Alcohol Dehydration on Monooxo W=O and Dioxo O=W=O Species

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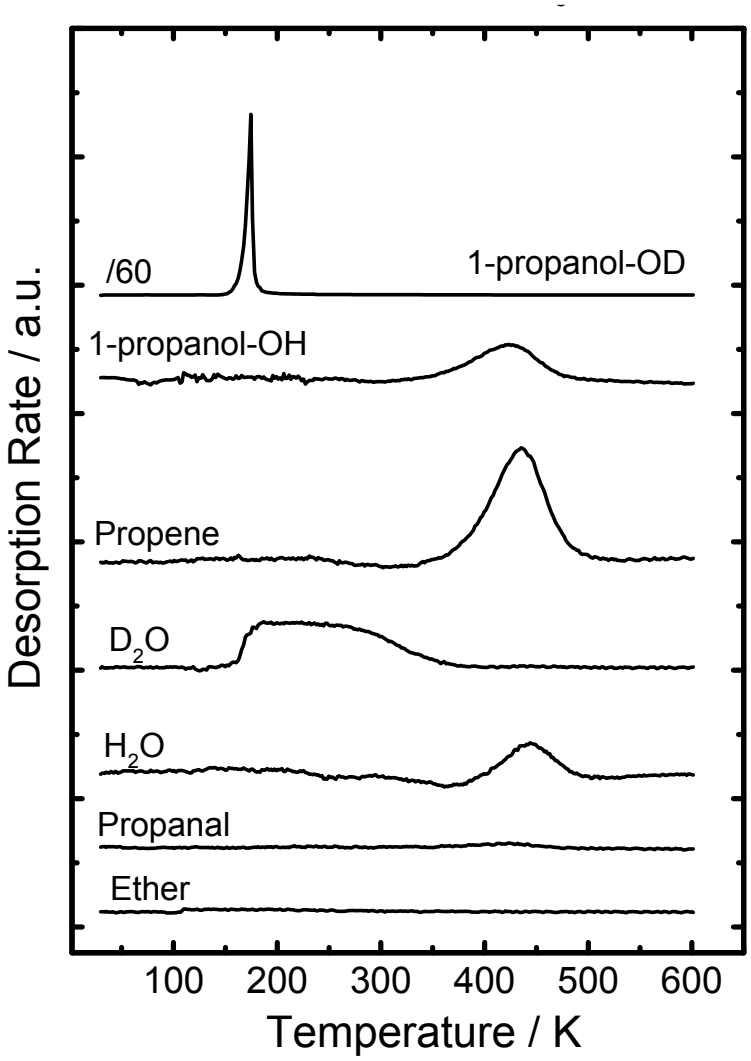


Figure S1. TPD spectra following 1-propanol-OD adsorption on 10 ML thick nanoporous WO_3 film that was deposited at 20 K and 65° angle of incidence. The 1-propanol-OD, 1-propanol-OH, propene, D_2O, H_2O, propanal, and di-n-propanyl ether spectra are obtained at m/e^- = 32, 31, 41, 20, 18, 58 and 73 amu, respectively. The contributions of 1-propanol-OD fragments at 41, 18, 20 and 58 amu have been subtracted using fragmentation pattern determined from the molecular desorption in the multilayer region.

