Heterogeneous Catalysis

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"Hydrogen-Catalyzed" Dehydrogenation: A Supercritical Conundrum**

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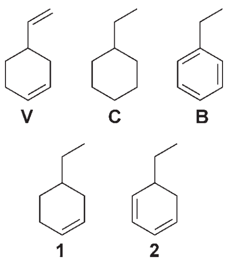
In recent years there has been increasing interest in organic reactions in supercritical carbon dioxide ($scCO_2$). These reactions have included Friedel–Crafts alkylations,[1–4] hydroformylation,[5–9] oxidation,[10–15] etherification,[16–18] and especially hydrogenation.[19–24] Apart from the environmental acceptability, the attractions of $scCO_2$ for hydrogenation are improved mass transport, ease of continuous operation, and potentially improved selectivity.[25] Much of this work has involved continuous reactors, which simplify scale-up. However, we show herein, that these reactors can produce apparently misleading results which, when correctly interpreted, can open up new routes to compounds which are difficult to synthesize otherwise.


V C B
1 2

Scheme 1. Structures of ethyl cyclohexane (**C**) and ethyl benzene (**B**) formed during the dehydrogenation of 1-vinyl cyclohex-4-ene (**V**); **1** and **2** are the intermediates detected in the course of this reaction and were identified by NMR spectroscopy (see Supporting Information).

The starting point for this paper was a report[26] of the attempted selective hydrogenation of 4-vinylcyclohex-1-ene (**V**; Scheme 1), in a small-scale (5 mL) continuous reactor. Unexpectedly, this approach resulted in the formation of ethyl benzene (**B**; which is a dehydrogenation product) even in the presence of a large excess of H_2 and at temperatures apparently as low as 40 °C. This report was significant firstly because the dehydrogenation of **V** is industrially important[27–31] and secondly because the reactor design is one which is very widely used for supercritical chemistry.

The dehydrogenation of cyclohexyl compounds to the corresponding benzene derivatives is an attractive route to aromatic compounds from cheap, plentiful biologically derived feedstocks. In batch reactors, this appears to be an overall disproportionation reaction, producing two mole of **B** for each mole of **C**. So, a surprising aspect of the reported dehydrogenation of **V** in $scCO_2$ was that **C** was not observed, making a simple disproportionation unlikely. The results presented herein provide an explanation of this conundrum and include the identification of two previously unsuspected intermediates, **1** and **2** in Scheme 1.

Initially, we investigated the effect of passing **V** + $scCO_2$ through the reactor in the absence of H_2. Our automated reactor (Figure 1)[16] was therefore programmed to ramp the temperature of the catalyst bed (Pd 2 %) from 80 °C to 200 °C over a period of 8 h at a constant pressure of 150 bar, analyzing the products by GLC every 5 minutes. Figure 2, shows that 1) in the absence of H_2, a reaction does occur; 2) this reaction yields both **B** and **C**, unlike the reaction in the presence of H_2 where **C** is not observed; 3) the ratio of **B** to **C** was found to be 2:1 close to the ratio expected for disproportionation;[27–31] 4) there are two additional products, **1** and **2**; 5) the reaction displays "light-off"[32] (i.e. there is an ignition over a small temperature interval of only 2–3 °C; similar behavior was also observed at 100, 200, and 250 bar) and 6) the reaction switches-off equally suddenly.

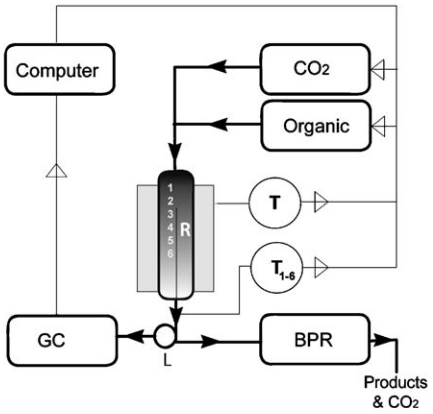


Figure 1. Schematic diagram of the automated apparatus. The organic substrates and CO_2 are delivered by HPLC pumps (Jasco PU–980 and CO_2–1580, respectively); system pressure in the reactor (R) is maintained by a Jasco Back Pressure Regulator (BPR) which also facilitates product separation. Samples of product are collected in-line by a sample loop (L; Valco/Vici) and injected into a gas chromatograph (GC) and the results are downloaded automatically to the computer. The high-pressure lines are designated by heavy filled arrowed lines, whilst data lines and the direction of data are depicted by light unfilled arrowed lines. T_{1-6} are optional thermocouples placed within the reactor.

