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

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Abstract

Mineral dust particles have photochemical properties that can promote heterogeneous reactions on their surfaces and therefore alter atmospheric composition. Even though dust photocatalytic nature has received significant attention recently, most studies have focused on inorganic trace gases. Here we investigated how light changes the chemical interactions between butanol and Arizona test dust, a proxy for mineral dust, under atmospheric conditions. Butanol uptake kinetics were measured, exploring the effects of UV light irradiation intensity (0 – 1.4 mW/cm), relative humidity (0 – 10%), temperature (283 – 298 K), and butanol initial concentration (20 – 55 ppb). The composition of the gas phase was monitored by a high-resolution proton-transfer-reaction mass spectrometer (PTR-ToF-MS) operating in H_3O^+ mode. Water was observed to play a significant role, initially reducing heterogeneous processing of butanol, but enhancing reaction rates once it evaporated. Gas phase products were identified, showing that surface reactions of adsorbed butanol led to the emission of a variety of carbonyl containing compounds. Under actinic light these compounds will photolyze and produce hydroxyl radicals, changing dust processing from a sink of VOC into a source of reactive compounds.

1 - Introduction

Every year, large amounts of mineral dust are emitted into the atmosphere and transported over several kilometers before being deposited. For instance, Kaufman and coworkers estimated that 240 ± 80 Tg of dust are transported annually from Africa to the Atlantic Ocean, and of these, 50 Tg arrives in the Amazon Basin.¹ During their lifetime in the troposphere, dust particles undergo physical interactions, including absorbing and scattering light, which influences radiative forcing and global albedo,² and inducing chemical reactions when acting as a substrate for the conversion or scavenging of various trace gases.³ Heterogeneous reactions of atmospheric relevant trace gases on mineral aerosols have received more attention lately, and the uptake of a few reactive gases by mineral aerosols has been studied using a variety of experimental approaches. For instance, the uptake kinetics of inorganic compounds such as NO_2 , HNO_3 , N_2O_5 , O_3 , SO_2 ,⁴⁻⁷ as well as some organics^{8,9} were investigated on mineral dust and various proxies. However, few studies have explored the effect of irradiation on the uptake.

Suspended dust particle composition varies depending on its sources location and may contain variable amounts of semiconductor metal oxides that show photocatalytic activity, such as TiO_2 and Fe_2O_3 , whose application in wastewater and air treatment have been extensively studied.¹⁰⁻¹³ Recently, the photocatalytic nature of dust particles has been suggested and discussed.^{14,15} However, up to now, the most investigations focused on inorganic compounds such as ozone,¹⁶ nitrogen dioxide,¹⁷ sulfur dioxide,^{18,19} and hydrogen peroxide,²⁰ and little is known about mineral dust photoreactivity towards volatile organic compounds (VOC).^{21,22}

To assess the importance of photocatalytic transformations of volatile organic compounds on mineral dust, we investigated the uptake kinetics of butanol on Arizona test dust (ATD). We performed experiments under dark and illuminated conditions and measured uptake coefficients as a function of several experimental parameters, including initial VOC concentration, relative humidity, external temperature, and light intensity. Additionally, we analyzed the gas phase products,

evaluating the role of dust and the influence of light, whose effects are quantified and discussed.

Butanol was selected as a proxy for small alcohols (and/or oxygenated VOCs; OVOC) that are abundant in the atmosphere. OVOCs are generally emitted directly by anthropogenic sources, biogenic sources, or produced from the degradation of other VOCs (hydrocarbon oxidation). Butanol, specifically, is an alcohol that does not absorb light in the UV or visible regions, but its incomplete oxidation products can generate photochemically active radicals.

