

Supporting Information

KINETICS AND PRODUCT FORMATION DURING THE PHOTOOXIDATION OF BUTANOL ON ATMOSPHERIC MINERAL DUST

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Lamps Irradiance

The experimental setup allows to switch on different number of lamps (from zero to 7) in different geometric configurations. Each lamp emits UV-A radiation, in wavelengths range from 300 to 420 nm, with a maximum around 350 nm. Lamps irradiance was measured with a Spectrometer AvaSpec-2048 (Avantes), using a calibration lamp AvaLight-DH-CAL and FC-UV400 fiber with cosine corrector.

For the study of the influence of light intensity, the number of lamps was varied, always maintaining a symmetrical configuration. The total irradiance for different configuration is shown in Figure S 1 and Table S1.

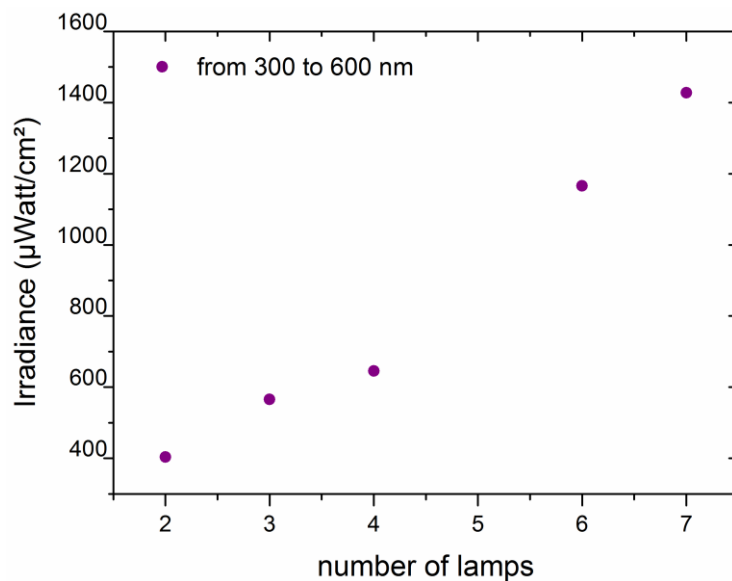


Figure S 1: Total irradiance for different configuration of lamps.

Table S 1: Total irradiance for different configuration of lamps for different ranges of wavelength: 300 to 400 nm, 400 to 600 nm and 300 to 600 nm

Irradiance ($\mu\text{Watt}/\text{cm}^2$)	Number of lamps				
	2	3	4	6	7
300 to 400 nm	349.4	484.16	553.04	1003.8	1226.1
400 to 600 nm	54.6	81.82	92.74	162.3	201.1