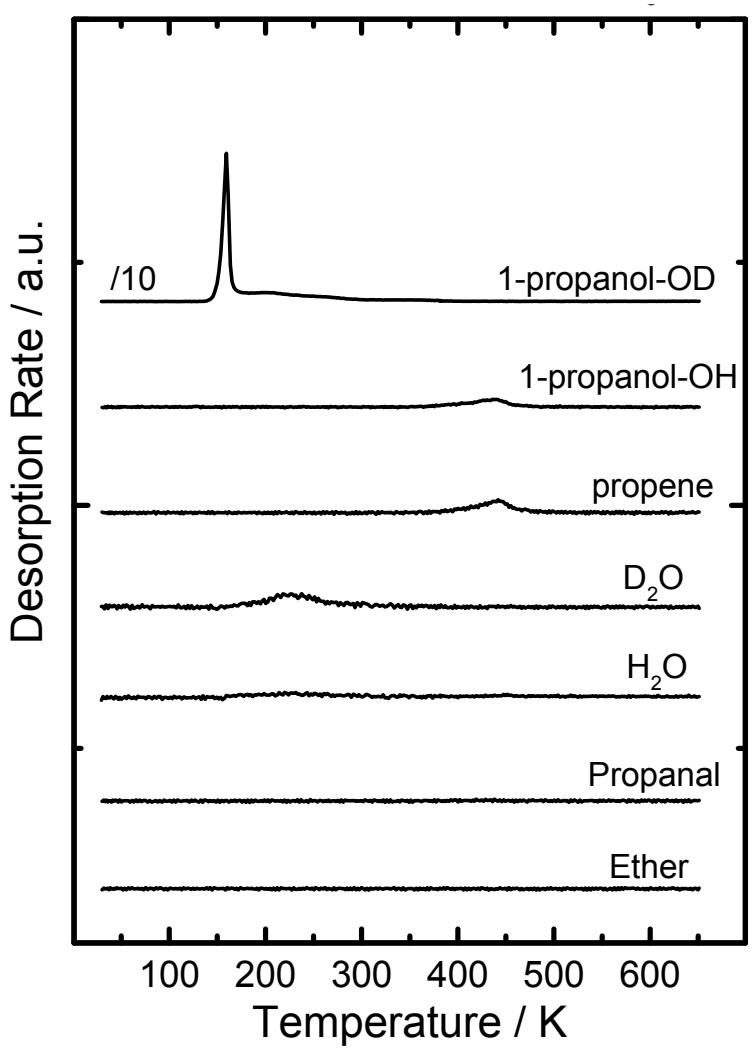


Figure S2. TPD spectra following 1-propanol-OD adsorption on ordered WO_3 /Pt(111) film at 20 K. The 1-propanol-OD, 1-propanol-OH, propene, D_2O, H_2O, propanal, and di-n-propanyl ether spectra are obtained at m/e^- = 32, 31, 41, 20, 18, 58 and 73 amu, respectively. The contributions of 1-propanol-OD fragments at 41, 18, 20 and 58 amu have been subtracted using fragmentation pattern determined from the molecular desorption in the multilayer region.

