ChemPubSoc Europe

DOI: 10.1002/chem.201400007

CHEMISTRY
A European Journal
Full Paper

Synthetic Methods

Mechanistic Investigation of the Reaction of Epoxides with Heterocumulenes Catalysed by a Bimetallic Aluminium Salen Complex

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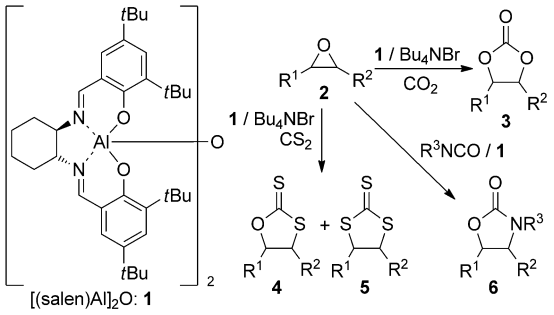
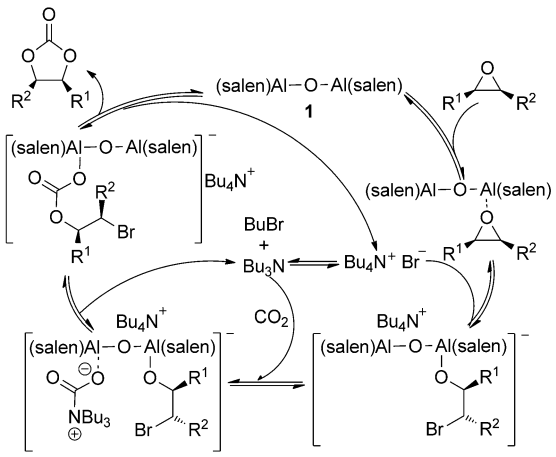
Abstract: The bimetallic aluminium(salen) complex $[(Al(salen))_2O]$ is known to catalyse the reaction between epoxides and heterocumulenes (carbon dioxide, carbon disulfide and isocyanates) leading to five-membered ring heterocycles. Despite their apparent similarities, these three reactions have very different mechanistic features, and a kinetic study of oxazolidinone synthesis combined with previous kinetic work on cyclic carbonate and cyclic dithiocarbonate synthesis showed that all three reactions follow different rate equations. An NMR study of $[Al(salen)]_2O$ and phenylisocyanate provided evidence for an interaction between them, consistent with the rate equation data. A variable-temperature kinetics study on all three reactions showed that cyclic carbonate synthesis had a lower enthalpy of activation and a more negative entropy of activation than the other two heterocycle syntheses. The kinetic study was extended to oxazolidinone synthesis catalysed by the monometallic complex Al(salen)Cl, and this reaction was found to have a much less negative entropy of activation than any reaction catalysed by $[Al(salen)]_2O$, a result that can be explained by the partial dissociation of an oligomeric Al(salen)Cl complex. A mechanistic rationale for all of the results is presented in terms of $[Al(salen)]_2O$ being able to function as a Lewis acid and/or a Lewis base, depending upon the susceptibility of the heterocumulene to reaction with nucleophiles.

Introduction

Bimetallic aluminium(salen) complex **1** was introduced as a catalyst by Jacobsen, who showed that it would catalyse asymmetric Michael additions.[1] Zhu subsequently reported Passerini type reactions between aldehydes, isocyanides and hydrogen azide catalysed by complex **1**,[2] and we demonstrated asymmetric cyanohydrin synthesis catalysed by a combination of complex **1** and triphenylphosphane oxide.[3] In recent papers, we have also reported the use of bimetallic aluminium(salen) complex **1** to catalyse the reaction between epoxides **2** and carbon dioxide,[4] carbon disulfide[5] or isocyanates[6] leading to cyclic carbonates[7] **3**, cyclic dithiocarbonates **4**,[8] cyclic trithiocarbonates[8] **5** and oxazolidinones[9] **6**, respectively (Scheme 1). Each of these studies was accompanied by a mechanistic investigation on that particular reaction, which resulted in the catalytic cycles shown in Scheme 2, 3 and 4 being suggested for the three reactions. It is clear, that despite the ap-



Scheme 1. Heterocycle synthesis achieved by use of catalyst **1**.



Scheme 2. Catalytic cycle for cyclic carbonate synthesis achieved by use of catalyst **1**.

