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Influence of reactor design on cyclic carbonate synthesis catalysed by a bimetallic aluminium(salen) complex

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Abstract

The influence of volume to surface area ratio on the rate of synthesis of cyclic carbonates from five epoxides and CO₂ catalysed by a bimetallic aluminium(salen) complex and tetrabutylammonium bromide in stirred batch reactors has been investigated. The results suggest that the rate of reaction is determined by the rate of CO₂ mass transfer from the gas phase into the reaction mixture rather than by the intrinsic kinetics of cyclic carbonate synthesis at liquid length scales of greater than 4mm. The solubility of CO₂ in the reaction mixtures was determined and shown to vary depending on the nature of the epoxide.

Keywords

Cyclic carbonate, epoxide, carbon dioxide, reactor design

1. Introduction

The chemicals industry is currently highly dependent on petrochemical precursors. However, the conversion of crude oil into useful chemicals requires large amounts of energy, resulting in significant CO₂ emissions. In addition, known reserves of crude oil are predicted to be consumed within the next 54 years [1]. Thus, the chemicals industry at present is neither green nor sustainable [2]. As a result, there is currently

considerable interest in developing new routes to commercially important chemicals starting from sustainable resources [3]. One such sustainable starting material is carbon dioxide and this has resulted in a significant increase in carbon dioxide chemistry over the last ten years [4]. There are two main problems with using carbon dioxide as a sustainable chemical feedstock: it is a very stable compound ($\Delta H_f = -394 \text{ kJ mol}^{-1}$), so many of its reactions are highly endothermic and they often have a high kinetic barrier [4]. The latter problem can however, be overcome through the development of effective catalysts. Despite these problems, there are examples of carbon dioxide chemistry which have been commercialized. Thus, the synthesis of urea from carbon dioxide and ammonia is highly exothermic ($\Delta H_r = -101 \text{ kJ mol}^{-1}$) and has been a commercial process since 1922 [5] and the synthesis of salicylic acids from carbon dioxide and phenols is also exothermic ($\Delta H_r = -31 \text{ kJ mol}^{-1}$) and has been a commercial process for over 100 years [6].

Scheme 1. Synthesis of cyclic carbonates and polycarbonates

Another exothermic reaction of carbon dioxide is its reaction with epoxides which can be controlled to produce either cyclic carbonates [7] or polycarbonates [8] (Scheme 1). Polycarbonates are attracting interest as replacements for petrochemically derived polymers. Cyclic carbonates have a number of commercial applications including as electrolytes for lithium ion batteries [9], polar aprotic solvents [10] and use as chemical intermediates [11]. The production of cyclic carbonates from epoxides and carbon dioxide has been a commercial process since the 1950s [12], though current commercial processes rely on quaternary ammonium or phosphonium salts as catalysts [11b, 13] and this necessitates the use of high temperatures and pressures. The energy required to obtain these high pressures negates any green aspects of the process as more carbon dioxide is produced generating the required energy than is incorporated into the cyclic carbonate.

Over the last six years we have developed bimetallic aluminium(salen) complexes (e.g. **1**) and related species (e.g. **2** and **3** [14]) as highly active catalysts for the synthesis of cyclic carbonates from epoxides and carbon dioxide in the presence of a tetraalkylammonium bromide cocatalyst. The combination of complex **1** and tetrabutylammonium bromide was shown to catalyse the synthesis of cyclic carbonates at 1 bar carbon dioxide pressure and room temperature [15,16] and kinetic studies revealed the full role of the tetrabutylammonium

bromide for the first time [16]. On the basis of the mechanistic studies, we prepared one-component and immobilized catalysts **4,5** [17,18] and showed that the immobilized catalysts could be used to form cyclic carbonates in a gas-phase flow reactor [18,19]. Immobilized catalysts **5** were shown to be compatible with both simulated [18] and real flue gas [20] and complex **1** was used as part of a next-generation, integrated energy and chemical production demonstration [21].

Whilst the gas-phase flow reactor is the optimal method for the large scale preparation of cyclic carbonates from volatile epoxides such as ethylene oxide and propylene oxide, other commercially important cyclic carbonates such as styrene carbonate and glycerol carbonate are needed on a smaller scale and prepared from non-volatile epoxides. For the synthesis of these cyclic carbonates, the use of stirred-tank batch reactors may be more appropriate. Previous studies have optimized the structure of catalysts **1-5** [14-19] and their synthesis [22]. However, batch mode reactions involving catalyst **1** are two-phase processes as the solid catalyst is dissolved in a liquid epoxide and exposed to gaseous carbon dioxide. Thus, it was anticipated that the reactor design could be an important part of optimizing the whole process. In this paper we report the results of a study to investigate the impact of reactor parameters on the rate of cyclic carbonate synthesis catalysed by complex **1** and tetrabutylammonium bromide.

2. Results and Discussion

The rate of cyclic carbonate synthesis using catalyst **1** can be determined by chemical or physical parameters. The intrinsic reaction rate (i.e. that determined by the chemical reaction) has been shown to obey the rate equation: $\text{rate} = k[\text{epoxide}][\text{CO}_2][\mathbf{1}][\text{Bu}_4\text{NBr}]^2$ [16]. However, this rate equation will only govern the overall kinetics when carbon dioxide transfer from the gas phase into the reaction solution and its subsequent diffusion from the gas–liquid interface into the bulk solution are rapid compared to the rate of cyclic carbonate synthesis. Therefore, experiments were designed to investigate the influence of volume to surface area ratio on reaction rate.

To determine the influence of surface area on reaction rate, a parallel reactor system was constructed consisting of four cylindrical reactors with diameters of 23.0 mm each fitted with a magnetic stirrer bar and located within a common plastic container equipped with a gas inlet and outlet. The plastic container was also fitted with a sampling port vertically above each reactor to allow samples to be removed by a syringe and needle. The reactors were filled with styrene oxide **6a** to six depths in the range of 4–21 mm. Each tube also contained catalyst **1** and tetrabutylammonium bromide (2.5 mol% each). The reactions were stirred at 200 rpm whilst 5% carbon dioxide in helium was passed through the plastic container at a steady rate of 0.17 mL s^{-1} (controlled by a mass-flow controller). These conditions were chosen to ensure that the conversion of epoxide **6a** into cyclic carbonate **7a** (Scheme 2) occurred sufficiently slowly that for at least the first 48 hours of reaction, the chemical reactions obeyed pseudo–zero order kinetics. At regular intervals, samples were removed from each cylindrical reactor and analysed by GCMS to determine the relative amounts of styrene oxide and styrene carbonate present. Each reaction was carried out in duplicate and one set of data are shown in Figure 1 [23]. It is apparent from this data that the volume specific rate of cyclic carbonate synthesis decreases as the depth of the reaction mixture increased. Figure 2 then shows that there is a linear relationship between the volume specific rate of reaction and $1/(\text{depth of reactor})$ or equivalently between total rate and surface area.

