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9th. Annual Conference on Carbon Capture and Sequestration

US-UK CCS Workshop
Pittsburgh, Pennsylvania
May 10th. 2010

Prof. Chris Rayner,
University of Leeds, UK

The University of Leeds

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- An international university
- Established in 1904 (from 1874 beginnings)
- Quality in teaching & research
- 2nd largest university in UK
- Modern & innovative
- Very popular with UK students,
- 2nd highest number UK applications
- Research income > £90 million
- Interdisciplinary and emerging fields encouraged

CCS at Leeds

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Major research area for Leeds

- Interdisciplinary research across Engineering, Chemistry and Earth and Environment.
- Current grants totalling ~ £ 6 M out of a total energy research portfolio of ~ £ 40 M.
- Important aspect of the EPSRC funded Energy Doctoral Training Centre at £ 6.5 M
- Yorkshire Forward funded Centre for Low Carbon Futures.
- Research Councils' Energy Programme, EPSRC highlighted Leeds' leadership in "Coal and CCS".
- Active international collaborations in CCS, e.g. strong partnership with Zhejiang University on pilot-scale research

Prof. Chris Rayner

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Research interest: synthetic organic chemistry, sustainable chemistry, natural products chemistry, CO_2 chemistry and applications in pharmaceutical synthesis.

- Degree and PhD, University of Liverpool UK.
- Postdoctoral research, Ohio State University, 1987-89
- University of Leeds since 1989
- Professor of Organic Chemistry, Head of Organic Chemistry

- 15 years experience in use of high pressure CO_2 in organic chemistry

- Director of C-Capture Ltd. and co-Director of DyeCat Ltd.
- Research interests relevant to CCS include amine degradation and CO_2 capture chemistry

Amines in carbon capture and storage

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- Amines, most commonly aqueous monoethanolamine (MEA), are used as solvents in post-combustion carbon capture processes.[1]
- They react reversibly with carbon dioxide.
- Thermal and oxidative solvent degradation limit the efficiency of this process.[2]
- Understanding degradation processes and products important for large scale but very difficult

Reactions between MEA and CO_2

[1] IEA Greenhouse Gas R&D Programme, 2004. *Improvement in power generation with post-combustion capture of CO_2*, IEA Greenhouse Gas R&D Programme Report No. PH4/33.

[2] Strazisar, B., Anderson, R., White, C., Degradation Pathways for Monoethanolamine in a CO_2 Capture Facility. *Energy and Fuels*, 2003, **17**, 1034-1039.

The oxidation of MEA analogues

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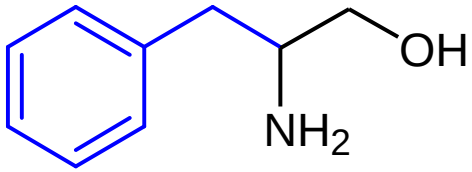
Alcohols