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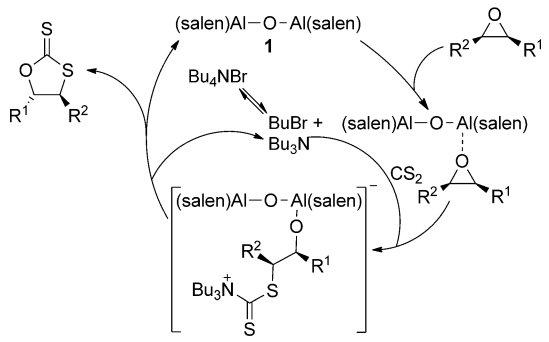
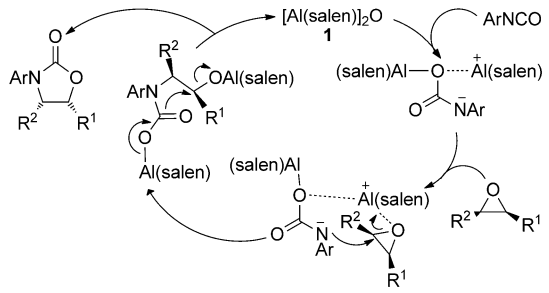
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201400007. It contains details on chemicals and instrumentations.



Scheme 3. Catalytic cycle for cyclic dithiocarbonate synthesis achieved by use of catalyst **1**.



Scheme 4. Catalytic cycle for oxazolidinone synthesis achieved by use of catalyst **1**.

parent similarities between the three reactions shown in Scheme 1, there are significant differences between them.

Thus, the reaction of epoxides with carbon dioxide requires the use of tetrabutylammonium bromide as a cocatalyst; for the reaction with carbon disulfide, the cocatalyst can be changed to tributylamine, and no cocatalyst is required in the reaction with isocyanates. The formation of cyclic carbonates **3** and oxazolidinones **6** was shown to preserve the epoxide stereochemistry, whereas the formation of cyclic di- and trithiocarbonates **4**/**5** was found to proceed with inversion of stereochemistry. Only bimetallic complexes were found to be active for cyclic carbonate synthesis, but monometallic aluminium(salen) complexes were also active catalysts for the reaction between epoxides and carbon disulfide or isocyanates. The complex **1** catalysed reactions between epoxides and carbon dioxide or carbon disulfide also had different kinetic equations represented by rate Equations (1) and (2).

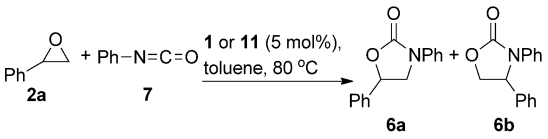
$$\text{rate} = k[\mathbf{1}][\text{Bu}_4\text{NBr}]_2[\text{epoxide}][\text{CO}_2] \text{ for cyclic carbonate synthesis} \quad (1)$$

$$\text{rate} = k[\mathbf{1}][\text{epoxide}] \text{ for cyclic dithiocarbonate synthesis} \quad (2)$$

The kinetics of the reaction between epoxides and isocyanates catalysed by complex **1** had not previously been reported. Therefore, we have undertaken an integrated kinetic study to investigate the origin of the differences in the reaction of epoxides with heterocumulenes catalysed by complex **1**, and to provide an overarching mechanistic understanding of all three processes. In this paper we report the results of this study.

Results and Discussion

Because the reaction between epoxides and isocyanates catalysed by complex **1** had not previously been studied kinetically, this was the starting point for this study, to allow the rate equation to be compared to those for the corresponding reactions with carbon disulfide and carbon dioxide. Our approach to acquiring kinetic data was to use reaction conditions that were as close to those used synthetically as possible. Therefore, the kinetic experiments were carried out at 80 °C in toluene using styrene oxide **2a** and phenylisocyanate **7** as substrates with 5 mol% catalyst **1** (Scheme 5). The reactions could



Scheme 5. Reaction used to study the kinetics of oxazolidinone synthesis.

be conveniently monitored by withdrawing samples at regular intervals and analysing them by ^{1}H NMR spectroscopy to determine the ratio of epoxide **2a** to oxazolidinones **6a**,**b** present. Compounds **6a**,**b** were formed in a 1:1.9 ratio in these reactions.

