ELECTRONIC SUPPLEMENTARY INFORMATION

Isosorbide bis(methyl carbonate) synthesis from isosorbide and dimethyl carbonate: The key role of dual basic-nucleophilic catalysts†

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Abbreviations

- ACN: Acetonitrile.
- C_{OH} (%): Conversion(s) of total hydroxyl groups contained by ISO and IMMC, as obtained by ATR-FTIR.
- IBMC: Isosorbide bis(methyl carbonate) (l,4:3,6-dianhydro-2,5-bis-O-(methoxy-carbonyl)-D-glucitol).
- IMMC: Isosorbide mono(methyl carbonate).
- ISO: Isosorbide (1,4:3,6-dianhydro-D-glucitol).

Contents

1. Multireactor Eyela

The experimental work was carried out in batchwise mode in an Eyela multireactor (**Picture P1**) consisting of 5 tube-shaped reactors, each one able to work with up to 60 mL of reaction mixture at different temperatures under the same magnetic stirring.

Picture P1. Eyela multirreactor.

2. Reaction monitorization by ATR-FTIR

Figure S1 show two spectra. In red at the reaction beginning corresponding to pure isosorbide. In blue at the end of a reaction with a high OH-conversion in which the intensity of the peak corresponding to OH close to 3500 cm^{-1} has decreased dramatically while an intense peak corresponding to C=O in linear carbonates can be observed. All spectra were recorded at 65 ºC after very quick evaporation of the solvent at the same temperature following the deposition of 1-2 drops of reaction medium on the sample holder of a Bruker ALPHA Platinum-ATR-FTIR Spectrometer.

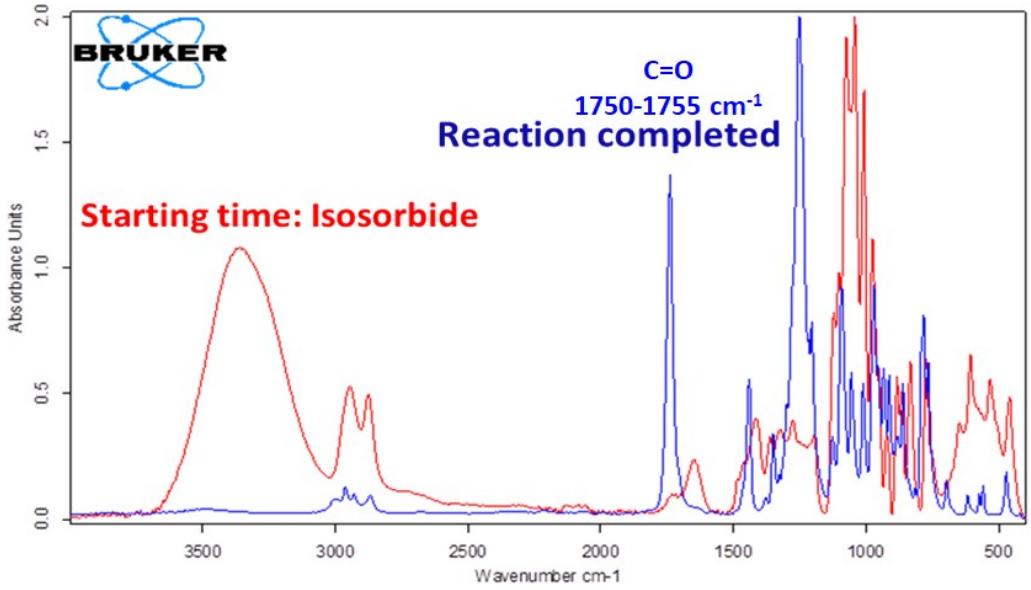

Figure S1. ATR-FTIR of a reaction at starting time (red) and after reaction completion (blue). In this case both spectra have been recorded after baseline correction and normalization to 2.

3. Reaction quantification

It was carried out by combining GPC and GC-MS as described in the paper. The GPC chromatogram for the reaction whose ATR-FTIR spectra is depicted in **Picture S1** is shown in **Figure S2**.

