



# A DFT study of the acid-catalyzed conversion of 2,5-dimethylfuran and ethylene to p-xylene

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## ABSTRACT

We present a detailed mechanism for the conversion of DMF (2,5-dimethylfuran) and ethylene to p-xylene, obtained by gas-phase DFT electronic structure calculations. The conversion consists of Diels–Alder cycloaddition and subsequent dehydration of the cycloadduct, an oxa-norbornene derivative. We present the energetics of both the uncatalyzed and acid-catalyzed (Brønsted and Lewis) reactions. Even though the DMF–ethylene cycloaddition is thermally feasible, we show that Lewis acids can further lower the activation requirements by decreasing the HOMO–LUMO gap of the addends. The catalytic effect may be significant or negligible depending on whether the Diels–Alder reaction proceeds in the normal or the inverse electron-demand direction. We also show that Brønsted acids are extremely effective at catalyzing the dehydration of the oxa-norbornene derivative, which, according to our calculations, cannot proceed uncatalyzed. On the other hand, we conclude that Brønsted acids do not catalyze the cycloaddition. Although strong Lewis acids like Li<sup>+</sup> can catalyze the dehydration, our calculations indicate that relatively elevated temperatures would be required as they are not as effective as Brønsted acids. We argue that the specific synthetic route to p-xylene is kinetically limited by the Diels–Alder reaction when Brønsted acids are used and by the dehydration when a Lewis acid is used, with the latter being slower than the former. Finally, we adduce experimental data that corroborate the theoretical predictions: we observe no activity in the absence of a catalyst and a higher turnover frequency to p-xylene in the Brønsted acidic zeolite HY than in the Lewis acidic zeolite NaY.

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## 1. Introduction

In 1982, Brion realized that furan can be converted into six-membered carbon rings in a simple two-step mechanism [1]. The key step in order to achieve such a structurally complex conversion is Diels–Alder cycloaddition between the furan and an alkene. The cycloadduct – an oxa-norbornene – may then undergo  $\beta$ -elimination of the heteroatom bridge and form cyclohexenols or cyclohexenediols, depending on the substituents on the alkene. In an attempt to produce difluorocyclohexadienol, using ethyl 3,3-difluoroacrylate as the alkene, Leroy et al. identified ethyl 2-fluoro-3-hydroxybenzoate – an aromatic compound – and again explained the mechanism through Diels–Alder cycloaddition followed by  $\beta$ -elimination [2]. Numerous studies followed in which substituted furans and alkenes were converted to a variety of oxa-norbornenes and 6-membered aromatic or non-aromatic rings [3]. All these reactions commonly proceeded through Diels–Alder

cycloaddition in the liquid phase and often in the presence of Lewis acid catalysts. Aromatization was exclusively achieved through base catalyzed  $\beta$ -elimination.

It was not until recently that an alternative route was discovered, based on similar principles, which would lead to aromatics. It was proposed that substituted benzenes can be synthesized by *dehydration* of oxa-norbornene derivatives which again may be synthesized from furan derivatives and alkenes by the Diels–Alder cycloaddition [4,5]. In the context of unraveling sustainable routes for the synthesis of base chemicals, this discovery can potentially have a tremendous impact as it enables the production of aromatics exclusively from renewable resources, if we consider that cellulosic biomass can be depolymerized into glucose which in turn may be dehydrated to hydroxymethylfurfural (HMF) – with or without prior isomerization to fructose – [6,7] while hydrodeoxygenation of HMF can yield alkylated furans [8].

Generally, the Diels–Alder reaction can easily take place under mild thermal conditions. The small activation energy is owed to the reaction being *symmetry allowed*, as one can readily see by applying the *conservation of orbital symmetry* theory of Woodward and Hoffmann [9]. It is a reaction whose mechanism has been

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studied extensively both experimentally and theoretically (*ab initio* or by DFT) and has sparked vigorous debates on whether it occurs in a concerted or in a stepwise (through a diradical intermediate) fashion. Notable are the femtosecond experiments of Zewail and co-workers and the calculations of Houk and co-workers on the retro-Diels–Alder of norbornene, in which the stepwise pathway has been found to lie higher in energy [10–14]. Computational studies of various Diels–Alder systems in the presence of Lewis acids have also been carried out in the gas phase or with dielectric solvent models [15–24]. A convenient framework to understand the observed Diels–Alder activity patterns at the electronic level is provided by the *frontier molecular orbital* (FMO) theory of Fukui [25]. Despite its qualitative character, it can provide very valuable insights that pertain to reactivity and selectivity [26,27]. Extracting from Fukui's work, the relevant passages about Diels–Alder reactions, two simple postulates can be formulated: (1) the smaller the energy gap between the highest occupied molecular orbital (HOMO) of the electron-rich reactant and the lowest unoccupied molecular orbital (LUMO) of the electron-deficient reactant, the lower the activation barrier; and (2) the symmetries of the interacting molecular orbitals must be compatible, that is, adequate for their mixing. The first statement implicates that if a Diels–Alder reaction is to be accelerated, then the HOMO–LUMO gap needs to be minimized. By supplying electron-withdrawing substituents to the more electron-deficient reactant and by adding electron-donating substituents to the electron-rich reactant, the electron-content disparity of the addends can be further increased, as for example in the Diels–Alder reaction between furan and acrylic monomers [28]. As a consequence, the polarity of the transition state – which has been shown to be a measure of the HOMO–LUMO gap as well as of the reaction rate – increases [27,29,30].