Schematic of the experimental set-up

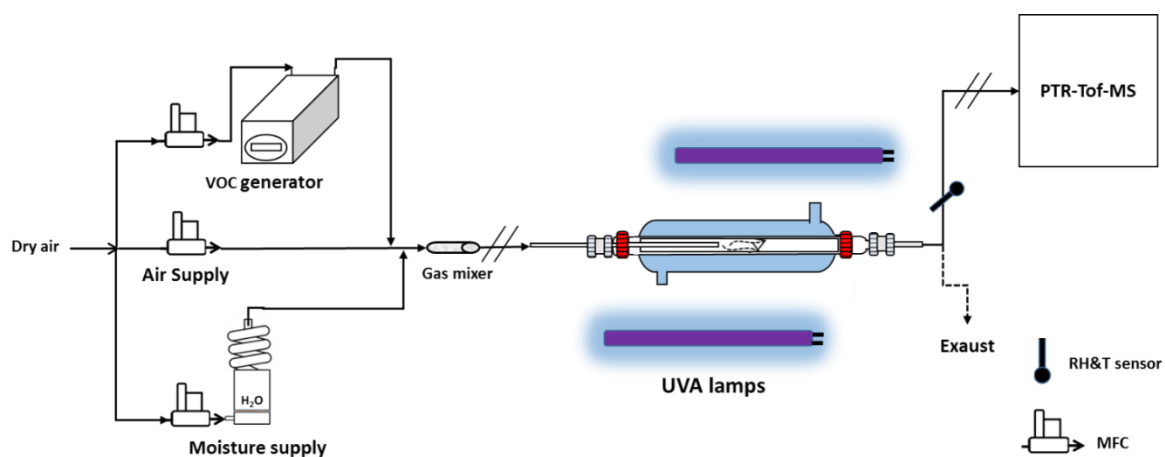


Figure S 2: A schematic overview of the experimental set-up

Butanol Uptake Kinetics

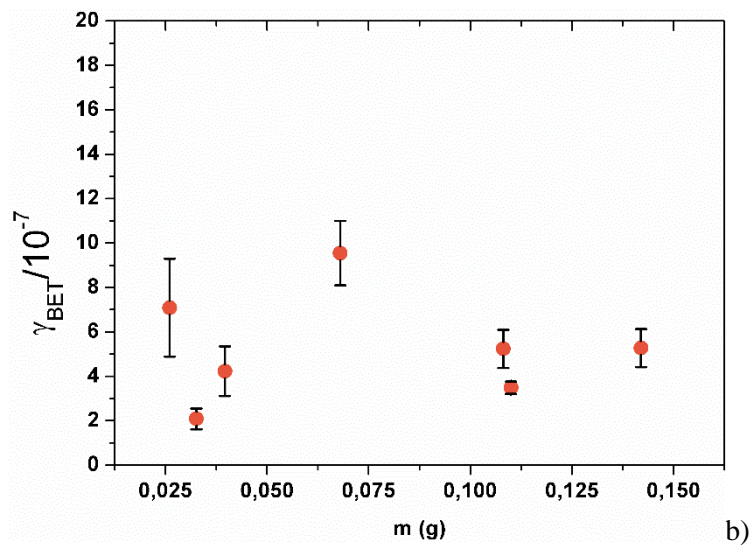
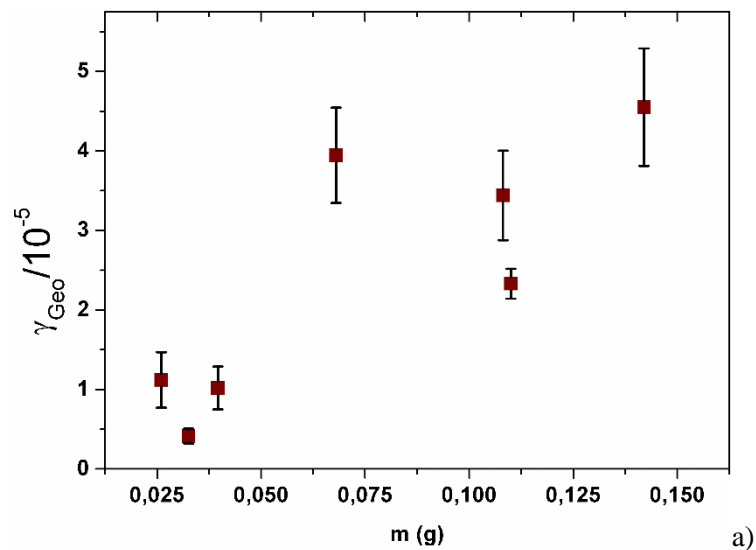


Figure S 3: Dependence of geometric uptake coefficient of butanol (a), and the BET uptake coefficients (b) as a function of film mass. For all experiments, Butanol initial concentration was 20 ppb, dry conditions, temperature of 293 K, for all, 7 lamps on (1.4 mWatt/cm²).