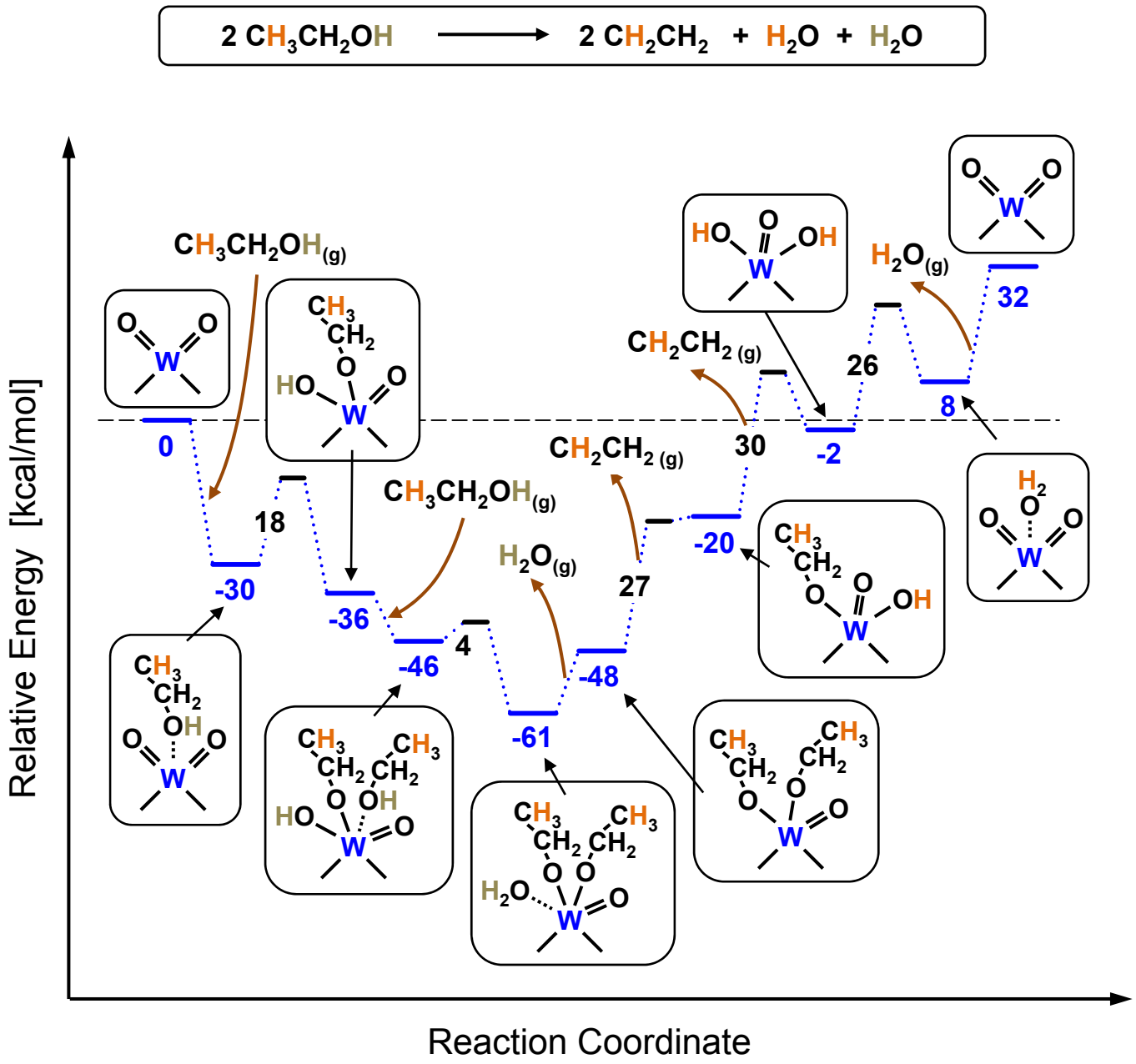


Figure S3. Reaction mechanisms for the dehydration of two ethanol molecules on the dioxo O=W=O moiety ofthe linear $(WO_3)_3$ cluster determined using DFT calculations.