Scheme 2. Synthesis of cyclic carbonates **7a–e** from epoxides **6a–e**

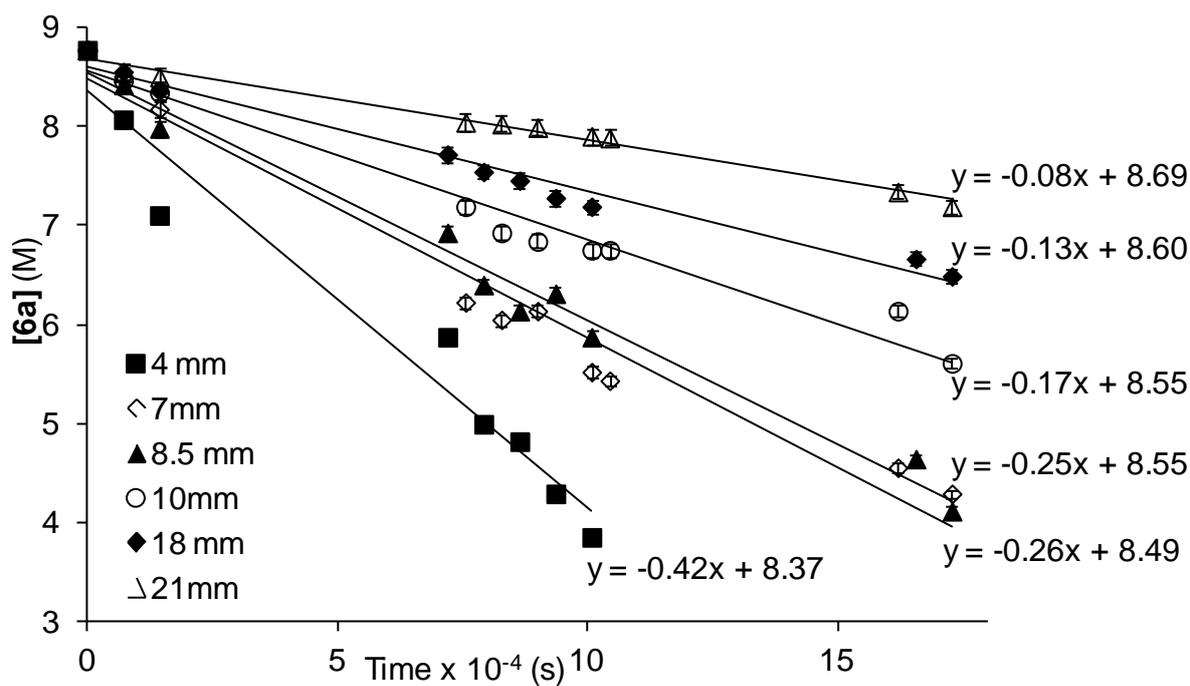


Figure 1. Influence of reactor depth on the rate of synthesis of styrene carbonate **7a**. The error bars on each point are set at $\pm 1\%$ (see error analysis section of experimental).

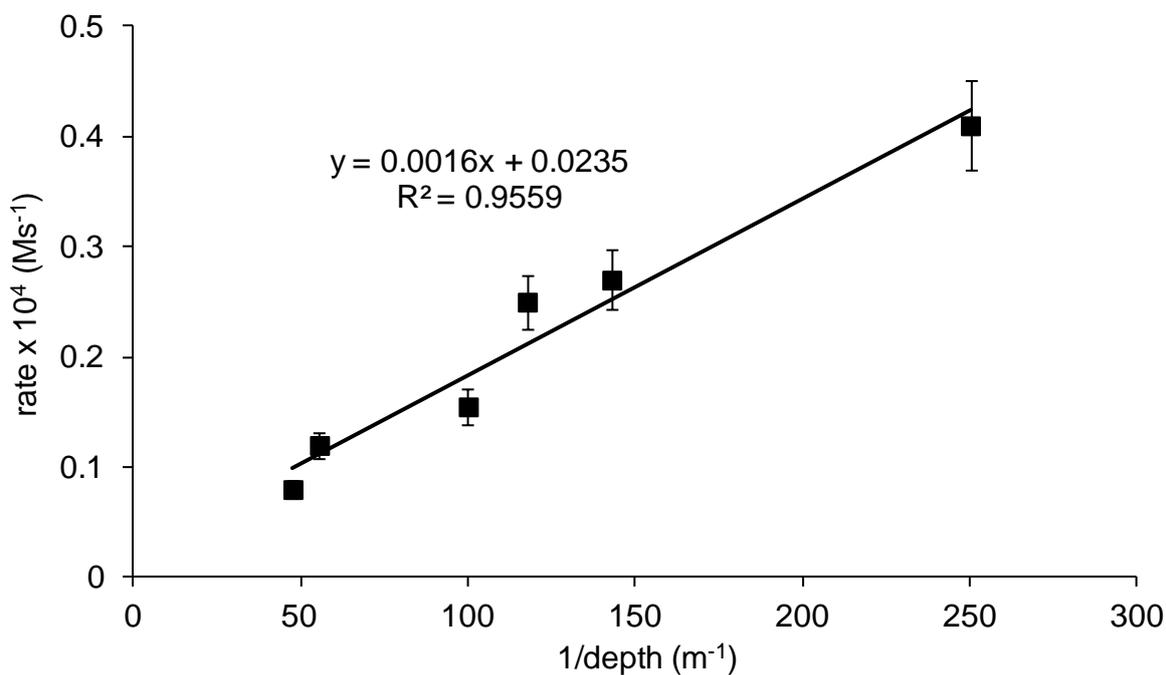


Figure 2. Relationship between rate of formation of cyclic carbonate **7a** and depth of reactor. The data plotted are the average of two rate constant determinations at each reaction depth. The error bars are $\pm 10\%$ of each point's value based on the maximum error between corresponding points the two data sets.

To investigate the generality of this result, the synthesis of four other cyclic carbonates **7b–e** from epoxides **6b–e** was investigated [23]. This selection included the synthesis of glycerol carbonate **7b** which is of growing commercial importance [24,25]. Figure 3 compares the results obtained with all five epoxides **6a–e** and in each case a linear relationship between the volume specific rate of reaction and $1/(\text{depth of reactor})$ was observed. However, whilst the gradients of the plots for epoxides **6a,b,d** and **e** were all similar, that for decene oxide **6c** (shown with a broken line in Figure 3) was much smaller (between a half and a third) than the others. It seemed likely that this was due to a difference in either the maximum solubility of CO_2 or the rate at which CO_2 dissolves in this epoxide. To investigate this, the solubility of CO_2 in epoxides **6a–e** was investigated at 0°C and gave the results shown in Figure 4. It is apparent from Figure 4 that on a mmole per mole of solvent basis, CO_2 is most soluble and most rapidly soluble in the very non-polar decene oxide. This higher solubility and rate of dissolution provides an explanation for the reduced gradient of volume specific rate versus $1/(\text{depth of reactor})$ (or total rate versus area) observed for reactions using decene oxide **6c** (Figure 3).

