

Supporting Information

**Ab initio Calculation of Rate Constants for Molecule–Surface  
Reactions with Chemical Accuracy**

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## 1. Methods:

To compute the hybrid MP2:PBE+D2 energies based on the subtractive scheme the MonaLisa program as described in ref. <sup>[1]</sup> has been used. It features interfaces to the VASP <sup>[2]</sup> and TURBOMOLE <sup>[3,4]</sup> codes. The VASP program applies periodic boundary conditions and uses plane wave basis sets. The present PBE+D2 calculations are performed at the  $\Gamma$  point only. An kinetic energy cutoff of 400 eV has been applied to the plane wave basis set and for all the atoms standard PAW potentials have been used.

PBE+D2 cluster calculations have been performed with the TURBOMOLE code. The triple-zeta valence basis set with polarization functions (TZVP) <sup>[5]</sup> named “def2-TZVP” in the TURBOMOLE library has been used.

MP2 energies are function counterpoise corrected for the basis set superposition error and extrapolated to the complete basis set (CBS) limit using Dunning’s correlation-consistent polarized valence triple- and quadruple-zeta basis sets (cc-pVXZ with X=T,Q) <sup>[6,7]</sup>. The “1s-frozen core” approximation is adopted.

Coupled cluster CCSD(T) calculations have been carried out with the TURBOMOLE code. Due to high computational effort, small cluster models (Fig. S3) have been considered using the TZVP basis set.

The evaluation of thermodynamic functions from vibrational partition functions and the anharmonic vibrational calculations have been performed using the in-house programs THERMO and EIGEN\_HESS\_ANHARM\_INT, respectively, see ref. <sup>[1]</sup>.

## 2. Transition state theory – working equations

The reaction rate constants and pre-exponentials are calculated following transition state theory

$$k = \frac{k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right)$$

$$A = \frac{k_B T}{h} \exp\left(1 + \frac{\Delta S^\ddagger}{R}\right)$$

where:

- $k_B$  – Boltzmann constant
- $T$  – Temperature
- $h$  – Planck constant
- $R$  – Gas constant

- $\Delta G^\ddagger$  – Apparent Gibbs free energy barrier
- $\Delta S^\ddagger$  – Apparent entropy barrier

For different thermodynamic functions  $X$ , apparent barriers are calculated as

$$\Delta X^\ddagger = X_{TS} - X_{\text{methanol}(ads)} - X_{\text{alkenes}(g)}$$

Each component of the above expression is calculated from partition functions.

In the case of the gas phase alkenes the total partition function is

$$Q_{tot} = Q_{tr} \cdot Q_{Rot} \cdot Q_{vib}$$

where:

- $Q_{Tr}$  – Translational partition function for the ideal gas, defined as

$$Q_{Tr} = \left( \frac{2\pi\mu k_B T}{h^2} \right)^{3/2} V = \frac{V}{\Lambda^3}$$

where:

- $\mu$  – Total mass of the molecule
- $V$  – Molar volume of the gas, defined by its partial pressure  $nRT/p$ , for one mole of gas it becomes  $RT/p$  and its units are

$$\frac{[\text{mol}][\text{kg m}^2 \text{s}^{-2} \text{mol}^{-1} \text{K}^{-1}][\text{K}]}{[\text{kg m}^{-1} \text{s}^{-2}]} = [\text{m}^3]$$

- $\Lambda$  – Thermal wavelength (having the units of an inverse of a length)
- $Q_{Rot}$  – Rotational partition function for the rigid rotor
- $Q_{vib}$  – Vibrational partition function calculated using the harmonic oscillator model (Harm) or direct sum over the states of the anharmonic oscillator (Anharm)

In the case of the methanol adsorption complex and the transition structures, the total partition function is simply

$$Q_{tot} = Q_{vib}$$

The Gibbs free energy is, by definition

$$G = H - TS$$

where

$$H = U - RT$$

for alkenes in the gas phase.

For the methanol adsorption complex and the transition structures (solid phases), the enthalpy is

$$H = U$$

Internal energy and entropy are calculated from the partition function as

$$U = k_B T^2 \frac{\partial \ln Q_{tot}}{\partial T} + E_{el}$$

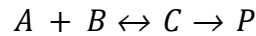
$$S = k_B \ln Q_{tot} + k_B T \frac{\partial \ln Q_{tot}}{\partial T}$$

where  $E_{el}$  is the electronic energy of the system.

### 3. Comparison with Arrhenius barriers

We follow Atkins, de Paula and Friedman <sup>[8]</sup>, topic 89

For the formation of products from the activated complex  $C^\ddagger$



with B and  $C^\ddagger$  being solids.