Alcohol

Aldehyde

Carboxylic Acid



Amines

Nitroso dimer

Imine

Amine

Hydroxylamine

Nitrosoalkane

Oxime

Nitrile

Nitroalkane

Oxidation studies 1

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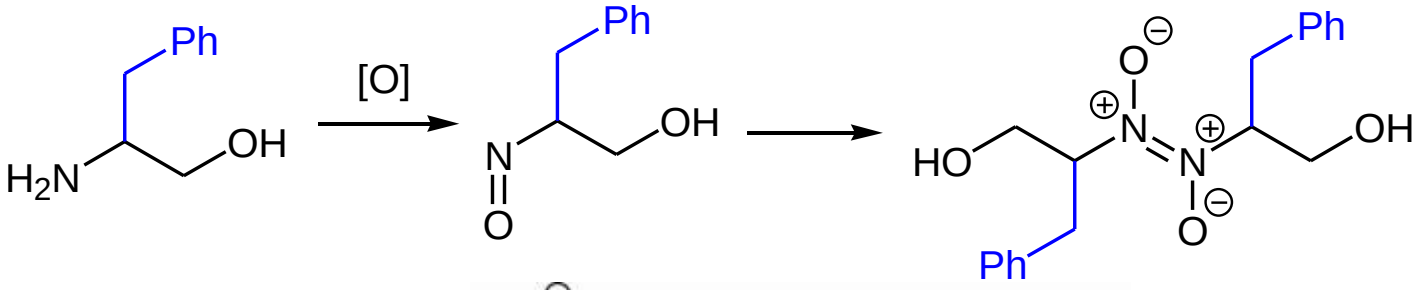
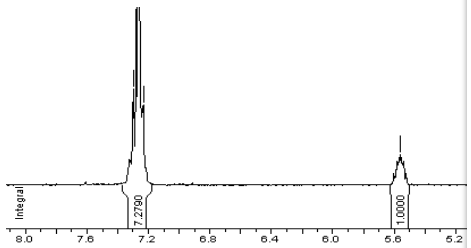
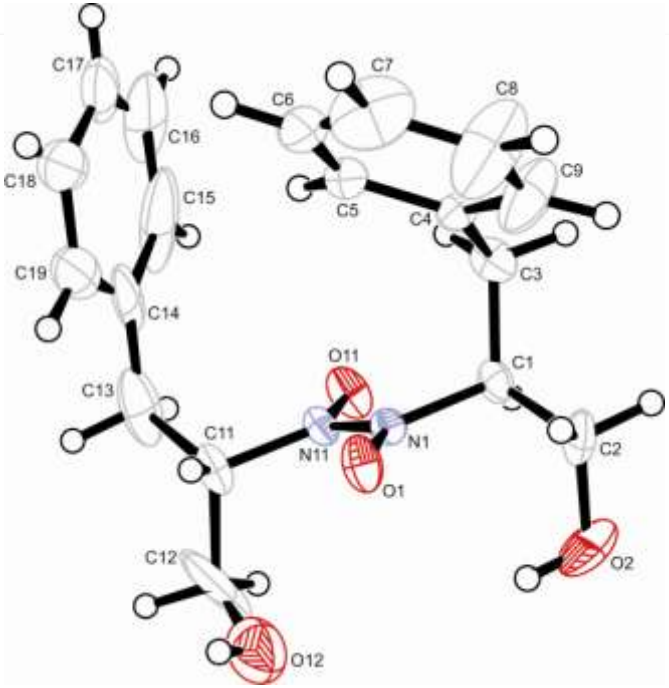


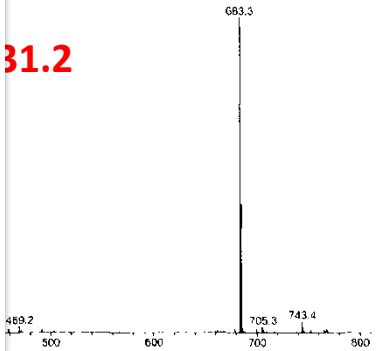


The obtained



Crystal structure of nitroso dimer

31.2



ition mass spectrum

Oxidation studies 2

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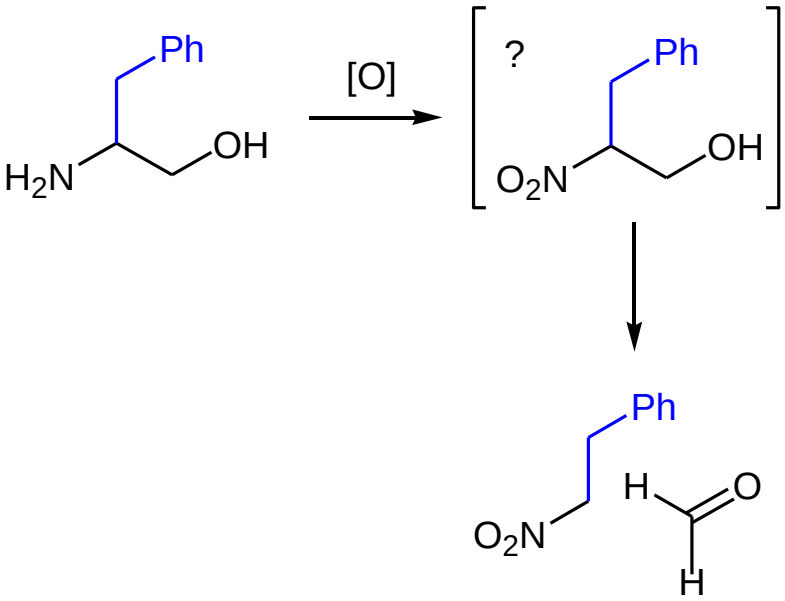
SLOW FAST