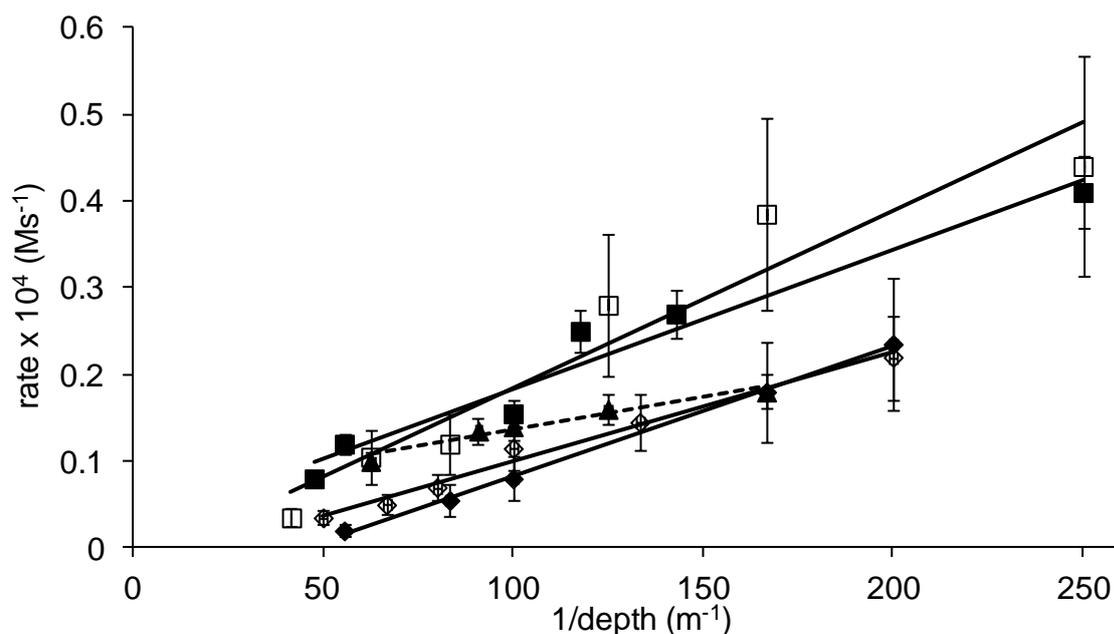


Figure 3. Relationship between rate of formation of cyclic carbonate **7a–e** and depth of reactor. The data plotted are the average of two rate constant determinations at each reaction depth. The error bars are based on the largest % difference between the duplicate runs for each substrate. Filled squares = styrene oxide **6a** ($y = 0.0016x + 0.0235$): Empty diamonds = glycidol **6b** ($y = 0.0013x - 0.0263$): Filled triangle and broken line = decene oxide **6c** ($y = 0.0007x + 0.0619$): Empty squares = epichlorohydrin **6d** ($y = 0.0021x - 0.0219$): filled diamonds = 3-phenoxypropylene oxide **6e** ($y = 0.0015x - 0.0673$).

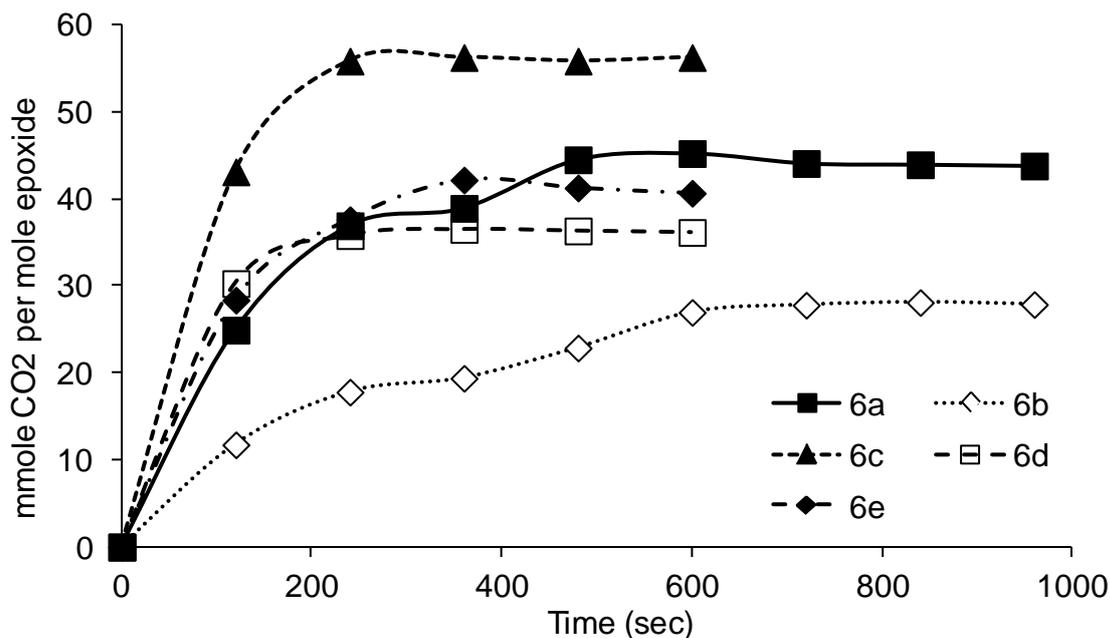


Figure 4. Solubility of CO₂ in epoxides **6a–e**.

Whilst the data shown in Figure 4 are representative of the early stages of cyclic carbonate synthesis during which the concentration of cyclic carbonate will be negligible, as the reaction progresses the reaction composition will change with the cyclic carbonate becoming the predominant species present. Most of cyclic carbonates **7a–e** are solids and (at least partly) precipitate from the reaction as they form. However, glycidol **6b** and glycerol carbonate **7b** are both liquids, so the solubility of CO₂ in mixtures of **6b** and **7b** was also determined to investigate how the solubility of CO₂ in the reaction mixture might vary as the reaction progresses. The results are shown in Figure 5 and show that there is a linear relationship between CO₂ solubility and the mole fraction of **7b** present in the reaction mixture. However, the solubility of CO₂ in cyclic carbonate **7b** is only 65% of the solubility of CO₂ in epoxide **6b** and the intrinsic reaction rate is known to be proportional to the concentration of dissolved CO₂ [16]. Therefore, under conditions where mass-transfer is not rate limiting, the rate of cyclic carbonate synthesis will decrease by 35% more than predicted if the concentration of dissolved CO₂ was assumed to be constant.

In conclusion, a batch reactor for the synthesis of cyclic carbonates from epoxides and carbon dioxide catalysed by the combination of catalyst **1** and tetrabutylammonium bromide should be designed to maximise the surface area between gaseous CO₂ and the liquid reaction mixture (increases in overall reaction rate are seen for decreasing liquid hold-up to gas-liquid surface area ratios to 4 mm). This could be achieved by appropriate

reactor design; use of high stirring rates and ensuring that the gas inlet ensures efficient mixing of the gaseous and liquid reactants.

Under the conditions employed here the overall kinetics are always controlled by mass transfer with the mass transfer coefficient being relatively insensitive to the nature of the epoxide, thus the results appear to be general to all syntheses of cyclic carbonates from epoxides and carbon dioxide and may also be relevant to the related synthesis of polycarbonates from the same substrates. The results obtained in this work provide important data needed to scale up reactions involving catalyst **1** as part of ongoing activities to commercialize this catalyst system for cyclic carbonate synthesis.