The rate of product formation

$$v = (d[P]/dt)$$

is

$$v = \tilde{k} \cdot V^o \cdot [A] = \tilde{k} \cdot (RT/p^o) \cdot [A] = k_c \cdot [A] \quad (1)$$

with  $\tilde{k} = (kT/h)K_p^\ddagger$ , or if the concentration is replaced by the partial pressure,  $[A] = p_A/RT$ ,

$$v = \tilde{k} \cdot (V^o/RT) \cdot p_A = \tilde{k} \cdot (1/p^o) \cdot p_A = k_p \cdot p_A \quad (2)$$

The molecular volume  $V^o$  in eq. (1) has to be given in the same units as the concentration  $[A]$  in the rate law (1), e.g.  $[A]$  in  $[mol \, dm^{-3}]$  and  $V^o$  in  $[dm^3 \, mol^{-1}]$ .

The units for the standard pressure  $p^o$  in eq. (2) must be chosen such that they match with the units in which the partial pressure  $p_A$  in the rate law (2) is given.

The Arrhenius activation energy  $E_A$  is defined as, <sup>[8]</sup>, see eq. 85.3, topic 85

$$E_A = RT^2 \left( \frac{\partial \ln k}{\partial T} \right) = RT^2 \frac{1}{k} \left( \frac{\partial k}{\partial T} \right)$$

For

$$\tilde{k} = \frac{k_B T}{h} K_p^\ddagger = \frac{k_B T}{h} \exp \left( -\frac{\Delta G^\ddagger}{RT} \right)$$

we obtain

$$RT^2 \frac{1}{\tilde{k}} \left( \frac{\partial \tilde{k}}{\partial T} \right) = \frac{RT^2}{\tilde{k}} \left( \left( \frac{k}{h} \right) \exp \left( -\frac{\Delta G^\ddagger}{RT} \right) + \tilde{k} \frac{\Delta H^\ddagger}{RT^2} \right) = RT + \Delta H^\ddagger$$

For rate law (1) with

$$k_c = V^o \tilde{k} = (RT/p^o) \cdot \tilde{k}$$

we get

$$E_A = RT^2 \frac{1}{k_c} \left( \frac{\partial k_c}{\partial T} \right) = RT^2 \left( \frac{1}{k_c} \left( \frac{R}{p^o} \right) \tilde{k} + \frac{1}{\tilde{k}} \left( \frac{\partial \tilde{k}}{\partial T} \right) \right) = RT + (RT + \Delta H^\ddagger)$$

$$E_A = 2 RT + \Delta H^\ddagger \quad (3)$$

For rate law (2) with

$$k_p = (1/p^o) \cdot \tilde{k}$$

we get

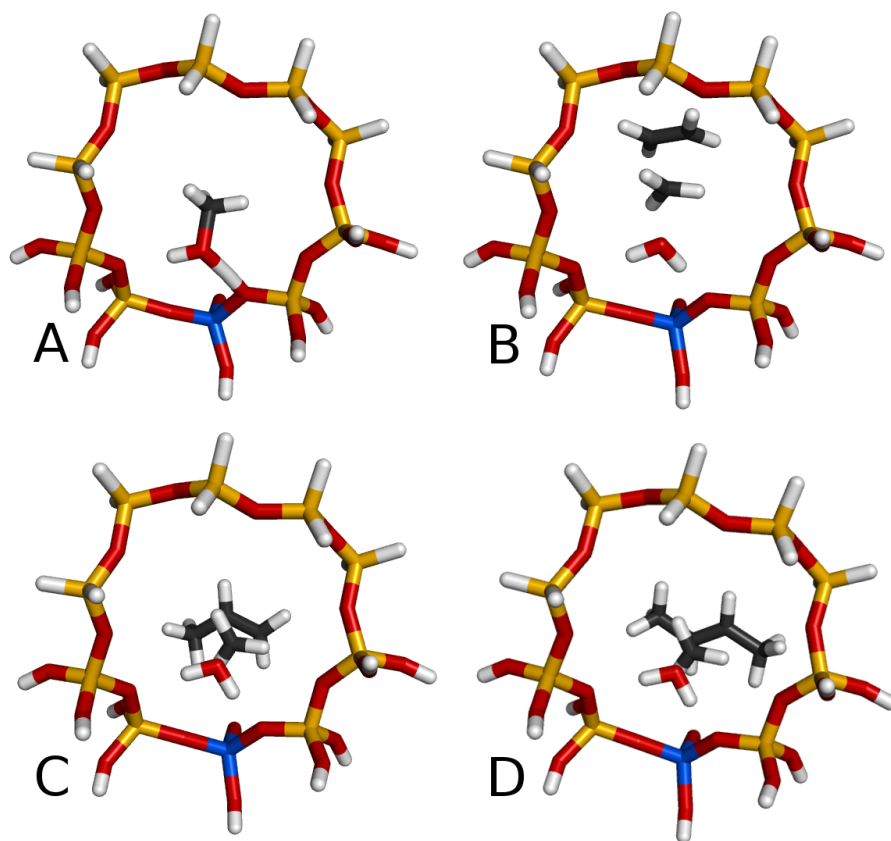
$$\frac{1}{k_p} \left( \frac{\partial k_p}{\partial T} \right) = \frac{1}{k_p} \left( \frac{1}{p^o} \right) \left( \frac{\partial \tilde{k}}{\partial T} \right) = \frac{1}{\tilde{k}} \left( \frac{\partial \tilde{k}}{\partial T} \right)$$

