the reactions reached equilibrium conversions of about 85%. The large dependence by the reaction rate on temperature as anticipated was again observed.

The NMR spectroscopy-derived data (Fig. 5) were used to determine the kinetics of reactions catalysed by **1c**. To model the system accurately it is necessary to determine both the reaction constant k_1 and the equilibrium constant K_{eq} . K_{eq} can be calculated from standard-state data (i.e. where data are collected under standard-state conditions). The change in the free energy of a system that occurs during a reaction can be measured under any set of conditions. If the data are collected under standard-state conditions, the result is the *standard-state free energy of reaction* (ΔG^0), given by the equation $\Delta G^0 = -RT \ln K_{eq}$ which can be rewritten as $K_{eq} = e_{-(\Delta G^0/RT)}$. However, reliable data for the current system are not available. Since both k_1 and K_{eq} needed to be determined, the system was modelled and both values were solved by iterative evaluation (see Sections 2.2 and 2.3).

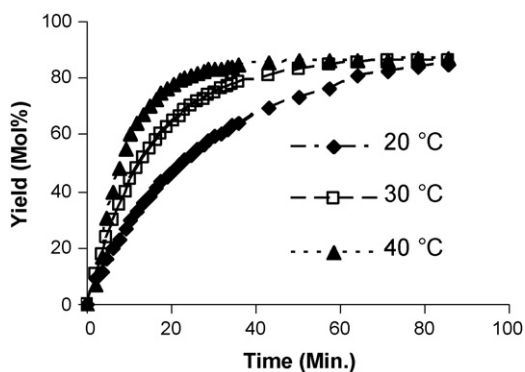


Fig. 6. TBD catalysis versus temperature (0.16 mol% catalyst, MeOH/PC 15:1), NMR studies.

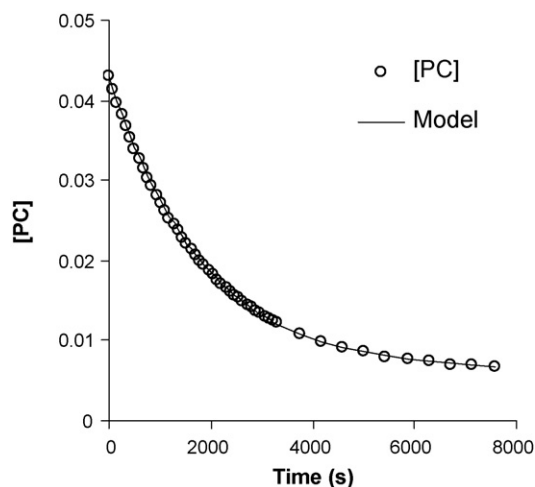


Fig. 7. [PC] versus reaction time at $T = 293$ K (calculated and recorded).

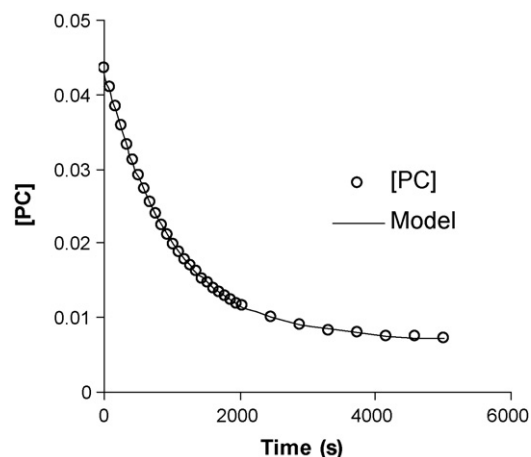


Fig. 8. [PC] versus reaction time at $T = 303$ K (calculated and recorded).

The reaction rates were calculated (20 °C = 293 K, 30 °C = 303 K, 40 °C = 313 K) with respect to the depletion of PC. The differences between the theoretical and experimental data with regard to the depletion of PC were calculated, and the k_1 constant was fitted for each temperature to minimise the differences. A good correlation between the experimental data and the modelled data was obtained and these are plotted in Figs. 7–10.

From the above figures it is evident that the model fits the experimental values very well. In general the errors are well distributed about 0 and do not show any particular bias. The largest disparity occurs for $T = 313$ K in the early part of the reaction. Apart from these points, the average disparity between model and experiments is below 2%. The iteratively determined K_{eq} values are presented in Table 2.

A plot of the equilibrium constants versus temperature (in Kelvin) afforded a straight line with a slope that defines the equilibrium constant at any given temperature (Fig. 11). The high R^2 -value

Table 2
Equilibrium constants at different temperatures for the Verkade base **1c** catalysed reactions.