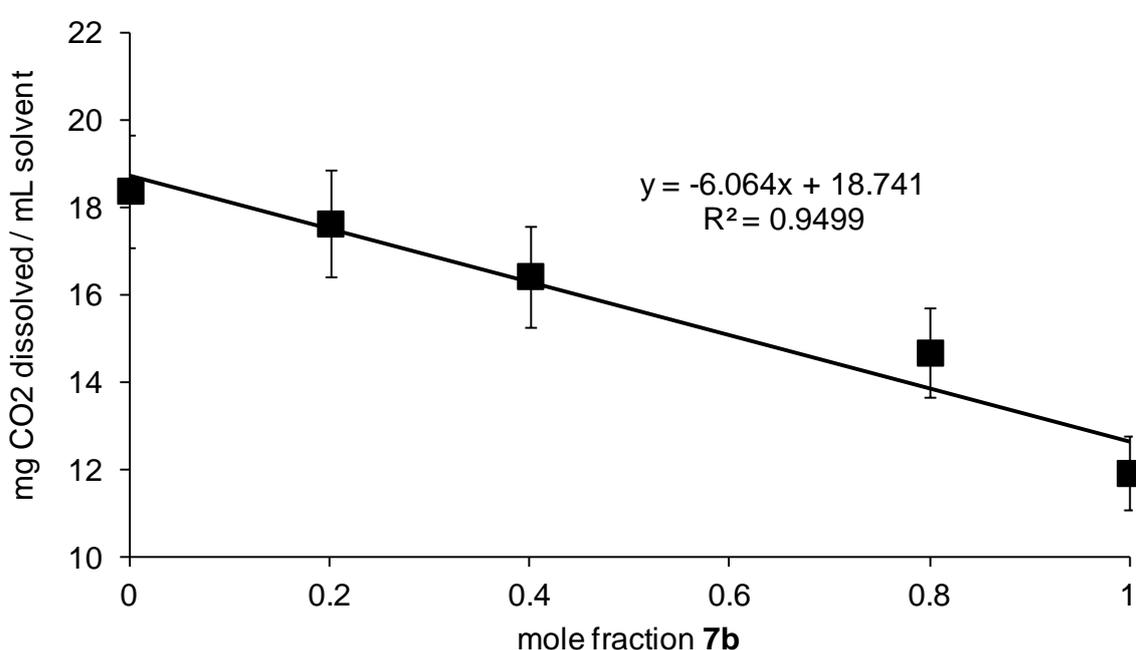


Figure 5. Solubility of CO₂ in **6b/7b** as a function of **7b** mole fraction. Each solubility measurement was carried out twice and the average value was used to construct the graph. The error bars are based on the largest % difference between the duplicate measurements ($\pm 7\%$).

3. Experimental

3.1 Instrumentation

Reactions involving styrene oxide were monitored by GCMS using a Varian CP-800-SATURN 2200 GCMS ion-trap mass spectrometer fitted with a FactorFour (VF-5 ms) capillary column (30 m x 0.25 mm) with helium as the carrier gas. The conditions used were: initial temperature 60 °C, hold at initial temperature for 3 minutes then ramp rate 15 °C/min to 270 °C; hold at final temperature for 5 minutes. T_R 7.33 minutes (styrene oxide), T_R 12.09 minutes (styrene carbonate). For the first 3.50 minutes, the eluent was routed away from the

mass detector. Subsequently, the detector was operated in full EI scan mode. The detector response was calibrated using solutions of styrene oxide of known concentration.

Reactions involving epoxides **6b–e** were monitored by ^1H NMR spectroscopy using a Bruker Avance 300 spectrometer at 300 MHz. All spectra were recorded in CDCl_3 at ambient temperature and were referenced to the residual solvent peak. The extent of reaction was determined by integration of the peaks corresponding to the epoxide and cyclic carbonate.

3.2 Error analysis

For reactions using styrene oxide which were analysed by GCMS, samples of ~1% and ~10% of styrene carbonate in styrene oxide were prepared and each was injected into the GCMS 10 times. These concentrations corresponded to those present towards the start and end of typical experiments. The results [23] showed that at both concentrations, all the readings were within $\pm 0.8\%$ of the mean value, so error bars of $\pm 1\%$ were applied to the data. For reactions involving epoxides **6b–e** which were analysed by ^1H NMR spectroscopy, at least three aliphatic peaks were available for both the epoxide and cyclic carbonate in the spectra. Comparison of the values of these integrals showed that the error was always less than $\pm 3\%$, so error bars of $\pm 3\%$ were applied to the data.

3.3 Investigation of influence of surface area on rate of synthesis of styrene carbonate **7a**

A reactor was constructed from a rectangular plastic container equipped with a gas inlet and outlet pipe and four sampling ports to allow liquids to be added and removed. Four vials with diameters of 10.0, 12.6, 17.5 and 26.9 mm were placed in the reactor immediately below the sampling ports, and a magnetic stirrer bar was placed in each vial. The vials were charged with catalyst **1** (0.18–0.72 g, 0.16–0.62 mmol) and Bu_4NBr (0.06–0.21 g, 0.16–0.62 mmol) so that each vial contained 1.25 mol% of each catalyst relative to the amount of epoxide **6a** to be used and was filled to a depth of 23 ± 1 mm. A flow (35 mL min^{-1}) of 5% CO_2 in He was then passed through the reactor to saturate the atmosphere above the vials. The gas flow rate was then reduced to 10 mL min^{-1} and styrene oxide **6a** (1.4–5.7 mL, 12.5–49.9 mmol) was added to each vial through the sampling ports such that each vial was filled to the same depth. Samples were taken from each vial at regular intervals through the sampling ports and each sample was analysed by GCMS to determine the relative concentrations of styrene oxide and styrene carbonate. This data was then used to derive the rate data.

3.4 Investigation of influence of reaction depth on rate of synthesis of cyclic carbonates 7a-e

A reactor was constructed from a rectangular plastic container equipped with a gas inlet and outlet pipe and four sampling ports to allow liquids to be added and removed. Four vials with a diameter of 23.0 mm were placed in the reactor immediately below the sampling ports, and a magnetic stirrer bar was placed in each vial along with 2.5 mol% of catalyst **1** and Bu₄NBr. Reactions involving epoxide **6a** were carried out at depths of 4–21 mm using **6a** (0.7–7.1 mL, 6.2–62.4 mmol), catalyst **1** (0.18–1.80 g, 0.16–1.56 mmol) and Bu₄NBr (0.05–0.50 g, 0.16–1.56 mmol). Reactions involving epoxide **6b** were carried out at depths of 5–20 mm using **6b** (0.8–3.3 mL, 12.7–50.6 mmol), catalyst **1** (0.37–1.47 g, 0.32–1.27 mmol) and Bu₄NBr (0.10–0.41 g, 0.32–1.27 mmol). Reactions involving epoxide **6c** were carried out at depths of 5–30 mm using **6c** (0.8–4.9 mL, 3.8–22.5 mmol), catalyst **1** (0.11–0.66 g, 0.09–0.56 mmol) and Bu₄NBr (0.03–0.18 g, 0.09–0.56 mmol). Reactions involving epoxide **6d** were carried out at depths of 4–24 mm using **6d** (0.5–3.1 mL, 6.6–39.8 mmol), catalyst **1** (0.19–1.15 g, 0.16–0.99 mmol) and Bu₄NBr (0.05–0.33 g, 0.16–0.99 mmol). Reactions involving epoxide **6e** were carried out at depths of 4–24 mm using **6e** (0.5–4.2 mL, 3.8–22.8 mmol), catalyst **1** (0.11–0.66 g, 0.09–0.56 mmol) and Bu₄NBr (0.03–0.18 g, 0.09–0.56 mmol). Reactions involving epoxide **6a** were again monitored by GCMS, whilst reactions involving epoxides **6b–6e** were monitored by ¹H NMR spectroscopy.

3.5 Determination of CO₂ solubility in epoxides 6a-e.

Epoxide **6a–e** (2 mL) was placed in a vial fitted with a magnetic stirring bar and weighed. The vial was placed in an ice bath and the contents stirred whilst CO₂ was bubbled through the solution as a flow rate of 10 mL min⁻¹. Every 2 minutes the vial was removed, dried and weighed before being returned to the ice bath. The process was repeated for up to 16 minutes until the weight of the vial and contents reached a constant value.

3.6 Determination of CO₂ solubility in mixtures of epoxide 6b and cyclic carbonate 7b.

A mixture of **6b** and **7b** containing the desired mole fraction of **7b** (2 mL) was placed in a vial fitted with a magnetic stirring bar and weighed. The vial was placed in an ice bath and the contents stirred whilst CO₂ was bubbled through the solution as a flow rate of 10 mL min⁻¹. Every 2 minutes the vial was removed, dried and weighed before being returned to the ice bath. The process was repeated for up to 16 minutes until the weight of the vial and contents reached a constant, maximum value.