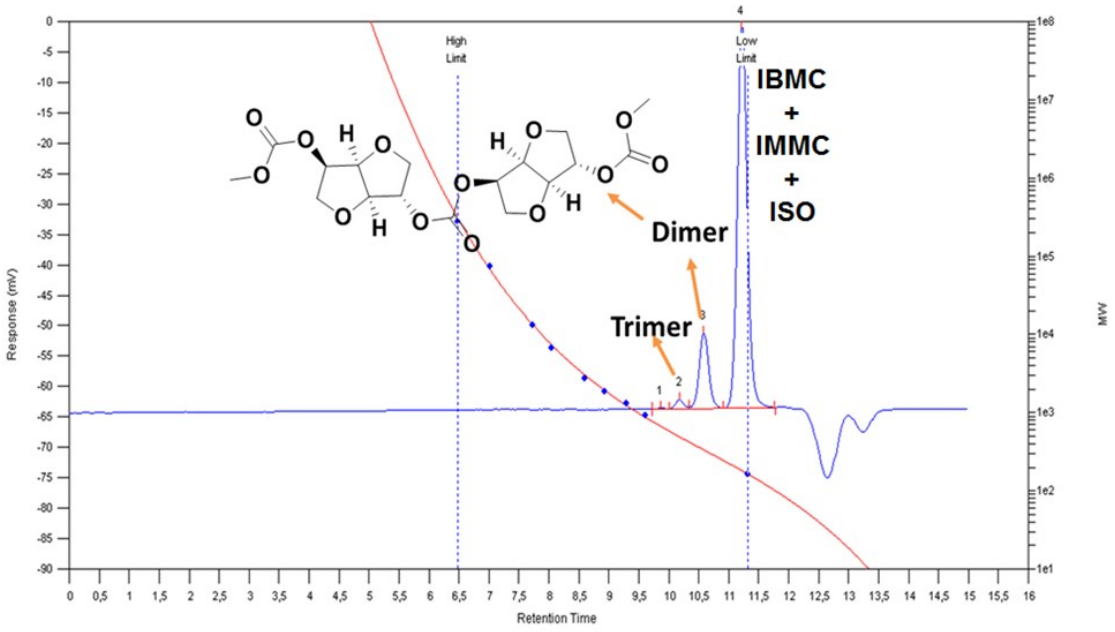

Figure S2. GPC chromatogram of a reaction leading to high oligomer content.

A typical GC-MS chromatogram of an incomplete reaction is depicted in **Figure S3**. Peaks at 17.57 min and 18.55 min have the same MS spectrum and correspond to the two IMMC isomers. The small peak at 31.42 min has an m/z of 429 indicating it is a dimer.