Hydroxylamine Nitrosoalkane Nitroso dimer

- Using fewer equivalents of oxidant did not lead to the hydroxylamine derivative being observed.
- The nitrosoalkane dimer is still the major product at temperatures up to 50 °C.
- Attempts to prepare the nitroalkane by a published method resulted in degradation.[3]



Nitroso dimer rearrangement

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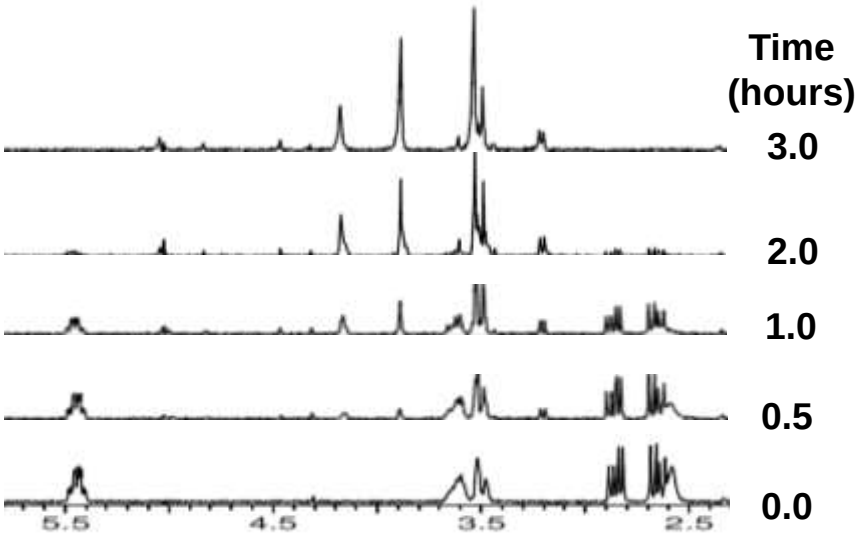
- The nitroso dimer is stable at 40 °C and 60 °C.
- At 100 °C it disassociates to nitrosoalkane and converts to an oxime.
- The oxime exists as two stereoisomers. Over time all the molecules convert to the more stable *syn* form.

syn *anti*

Heating the nitroso dimer in toluene:



Nitroso dimer Nitrosoalkane Oxime

Rearrangement of oximes

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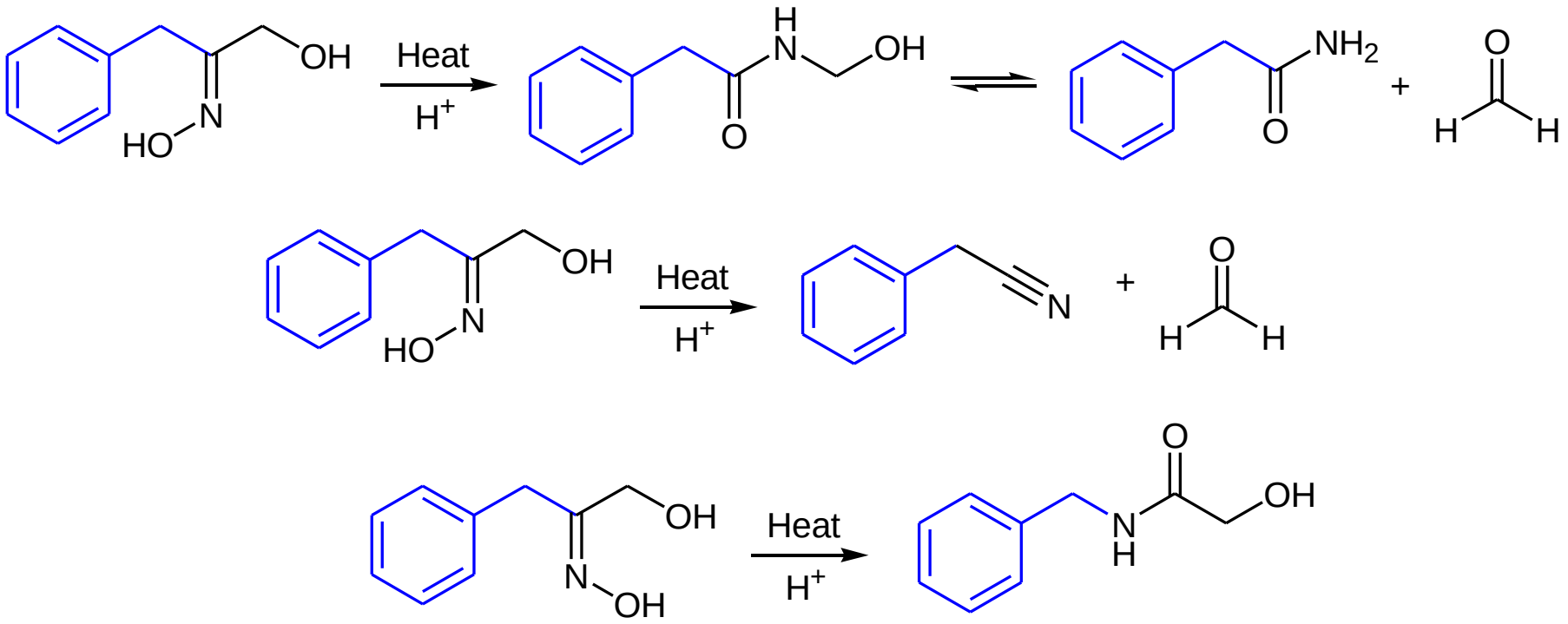
- Oximes well known to undergo Beckmann rearrangement under acidic conditions and at elevated temperatures