Supporting Information

Each individual set of kinetic data and GCMS error analysis.

Vitae

Michael North obtained his BSc. from Durham University and his D.Phil from the University of Oxford. After a postdoctoral position at the University of Nottingham, and academic posts at the Universities of Wales and London, he was appointed to his current position as Professor of Organic Chemistry and joint director of the University Research Centre in Catalysis and Intensified Processing at Newcastle University. His research interests are centred on the design of new catalysts for asymmetric carbon-carbon bond formation and carbon dioxide chemistry. In 2001 he was awarded the Descartes Prize by the European Commission.



Ian Metcalfe is Professor of Chemical Engineering at Newcastle University. He received his undergraduate degree from Imperial College and his PhD from Princeton University. He is a Chartered Engineer, a Fellow of the Institution of Chemical Engineers, a Chartered Chemist and a Fellow of the Royal Society of Chemistry. Ian was elected a Fellow of the Royal Academy of Engineering in 2012. His work is primarily in the area of catalyst kinetics and high temperature membrane systems applied to energy systems. He is joint director of the University Research Centre in Catalysis and Intensified Processing.



Pedro R. Villuendas obtained his BSc in Chemistry at Universidad de Zaragoza (Spain) in 2002 and his PhD at the University of Leicester in 2007 under the supervision of Dr. Alison Stuart and Professor Eric Hope. He then joined Professor Michael North's group at Newcastle University in 2007 as a Research Associate. He is currently working at the University of Zaragoza (Spain) as a postdoctoral fellow. His work is centred on catalysis and reaction mechanisms.



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Influence of reactor design on cyclic carbonate synthesis catalysed by a bimetallic aluminium(salen) complex

Supporting information

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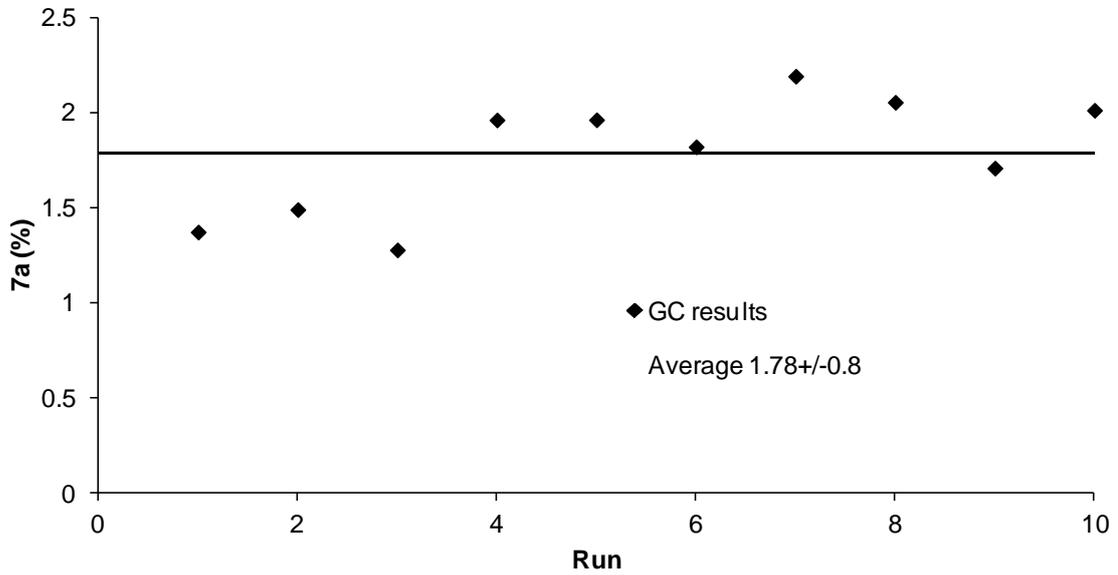
- a) School of Chemical Engineering and Advanced Materials and University Research Centre in Catalysis and Intensified Processing, Newcastle University, Mertz Court, Newcastle upon Tyne, England, UK, NE1 7RU.
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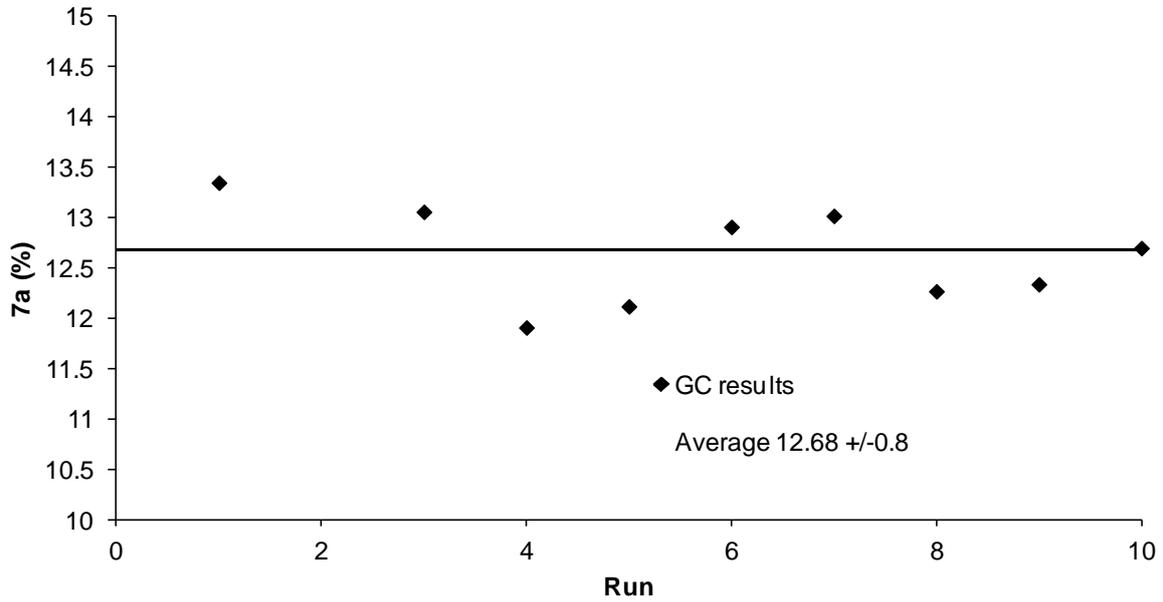
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GCMS error analysis

Results for 1% styrene carbonate in styrene oxide



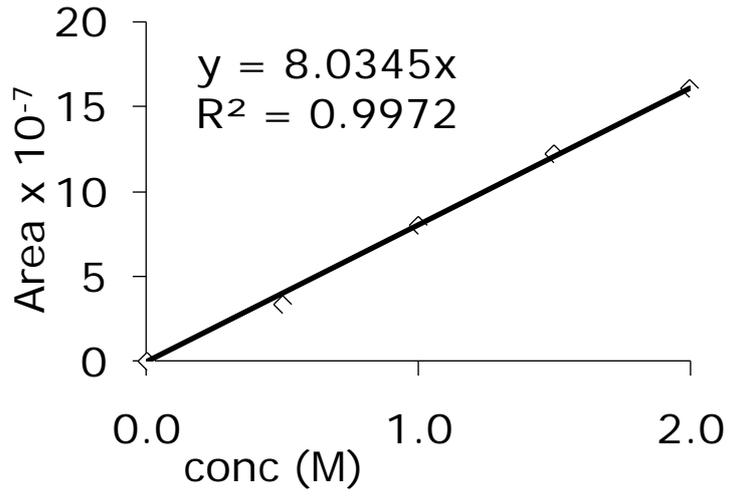
Results for 10% styrene carbonate in styrene oxide



