Supporting Information

Optimizing the reaction conditions for the formation of fumarate via trans-hydrogenation

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Contents:

1. Catalytic mechanism

The catalyst mechanism is illustrated in figure S1. It is assumed that the substrate can leave the catalytic circle after the first reaction step to fumarate or can stick to the catalyst and reacts further to succinate without leaving the catalyst in between.

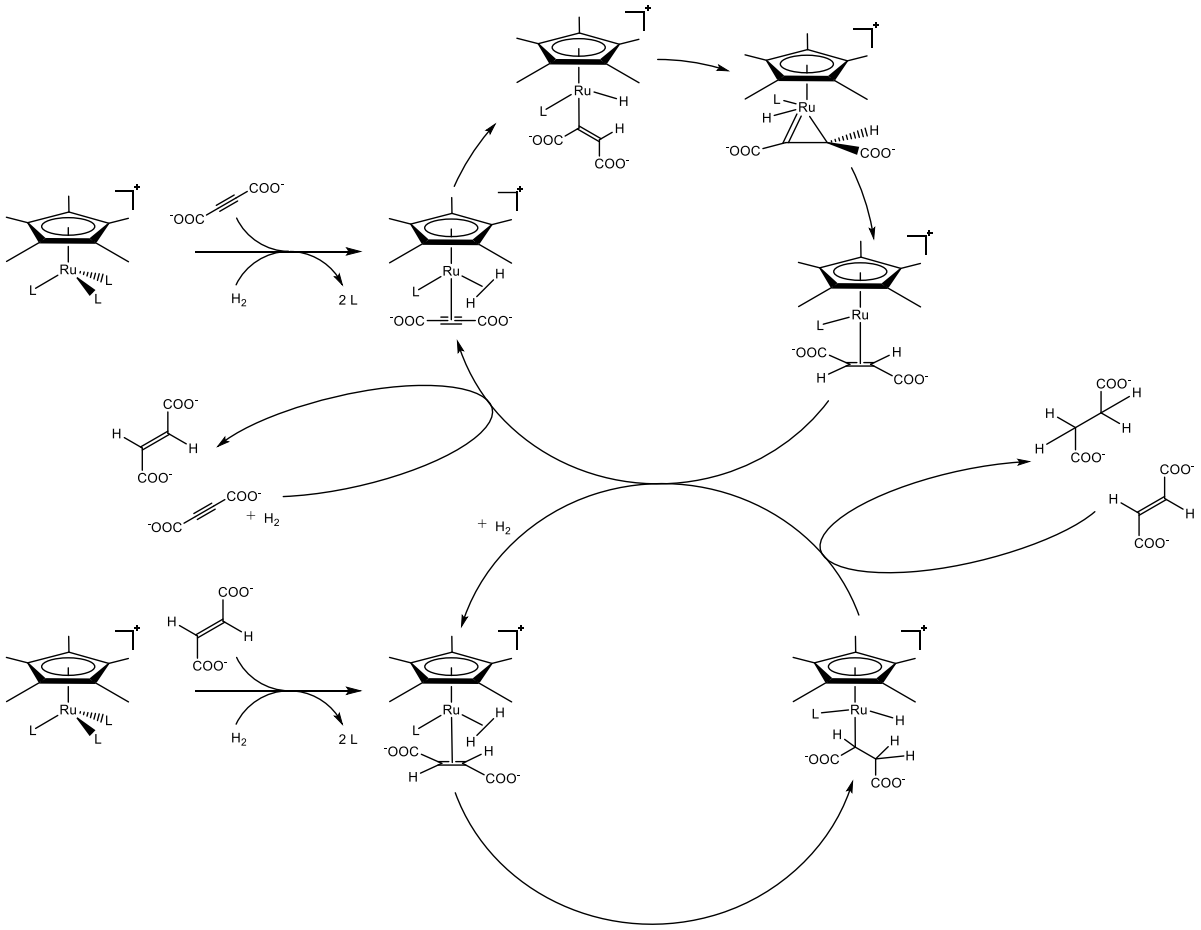

Figure S1: Reaction of ADC with hydrogen in presence of the catalyst to fumarate and then to succinate. Suggested catalyst mechanism.