- Three different pathways possible, all giving different products



[4] Ferris, A.F., α-Oximino Ketones. IV. The "Normal" and "Abnormal" Beckmann Rearrangements. *J. Org. Chem.,* 1960, **25**(1), 12-18.

Suggested MEA degradation products

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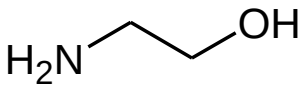
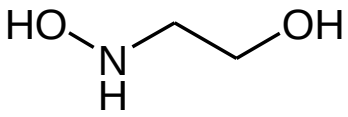
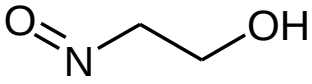
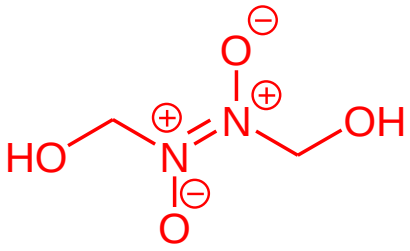
Primary oxidation

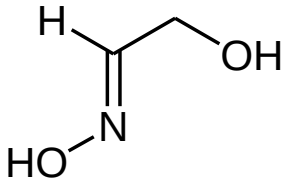


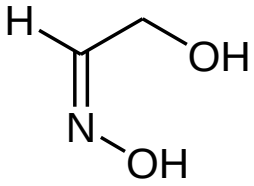


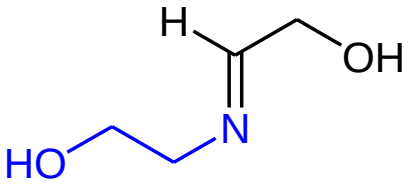




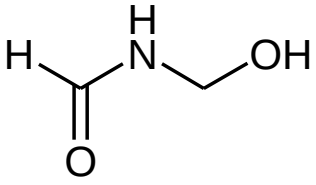
Primary degradation

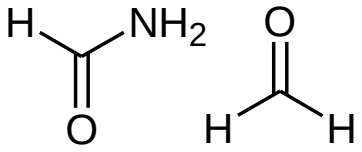


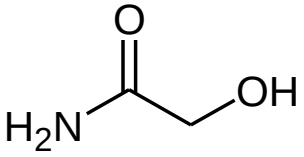


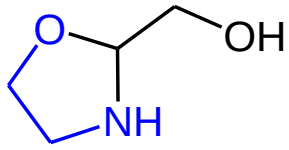


Secondary degradation

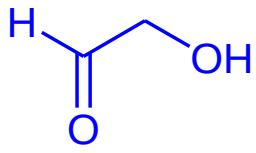


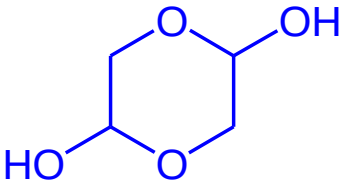


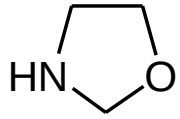


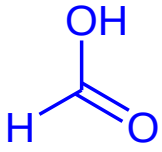


Hydrolysis

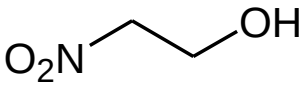


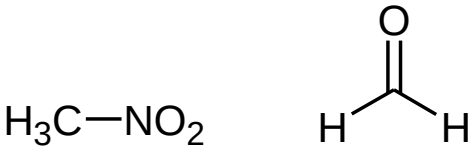






and other N-nitroso species?