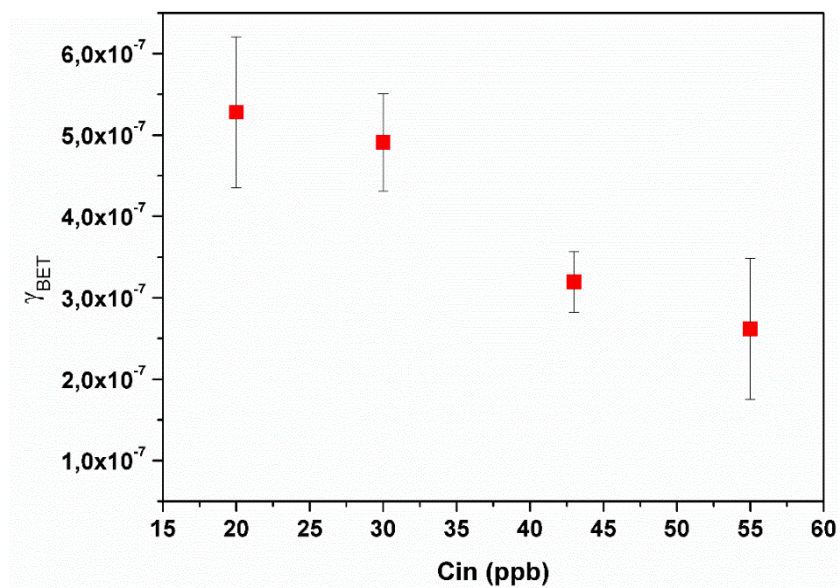


Figure S 4: γ_{BET} as function of butanol concentration. For butanol initial concentration from 20 to 55 ppb, dry conditions, temperature 293 K, for all 7 lamps irradiation (1.4 mWatt/cm).

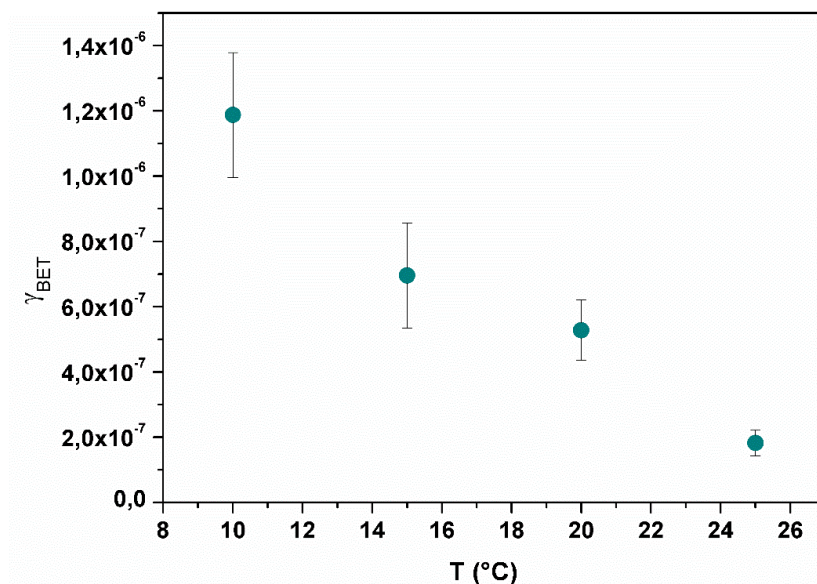


Figure S 5: Uptake coefficient, γ_{BET} , as a function of reactor temperature. For initial concentration of 20 ppb of butanol, dry conditions (0% relative humidity), irradiation of 7 lamps (1.4 mWatt/cm²).