Reactions carried out under these conditions showed a good fit to first-order kinetics, and reactions using three different initial concentrations of styrene oxide **2a** showed no change in the rate of reaction, whereas reactions carried out using three different initial concentrations of phenyl isocyanate **7** showed that the reaction rate increased as the concentration of isocyanate **7** increased.[10] The only other species present in this reaction was catalyst **1**, and the order with respect to catalyst **1** was determined by carrying out reactions using 5–13 mol% of the catalyst. These reactions were carried out in duplicate,[10] and the resulting plot of log[**1**] versus log(k_{1avg}) is shown in Figure 1. The data could be fitted to a straight line

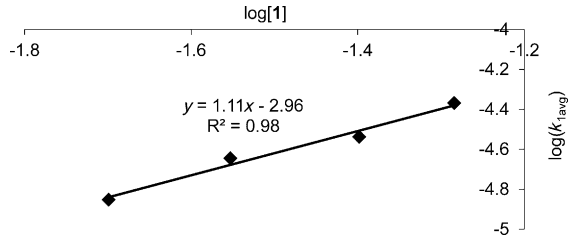


Figure 1. Plot of log[**1**] versus log(k_{1avg}) for the synthesis of oxazolidinones **6a** and **b**. Reactions carried out in toluene at 80 °C with [**2a**]$_0$ = 0.40 M and [**7**]$_0$ = 0.42 M.

with a slope of 1.1, suggesting that the reaction was first order in complex **1** concentration, and this was confirmed by a plot of [**1**] versus k_{1avg}, which also fitted to a straight line.[10] Thus, the kinetic equation for the reaction shown in Scheme 5 is given by Equation (3).

$$\text{rate} = k[\mathbf{1}][\text{isocyanate}] \quad (3)$$

This rate equation is very different to those observed for the reaction of epoxides with carbon dioxide and carbon disulfide [Eq. (1) and (2)] and suggests that the initial interaction on the catalytic cycle is between catalyst **1** and the isocyanate. This was supported by a ^{13}C NMR spectroscopic study of a mixture of complex **1** and phenylisocyanate **7**, which showed both an increase in the number of peaks and changes in their chemical shift, consistent with the formation of a new species with lower symmetry than complex **1**. In contrast, no change in the spectrum of complex **1** was observed when styrene oxide **2a** was added. Figure 2 shows the aliphatic region of spectra recorded in $CDCl_3$ with signals corresponding to the cyclohexyl ring carbon atoms and the *tert*-butyl methyl groups. The spectrum of complex **1** shows two signals above 55 ppm corresponding to the CH-N groups. In the spectrum of the mixture, these signals are shifted to above 60 ppm, and one of them is resolved into two separate signals. Similarly, the spectrum of complex **1** shows two peaks for the *tert*-butyl groups (either side of 30 ppm) and in the mixture, one of these is resolved into two separate signals. The other four peaks in the spectrum of complex **1** correspond to the four CH_2 groups within the cyclohexyl ring and, again, when phenylisocyanate is added, two of these signals are resolved into two peaks.

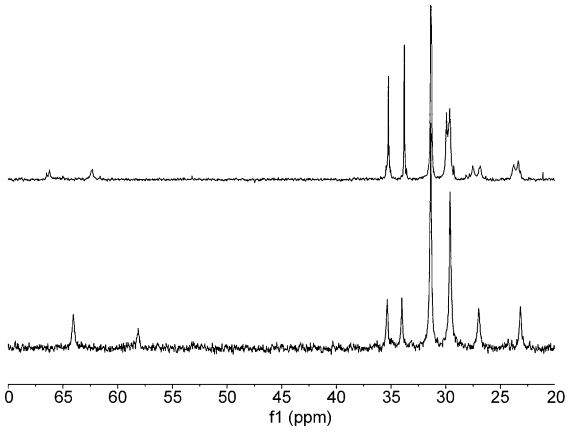
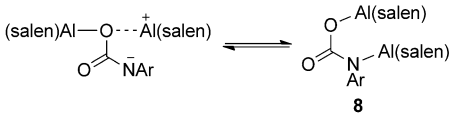


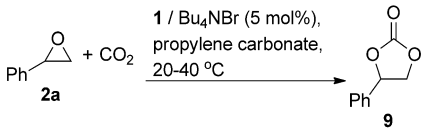
Figure 2. Partial ^{13}C NMR spectra of complex **1** (bottom) and a mixture of complex **1** and isocyanate **7** (top).

