PRESSURE AND SUPERCRITICAL CO_2 CONDITIONS IMPROVE THE ESTERIFICATION REACTION OF PHTHALIC ANHYDRIDE WITH METHANOL IN GLASS MICROREACTORS

F. Benito-López[1], R.M. Tiggelaar[2], R.J.M. Egberink[1], J.G.E. Gardeniers[2], W. Verboom[1], A. van den Berg[2], and D.N. Reinhoudt[1]

MESA$^+$ Institute for Nanotechnology, University of Twente, Enschede, The Netherlands
[1] Supramolecular Chemistry and Technology Group
[2] BIOS Lab-on-a-Chip Group

Abstract

We have developed a new microreactor platform for studying high pressure synthetic chemistry near/under supercritical conditions. A simple reaction, the esterification of phthalic anhydride with methanol, was studied at high pressures as well as under *sc*CO_2 conditions using a continuous flow glass microreactor. The unique design of this system is such that supercritical conditions can be generated in the microreactor, by controlling the pressure and temperature. The microreactor design allows to study the influence of different *p*,*T*-conditions on the rate constants in an easy way.

Keywords: microreactor, high-pressure, kinetics, supercritical CO_2

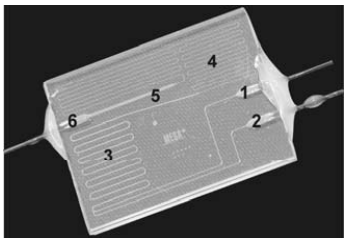
1. Introduction

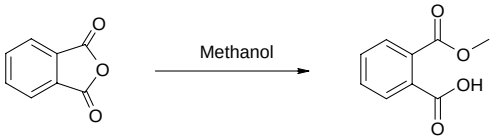
High-pressure conditions can have a positive effect on the rate constant, yield, and selectivity of chemical reactions. However, work in this area has been limited due to the requirement of special equipment. The small characteristic dimensions of microreactors make them suitable for performing chemical reactions that need extreme conditions, like high pressures or temperatures, without extensive safety precautions. In this contribution the results of a study on the reaction kinetics of an esterification reaction are presented when performed in a glass microreactor under high pressures and supercritical CO_2 (*sc* CO_2) conditions.

2. Experimental

In Figure 1(a) a picture of the microreactor, made of Borofloat glass, is shown. It has two inlets for the introduction of pressurized fluids. In the following channel (70×30 μm^2, length 13.5 mm) mixing of the fluids takes place as well as the chemical reaction. This channel connects to a narrow channel (20×5 μm^2; length 177 mm), which acts as a hydraulic resistance that ensures a constant pressure in the reaction zone.

In this chip the esterification of phthalic anhydride in methanol was performed (Figure 1(b)). In Figure 2 the kinetic values are depicted as a function of pressure for different temperatures.





(a) **(b)**

Figure 1. (a) Microreactor chip (20 × 15 × 2.2 mm). Legend: **1** inlet liquid-CO_2, **2** inlet sample solutions, **3** reaction zone, **4** fluidic resistor, **5** expansion zone, **6** outlet. (b) Scheme of the esterification of phthalic anhydride with methanol.

Substantial increases in kinetic values were found when the reaction was done at high pressures. For all investigated temperatures, there is a sharp increase in the rate constants. For instance, at 20 °C 42-fold and 79-fold increases were found for a pressure increase of 90 or 110 bar, respectively. In Table 1 an overview is given of the rate constants obtained from experiments done at high pressures (90 and 110 bars) and for experiments where *sc*CO_2 is used as cosolvent. *sc*CO_2 is generated in the microreactor by changing the phase of $CO_2(l)$ by increasing the temperature of the reaction zone above the critical temperature (T_C) of CO_2. When *sc*CO_2 is used as cosolvent, at pressures of 90 and 110 bar very high enlargements of the rate constants were observed,for example, 161-fold and 296-fold increases at 40 °C.

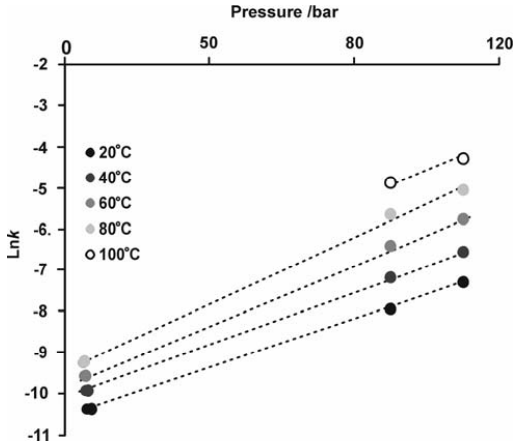


Figure 2. Kinetic values as a function of pressure for different temperatures.

3. Discussion

Theoretically, for labscale experiments a pressure of 110 bar should not affect the reaction kinetics. However, when performed in the microreactor, significant increases were found. These enlarged reaction rates might be attributed to the distinctive

conditions under which the continuous flow microreactor is operated, such as diffusive mixing under laminar-flow regime in small reaction volumes (~260 nL of the reaction zone) [1].

Table 1. Kinetic values for different temperatures at 90 and 110 bars with and without *sc*CO_2 as cosolvent.

	k /M^{-1} s^{-1} (90 bar) [a]		k /M^{-1} s^{-1} (110 bar) [a]	
T /°C	methanol	Methanol + *sc*CO_2	methanol	Methanol + *sc*CO_2
20	3.5×10^{-4}	--	6.7×10^{-4}	--
40	7.6×10^{-4}	1.2×10^{-1}	1.4×10^{-3}	2.0×10^{-1}
60	1.6×10^{-3}	1.8×10^{-1}	3.1×10^{-3}	3.1×10^{-1}
80	3.5×10^{-3}	2.7×10^{-1}	6.4×10^{-3}	4.6×10^{-1}
100	7.5×10^{-3}	3.6×10^{-1}	1.3×10^{-2}	6.9×10^{-1}

[a] Mean values from duplicate experiments.

Other aspects, like material properties (hydroxy and silanol groups in the surface), could also play a role since the esterification reaction is acid catalyzed, and are currently examined. In case of *sc*CO_2 as cosolvent, extremely high rate constants were found. This is attributed to the unique properties of *sc*CO_2, which dramatically change reaction rates with relatively small changes in temperature and pressure [2].

4. Conclusions

Clearly, the results of this study show that glass microreactors in continuous flow mode operated at high pressure conditions give rise to significant rate enhancements. Since temperature and pressure can be regulated and their influence on continuous flow reactions can be observed easily and fast, this microreactor has a great potential for high-throughput screening at high pressures. Implementation of high-pressure processes in microreactors offer important advantages in terms of safety and therefore makes high pressure research easier accessible.

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References

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