Hence,

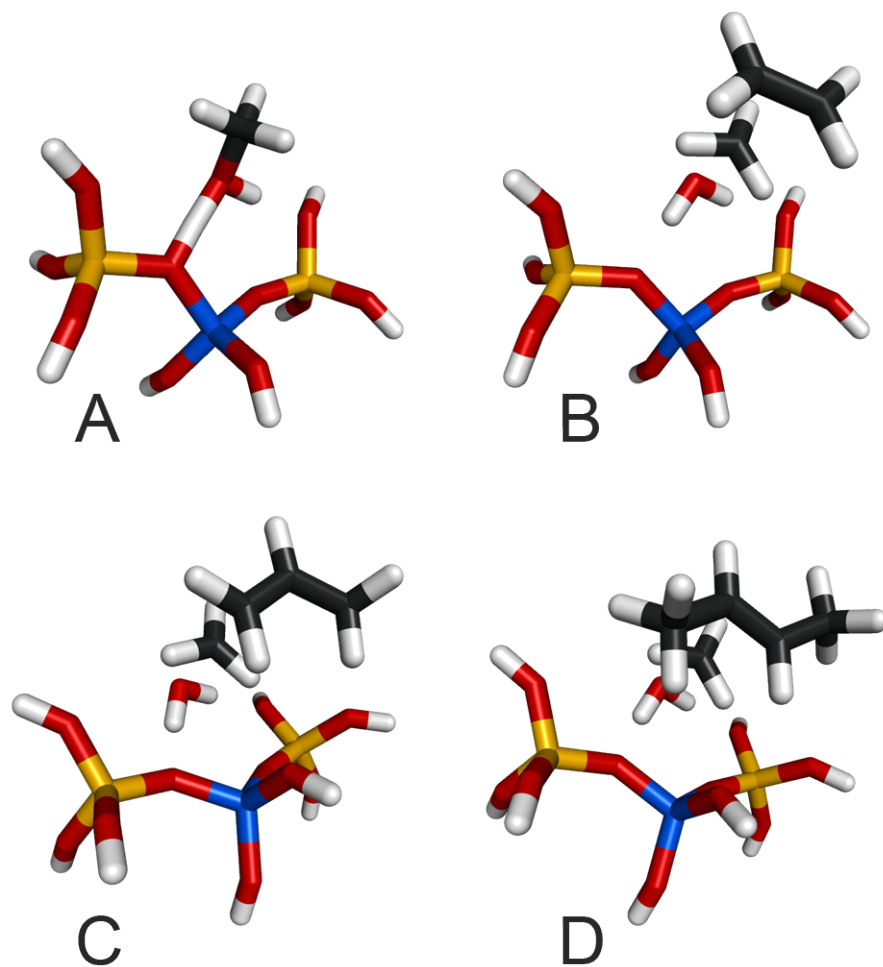
$$E_A = RT + \Delta H^\ddagger \quad (4)$$

We get different relations between the heat of activation and the Arrhenius activation energy depending on the rate law. The difference is RT. The reason is that the Arrhenius equation describes the temperature dependence of the rate constants only approximately, and the deviations are different when the rate law is formulated in terms of concentration or partial pressure. Since the experiments we are referring to measure partial pressures <sup>[9,10]</sup> we use eq. (4) to derive “experimental” enthalpy barriers from the measured Arrhenius barriers.