In Scheme 4, the adduct between complex **1** and phenylisocyanate **7** is drawn with both aluminium atoms still bound to the μ-oxygen to emphasise the increased Lewis acidity of the positively charged ion. In such a structure, the two aluminium ions and their salen ligands would be expected to be identical, with the positive charge delocalised between them. However, this adduct can also be drawn as uncharged species **8** (Scheme 6) in which the two aluminium ions and hence the two salen ligands are clearly different. This would be consistent with the ^{13}C NMR data.



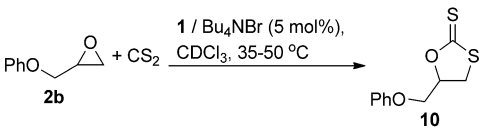
Scheme 6. Adduct formation between complex **1** and phenylisocyanate **7**.

Having determined the kinetic equations for all three reactions, a variable-temperature kinetic study was carried out to allow the enthalpy and entropy of activation as well as the Gibbs free energy of activation for each reaction to be determined. For oxazolidinone synthesis, the variable-temperature study was carried out in duplicate using epoxide **2a** and isocyanate **7** with 5 mol% catalyst **1** in toluene at temperatures of 70 to 110 °C; the resulting rate data were then used to create an Eyring plot.[10] A variable-temperature kinetic study of the reaction between styrene oxide **2a** and excess carbon dioxide to form styrene carbonate **9** catalysed by 5 mol% complex **1** and 5 mol% tetrabutylammonium bromide was carried out in propylene carbonate at temperatures of 20 to 40 °C (Scheme 7). The reactions were monitored by removing samples for analysis by ^{1}H NMR spectroscopy and the rate data were used to create an Eyring plot.[10]



Scheme 7. Reaction used to study the kinetics of cyclic carbonate synthesis.

For the reaction between epoxides and carbon disulfide, epoxide **2b** was used as substrate because this substrate gives almost exclusively (>96%) dithiocarbonate **10** as the product,[5] so complications due to trithiocarbonate formation were avoided. In this case, the kinetics of reactions carried out at 35–50 °C in $CDCl_3$ using 5 mol% complex **1** and tetrabutylammonium bromide as catalyst and cocatalyst, respectively, were monitored by ^{1}H NMR spectroscopy (Scheme 8).[10] The resulting Eyring plot is given in the Supporting Information and the thermodynamic parameters extracted from all the Eyring plots are collected in Table 1.



Scheme 8. Reaction used to study the kinetics of cyclic dithiocarbonate synthesis.

Table 1. Activation parameters for reactions catalysed by complex **1** or **11**[a,b]

Catalyst	Heterocumulene	$\Delta H^{\neq}$ [kJ mol^{-1}]	$\Delta S^{\neq}$ [J mol^{-1} K^{-1}]	$\Delta G^{\neq}$ [kJ mol^{-1}]
1	PhNCO	58.9 ± 2.0	−140 ± 6	97.0 ± 3.6
1	CO_2	25.8 ± 0.5	−185 ± 2	76.3 ± 1.1
1	CS_2	61.1 ± 0.6	−123 ± 2	94.7 ± 1.2
11	PhNCO	80.2 ± 2.3	−49 ± 7	93.7 ± 4.2

[a] Data based on the average of two data sets with the error limits derived from the two individual data sets. [b] $\Delta G^{\neq}$ at 273 K.

Table 1 shows that the Gibbs free energy of activation for cyclic carbonate synthesis is approximately 20 kJ mol^{-1} lower than that for the synthesis of cyclic dithiocarbonates or oxazolidinones. This is consistent with the facts that complex **1** was originally optimized for cyclic carbonate synthesis and that cyclic carbonate synthesis catalysed by complex **1** occurs at 20 °C, whereas the formation of cyclic dithiocarbonates or oxazolidinones requires temperatures of 50–90 °C. The enthalpies and entropies of activation for cyclic dithiocarbonate or oxazolidinone synthesis are also very similar. The rate equations for cyclic dithiocarbonate synthesis [Eq. (2)] and oxazolidinone synthesis [Eq. (3)] both suggest that the first step in both of the catalytic cycles shown in Scheme 3 and 4 is the rate-determining step. In both cases, this involves a homogeneous liquid-phase reaction between complex **1** and a second species, to form a single activated complex. Thus, both reactions would be expected to have similar and negative entropies of activation.