Analysis of the product stream by off-line GC/MS showed that **2** had a parent ion with m/z 108, identical to that of **V**. By contrast **1**, had m/z 110, consistent with a partially hydrogenated product. Further experiments, detailed in the ESI, provided sufficient NMR spectroscopic data to identify the structures of **1** and **2** (see Scheme 1).

Estimating the residence times in these reactors is straightforward but slightly convoluted.[33] However, once the relationship between flow rate and residence time has

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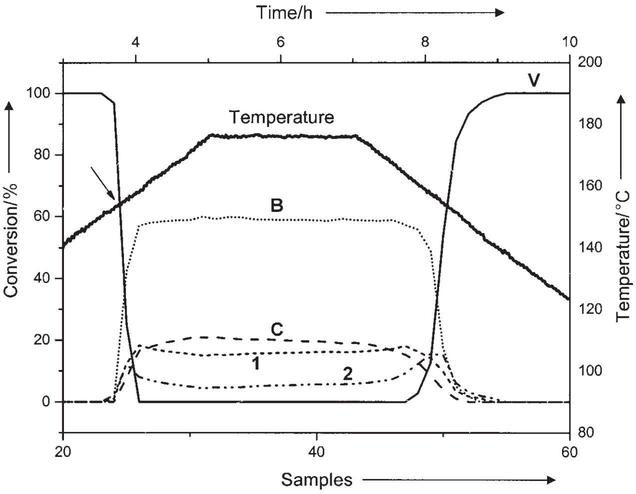


Figure 2. Plot of the product distribution observed whilst the catalyst bed is heated (bold line) between 140 and 180 °C. Note the arrowed auto-thermal ignition point at around 150 °C, and the presence of intermediates **1** and **2**. Flow rates: CO_2 1 mL min^{-1}, **V** 0.2 mL min^{-1}. The product composition was sampled every 15 minutes over the 10-hour period.

been established, it is relatively simple to investigate the variation of reaction products with residence time. Figure 3 shows that 1) reaction products are detected at residence times longer than 2 s; 2) the yields of **B** and **C** grow steadily with increasing residence time, confirming that **B** and **C** are final products; 3) the yields of **1** and **2** reach maxima and then decrease, suggesting that **1** and **2** are intermediates, and 4) the initial rates of formation of **2** and **B** are similar, suggesting that **2** is not an intermediate in the formation of **B**.

However, additional evidence for the relative positions of the different species in the reaction scheme can be obtained by analyzing the GC data with the new analytical technique, 2DCOR-GC,[1,34] which is an extension of the generalized correlation function to chromatographic data.[34] The 2DCOR-GC maps shown in Figure 4, are calculated from the same experiment that gave the data in Figure 3. The off-diagonal peaks in Figure 4a show that the formations of all of the products are correlated to **V** but not necessarily to each other, reflecting the existence of two parallel reaction pathways, namely hydrogenation and dehydrogenation. Together, the two maps can be used to deduce the sequence of formation of **B**, **C**, **1**, and **2**, see Scheme 2. The 2DCOR-GC maps provide evidence for two additional intermediates, **X** and **Y**, which are difficult to discern in the 1D chromatograms but are easily seen in the maps. **X** and **Y**, correlate with **2** but are formed before it. Although **X** and **Y** were not identified spectroscopically, a simple GC structural–elution simulation[35] suggests that they may have the structures shown in Scheme 2. An additional weak peak, **A** in Figure 4, was