Lewis acids have been the catalysts of choice and the most efficient way to enhance the Diels–Alder reaction rates [31–35] – more so than solvent effects [36]. By lowering the frontier orbital energies of the coordinated addend, they may accelerate the reaction by several orders of magnitude. The associated effect of Lewis acids on the system's geometry may range from leaving it largely unaffected to forcing the reaction to proceed through a stepwise mechanism, depending on the system of reactants and catalyst as described elsewhere [32,33]. Among the numerous Lewis acids that were tested, alkali and alkaline perchlorates showed particularly promising results. Alkali and alkaline perchlorates [37] were employed as catalysts, recording dramatic rate improvements over the uncatalyzed reaction. The observed rates for the different cations were found to follow the order  $Mg^{2+} > Ba^{2+} \geq Li^+ > Na^+$  and to be in direct correlation with the respective charge/radius ratios [38].

It is well established that the hydrophobic effect increases the rate of the Diels–Alder reaction [39]. Thus, it is not surprising that confinement of the addends, like inside zeolite pores, can have the same effect on the rate [40]. In the case of zeolites, it has also been reported that extra-framework cations can be beneficial, presumably because they function as Lewis acid catalysts. Murthy and Pillai found that when furan was mixed with acrolein in Na-containing zeolite Y, the Diels–Alder yield increased [41]. Imachi and Onaka have observed higher Diels–Alder activity in solvent-free NaY than in organic or aqueous media [42].

In a recent study, Williams et al. introduced a procedure to synthesize p-xylene from DMF and ethylene in zeolite HY [5]. The authors reported selectivity of 51% to p-xylene at 573 K, which they were able to increase to 76% with the use of an aliphatic solvent. They proposed that the reaction proceeds by Diels–Alder cycloaddition and subsequent dehydration of the resulting cycloadduct. (Fig. 1) In this paper, we study the specific reaction by carrying out electronic structure calculations and investigate how Brønsted acid catalysis alters the mechanism and energetics.

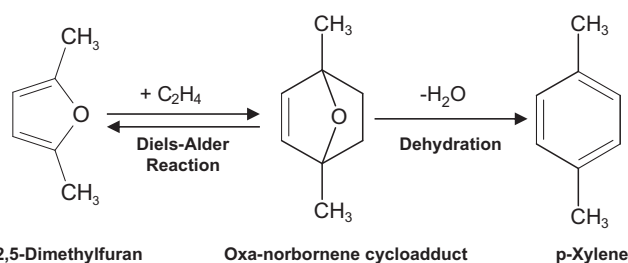


Fig. 1. Proposed reaction for the conversion of DMF to p-xylene (adapted from Williams et al. [5]).

Furthermore, we investigate whether extra-framework alkali cations can achieve Lewis acid catalysis and whether the latter can be an alternative to Brønsted acid catalysis. Lewis acids are known to have a catalytic effect on dehydration, for example, alkali cation-exchanged X and Y zeolites promote the dehydration of short alcohols [43]. We use experiments to test our theoretical predictions about different catalytic systems and their turnover frequencies to p-xylene. To the best of our knowledge, no computational studies of the dehydration of oxa-norbornene or its derivatives have been published to date, either in the uncatalyzed or in the catalyzed case.

## 2. Methods

### 2.1. Experimental setup

#### 2.1.1. Catalyst preparation

Two commercial zeolitic catalysts from Zeolyst International – NaY (CBV100, Si/Al = 2.55) and HY (CBV600, Si/Al = 2.6) – have been used in our experiments. The NaY sample has been washed at 298 K with 0.05 M  $NaHCO_3$  solution for 30 min in order to preclude trace Brønsted acidity. Subsequently, the two samples were calcined at 823 K for 4 h in 100 cc/min helium flow to remove any organic residual. The total acid sites and BET surface areas were quantified using techniques described elsewhere [5].

#### 2.1.2. Measurement of catalytic properties

The reaction of DMF (99% purity, Sigma–Aldrich) with ethylene (Scotts Specialty Gas, Inc) was carried out in a 45 mL-closed Parr reactor (series 4740). The vessel was heated by a Chemglass oil-bath unit. The mixing of both reactants was done by use of a magnetic stirrer. 7.2 g (0.075 mol) of DMF and 4.69 MPa (680 psig) of ethylene (0.07 mol) were charged to the reactor and reacted at 493 K for 6 h. n-Decane was found to be inactive under the experimental conditions and thus was used as an internal standard. After the end of reaction, product mixtures were collected, filtered with 0.2  $\mu$ m-syringe filter, and diluted in ethyl acetate (HPLC-grade, Sigma–Aldrich) for the subsequent gas chromatography (GC) analysis (7890A Agilent). Product identification was confirmed with an Agilent 6850 series GC, a 5973 MS detector and injection of the standards. Details for the determination of the acid site density in the zeolitic catalysts can be found elsewhere [5].

### 2.2. Computational model

All the calculations were performed at the restricted-DFT M062X/6-311+(d,p) theory level [44,45] with the Gaussian software package (Gaussian 09, Revision A.2) [46]. Rubidium and Cesium atoms were modeled with the effective core potential LANL2DZ. All the structures were fully relaxed, and vibrational frequencies were calculated. Transition states were confirmed by the presence of a single imaginary frequency and by IRC (intrinsic

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