The enthalpies and entropies of activation for cyclic carbonate synthesis are, however, very different to those for cyclic dithiocarbonate or oxazolidinone synthesis. The rate equation [Eq. (1)] suggests that the rate-determining step is much later in the catalytic cycle because all components of the reaction appear in the rate equation. This, combined with the fact that the carbon dioxide starts as a gas rather than in solution, accounts for the much more negative entropy of activation for this reaction. However, this is more than offset by the much lower enthalpy of activation for cyclic carbonate synthesis, which is consistent with a rate-determining step late in the catalytic cycle, after the epoxide has been ring-opened and its strain energy released.

Monometallic aluminium(salen) chloride **11** is also an active catalyst for the synthesis of oxazolidinones from epoxides and isocyanates, and is about half as catalytically active as complex **1**.[6] Complex **11** is also known to catalyse the reaction between epoxides and carbon disulfide, displaying similar catalytic activity to complex **1**,[5] but was inactive for the synthesis of cyclic carbonates from epoxides and carbon dioxide. The latter two results are easily explained because the catalytic cycle for cyclic carbonate synthesis (Scheme 2) requires a bimetallic catalyst, whereas the catalytic cycle for cyclic dithiocarbonate synthesis (Scheme 3) requires only a single metal ion. However, the catalytic cycle proposed for oxazolidinone synthesis (Scheme 4) involves interconversion between bimetallic and monometallic species. Therefore, a kinetic study of the reaction between styrene oxide **2a** and phenylisocyanate **7** catalysed by complex **11** was undertaken under the same conditions used for reactions catalysed by complex **1** (Scheme 5).

Reactions in which the initial concentrations of epoxide **2a** and isocyanate **7** were varied again showed that these reactions were first order in isocyanate concentration and zero order in epoxide concentration.[10] Compounds **6a**,**b** were again formed in a 1:1.9 ratio in these reactions. Then, reactions were carried out (in duplicate) at four different concentrations of catalyst **11**, and the resulting plot of log([**11**]) versus log(k_1) (Figure 3) indicated that the reaction was third order in catalyst

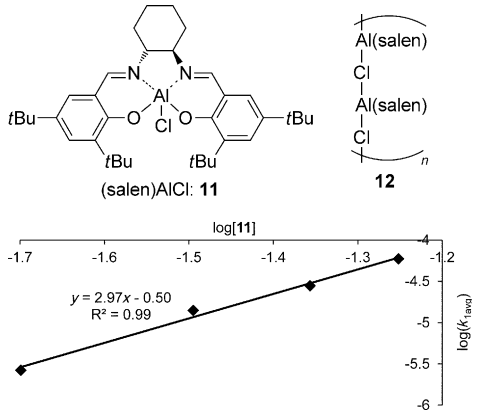


Figure 3. Plot of log[**11**] versus log(k_{1avg}) for the synthesis of oxazolidinones **6a** and **b**. Reactions carried out in toluene at 80 °C with [**2a**]$_0$ = 0.40 M and [**7**]$_0$ = 0.42 M.

concentration. This was confirmed by a plot of [**11**] versus (k_1·[**11**]$^{-2}$), which was also found to be a straight line passing through the origin (Figure 4). Thus, the rate equation for oxazolidinone synthesis catalysed by complex **11** is represented by Equation (4).

$$\text{rate} = k[\mathbf{11}]^3[\text{isocyanate}] \quad (4)$$

A possible explanation for the third-order kinetics with respect to complex **11** is that complex **11** exists as chloride bridged oligomers, giving a structure such as **12**. There is ample literature precedent for chloride to bridge between two aluminium ions[11,12] and for this bridging to result in the formation of oligomers or clusters.[12] To investigate this aspect of

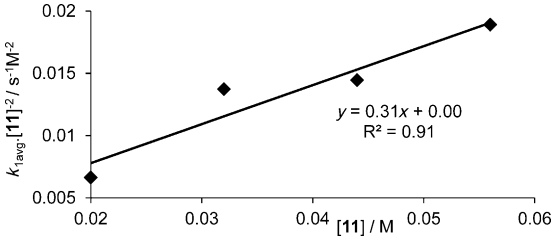


Figure 4. Plot of [**11**] versus k_{1avg}[**11**]$^{-2}$ for the synthesis of oxazolidinones **6a** and **b**. Reactions carried out in toluene at 80 °C with [**2a**]$_0$ = 0.40 M and [**7**]$_0$ = 0.42 M.

the catalysis further, and to allow a direct comparison with the results obtained using complex **1**, a variable-temperature study of the synthesis of oxazolidinones **6a**,**b** was carried out to allow an Eyring plot to be constructed;[10] the thermodynamic parameters extracted from this Eyring plot are included in Table 1.