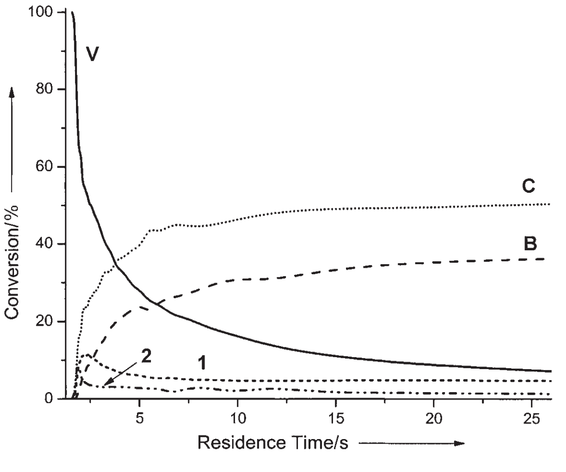


Figure 3. Plot of the product distribution for the dehydrogenation of **V** in the absence of H_2 as the residence time is varied. The traces are labeled **1**, **2**, **V**, **C**, **B** as in Scheme 1. In principle, such data can be used to model the kinetics of the reaction and hence to extract rate constants for the different stages. However, we are limited in this case by the fact that H_2 is a key component in the reaction but its concentration is unknown and indeed, will vary at different points in the reactor.

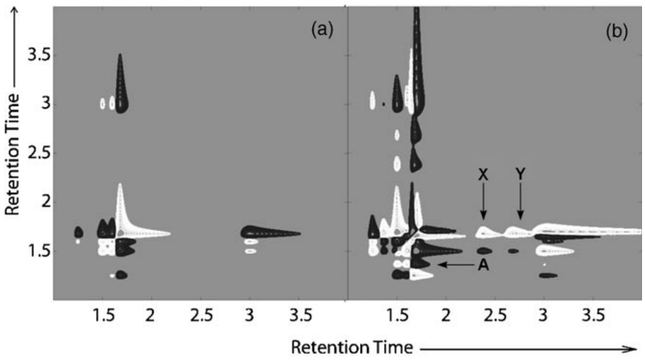
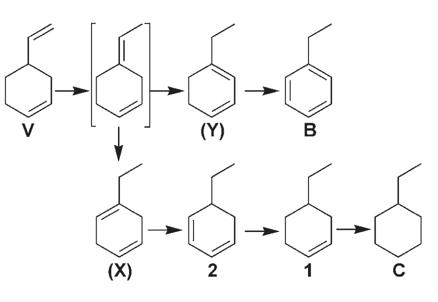


Figure 4. 2D-correlation analysis of the complete GC data from the experiment illustrated in Figure 3. This analysis is mathematically similar to the 2DCOS methodology for FTIR.[38] The principle of analysis for GC and FTIR are the same. The sequence in which the various compounds occur in response to a perturbation (in this case residence time) is obtained by comparing the signs (white positive, black negative) of the off-diagonal peaks in the synchronous and asynchronous plots and applying Noda's Rules.[38] a) Synchronous map showing the simultaneous relationships between products; b) asynchronous map showing the "out-of-phase" relationships. In this plot, further products, **A**, **X**, and **Y**, have been highlighted. High-resolution color copies are available in the Supporting Information.



Scheme 2. Postulated mechanism for the dehydrogenation/hydrogenation of **V** to form **B** and **C**. Compounds **1** and **2**, have been identified by NMR spectroscopy, and **X** and **Y** have been tentatively identified by elution–structure relationships.

identified as vinyl cyclohexane, by comparison with an authentic sample. Compound **A** does not correlate synchronously with any other species and is probably the product of a side reaction.

We now return to the original conundrum, namely why H_2 apparently catalyzes the dehydrogenation of **V** at temperatures close to ambient.[26] Figure 5 shows thermal images of the reactor, which reveal that H_2 causes a highly exothermic reaction and the generation of a distinct hot spot. A separate experiment with an internal thermocouple, deliberately located in the region of the hot spot, indicated that the temperature of the catalyst bed rose to approximately 200 °C. A further experiment with a series of six thermocouples positioned at regular intervals down the length of an 8 cm reactor showed that over 24 h the hot spot gradually moves down the catalyst bed; presumably the catalyst gradually becomes deactivated through charring or coking.[36] Thus, the explanation of the "catalysis" by H_2 is that hydrogenation of **V** rapidly heats a thin layer at the top of the catalyst bed to a temperature well above the light-off temperature for dehydrogenation of **V**. Since the dehydrogenation is itself exothermic, the reaction becomes almost self-sustaining and therefore can continue with almost 100 % yield of **B** without the formation of **C**.