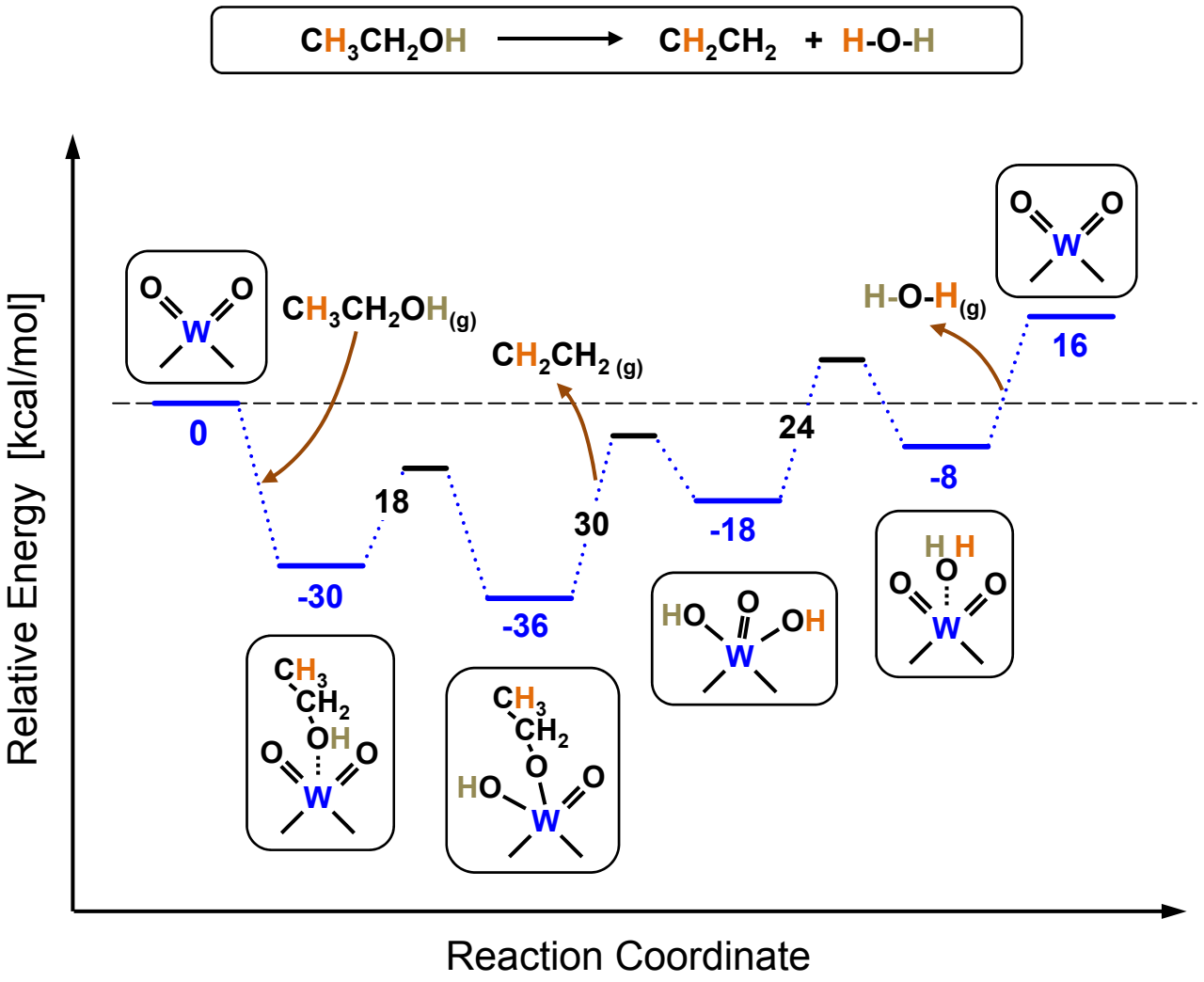


Figure S4. Reaction mechanisms for the dehydration of a single ethanol molecules on the dioxo O=W=O moiety of the linear $(WO_3)_3$ cluster determined using DFT calculations.