HCN

Analysis of used sample of MEA

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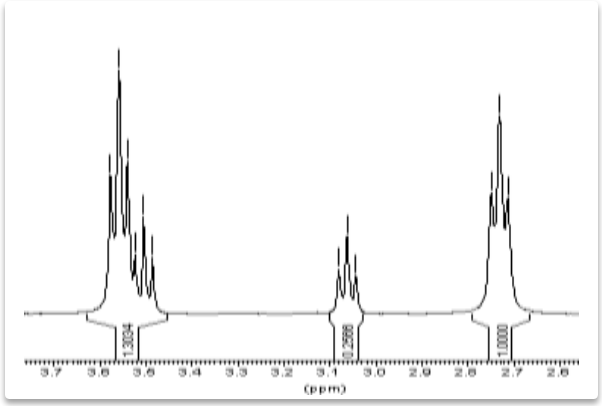
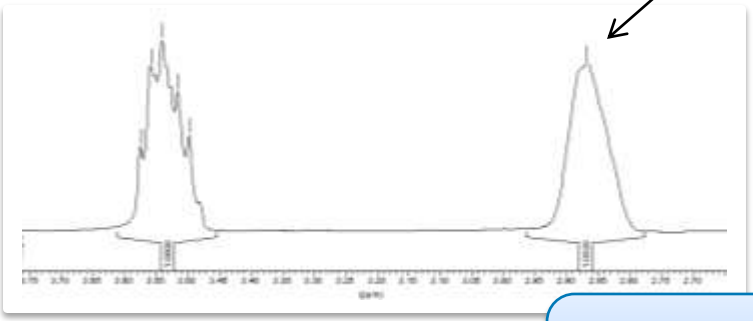
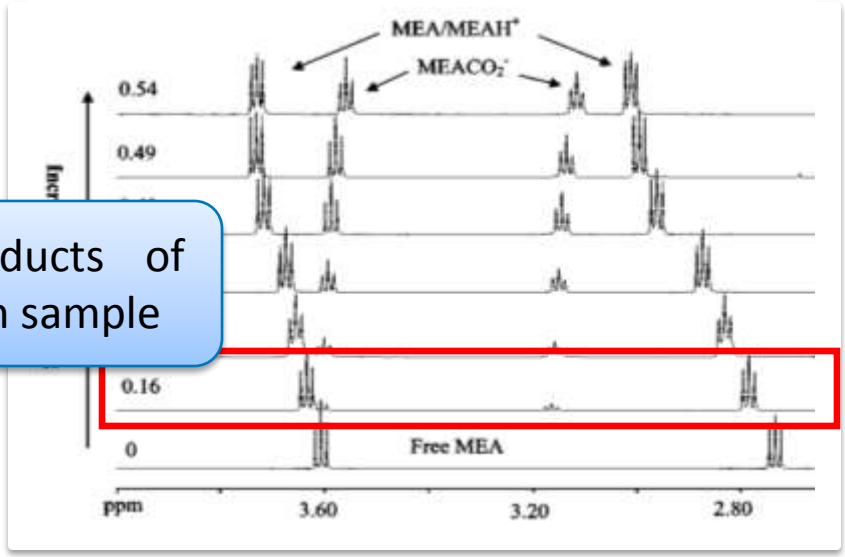
1. Addition of conc. hydrochloric acid, both species convert to ammonium chloride salt.



2. Comparison with a study by Fan *et al.* indicates the sample is loaded with ~0.16 mol CO_2/mol MEA.[5]



3. No obvious products of degradation present in sample



[5] Fan, G., Wee A., Idem, R., Tontiwachwuthikul, P., NMR studies of amine species in MEA-CO2-H2O system: Modification of the model of vapor-liquid equilibrium (VLE). *Ind. Eng. Chem. Res.,* 2009, **48**, 2717-2720.