The most striking feature of the activation parameters for the reaction catalysed by complex **11** is the entropy of activation, which is only about one third that of the corresponding reaction catalysed by complex **1**. Because both reactions involve the same substrates reacting to give the same products in the same solvent and at the same temperatures, this difference in entropies of activation can be accounted for by dissociation of oligomeric species **12** resulting in a large increase in entropy during the transition state, which largely offsets the decrease in entropy associated with the aluminium(salen) unit and isocyanate coming together. In contrast, the enthalpy of activation for the reaction catalysed by complex **11** is significantly higher than that for the reaction catalysed by complex **1**. This presumably reflects the fact that no bridging oxygen is available in complex **11** to bond to the isocyanate during the transition state. The net result of these differences in enthalpy and entropy of activation largely cancels out, so that reactions catalysed by complexes **1** and **11** have the same Gibbs free energy of activation, within the experimental error.

Conclusion

Complex **1** catalyses the formation of five-membered ring heterocycles from epoxides and carbon dioxide, carbon disulfide and isocyanates. These three reactions follow three different rate equations [Eq. (1–3)]. The rate equations for the reactions with carbon disulfide and isocyanates [Eq. (2) and (3), respectively] are both of the form: rate $= k$[substrate], but differ in which substrate the rate does (and does not) depend upon. This suggests that for the reaction with carbon disulfide, the initial interaction is between complex **1** and the epoxide, whereas for the reaction between complex **1** and isocyanates, the initial interaction is between complex **1** and the isocyanate. In both cases, this initial interaction appears to be rate determining. The ^{13}C NMR spectrum of a mixture of complex **1** and phenylisocyanate was consistent with the latter interaction. In contrast, the rate equation for cyclic carbonate synthesis catalysed by complex **1** [Eq. (1)] has a much more complex form, involving both substrates and the tetrabutylammonium bromide cocatalyst, as well as complex **1**. This suggests that for this reaction the rate-determining step is later in the catalytic cycle.

The above results can be explained on the basis of the relative susceptibility of the three heterocumulenes to attack by nucleophiles. Isocyanates are particularly susceptible to attack by nucleophiles, including oxygen-based nucleophiles.[13] Carbon dioxide and carbon disulfide are less susceptible to attack by nucleophiles, although they are known to react with oxygen- and nitrogen-based nucleophiles.[14,15] The bridging oxygen of complex **1** is potentially a good, hard nucleophile,[16,17] and for the reaction with isocyanates this appears to initiate the catalytic cycle as shown in Scheme 4. In contrast, for reactions with heterocumulenes, which are less susceptible to attack by nucleophiles (carbon dioxide and carbon disulfide), the coordinatively unsaturated aluminium ions of complex **1** can act as Lewis acids and coordinate to the epoxide. For the reaction with carbon disulfide, this initial epoxide coordination appears to be rate determining, with all subsequent steps in the catalytic cycle shown in Scheme 3 involving very good nucleophiles or leaving groups. In contrast, for cyclic carbonate synthesis, initial coordination of the epoxide to the aluminium ion appears not to be the rate-determining step of the catalytic cycle, resulting in a more complex rate equation.

The entropies of activation determined from variable-temperature kinetic data also support the above hypothesis. The reactions of epoxides with carbon disulfide and isocyanates have very similar negative entropies of activation, consistent with two species coming together to form a single adduct in the rate-determining transition state. The reaction with carbon dioxide has a much more negative entropy of activation, consistent with more species having come together by the time the reaction reaches the rate-determining transition state.

The overall analysis suggests that for future catalyst design, for reactions involving heterocumulenes that have relatively low susceptibility to attack by nucleophiles, the Lewis acidity of the catalyst should be optimized to facilitate its reaction with and activation of epoxides, whereas for reactions involving isocyanates and other heterocumulenes that are highly susceptible to attack by nucleophiles, the Lewis basicity of the catalyst should be optimized because this interaction determines the overall rate of reaction. The data suggest that catalyst **1** is significantly more suitable for reaction with carbon dioxide than with carbon disulfide or isocyanates because both the enthalpy and Gibbs free energy of activation for cyclic carbonate synthesis are 20–30 kJ mol^{-1} lower than those for cyclic dithiocarbonate or oxazolidinone synthesis. This analysis will guide future catalyst development for these and related reactions.