2. ^{1}H NMR spectra

In figure S2 the ^{1}H NMR spectrum of the 0 mM of Na_2SO_3 concentrated sample after the kinetic experiments is given. It Is visible that more than just fumarate (6.98 ppm) was formed. Also, the cis product maleate can be observed at a chemical shift of 6.45 ppm. The side products are not part of this work and are not further investigated. More details of geminal side products can be found in literature from Laurynas Dagys et al. [1]

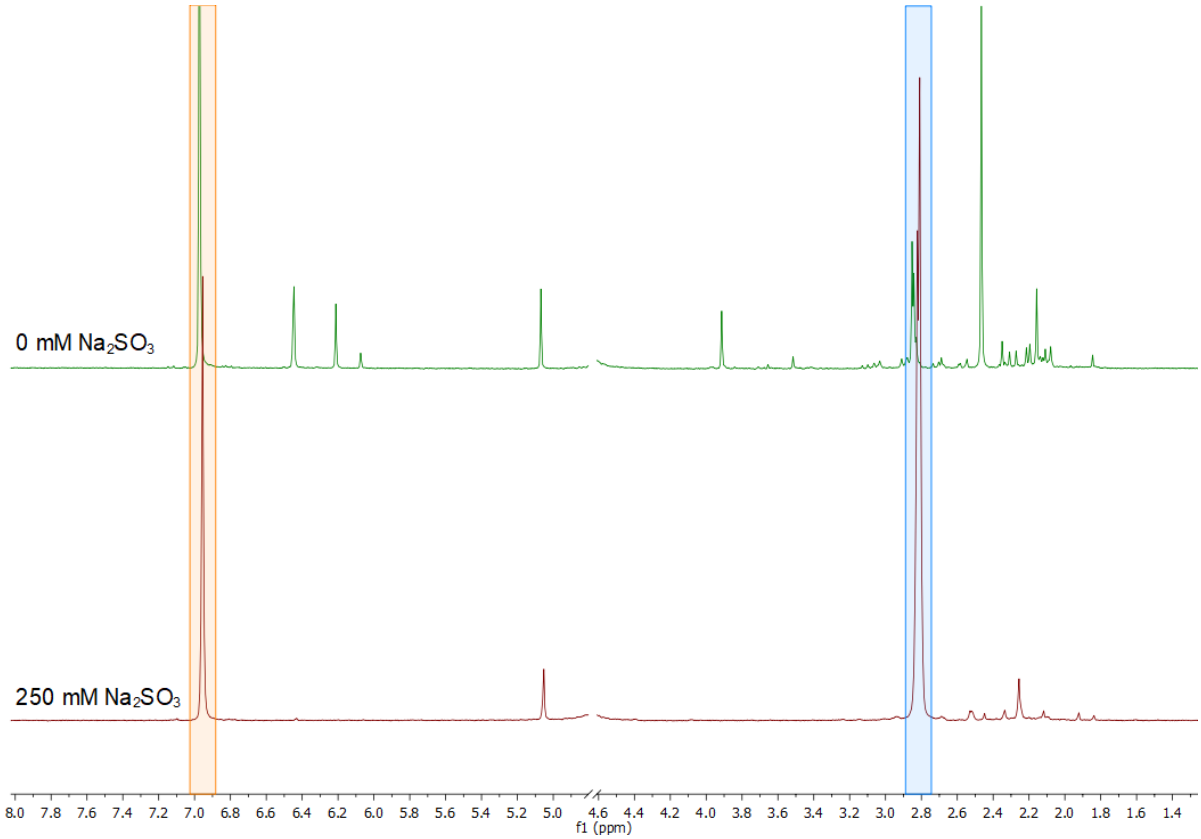

Figure S2: ^{1}H NMR spectra of the sample without Na_2SO_3 (green) and with 250 mM Na_2SO_3 (red) with marked fumarate peak at 6.9 ppm (orange) and succinate peak at 2.8 ppm (blue) measured after the kinetic reactions

3. Isotope shift by partial deuteration

The effect of the isotope shift of the succinate peak originated in the partially-deuterated molecules can be seen in figure S3 in the three peaks of the succinate. By adding pure succinic acid just one peak of the three increases which is an indication of the different molecules.