Implications for MEA degradation

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- Amine group more susceptible to oxidation than alcohol
- Wide range of small, structurally similar, highly polar species formed
- Unambiguous characterisation challenging
- Many will be thermally unstable and may undergo further degradation
- Particularly hazardous materials may be formed, e.g. HCN, N-nitrosamine derivatives
    - Issue for process operation and disposal
- Further studies required on MEA itself and spent samples

Reaction of novel amines with CO_2

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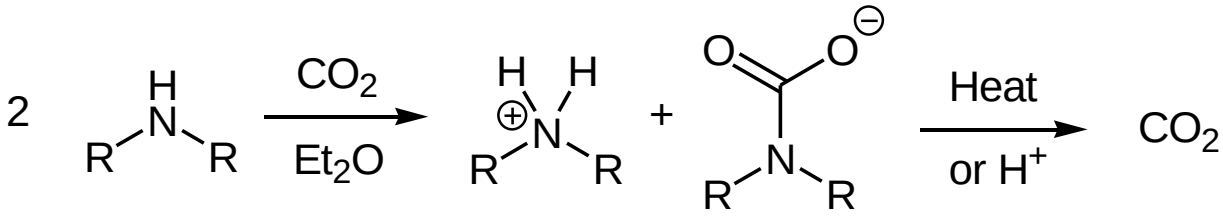


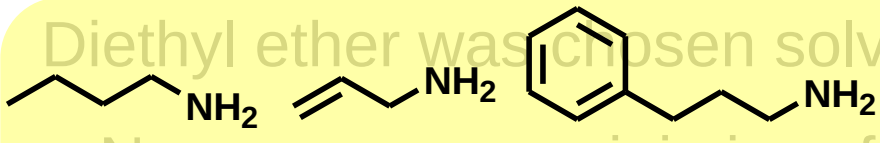
Selected amines

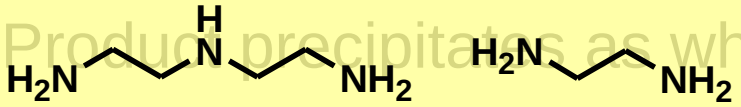
Instant formation of solid turning quickly gel-like

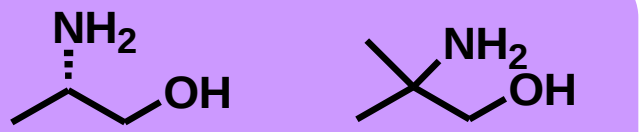
Up to 5 mins of CO_2 require to form colourless solid

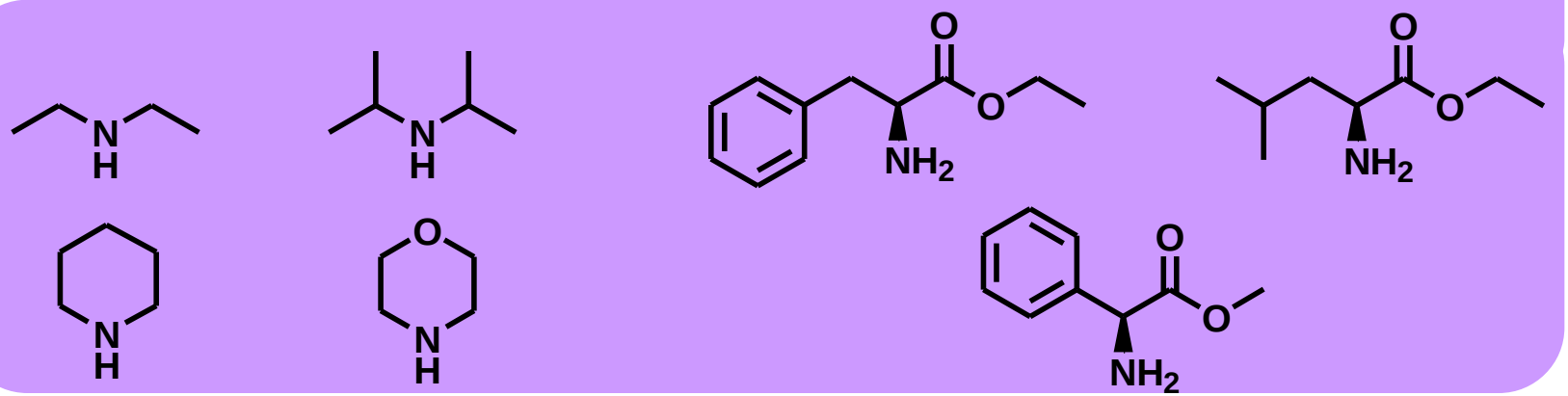
Diethyl ether was chosen solvent:

- Non-aqueous – minimises formation of bicarbonate
- Product precipitates as white so









Structure of carbamate salts

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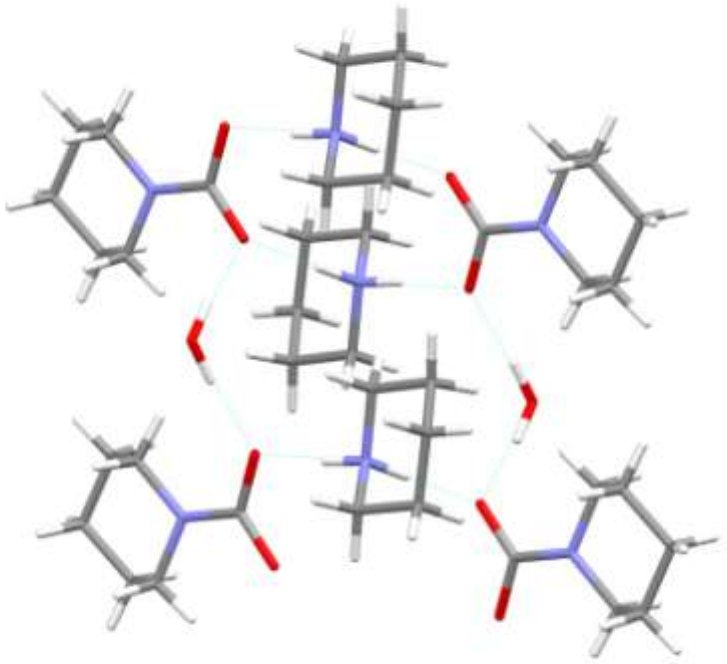
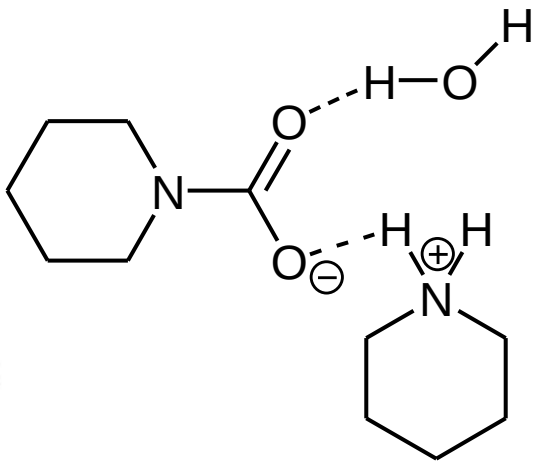
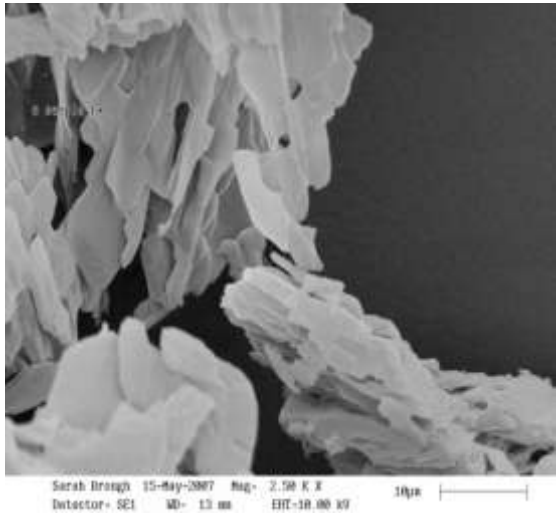
- Carbamates highly crystalline and reasonably stable, X-ray crystal structure obtained
- Hygroscopic – water of crystallisation present, even though apparent anhydrous conditions
- Extensive hydrogen bonding between species
- Decarboxylates on heating to 80 C







