SUPPORTING INFORMATION

Route to Renewable PET: Reaction Pathways and Energetics of Diels-Alder and Dehydrative Aromatization Reactions Between Ethylene and Biomass-Derived Furans Catalyzed by Lewis Acid Molecular Sieves.

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A. Figures and Tables

Figure S.1 XRD pattern of Sn-Beta. (Si/Sn = 129).
Figure S.2 XRD patterns of Zr-Beta-92, Zr-Beta-155, Zr-Beta-264, and Zr-Beta-492.
Figure S.3 SEM image of Zr-Beta-92.

Figure S.4 SEM image of Zr-Beta-155.
Supporting Information
J. J. Pacheco, J. A. Labinger, A. L. Sessions, M.E. Davis

Figure S.5 SEM image of Zr-Beta-264.

Figure S.6 SEM image of Zr-Beta-492.
Figure S.7  EI mass spectrum of Compound I.
Figure S.8  EI mass spectrum of Compound II.
Figure S.9  EI mass spectrum of Compound III.
Figure S.10 GC-FID chromatogram of TLC fraction containing Compound I (MW=166) and MMFC.

Figure S.11 $^1$H NMR spectrum (in CDCl$_3$) of TLC fraction containing Compound I (#1-6) and MMFC (marked by *).
Table S.1 Relative areas of numbered peaks corresponding to Compound I in Figure S.11.

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Area</th>
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<tbody>
<tr>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0.93</td>
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<tr>
<td>3</td>
<td>1.03</td>
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<td>4</td>
<td>3.22</td>
</tr>
<tr>
<td>5</td>
<td>2.09</td>
</tr>
<tr>
<td>6</td>
<td>2.08</td>
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</table>
Figure S.12  El TOF-mass spectra of Compound I (top) and Compound II (bottom).
Figure S.13  Formation of a bicyclo[2.2.2]oct-2-ene product from the Diels-Alder addition of C$_2$H$_4$ with a cyclohexadiene side product observed by Do, et al.$^1$
Figure S.14 El mass spectrum of methyl 4-formyl benzoate in Figure 4.
Figure S.15  EI mass spectrum of dimethyl 2,5-furandicarboxylate in Figure 4.
Figure S.16 EI mass spectrum of dimethyl terephthalate in Figure 4.
Supporting Information
J. J. Pacheco, J. A. Labinger, A. L. Sessions, M.E. Davis

Figure S.17 Oxidation of cyclohexadiene side products to the corresponding aromatics observed by Do, et al.¹

Figure S.18 Thermal oxidation of α-terpinene to p-cymene, thymol, and carvacrol reported by Mcgraw, et al.²

Figure S.19 Alternate Bronsted acid-catalyzed pathways for the ring-opening of the Diels-Alder adduct between ethylene and the DMF. Do, et al. observed formation of 4¹, and Li, et al. used computational methods to predict the formation of both 3 and 4³.
B. Methods for determining initial rates

The measurement of PX yield was performed by GC/FID using triglyme as internal standard in dioxane solvent. Due to the similarity in boiling points, the DMF reactant elutes at the same time as dioxane in the GC. Therefore, DMF conversion (and PX selectivity) was unable to be determined by GC-FID. Quantitative $^1$H NMR analysis was used to measure DMF conversion, and it was found that PX selectivities were ~40%. This is in agreement with previous reports of PX selectivity at low PX yields.\(^4\) Due to the low PX selectivities at low yields, the PX yields were used (rather than DMF conversion) for determining the initial rates and apparent $E_a$.

The MMF conversion and MPT yield was measured by GC/FID using triglyme as internal standard in dioxane solvent. The MMF conversion profiles at low conversion were unreliable and exhibited a larger amount of error. This was due to irreproducibility in the area ratio of the MMF/triglyme peaks in the gas chromatogram from injection to injection, and the source of the irreproducibility was unresolved. The area ratios of the MPT/triglyme peaks were very reliable from injection to injection and, therefore, the MPT yield profiles were used for determining the initial rates and apparent $E_a$.

Figures S.20-S.21 show how initial rates were estimated using the collected PX and MPT yield profiles by drawing maximum and minimum slopes of the profiles at $t = 0$ that one may reasonably argue. The reported rates are the average of these maximum and minimum slopes. The maximum and minimum slopes were used as the +/- error bars in Figure 8 and Figure 10. Tables S.2 and S.3 summarize the maximum, minimum, and average slopes in Figures S.20-S.21.
Supporting Information
J. J. Pacheco, J. A. Labinger, A. L. Sessions, M.E. Davis

The scatter in the data can be (in part) attributed to the separate batch reaction experiments required to collect each individual time point.
Figure S.20 Plots used for measuring the initial rates from the collected PX yield profiles.
Figure S.20 continued. Plots used for measuring the initial rates from the collected PX yield profiles.
Figure S.20 continued. Plots used for measuring the initial rates from the collected PX yield profiles.
Figure S.20 continued. Plots used for measuring the initial rates from the collected PX yield profiles.
Figure S.21 Plots used for measuring the initial rates from the collected MPT yield profiles. Error bars are +/- standard deviation for multiple injections on GC/FID.
Figure S.21 continued  Plots used for measuring the initial rates from the collected MPT yield profiles. Error bars are +/- standard deviation for multiple injections on GC/FID.
Figure S.21 continued  Plots used for measuring the initial rates from the collected MPT yield profiles. Error bars are +/- standard deviation for multiple injections on GC/FID.
Figure S.21 continued  Plots used for measuring the initial rates from the collected MPT yield profiles. Error bars are +/- standard deviation for multiple injections on GC/FID.