GCMS calibration for styrene oxide

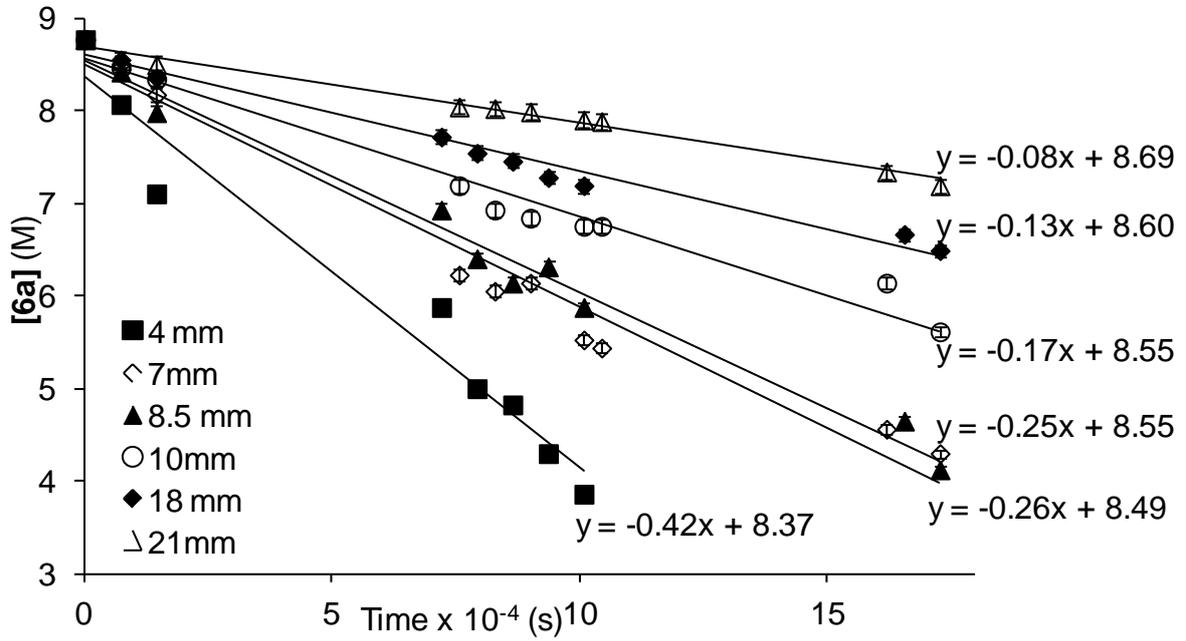
Styrene oxide
Concentration
0
0.5 M
1.0 M
1.5 M
2.0 M

Area of GC peak with retention time 7.33 minutes
0
 3.353×10^7
 8.022×10^7
 1.224×10^8
 1.610×10^8

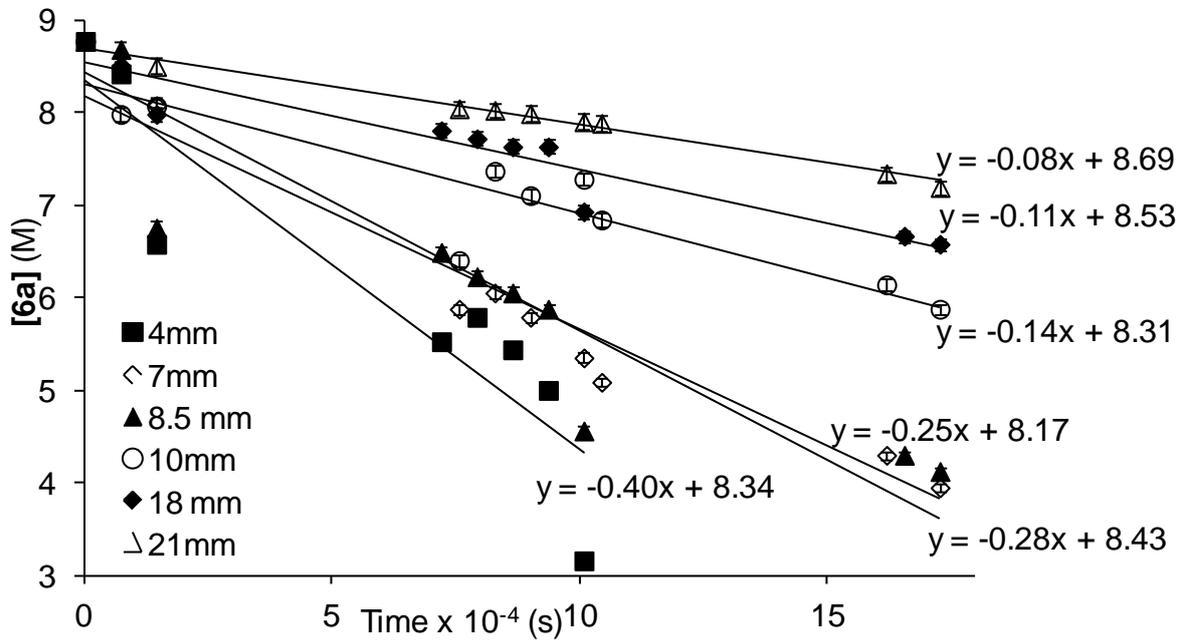


Plots of both data sets of [6a] versus time at six different reaction depths.