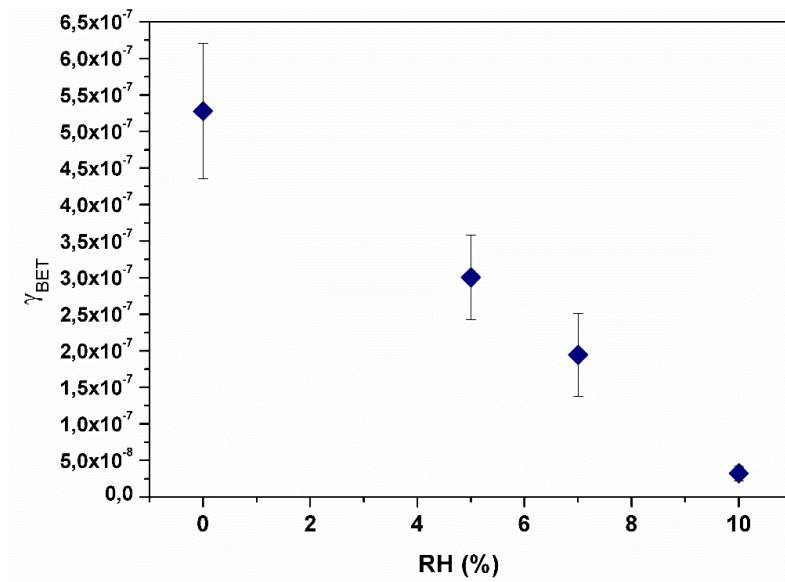
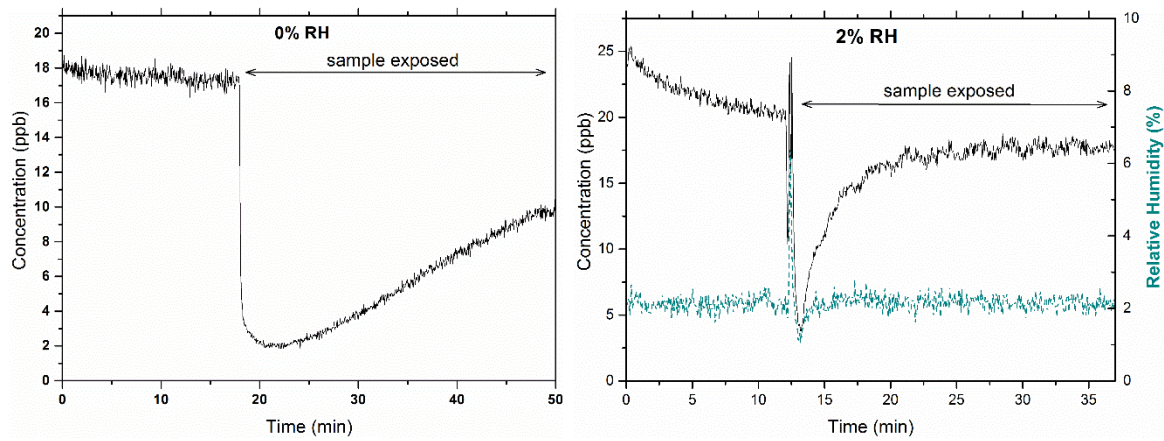


Figure S 6: Uptake coefficient, γ_{BET} , as a function of relative humidity. For initial concentration of 20 ppb of butanol, temperature 293 K and illumination of 7 lamps (1.4 mWatt/cm²).



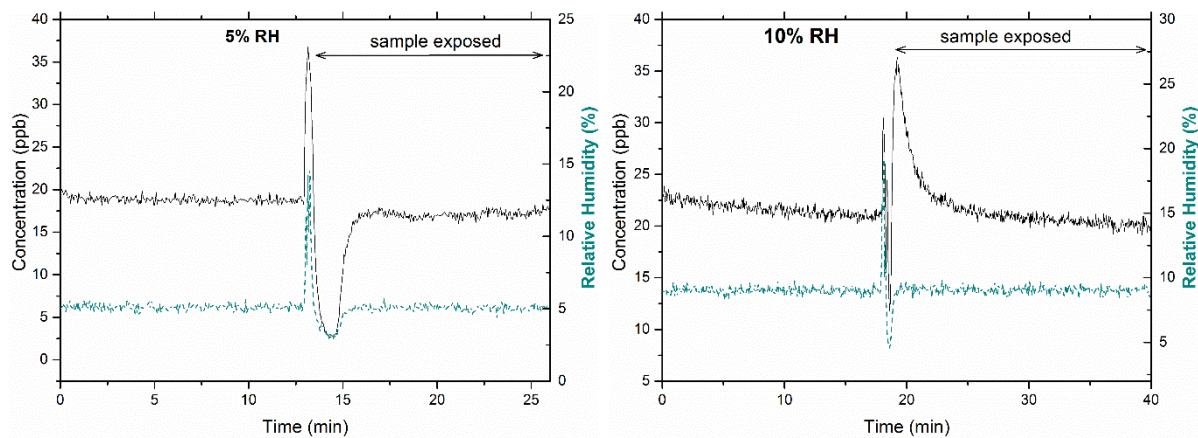


Figure S 7: Butanol loss, exposing an ATD film to different relative humidity levels under dark conditions. For initial concentration of 20 ppb of butanol, temperature 293 K.

