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Electronic Supplementary Information (ESI) for:

DFT and Experimental Analysis of Aluminium Chloride as a Lewis Acid Proton Carrier Catalyst for Dimethyl Carbonate Carboxymethylation of Alcohols

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Table of contents

1 Characterisation
1.1 Mass spectrum electron ionisation (EI) of methyl octyl carbonate (MOC)3
1.2 ¹ H NMR of MOC4
1.3 ¹³ C NMR of MOC4
1.4 1 H NMR of pure dimethyl carbonate (DMC)5
1.5 ^{1}H NMR of complex of DMC and AlCl ₃ 5
1.6 ¹³ C NMR of pure DMC6
1.7 $^{\rm 13}C$ NMR of complex of DMC and AlCl_36
2 Experimental and DFT calculation of FT-IR spectrum7
3 Potential complexes of DMC and AlCl ₃ 8
4 AICl ₃ – DMC complexes through AI-O interactions
5 Path A2 and path B2: the four-membered ring transition state9
6 Path D1: the AlCl $_3$ catalysed reaction pathway with coordination occurring through the

carbonyl oxygen of DMC11
7 The thermodynamic quantities obtained by M06-2X functional14
8 The optimised structures of the stationary points17
8.1 A2-RC17
8.2 A2-TS17
8.3 A2-PC
8.4 B2-RC
8.5 B2-TS1
8.6 B2-IM19
8.7 B2-TS2
8.8 B2-PC19
8.9 A-RC20
8.10 A-TS
8.11 A-PC21
8.12 B-RC21
8.13 B-TS1
8.14 B-IM
8.15 B-TS223
8.16 B-PC23
8.17 C-RC23
8.18 C-TS124
8.19 C-IM124
8.20 C-TS225
8.21 C-IM225
8.22 C-TS325
8.23 C-PC26
8.24 D1-RC
8.25 D1-TS
8.26 D1-PC27

1 Characterisation



1.1 Mass spectrum electron ionisation (EI) of methyl octyl carbonate (MOC)





1.2 $^{1}\mathrm{H}$ NMR of MOC

Figure S2. ¹H NMR of MOC

1.3¹³C NMR of MOC



Figure S3. ¹³C NMR of MOC

1.4 ¹H NMR of pure dimethyl carbonate (DMC)



Figure S4. ¹H NMR of pure dimethyl carbonate (DMC)

1.5 ^{1}H NMR of complex of DMC and AlCl₃



Figure S5. ¹H NMR of complex of DMC and AlCl₃ (mole ratio of DMC to AlCl₃ is 10:1)



1.6¹³C NMR of pure DMC

Figure S6. ¹³C NMR of pure DMC

1.7 $^{\rm 13}{\rm C}$ NMR of complex of DMC and AlCl_



Figure S7. ¹³C NMR of complex of DMC and AlCl₃ (mole ratio of DMC to AlCl₃ is 10:1)



2 Experimental and DFT calculation of FT-IR spectrum

Figure S8. FT-IR of pure AlCl₃ (green line), pure DMC (red line) and AlCl₃-DMC complex and (mole ratio of DMC to AlCl₃ is 10:1) (blue line), with the stretching vibration of Al- O_{sp3} (455 cm⁻¹) and Al- O_{sp2} (488 cm⁻¹) clearly visible.



Figure S9. Theoretical FT-IR of (a) DMC, (b) $AlCl_3$ coordinating with DMC through the sp² hybridised carbonyl oxygen and (c) $AlCl_3$ coordinating with DMC through the sp³ hybridised oxygen. Data obtained by DFT calculations at the CAM-B3LYP-D3/6-311+G(d,p) level.

3 Potential complexes of DMC and AlCl₃

In this research, dimeric aluminium chloride has been employed as a simplified structure to carry out density functional theory (DFT) analysis in place of the polymeric lattice of solid AlCl₃. The latter would be impossible to model, due to complexity, while the former should sufficiently correlate for the calculations to be valid.



Figure S10. The optimised structures of the stationary points for (a) dimeric aluminium chloride, (b) Al_2Cl_6 coordinating to the carbonyl of DMC and (c) Al_2Cl_6 coordinating to the sp³ hybridised oxygen atom of DMC; significant bond lengths (angstroms) are given.



4 AICl₃ – DMC complexes through AI-O interactions

Figure S11. The optimised structures of the stationary points for (a) DMC, (b) $AICI_3$ coordinating to the carbonyl of DMC and (c) $AICI_3$ coordinating to the sp³ hybridised oxygen

atom of DMC. Significant bond lengths (angstroms) are also given.

Reaction	ΔΕ	ΔН	ΔG
$DMC + 1/2(Al_2Cl_6) \rightarrow Structure-A$	-19.8	-20.1	-15.3
$DMC + 1/2(Al_2Cl_6) \rightarrow Structure-B$	-9.0	-9.2	-4.5

Table S1. The changes in energy (ΔE , kcal mol⁻¹), enthalpy (ΔH , kcal mol⁻¹) and Gibbs free energy (ΔG , kJ mol⁻¹) for complex reaction obtained by DFT calculations.

5 Path A2 and path B2: the four-membered ring transition state

Calculations imply that there are an additional two possible pathways for catalyst-free carboxymethylation of 1-octanol by DMC, requiring a four-membered transition state. The schematic descriptions of these two pathways are shown in Figure S12.



Figure S12. The two four-membered transition state reaction pathways for the carboxymethylation of 1-octanol by DMC under catalyst-free conditions (R = n-octyl).



Figure S13 Optimised 4-membered transition state (TS) structures for catalyst-free carboxymethylation of 1-octanol by DMC. The imaginary frequency and significant bond lengths (angstroms) are also given (R = n-octyl).