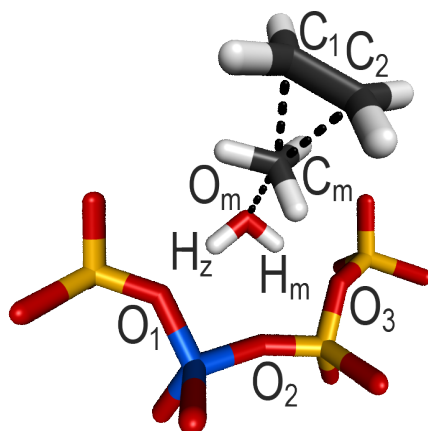
## 4. Additional Results



**Fig. S1.**  $10T_{10H}$  type clusters employed in the hybrid MP2:PBE+D scheme for A) methanol adsorption structure, B) ethene transition structure, C) propene transition structure, and D) *t*-2-butene transition structure. Color key: yellow, silicon; red, oxygen; blue, aluminum; black, carbon; and white, hydrogen. “10H” denotes 10 terminating H atoms at Si, the remaining terminating groups are OH groups.



**Fig. S2.** 4T-size clusters employed for the CCSD(T) correction for A) methanol adsorption structure, B) ethene transition structure, C) propene transition structure, and D) *t*-2-butene transition structure. Color key: yellow, silicon; red, oxygen; blue, aluminum; black, carbon; and white, hydrogen.



**Fig. S3.** Characteristic distances for the transition structure of ethene. The same nomenclature is kept for all other complexes following Svelle et al.<sup>[11]</sup>. Color key: yellow, silicon; red, oxygen; blue, aluminum; black, carbon; and white, hydrogen.

Table S1. Atomic distances (pm, see Fig. S 3) for relaxed transition structures of ethene, propene, and *t*-2-butene.

Bond <sup>x</sup>	ethene		propene		<i>t</i> -2-butene		adsorbed methanol		
	PBE <sup>a</sup>	PBE+D2 <sup>b</sup>	PBE <sup>a</sup>	PBE+D2 <sup>b</sup>	PBE <sup>a</sup>	PBE+D2 <sup>b</sup>	Bond <sup>x</sup>	PBE <sup>a</sup>	PBE+D2 <sup>b</sup>
O <sub>z1</sub> H <sub>z</sub>	184	176	177	179	177	178	O <sub>z1</sub> H <sub>z</sub>	111	119
O <sub>z2</sub> H <sub>m</sub>	198	252	208	259	218	259	O <sub>z2</sub> H <sub>m</sub>	179	250
O <sub>z3</sub> H <sub>m</sub>	266	208	259	205	261	204	O <sub>z3</sub> H <sub>m</sub>	265	196
O <sub>m</sub> C <sub>m</sub>	218	217	209	208	206	205	H <sub>z</sub> O <sub>m</sub>	136	134
C <sub>m</sub> C <sub>1</sub>	216	218	215	218	234	234	H <sub>m</sub> O <sub>m</sub>	100	99
								(97) <sup>c</sup>	(97) <sup>c</sup>
C <sub>m</sub> C <sub>2</sub>	221	221	244	242	230	229	O <sub>m</sub> C <sub>m</sub>	145	145
								(143) <sup>c</sup>	(143) <sup>c</sup>

<sup>a</sup> Ref.<sup>[11]</sup>. <sup>b</sup> This work. <sup>c</sup> Gas phase methanol.



Table S2. Energy and enthalpy barriers and their contributions (kJ mol<sup>-1</sup>) for the reaction of ethene, propene, and *t*-2-butene with methanol adsorbed in H-MFI. C – cluster model (Fig. S2), pbc – periodic boundary conditions (Fig. S1).

		ethene	propene	<i>t</i> -2-butene
Energy, $\Delta E_{el}^{\ddagger}$	PBE+D (pbc)	79.2	32.7	17.6
	$\Delta$ MP2/CBS(C)	17.6	21.5	17.8
	Hybrid MP2/CBS:PBE+D2	96.8	54.2	35.4
	MP2/CBS(C) – CCSD(T)	3.2	2.3	2.9
ZPVE	harmonic	11.7	7.8	5.7
	anharmonic	10.9	5.4	5.3
finite temperature corr. <sup>a</sup>	harmonic	6.9	7.9	10.8
	anharmonic	-0.3	5.2	5.3
Enthalpy, $\Delta H_{623}^{\ddagger}$	harmonic	113.4	67.0	49.7
	anharmonic	105.4	61.9	43.8
	harmonic, Svelle <sup>b</sup>	104	77	48
	harmonic, Van Speybroeck <sup>c</sup>	83.2	51.6 <sup>d</sup>	28.9 <sup>d</sup>
	experiment <sup>e</sup>	104	64	40

<sup>a</sup> Includes  $RT = 5.2$  kJmol,  $\Delta H^{\ddagger}(T) = \Delta E^{\ddagger}(T) - RT$ . <sup>b</sup> Ref. <sup>[11]</sup>. <sup>c</sup> Ref. <sup>[12]</sup>. <sup>d</sup> Derived from the  $E_a$  values in Table. 3 of ref. <sup>[12]</sup>. <sup>e</sup>  $\Delta H_{623}^{\ddagger} = E_A - RT$ , see section 3.