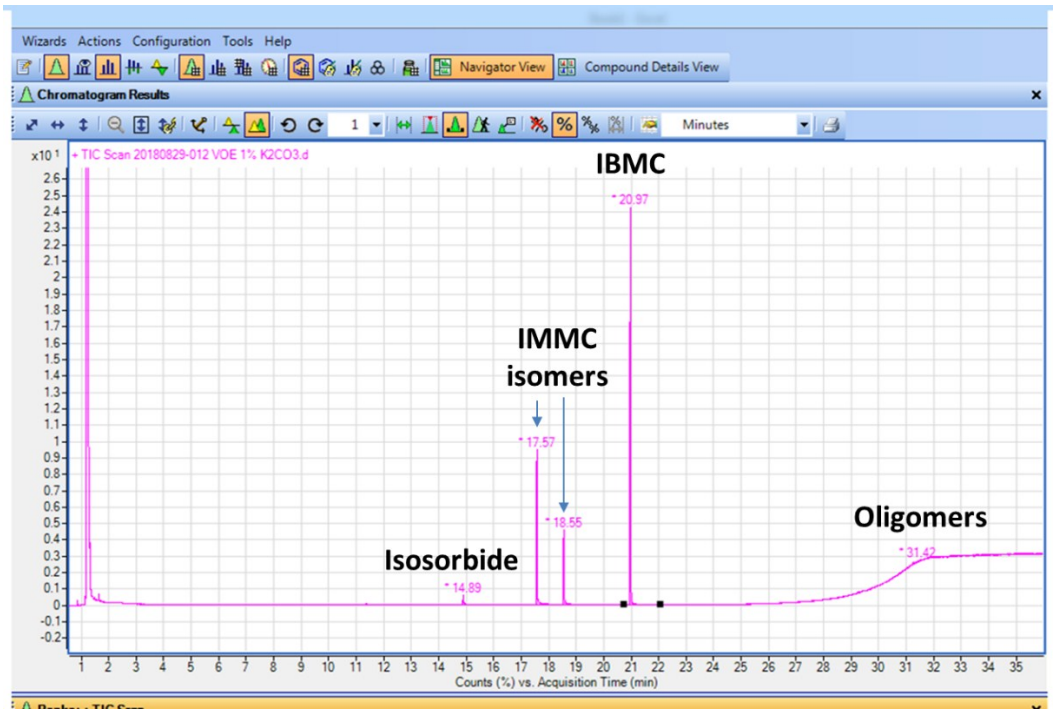

Figure S3. GC-MS chromatogram of an incomplete reaction.

Figure S4 shows why yield and selectivity cannot be determined by GC-MS. It provides analytical results from GC-MS and GPC for a reaction carried out under continuous methanol removal for getting a full conversion of both ISO and IMMC so that the only monomeric species existing in the reaction medium is IBMC. The GC-MS chromatogram of the solid obtained after complete evaporation of the solvent following reaction completion show only a peak corresponding to IBMC. Consequently, it could be deduced that a 100% OH-conversion, a 100% IBMC yield and a 100% IBMC selectivity are obtained. However, these results are misleading as shown by the results obtained by GPC. A content of 9.2 wt% and 0.4 wt% of a dimer and a trimer, respectively, are detected by GPC.

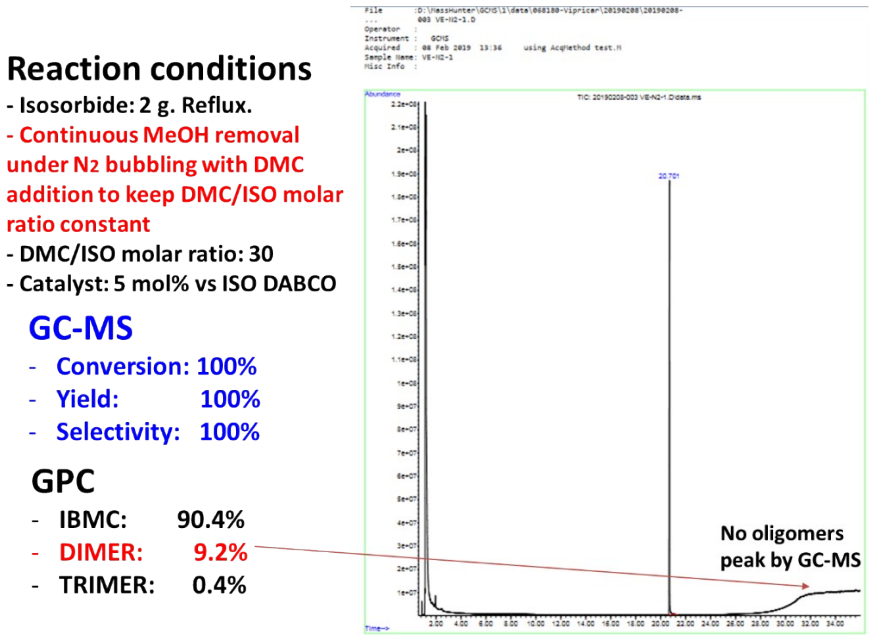

Figure S4. Data showing that results based on GC-MS are misleading.

