**Table 1.** Chemical formula and molecular structure of the investigated small molecule inhibitors.

|  |  |  |  |
| --- | --- | --- | --- |
|  | **HAc** | **Hacac** | **Hthd** |
| IUPAC name | ethanoic acid | 2,4-pentadione | 2,2,6,6-tetramethyl-3,5-heptanedione |
| Chemical formula | CH3COOH | CH3COCH2COCH3 | (CH3)3CCOCH2COC(CH3)3 |
| Ball-stick model  (side-view) |  |  |  |
| Model with Van der Waals radius (top-view) |  |  |  |
| \* Note that Hacac and Hthd are depicted in their enol forms, instead of keto forms, since enols are the more stable tautomers in the gas phase out of the keto-enol equilibrium for diketones.24,38–40 | | | |

**Table 2.** Experimental observations: overall blocking performance of HAc, Hacac and Hthd in terms of SiO2 nucleation delay from spectroscopic ellipsometry (Figure 1) and BDEAS blocking based on FTIR (Figure 2). Theoretical studies: overview of the packing of the studied SMIs on an Al2O3 surface in terms of their covered area and surface density from random sequential adsorption (RSA) simulations (see Figure 5 and Figure 6). The covered area (see Equation (4)) and surface density of SMIs are relevant for elucidating the contributions of steric shielding and chemical passivation components. Specifically, the increase of covered area as a function of SMI size reflects a larger steric shielding contribution, whereas a decrease of SMI surface density as a function of SMI size indicates a smaller chemical passivation component. These will be discussed in more detail in section IV. DISCUSSION.

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| --- | --- | --- | --- | --- |
|  | Experimental | | Theoretical | |
|  | SiO2 nucleation delay  (Cycles) | BDEAS blocking  (%) | Covered area  (%) | Surface density  (nm-2) |
| HAc | 58 ± 2 | 97.4 ± 0.4 | 50.1 ± 0.3 | 2.21 ± 0.01 |
| Hacac | 30 ± 3 | 92.0 ± 1.1 | 50.6 ± 0.4 | 1.46 ± 0.01 |
| Hthd | 44 ± 2 | 96.0 ± 0.6 | 53.1 ± 0.3 | 0.76 ± 0.01 |

Table 3. Summary of the most relevant binding energies and activation barrier for water formation of HAc, Hacac, and Hthd on an Al2O3 surface in various configurations calculated by DFT. In certain cases, we include the values for the adsorbate and the adsorbed byproduct in parenthesis. For chelate structures we have included the total energy (Eads = Eads(dispersion) + Eads(electronic)), the dispersion and electronic contribution to the total energy. All energies are in eV.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **(eV)** | | **HAc** | **Hacac** | **Hthd** |
| Physisorption | | -0.93 | -0.75 | -0.72 |
| monodentate before H2O formation | | -1.13 | -0.97 | -1.01 |
| activation barrier (Ea) | | 0.37 | 0.25 | 1.30 |
| monodentate after H2O formation | | -0.64  -1.61 (+H2O ads.) | -0.91 (+H2O ads.) | -0.94 |
| Chelate | Total | -- | -0.98  -1.24 (+H2O ads.) | -0.84  -0.96 (+H2O ads.) |
| Dispersion. | -- | -0.54 | -1.04 |
| Electronic. | -- | -0.44 | +0.20 |