Data set 1

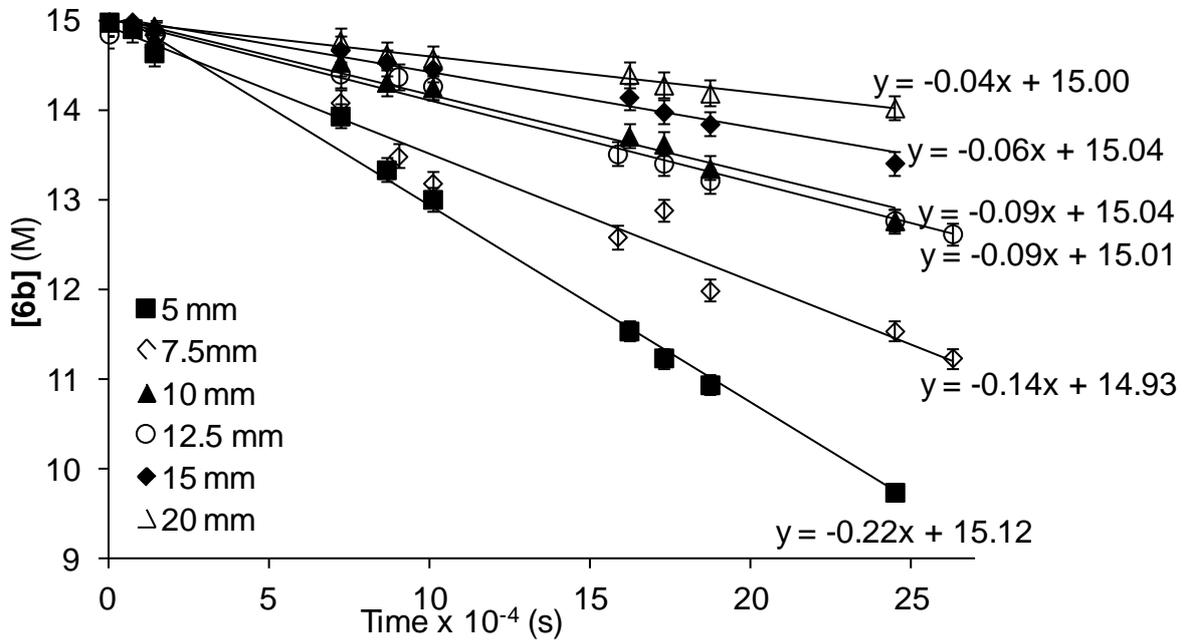


Data set 2

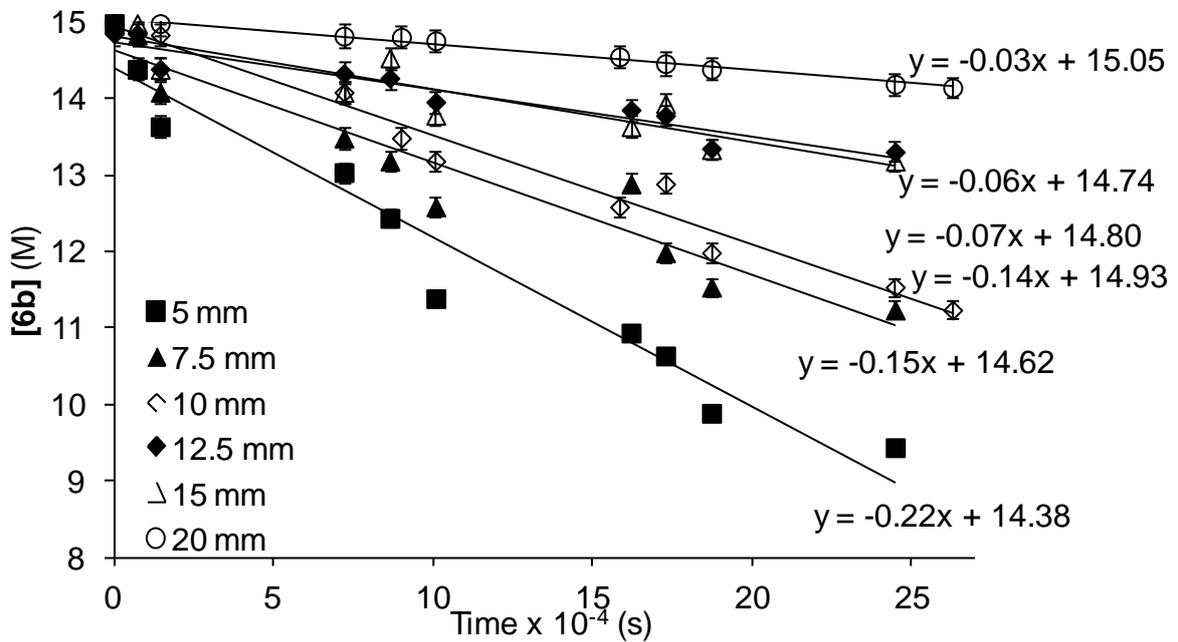


Plots of both data sets of [6b] versus time at different reaction depths.

Data set 1

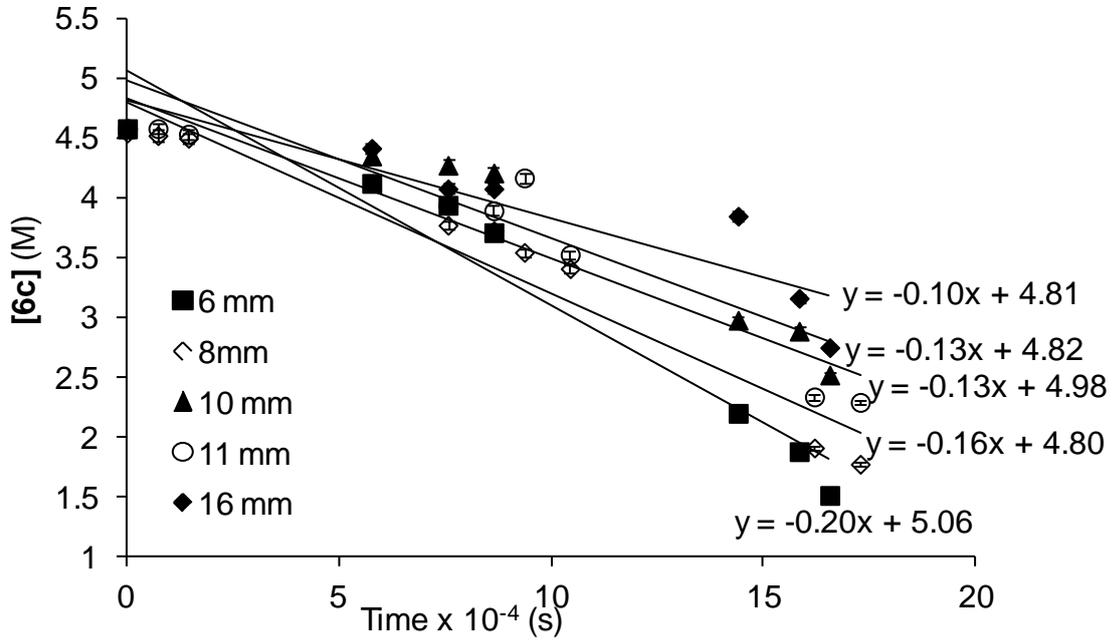


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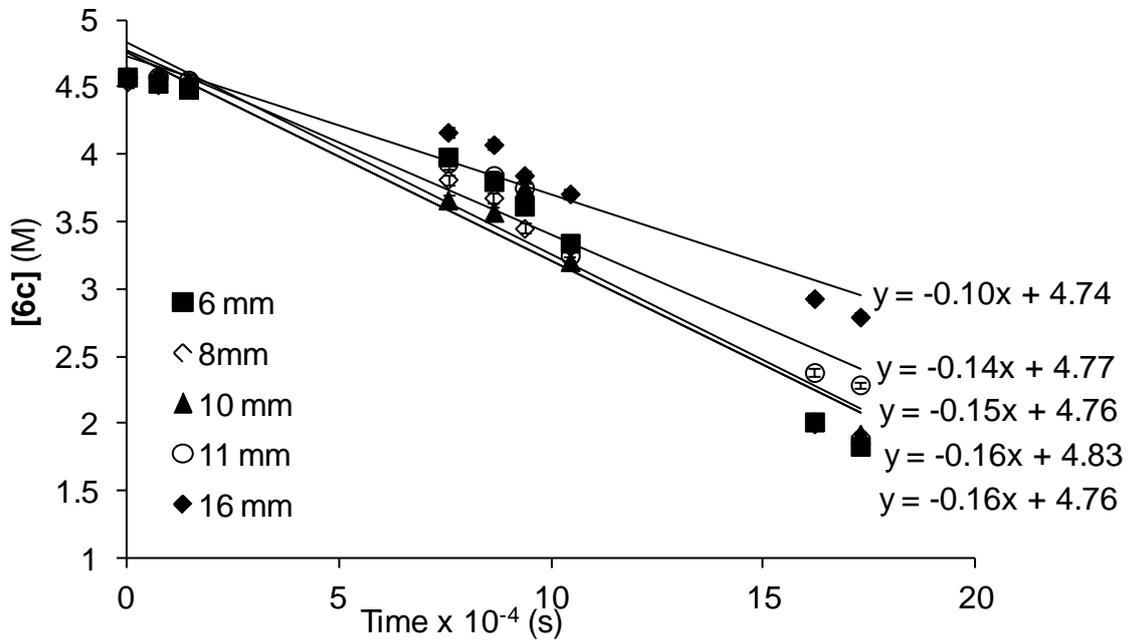


Plots of both data sets of [6c] versus time at different reaction depths.