Table S3. Pre-exponential and rate constants (mbar<sup>-1</sup> s<sup>-1</sup>) for the methylation reaction of ethene, propene, and *t*-2-butene with methanol adsorbed in H-MFI. Observed experimental values <sup>[9,10]</sup> and calculated ones obtained with anharmonic and harmonic frequencies using normal mode distortions in internal coordinates, Anharm-Hybrid and Harm-Hybrid, respectively, and with harmonic frequencies obtained using finite differences of Cartesian distortions for part of the system <sup>[11]</sup>, Harm-Svelle. The Harm-VanSp results <sup>[12]</sup> have been obtained with a 46 tetrahedra cluster model. For each of the calculated values the ratio with experiment is reported.

	ethene		propene		<i>t</i> -2-butene	
	<i>A</i>	Obsd/Cald	<i>A</i>	Obsd/Cald	<i>A</i>	Obsd/Cald
Observed	$2.7 \times 10^5$	-	$2.1 \times 10^3$	-	$5.9 \times 10^1$	-
Anharm-Hybrid	$1.1 \times 10^5$	3.4	$2.5 \times 10^2$	8.4	$1.7 \times 10^1$	3.4
Harm-Hybrid	$4.2 \times 10^1$	6395.4	$5.0 \times 10^0$	423.2	$1.0 \times 10^2$	0.6
Harm-VanSp	$1.0 \times 10^4$	26.8	$4.8 \times 10^2$	4.4	$1.5 \times 10^2$	0.4
Harm-Svelle	$4.0 \times 10^3$	67.4	$7.5 \times 10^2$	2.8	$4.6 \times 10^2$	0.1
	<i>k</i>	Obsd/Cald	<i>k</i>	Obsd/Cald	<i>k</i>	Obsd/Cald
Observed	$2.0 \times 10^{-4}$	-	$3.5 \times 10^{-3}$	-	$1.0 \times 10^{-2}$	-
Anharm-Hybrid	$6.1 \times 10^{-5}$	3.3	$6.0 \times 10^{-4}$	5.8	$1.4 \times 10^{-3}$	7.3
Harm-Hybrid	$4.8 \times 10^{-9}$	41483.7	$4.5 \times 10^{-6}$	772.9	$2.6 \times 10^{-3}$	2.9
Harm-Svelle	$7.2 \times 10^{-6}$	27.7	$2.2 \times 10^{-4}$	15.6	$4.1 \times 10^{-2}$	0.2

## References:

- [1] G. Piccini, M. Alessio, J. Sauer, Y. Zhi, Y. Liu, R. Kolvenbach, A. Jentys, J. A. Lercher, *J. Phys. Chem. C* **2015**, *119*, 6128-6137.
- [2] G. Kresse, J. Furthmuller, *Phys. Rev. B* **1996**, *54*, 11169-11186, *Phys Rev B*.
- [3] TURBOMOLE V6.5 2013, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from <http://www.turbomole.com>.
- [4] C. Hättig, A. Hellweg, A. Köhn, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1159-1169.
- [5] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305, *Phys Chem Chem Phys*.
- [6] T. H. Dunning, *J. Chem. Phys.* **1989**, *90*, 1007-1023, *J Chem Phys*.
- [7] D. E. Woon, T. H. Dunning, *J. Chem. Phys.* **1993**, *98*, 1358-1371, *J Chem Phys*.
- [8] P. Atkins, J. d. Paula, R. Friedman in *Physical Chemistry. Quanta, Matter, and Change*, Oxford University Press, Oxford, **2013**.
- [9] S. Svelle, P. O. Rønning, U. Olsbye, S. Kolboe, *J. Catal.* **2005**, *234*, 385-400.
- [10] S. Svelle, P. O. Rønning, S. Kolboe, *J. Catal.* **2004**, *224*, 115-123.
- [11] S. Svelle, C. Tuma, X. Rozanska, T. Kerber, J. Sauer, *J. Am. Chem. Soc.* **2009**, *131*, 816-825, article.
- [12] V. Van Speybroeck, J. Van der Mynsbrugge, M. Vandichel, K. Hemelsoet, D. Lesthaeghe, A. Ghysels, G. B. Marin, M. Waroquier, *J. Am. Chem. Soc.* **2011**, *133*, 888-899.