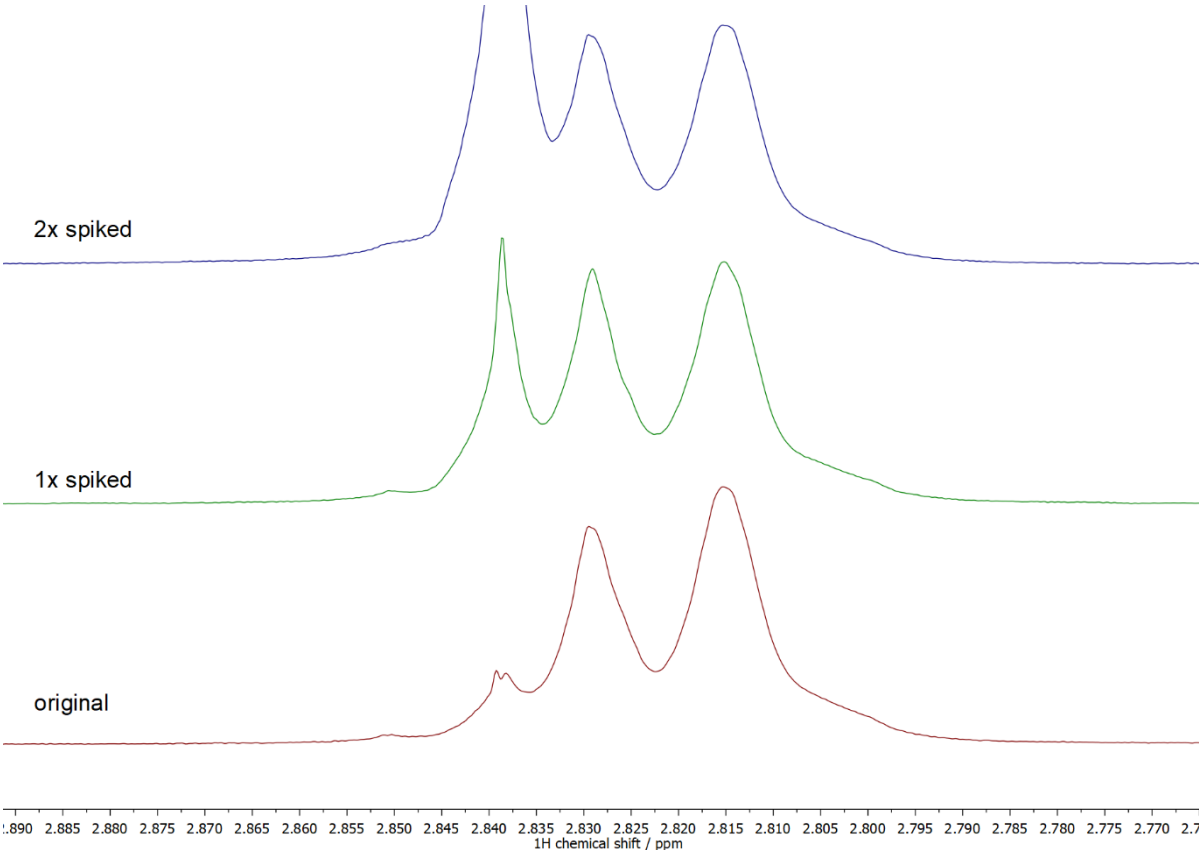

Figure S3: ^{1}H NMR spectra after hydrogenation (90° excitation pulse, RG 191.11) zoomed in on the succinate peak. The red spectrum is the original sample, while the green and blue spectrum are spiked samples with succinic acid.

4. Solid precipitation after reaction

Figure S4 shows an NMR tube after the hydrogenation reaction. It is obvious that some substance precipitates out of the solution. Up to this point, it is not yet known what substance is involved here. The nature of this substance will be investigated in further work.

Figure S4: Pictures of the NMR tube after the reaction.

References

1. L. Dagys, B. Ripka, M. Leutzsch, G.A.I. Moustafa, J. Eills, J.F.P. Colell and M.H. Levitt, *Magnetic Resonance*, 2020, **1**, 175.