Data set 1

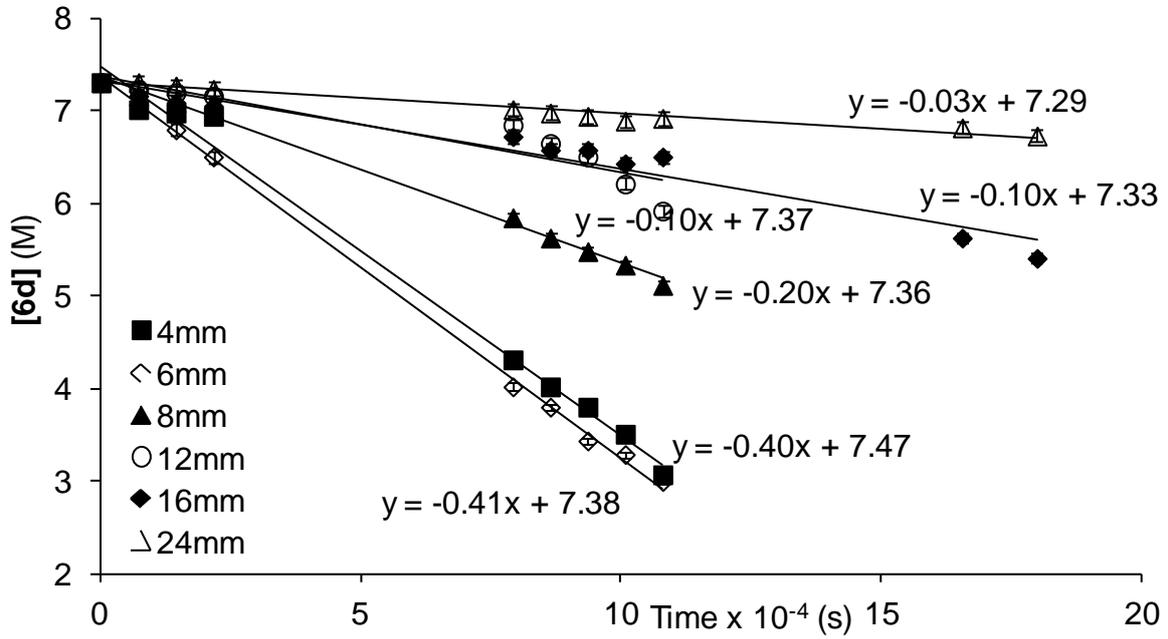


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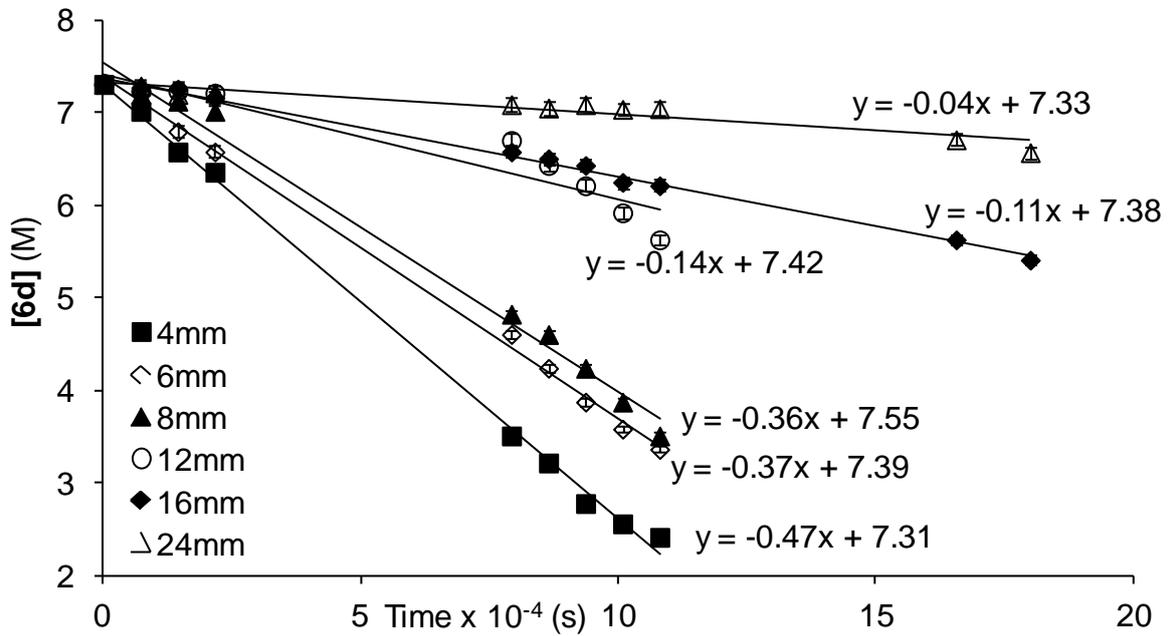


Plots of both data sets of [6d] versus time at different reaction depths.

Data set 1

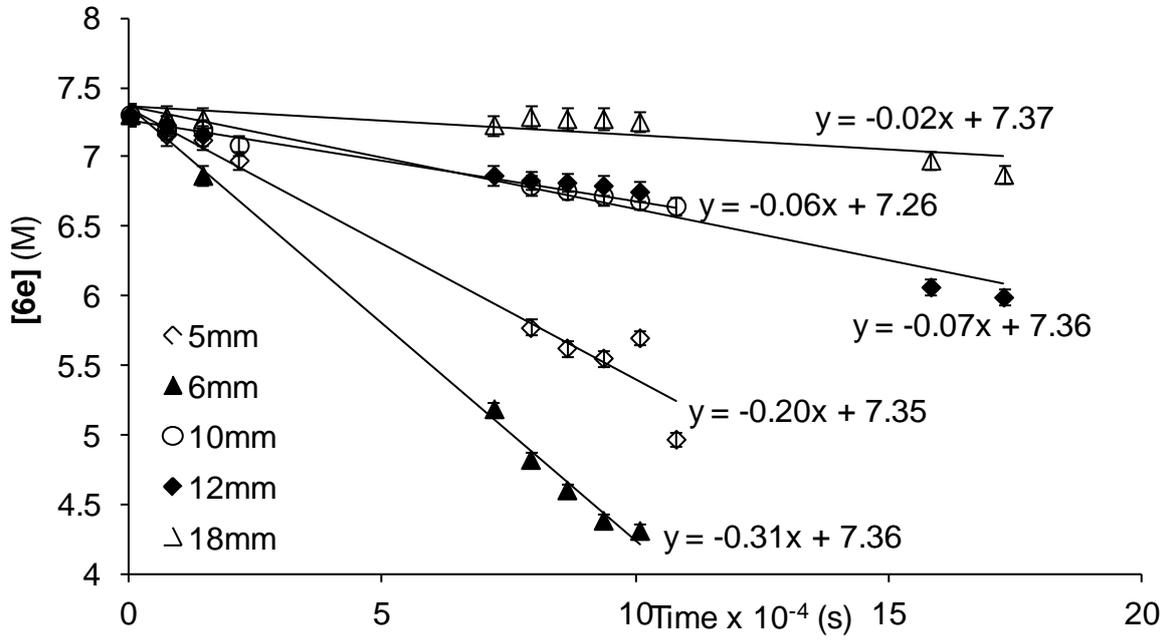


Data set 2



Plots of both data sets of [6e] versus time at different reaction depths.

Data set 1



Data set 2