In path A2, the nucleophilic 1-octanol (O_{a1}) bonds to the electrophilic carbon atom C_1 , and proton transfer of H_{a1} to the oxygen atom O_2 simultaneously occurs (Figure S13(a)). The transition state (A2-TS) has a four-membered ring structure constituted by C_1 , O_{a1} , H_{a1} and O_2 atoms, and the imaginary frequency is 1261.1i cm⁻¹.

The path B2 is a two-step addition/elimination mechanism. As described Figure S12, this pathway begins with the addition of 1-octanol to the C₁ carbon of C₁=O₁, proceeding through two different transition states (B2-TS1 and B2-TS2). In the first four-membered ring transition state B2-TS1 (see Figure S13(b)), the imaginary frequency is 1367.5i cm⁻¹, associated with the nucleophilic attack of alcohol molecule (O_{a1}) at the C₁ carbon atom, and the simultaneous H_{a1} proton transfer from 1-octanol (O_{a1}) to the carbonyl oxygen O₁. The second step of this pathway was the elimination process (see Figure S13(c)), through the breaking of the C₁–O₂ σ bond and the simultaneous restoration of the C₁=O₁ π bond.



Reaction Coordinate

Figure S14 Relative energy profiles (in kcal mol⁻¹) for the catalyst-free carboxymethylation of 1-octanol by Path A2 and Path B2 obtained by the CAM-B3LYP/6-311+G(d,p) method.

6 Path D1: the AlCl₃ catalysed reaction pathway with coordination occurring through the carbonyl oxygen of DMC

In addition to the 6 membered transition state for AlCl₃ catalysed carboxymethylation of 1octanol proposed in the paper, pathways by a four membered transition state are also possible. These are shown in Figure S15. We found that the energy barrier for Path C (19.9 kcal mol⁻¹) is much lower than that for Path D1 (40.9 kcal mol⁻¹), which suggests that Structure-B is most advantageous for catalysis to occur. Moreover, the energy barrier for catalyst-free pathway path B (31.4 kcal mol⁻¹) is also much lower than that for catalysed pathway Path D1. Additionally, based on DFT calculations the AlCl₃ catalysed process cannot proceed through a 6 membered transition state (where the carbonyl oxygen is coordinated to AlCl₃) due to steric hindrance.



Figure S15 The carboxymethylation reaction of 1-octanol *via* a 4 and 6 membered transition states, in which the AlCl₃ catalysed 6 membered transition state (where the carbonyl oxygen is coordinated to AlCl₃) cannot form due to the steric hindrance.



Figure S16 Optimised 4 membered TS structure of the catalysed reaction pathway D1. imaginary frequency and significant bond lengths (angstroms) are given (R = n-octyl).

Of note is that although the activation energy barrier of Path D1 is lower than Path A2, it remains significantly higher than that of Path C, Scheme 2.



Reaction Coordinate

Figure S17 Relative energy profiles (in kcal mol⁻¹) for the carboxymethylation reaction of 1octanol *via* a 4-membered transition state, both catalyst-free (Path A2) and AlCl₃ catalysed with coordination through the carbonyl oxygen atom (Path D1), obtained by the CAM-B3LYP/6-311+G(d,p) method.



Reaction Coordinate

Figure S18. Relative enthalpy profiles (in kcal mol⁻¹) for the carboxymethylation reaction of 1-octanol for three pathways obtained by the CAM-B3LYP/6-311+G(d,p) method (Path A and Path B are catalyst-free; Path C is AlCl₃ catalysed).



Reaction Coordinate

Figure S19. Relative Gibbs free energy profiles (in kcal mol⁻¹) for the carboxymethylation reaction of 1-octanol along three pathways obtained by the CAM-B3LYP/6-311+G(d,p) method (Path A and Path B are catalyst-free; Path C is AlCl₃ catalysed).

7 The thermodynamic quantities obtained by M06-2X functional

All of the geometric structures were fully optimised at the M06-2X/6-311+G(d,p) level of theory, and the thermodynamic quantities were calculated at the same level of theory.



Reaction Coordinate

Figure S20. Relative energy profiles (in kcal mol⁻¹) for the carboxymethylation reaction of 1octanol for three pathways obtained by the M06-2X/6-311+G(d,p) method (Path A and Path B are catalyst-free; Path C is catalysed by AlCl₃).



Reaction Coordinate

Figure S21. Relative enthalpy profiles (in kcal mol⁻¹) for the carboxymethylation reaction of 1-octanol for three pathways obtained by the M06-2X/6-311+G(d,p) method (Path A and Path B are catalyst-free; Path C is catalysed by $AICI_3$).



Figure S22. Relative Gibbs free energy profiles (in kcal mol⁻¹) for the carboxymethylation reaction of 1-octanol along three pathways obtained by the M06-2X/6-311+G(d,p) method (Path A and Path B are catalyst-free; Path C is catalysed by $AlCl_3$).



Reaction Coordinate

Figure S23 Relative energy profiles (in kcal mol⁻¹) for the catalyst-free pathways (Path A2 and Path B2) and AlCl₃ catalysed pathway (Path D1) obtained by the M06-2X/6-311+G(d,p) method.

8 The optimised structures of the stationary points

8.1 A2-RC



8.2 A2-TS







8.4 B2-RC





8.6 B2-IM



8.7 B2-TS2











8.11 A-PC





8.13 B-TS1



8.14 B-IM



8.15 B-TS2





8.17 C-RC



8.18 C-TS1







8.20 C-TS2



8.21 C-IM2



8.22 C-TS3



8.23 C-PC



8.24 D1-RC



8.25 D1-TS







S26