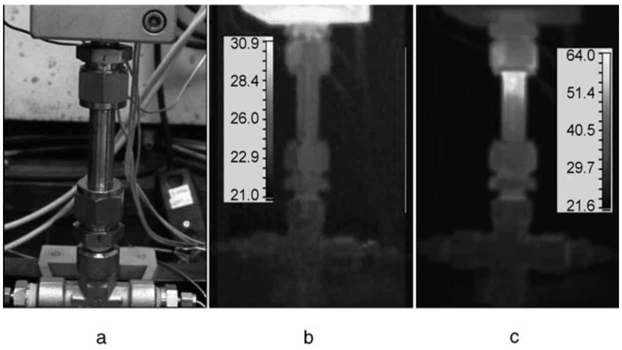


Figure 5. Evidence for hot spots during the dehydrogenation of **V** in the presence of H_2. a) photograph of the reactor; b) and c) thermal images of the same reactor with b) the pre-heater set to 40 °C, and CO_2 and **V** both flowing through it. Note the maximum temperature is 31 °C and c) with H_2 flowing and all other conditions unchanged. Note that the reactor skin has now reached nearly 65 °C. A thermocouple place at the center of the reactor reads over 200 °C. The exit temperature remained close to ambient. High-resolution color copies are available in the Supporting Information.

It is possible to suppress the dehydrogenation completely by deliberately cooling the reactor to 10 °C, although the catalyst bed itself is presumably at a higher temperature. This approach was used to generate sufficient quantities of **1** and **2** for their identification by NMR spectroscopy (see Supporting Information). Note that this low-temperature hydrogenation of **V** is a much simpler route to **2** than the original synthesis by Trost and co-workers,[37] which involved a Diels–Alder or cycloaddition reaction, and thus opens up the possibility of manufacturing this compound on a larger-scale if required.

The apparent catalytic effect of H_2 in the dehydrogenation **V** is the result of thermal hot spots generated in the catalyst bed by an initial exothermic hydrogenation "light-off" forcing the dehydrogenation reaction. The important point is that the possible presence of such hot spots in small-scale reactors should not be overlooked in other exothermic reactions in fixed bed reactors. Clearly it will be worth investigating the effects of different supercritical solvents on hot spots since different fluids can have significantly different thermal properties. In addition our study has resulted in the isolation of the diene, **2** by a potentially much simpler route than that previously reported.[37]

Many of our experiments would not have been possible on manually operated equipment because it was necessary to collect large amounts of data over a whole series of different reaction conditions, a process which would be impractically long without automation. However, handling such large volumes of data in itself presents problems and herein we have demonstrated again the value of 2DCOR-GC for presenting these data in a more easily interpretable form. Overall, one of the more important lessons from this work is that even apparently simple catalytic reactions are in reality quite complex, but that current techniques for supercritical chemistry are now capable of unraveling these complexities.

Experimental Section

Our automated continuous supercritical apparatus has recently been described in detail elsewhere.[16] Figure 1 shows a schematic of the design. Computer controlled HPLC pumps (Jasco CO_2–1580 and Jasco PU–980) deliver the CO_2 and organic substrate. The preheated CO_2/organic mixture is passed over the catalyst bed (2 % Pd/SiO_2/Al_2O_3 supported: Johnson Matthey), which is heated by cartridge heaters and aluminum blocks. The temperature of the catalyst bed is controlled by a programmable Eurotherm. After the reaction has occurred and left the catalyst bed, the mixture of products and gases are passed through a HPLC 4-port sample loop (Valco/Vici), which samples 0.06 μL periodically into a GLC (Shimadzu GC17–A v.4), whereupon product separation and analysis is carried out. The system pressure and product separation is facilitated by a programmable Back Pressure Regulator (Jasco BPR BP-1580-81). Data analysis is performed off-line after the experimental is completed.

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