SEM of a carbamate

Decarboxylation of carbamates

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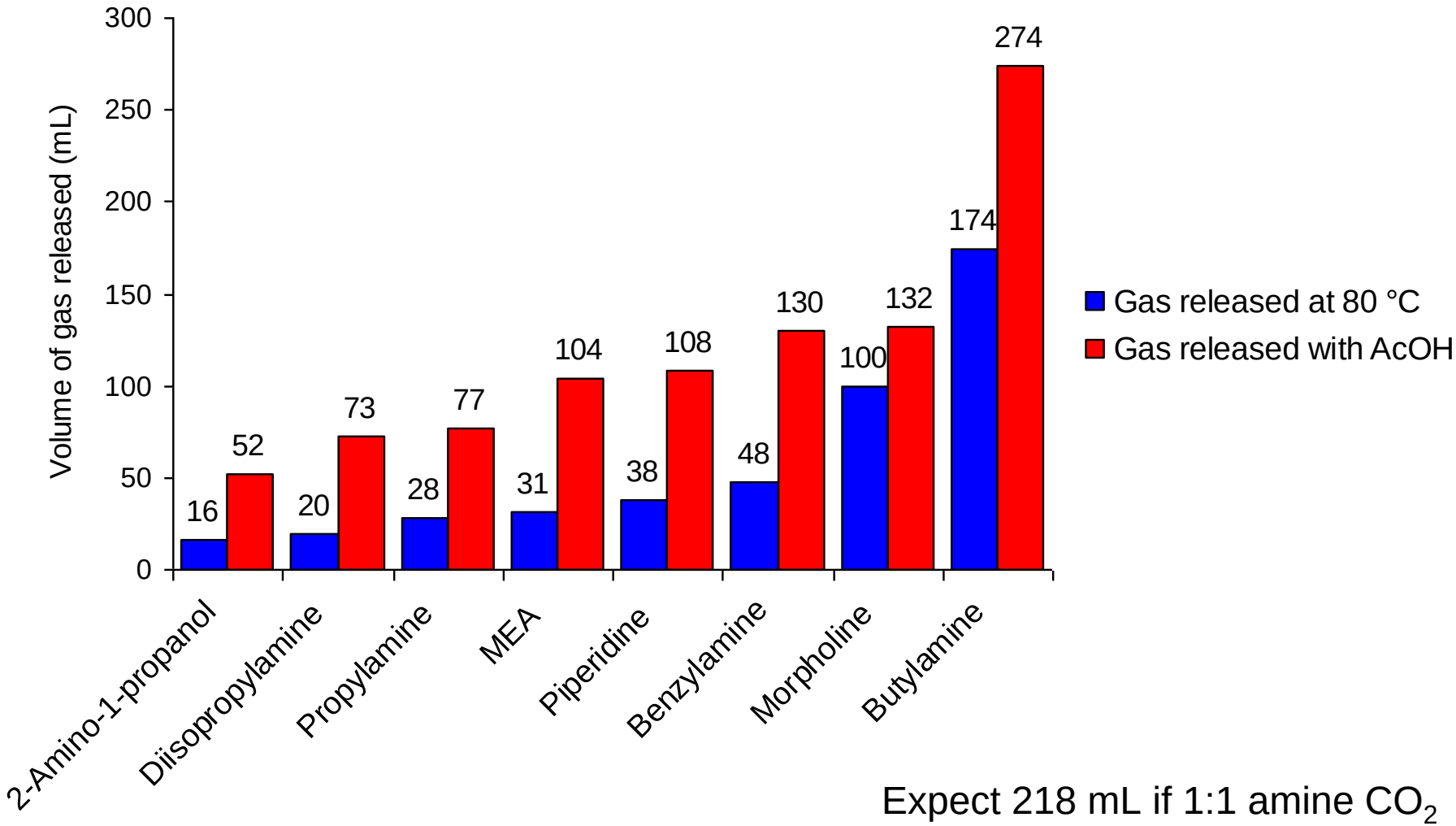

Expect 218 mL if 1:1 amine CO_2

C-Capture Ltd.

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- Established to commercialise novel non-amine based solvents for CO_2 capture.
- Solvents based on renewable, non-toxic materials
- Non-amine based
- Inexpensive
- Favourable energetic characteristics, enthalpy of decarboxylation typically half that for MEA
- Enhanced kinetic profile for CO_2 absorption
- Compatible with amine based post-combustion capture equipment
- Further discussions possible under appropriate confidentiality agreement

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