Table S.2 Initial rates of PX formation for profiles in Figure S.20.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Si/Zr</th>
<th>Initial rate (mM PX/hr)</th>
<th>Min</th>
<th>Max</th>
<th>Average</th>
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<tr>
<td>230</td>
<td>92</td>
<td>8.40</td>
<td>5.16</td>
<td>6.22</td>
<td>9.54</td>
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<td>230</td>
<td>155</td>
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<td>1.86</td>
<td>1.86</td>
</tr>
<tr>
<td>230</td>
<td>492</td>
<td>1.56</td>
<td>1.56</td>
<td>1.56</td>
<td>1.56</td>
</tr>
<tr>
<td>210</td>
<td>155</td>
<td>3.78</td>
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<td>1.56</td>
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<tr>
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<td>155</td>
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</table>
Supporting Information
J. J. Pacheco, J. A. Labinger, A. L. Sessions, M.E. Davis

**Table S.3** Initial rates of MPT formation for profiles in Figure S.21.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Si/Zr</th>
<th>Initial rate (mM PX/hr)</th>
<th>Min</th>
<th>Max</th>
<th>Average</th>
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<td>9.00</td>
<td>10.62</td>
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<td>155</td>
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<td>492</td>
<td>2.70</td>
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<td>5.04</td>
<td>6.84</td>
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<td>2.52</td>
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<td>2.97</td>
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C. Method for calculating the \( \frac{R}{R_0} \) values in Table 3.

Method to solve for quantity \( \frac{R}{R_0} = \left( \frac{\delta^{13}C}{\delta^{12}C} \right)_{C_{2,5}} \) where \( C_{2,5} \) denotes a carbon atom at the 2- or 5- position of the reacting furan molecule and \( \left( \frac{\delta^{13}C}{\delta^{12}C} \right)_0 \) is the ratio of the starting furan.

1. \( \delta_0 \): \( \delta^{13}C \) for starting furan (fractional conversion, \( F = 0 \))

\[
\delta_0 = \left[ \frac{\left( \frac{\delta^{13}C}{\delta^{12}C} \right)_0}{\left( \frac{\delta^{13}C}{\delta^{12}C} \right)_{PDB}} - 1 \right] \times 1000 \quad \text{OR} \quad \frac{\delta_0}{1000} + 1 = \frac{\left( \frac{\delta^{13}C}{\delta^{12}C} \right)_0}{\left( \frac{\delta^{13}C}{\delta^{12}C} \right)_{PDB}}
\]

2. \( \delta - \delta_0 \): Difference in \( \delta^{13}C \) between unreacted furan at conversion \( F \) and of starting furan (\( F = 0 \)).

\[
\delta - \delta_0 = \left[ \frac{\left( \frac{\delta^{13}C}{\delta^{12}C} \right)_{C_{2,5}} - \left( \frac{\delta^{13}C}{\delta^{12}C} \right)_0}{\left( \frac{\delta^{13}C}{\delta^{12}C} \right)_{PDB}} \right] \times 1000
\]

3. \( \delta_{C_{2,5}} - \delta_0 \): Difference in \( \delta^{13}C \) of C-2 or C-5 carbons in unreacted furan at conversion \( F \) and of starting furan (\( F = 0 \)). \( N \) is number of carbons in the furan molecule.

\[
\delta_{C_{2,5}} - \delta_0 = (\delta - \delta_0) \times \frac{N}{2} = \left[ \frac{\left( \frac{\delta^{13}C}{\delta^{12}C} \right)_{C_{2,5}} - \left( \frac{\delta^{13}C}{\delta^{12}C} \right)_0}{\left( \frac{\delta^{13}C}{\delta^{12}C} \right)_{PDB}} \right] \times 1000
\]

4. Divide quantity \( (\delta - \delta_0) \times (N/2) \times (1/1000) \) by quantity \( \delta_0/1000 + 1 \) from step 1.

\[
\frac{(\delta - \delta_0) \times \frac{N}{2} \times \frac{1}{1000}}{\delta_0/1000 + 1} = \frac{\left( \frac{\delta^{13}C}{\delta^{12}C} \right)_{C_{2,5}} - \left( \frac{\delta^{13}C}{\delta^{12}C} \right)_0}{\left( \frac{\delta^{13}C}{\delta^{12}C} \right)_0} = \frac{\left( \frac{\delta^{13}C}{\delta^{12}C} \right)_{C_{2,5}}}{\left( \frac{\delta^{13}C}{\delta^{12}C} \right)_0} - 1 = \frac{R}{R_0} - 1
\]
Supporting Information
J. J. Pacheco, J. A. Labinger, A. L. Sessions, M.E. Davis

\[ \frac{R}{R_0} = \frac{^{13}C}{^{12}C}_{C_{2.5}} = \frac{\left( (\delta - \delta_0) \cdot N \right)}{1000 \cdot 2} + 1 = \frac{(\delta - \delta_0) \cdot N}{\delta_0 + 1000} + 1 \]

Equation S.1  \[ KIE = \frac{\ln(1-F)}{\ln[(1-F)R/R_0]} \]

D. References


