Supporting Information

Alcohols on the rocks: solid-state formation in a $H_3CC \equiv CH + OH$ cocktail under dark cloud conditions

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S1 Additional TPD-QMS spectra



Figure S1: TPD-QMS fragment spectra acquired after deposition of i-propanol (top; exp. 3.1) and i-propanol + H + O_2 (bottom; exp. 3.2) on a 10 K surface. Note the 10 K shift of the main desorption peak of i-propanol between the two experiments.

S2 Pathways and benchmark calculations

S2.1 IRC paths

For the reaction $H_3CC \equiv CH + OH$, we perform IRC calculations to confirm that the found transition state structures connect the relevant pre-reactive complex and desired product. The resulting paths are presented in Figures S2 and S3. The pre-reactive complex energy is set to zero, acting as the reference value for the energy.

Examining Figure S3, it also becomes clear why the activation energy for the reaction $H_3CC\equiv CH + OH$ on the exterior carbon atom has such a high activation energy in comparison to that at the center carbon. This is because there is an extra rotation of the OH radical involved in order to reach the transition state structure. In other words, this only plays a role for a starting geometry where the OH and $H_3CC\equiv CH$ are fully relaxed.



Figure S2: Intrinsic reaction coordinate path for the reaction $H_3CC \equiv CH + OH$ on the centered carbon atom. The geometries corresponding to the pre-reactive complex, transition state, and product are displayed above.



Figure S3: Intrinsic reaction coordinate path for the reaction $H_3CC \equiv CH + OH$ on the exterior carbon atom. The geometries corresponding to the pre-reactive complex, an intermediate state, the transition state, and product are displayed above.

S2.2 NEB paths



Figure S4: Nudged-elastic band path for the reaction $H_3CCH=CH_2 + OH$ on the centered carbon atom.



Figure S5: Nudged-elastic band path for the reaction $H_3CCH=CH_2 + OH$ on the exterior carbon atom.

S2.3 M06-2X validity check

In order to test if the use of the MPWB1K is valid, the activation energies have been recalculated with the M06-2X functional with the same basis set (def2-TZVP). This is a functional very commonly used for these types of reactions as well and is thought to be able to reasonably describe the reaction paths. Indeed, it is shown in Table S1 that the activation energies that are responsible for determining the reactivity differ by at most 240 K, indicating a proper choice of functional.

Table S1: Reaction of $H_3CC \equiv CH + OH$ and $H_3CCH = CH_2 + OH$, respectively. E and I refer to the exterior and interior carbon, respectively. All values are in units of Kelvin.

		$HC \equiv CCH_3 + OH$		
		MPWB1K		
Energy type	E or I carbon	PES	ZPE	Total
Activation	Ι	-126	763	636
Activation	${ m E}$	-358	738	380
Reaction	Ι	-16928	2089	-14839
Reaction	${ m E}$	-18122	2333	-15790
		M06-2X		
Energy type	E or I carbon	PES	ZPE	Total
Activation	Ι	-59	773	714
Activation	${ m E}$	-110	729	619
Reaction	Ι	-17224	2054	-15170
Reaction	${ m E}$	-18006	2296	-15710
		$H_2C = CHCH_3 + OH$		
		MPWB1K		
Energy type	E or I carbon	PES	ZPE	Total
Activation	Ι	-1490	799	-691
Activation	${ m E}$	-1358	687	-671
Reaction	Ι	-15736	1692	-14045
Reaction	${ m E}$	-16088	1825	-14263
		M06-2X		
Energy type	E or I carbon	PES	ZPE	Total
Activation	Ι	-1557	837	-720
Activation	${ m E}$	-1420	775	-645
Reaction	Ι	-11299	2160	-9139
Reaction	${ m E}$	-16772	1901	-14871

S2.4 CCSD(T)-F12/cc-VDZ-F12 validity check

As a further validity check, the interaction energies of the $OH-C_3H_n$ pre-reactive complexes calculated with MPWB1K (DFT) are compared to those calculated with CCSD(T)-F12/cc-VDZ-F12. The interaction energies of the $OH-C_3H_n$ pre-reactive complexes differ by at most 115 K between MPWB1K and CCSD(T)-F12/cc-VDZ-F12 calculations, as shown in Table S2. This shows again that the used functional can accurately describe these reaction paths. For the pre-reactive complex of OH with $H_3CC\equiv CH$ on the exterior carbon atom, convergence is not achieved for the CCSD(T)-F12/cc-VDZ-F12 calculation.

Table S2: Interaction energies of OH with $H_3CC\equiv CH$ and $H_3CCH=CH_2$. E and I refer to the exterior and interior carbon, respectively. All values are in units of Kelvin.

	$HC \equiv CCH_3 + OH$	
E or I carbon	PES MPWB1K	PES $CCSD(T)$ -F12/cc-VDZ-F12
Ι	-1342	-1333
${ m E}$	-2073	-
	$H_3CCH=CH_2+OH$	
E or I carbon	PES MPWB1K	PES $CCSD(T)$ -F12/cc-VDZ-F12
Ι	-1543	-1509
${ m E}$	-1624	-1510