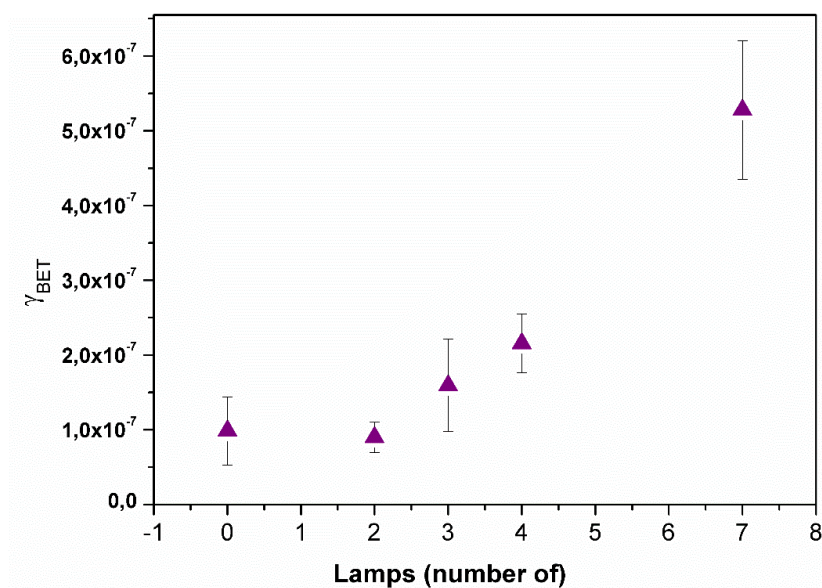


Figure S 8: Uptake coefficient, γ_{BET} as a function of number of lamps. For initial concentration of 20 ppb of butanol, dry conditions, temperature 293 K.

Product identification and PTR-MS Standards

The fragmentation patterns of the main products were examined by measuring the signals of vaporized liquid standards under the same experimental conditions (i. e. the compounds passed on the same pathway, using the same setup and air as carrier gas). The standards were performed using the exponential dilution method¹: small volumes (< 2 μL , in function of the volatility of the compound) were added in an empty flask well stirred and flushed continuously with air ($Q_{\text{air}} = 500 \text{ ml/min}$ plus 3L/min of dilution) and sent to the PTR-MS inlet. The setup is depicted in Figure S 9 and results are summarized on Table S 2.

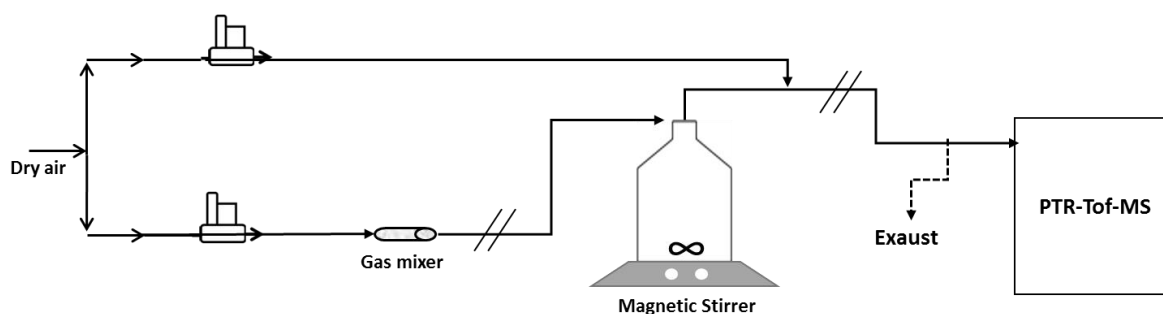


Figure S 9: Setup for fragmentation patterns for standards compounds on PTR-Tof-MS operating on H_3O^+ .