T (°C)	T (K)	K_{eq}
20	293	0.2934
30	303	0.2546
40	313	0.2125

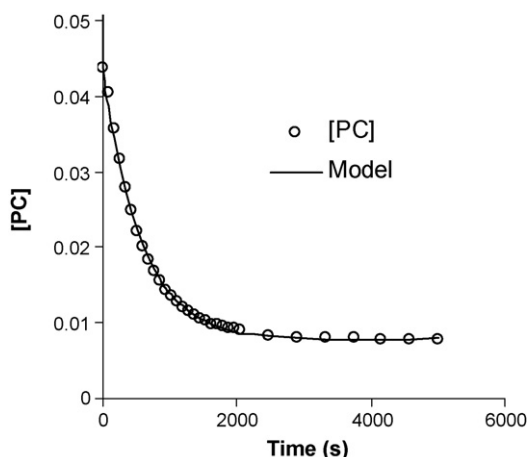


Fig. 9. [PC] versus reaction time at $T = 313$ K (calculated and recorded).

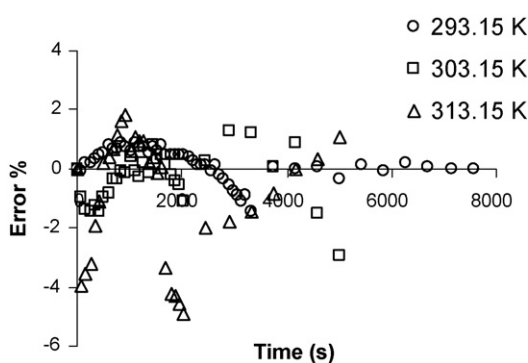


Fig. 10. Calculated errors in the model for three reaction temperatures.

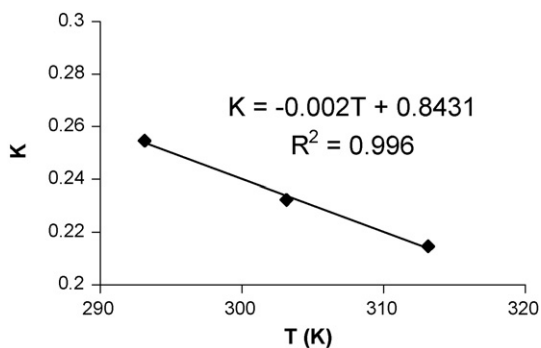


Fig. 11. Dependence of equilibrium constant on temperature.

(0.996) is indicative of a good fit between the data points calculated from the experimental data and the trend line fitted to the data.

The fitted k -values obtained from the model at different temperatures are shown in Table 3.

The rate constant can be expressed mathematically as a function of temperature according to Eq. (4) (Arrhenius equation) where k_0

Table 3
Calculated k -values.

T (K)	$1/T$ (K^{-1})	k (mol K^{-1})	$\ln k$
293	0.003411	0.000523	-7.56
303	0.003299	0.000944	-6.94
314	0.003193	0.001614	-6.43

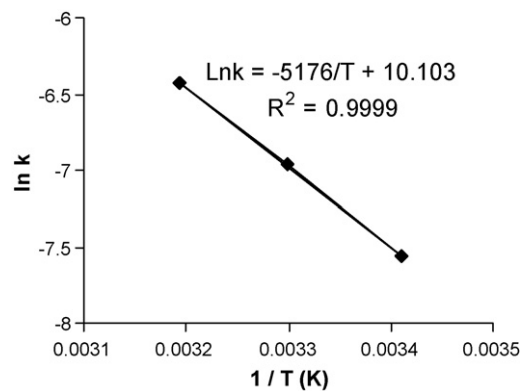


Fig. 12. Dependence of transesterification reaction rate on temperature.

is the initial rate of reaction.

$$k(T) = k_0 e^{E_a/RT} \quad (4)$$

When taking the natural logarithms of Eq. (4), a simple straight line equation is found in

$$\ln(k(T)) = \ln(k_0) - \left(\frac{E_a}{R}\right) \times \frac{1}{T} \quad (5)$$

Plotting the graph of $\ln(k)$ versus $1/T$ results in a straight line represented by Eq. (5) (Fig. 12). The high R^2 -value again indicated a good fit between the theoretical values (solid line) and the experimental data points.

From this plot we were able to calculate values for k_0 (intercept) and E_a (slope), namely $k_0 = 2.4416 \times 10^4$ mol/min and $E_a = 4.3033 \times 10^4$ kJ mol $^{-1}$.

4. Conclusion

The results contained herein show that basic homogenous catalysts such as strong nitrogen bases and, specifically, Verkade proazaphosphatranes were selective highly efficient catalysts for this particular reaction. To our best knowledge, proazaphosphatranes **1a–c** have not previously been employed for the transesterification reaction between propylene carbonate and methanol and this work shows that low catalyst loadings are suitable to this transformation. The NMR spectroscopy-monitored transesterification reactions closely mimic the reactions performed in the autoclave showing no significant difference in the equilibrium conversion between the two experimental techniques. The overall activity of the proazaphosphatranes followed the order **1c** > **1b** > **1a**, and that of the nitrogen bases followed the order TBD > DBU > DBN > DABCO. The results obtained from the NMR studies were used to determine the reaction kinetics and a good correlation was obtained between the theoretical and experimental data.

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