4. Variations of OH-conversion vs time

Variations of OH-conversions with reaction time for reactions carried out with catalysts reported in **Table 3** of paper are depicted in **Figure S5**.

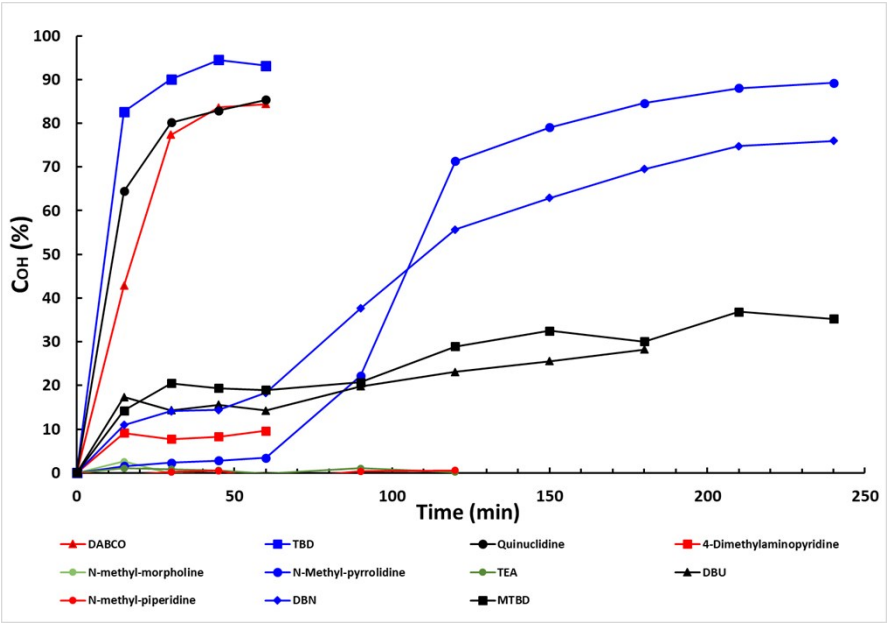

Figure S5. Variation of OH-conversion with time for several catalysts at 5 mol% vs ISO-2.81.

5. Calculation of pKa for conjugate acid of perhydroazepine in ACN

It has been based on the correlation between the pKas in ACN and those in water for three structural analogous compounds (cycloaliphatic secondary amines) of perhydroazepine: Morpholine, piperidine and pyrrolidine. The method consists of calculating the differences between the pKas in ACN and in water for the conjugate acids of these amines, working then out the average of the three values and adding finally the resulting value to the pKa in water for the conjugate acid of perhydroazepine. As it can be seen in **Table S1**, the relative uncertainty for the mean value (8.24) is as low as 1.54%. Consequently, pKa in ACN for the conjugate acid of perhydroazepine is 11.07[1] (pKa in water) + 8.24 = 19.31. The good correlation between the pKas in water and ACN has been shown for other bases, such as, e.g., for anilines,[2] and pyridines.[3]

Table S1. Correlation between pKas in ACN and water for conjugate acids of three structural analogous of perhydroazepine.

Cycloaliphatic amine	pKa_{water}	pKa_{ACN}	pKa_{ACN} - pKa_{wate}
Morpholine	8.36	16.61	8.25
Piperidine	11.22	19.35	8.13
Pyrrolidine	11.27	19.62	8.35
		Average	8.24
		SD[1]	0.11
		U	0.13
		Ur (%)[3]	1.54

[1]Standard deviation; [2] Uncertainty for k = 2 (95% confidence level); [3] Relative uncertainty

References

1. Perrin D., Dissociation constants of organic bases in aqueous solution. IUPAC Chem Data Ser, Buttersworth, London, 1965.
2. I. Kaljurand, A. Kütt, L. Soovaäli, R. Rodima, V. Mäemets, I. Leito and I. Koppel, *J. Org. Chem.*, 2005, **70**, 1019-1028.
3. D. Augustin-Nowacka and L. Chmurzyñski, *Anal. Chim. Acta*, 1999, **381**, 215-220.