Experimental Section

Procedure for Measuring the Kinetics of the Reaction between Epoxide 2a and Phenylisocyanate 7 Catalysed by Complex 1

Complex **1** (0.04–0.11 mmol) and styrene oxide **2a** (0.1 mL, 0.84 mmol) were dissolved in toluene (2 mL) and the solution was heated to 80 °C, after which phenylisocyanate **7** (0.1 mL, 0.84 mmol) was added. An aliquot of the reaction mixture was removed and immediately quenched with $CDCl_3$ every 30 min for 4–5 h. Each sample was analysed by ^1H NMR spectroscopy to determine the ratio of epoxide **2a** to oxazolidinones **6a**,**b**.

Procedure for Measuring the Kinetics of the Reaction between Epoxide 2a and CO_2 Catalysed by Complex 1

Complex **1** (50 mg, 0.04 mmol) and Bu_4NBr (12.9 mg, 0.04 mmol) were placed in a test tube fitted with a side-arm and dissolved in propylene carbonate (0.5 mL). A round-bottom flask was filled with dry-ice pellets and attached to the side-arm. The test tube was

sealed with a Suba seal pierced with an empty balloon. The CO_2 was allowed to flush the system and fill the balloon. The solution was then heated (20–40 °C), and styrene oxide **2a** (0.1 mL, 0.84 mmol) was added to the solution. An aliquot of the reaction mixture was removed and immediately quenched with $CDCl_3$ every 30 min for 4–5 h. Each sample was analysed by ^{1}H NMR spectroscopy to determine the ratio of epoxide **2a** to cyclic carbonate **9**.

Procedure for Measuring the Kinetics of the Reaction between Epoxide 2b and CS_2 Catalysed by Complex 1

Complex **1** (50 mg, 0.04 mmol), Bu_4NBr (12.9 mg, 0.04 mmol) and 3-phenoxypropylene oxide **2b** (0.113 mL, 0.84 mmol) were dissolved in $CDCl_3$ (0.37 mL). The solution was added to an NMR tube followed by addition of carbon disulfide (0.09 mL, 1.5 mmol). The tube was inserted into the NMR spectrometer with the probe heated (35–50 °C). A ^{1}H NMR spectrum was collected every 30 min for 12.5 h and used to determine the ratio of epoxide **2b** to cyclic dithiocarbonate **10**.

Procedure for Measuring the Kinetics of the Reaction between Epoxide 2a and Phenylisocyanate 7 Catalysed by Complex 11

Complex **11** (5–13 mol%) and styrene oxide **2a** (0.1 mL, 0.84 mmol) were dissolved in toluene (0.5–2 mL) and the solution was heated to 80 °C, after which phenylisocyanate **7** (0.1 mL, 0.835 mmol) was added. An aliquot of the reaction mixture was removed and immediately quenched with $CDCl_3$ every 30 min for 4–5 h. Each sample was analysed by ^{1}H NMR spectroscopy to determine the ratio of epoxide **2a** to oxazolidinones **6a**,**b**.

Acknowledgements

The authors thank EPSRC for a studentship to C. B.

Keywords: aluminium · carbon dioxide · carbon disulfide · epoxides · kinetics · ring-opening · reaction mechanisms

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Received: February 1, 2014
Published online on ■■ ■■, 0000

FULL PAPER

Synthetic Methods

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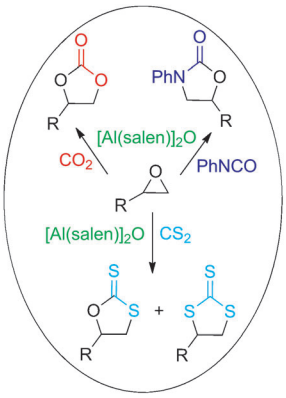
Mechanistic Investigation of the Reaction of Epoxides with Heterocumulenes Catalysed by a Bimetallic Aluminium Salen Complex



One ring to rule them all: Kinetic studies on the reaction of epoxides with carbon dioxide, carbon disulfide and phenylisocyanate catalysed by $[Al(salen)]_2O$ provide an overarching mechanistic understanding of these reactions, which follow three different rate equations (see scheme). The results highlight the potential of $[Al(salen)]_2O$ to act as both a Lewis acid and a Lewis base with the relative importance of these determined by the heterocumulene.