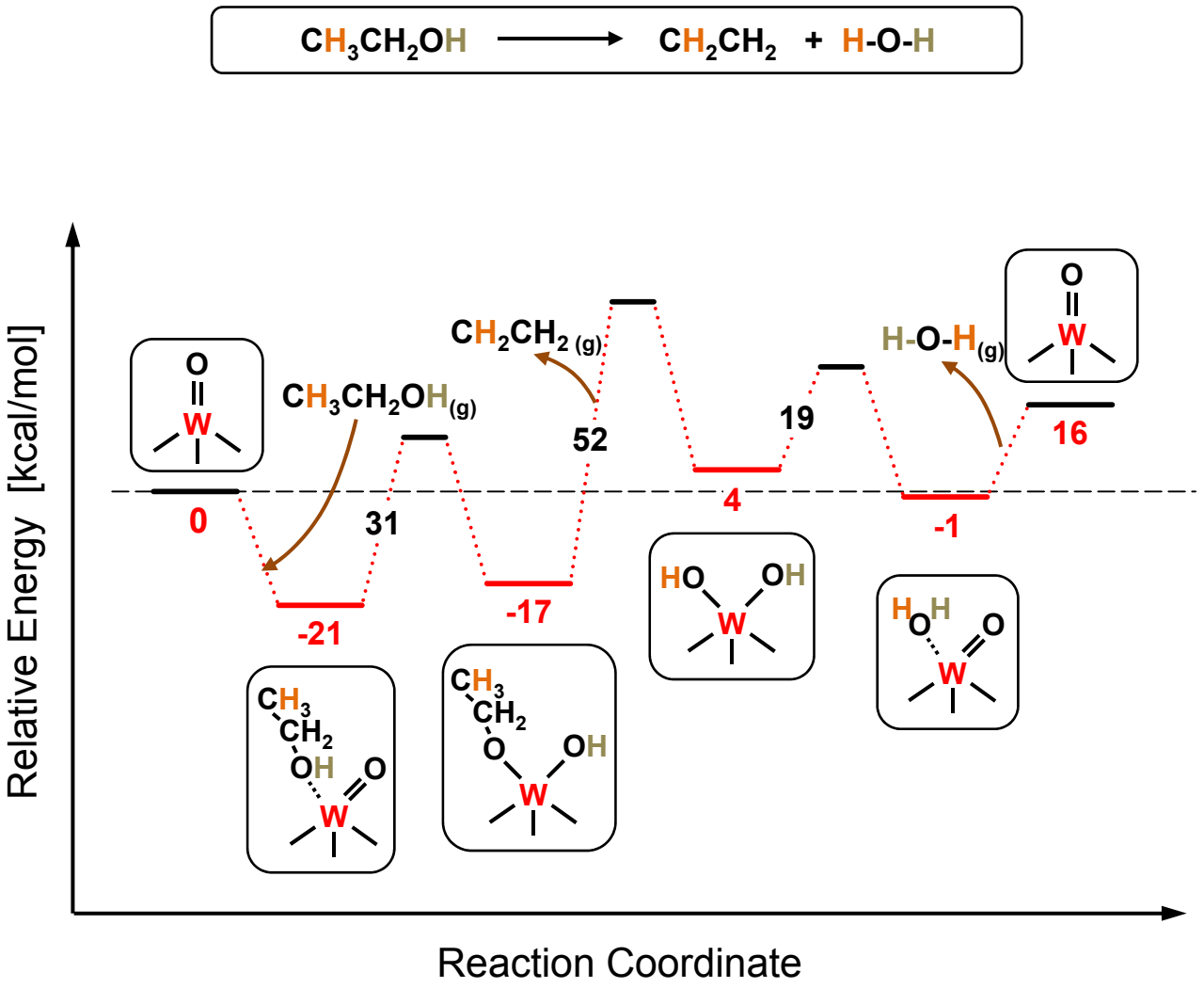
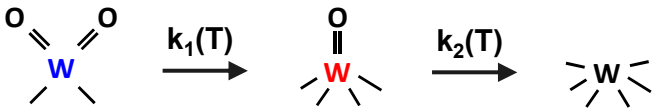


Figure S5. Reaction mechanisms for the dehydration of a single ethanol molecules on the monooxo W=O moiety of the linear $(WO_3)_3$ cluster determined using DFT calculations.

First Order Kinetics of Sequential Reactions

Conversion of O=W=O species as described in Equation 1 in the main text:

Reactions: 

Concentrations:	$[WO_2]$	$[WO]$	$[W]$
Initial concentrations:	$[WO_2]_0$	0	0

Rate equations:

$$\frac{d[WO_2]}{dt} = -k_1[WO_2]$$

$$\frac{d[WO]}{dt} = k_1[WO_2] - k_2[WO]$$

$$\frac{d[W]}{dt} = k_2[WO]$$

Analytic solution:

$$[WO_2] = [WO_2]_0 \exp(-k_1 t)$$

$$[WO] = \frac{k_1}{k_2 - k_1}\left(\exp(-k_1 t) - \exp(-k_2 t)\right)[WO_2]_0$$

$$[W] = \left(1 + \frac{k_1 \exp(-k_2 t) - k_2 \exp(-k_1 t)}{k_2 - k_1}\right)[WO_2]_0$$

Expressions plotted on *x* and *y* axes in Figure 4 during the course of reaction represented by reaction time, *t*:

$$x = \frac{[WO_2] + [WO]}{[WO_2]_0} = \left(\frac{k_1 \exp(-k_2 t) - k_2 \exp(-k_1 t)}{k_2 - k_1}\right)$$

$$y = \frac{[WO_2]}{[WO_2]_0} = \exp(-k_2 t)$$