Table S 2: Results for fragmentation patterns of standards compounds on PTR-Tof-MS operating on H_3O^+ .

Compound	Formula	Mw	Proposed Ions	m/z detected	Ratio (%)
Acetaldehyde	$\text{C}_2\text{H}_4\text{O}$	44.05	$[\text{MH}^+]$	45.033	100%
Propanal	$\text{C}_3\text{H}_6\text{O}$	58.08	$[\text{MH}^+]$	59.049	88.2%
			$[\text{MH}^+] + (\text{C}_2\text{H}_4)$	31.017	11.8%
			$[\text{MH}^+] - \text{H}_2\text{O}$	55.054	80.0%
Butanal	$\text{C}_4\text{H}_8\text{O}$	72.11	$[\text{MH}^+]$	73.063	15.6%
			$[\text{MH}^+] - \text{H}_2\text{O}$ isotope	56.057	4.4%

			[MH ⁺] - H ₂ O	97.096	50.6%
Heptanal	C ₇ H ₁₄ O	114.18	[MH ⁺] + (C ₃ H ₈ O)	55.054	28.5%
			[MH ⁺]	115.11	14.9%
			[MH ⁺] - H ₂ O isotope	98.10	5.9%
			C ₃ H ₉ ⁺ (+ C ₃ H ₅ ⁺)	69.069	29.3%
Octanal	C ₈ H ₁₆ O	128.21	[MH ⁺] - H ₂ O	111.11	24.0%
			[MH ⁺]	129.12	21.5%
			C ₃ H ₅ ⁺ (+ C ₅ H ₉ ⁺)	41.038	10.1%
			[MH ⁺] isotope	112.12	8.0%
			[MH ⁺] + (C ₄ H ₁₀ O)	55.054	7.1%
Acetone	C ₃ H ₆ O	58.08	[MH ⁺]	59.049	100%
Butanol	C ₄ H ₁₀ O	74.12	[MH ⁺] - H ₂ O	57.069	90%
			[MH ⁺] - H ₂ O - CH ₄	41.039	10%

Summarizing the results from the standards procedure and what has been reported on literature,^{2,3} we can assign fragments of a determined m / z to compounds that originated them, Table S 3.

Table S 3: Product identification and m/z to molecules assignments.

Major Products			Minor Products		
m/z	Formula	Compound	m/z	Formula	Compound
45.033	C ₂ H ₅ O ⁺	Acetaldehyde	83.085	C ₆ H ₁₁ ⁺	fragment Hexanal
31.017	CH ₃ O ⁺	Formaldehyde / fragment Propanal	87.080	C ₅ H ₁₁ O ⁺	Pentanal

59.049	$C_3H_7O^+$	Propanal/ Acetone	97.101	$C_7H_{13}^+$	fragment Heptanal
33.033	CH_4O^+	Metanol	111.116	$C_8H_{15}^+$	fragment Octanal
69.069	$C_5H_9^+$	fragment Octanal / Pentanal	129.127	$C_8H_{17}O^+$	Octanal
115.111	$C_7H_{15}O^+$	Heptanal			

References

- (1) McKinley, J. and Majors, R.E. The Preparation of Calibration Standards for Volatile Organic Compounds - A Question of Traceability, *LCGC Magazine*, **2000**, (10), 18.
- (2) Buhr, K., Van Ruth, S., Delahunty, C. "Analysis of Volatile Flavour Compounds by Proton Transfer Reaction-Mass Spectrometry: Fragmentation Patterns and Discrimination between Isobaric and Isomeric Compounds." *Int. J. Mass Spectrom.*, **2002**, 221 (1): 1–7.
- (3) Španěl, P., Yufeng J., and Smith, D. SIFT Studies of the Reactions of H_3O^+ , NO^+ and O_2^+ with a Series of Aldehydes and Ketones *Int. J. Mass Spectrom. Ion Process.* **1997**, 165–166, 25–37.