2 - Experimental

Coated wall flow tube

Experiments were performed in a horizontal coated wall flow tube reactor described in detail previously.²³ The temperature was maintained constant during each experiment by circulating thermostatically controlled water around an outer jacket. Dust was coated on the inner surface of a removable Pyrex insert (id 0.55 cm, length 20 cm), which fit within a larger tube, providing good contact with the jacket. Seven actinic lamps (Phillips 20 W) surrounded the reactor and could be switched on or off to modify the light intensity between 0 and 1.4 mW/cm² (see Supplementary Information, Figure S1) measured at the outer surface of the reactor. It is important to highlight that in this layout, UV light was irradiated from the back of the coatings, which were relatively thin (μm) with a maximum absorption of 15% i.e., the film is mostly homogeneously illuminated. Also, our approach does not consider light scattering in the dust film. However, Dupart et al²⁴ showed that this approach led, nevertheless, to similar uptake kinetics measured in more complex aerosol flow tube experiments where such limitations do not exist. Therefore, we believe that the light intensity measured is appropriate for the experiments described herein.

All experiments were carried out at atmospheric pressure using filtered dry air as a carrier gas at a total flow of 200 mL min⁻¹, except when stated otherwise. For humid experiments, water vapor

was introduced into the reactor by bubbling air through a thermostated gas bubbler filled with deionized water. Humidity and temperature were monitored by a SP UFT75 sensor. A schematic overview of the experimental setup is given in Figure S3. Gas phase butanol was generated using a calibrated permeation tube (*Dynacal*® - permeation rate 100 ng/min at 60 °C) placed in a temperature-controlled permeation device (VICI Metronics Dynacalibrator, Model 150).

Gas phase analysis

The coated wall flow tube was coupled to a high-resolution proton transfer reaction time of flight mass spectrometer (SRI-PTR-TOF-MS 8000 from Ionicon Analytik GmbH – Innsbruck, Austria) enabling on-line monitoring of the disappearance of butanol and the identification and quantification of products. The instrument continuously sampled 50 sccm at the flow tube outlet and its inlet temperature was 60 °C. Spectra were collected at a time resolution of 3.2 s. All measurements were performed using the following parameters: source current of 4.6 mA, drift voltage of 600 V, drift temperature of 60 °C, and a drift pressure of 2.42 mbar. E/N was about 125 Td ($1 \text{ Td} = 10^{-17} \text{ V cm}^2$). All results presented here were acquired using the H_3O^+ ionization mode as the reaction rates and fragmentation patterns for OVOCs such as alcohols, aldehydes, ketones, etc., have been extensively studied and documented.^{25–28}

Ideally, the proton transfer reaction should provide soft ionization resulting in very little or no fragmentation of compounds. However, in practice, fragmentation is observed. Fragmentation patterns for small OVOCs have already been studied, but it may be altered depending on the actual experimental conditions (for example, humidity) and instrument settings.²⁹ Therefore, fragmentation patterns of the main products were examined by measuring the signals of vaporized liquid standards under the same experimental conditions. Details about this procedure are available in the Supplementary Information.

Film Preparation

104

105 Arizona Test Dust (ATD) was used as provided by Powder Technology Inc. without further
106 pretreatment. The ATD Brunauer – Emmett – Teller surface area (BET) is $4.2 \pm 0.012 \text{ m}^2 \text{ g}^{-1}$ as
107 measured with a Micromeritics Tristar 3000, with particles having an average grain size of $4.08 \pm$
108 $2.91 \text{ }\mu\text{m}$.

109 ATD suspensions in ethanol were prepared to facilitate coating the inner surface of the Pyrex
110 tube insert. These suspensions were sonicated for 10 minutes and then dripped into the insert, which
111 was rotated to produce a uniform film. Once coated, the excess solution was allowed to flow out and
112 the tube was dried by flowing nitrogen through it. This step was repeated few times until a visually
113 homogeneous film was obtained. Finally, the insert was placed in an oven to dry at $60 \text{ }^\circ\text{C}$ for 24 h.
114 After drying, all tubes were weighed, and the mass of ATD films varied from 20 to 150 mg.

115

116 Uptake Experiments

117

118 Butanol loss was measured as a function of the movable injector position, that is, interaction time
119 between the VOC and dust surface. In a typical experiment, a freshly coated tube was placed in the
120 reactor and the injector was set to bypass the reactor, so that no surface was exposed to the gas flow
121 (position 0). The flow of butanol was then established and its concentration monitored. When it was
122 constant, lights were switched on. After 60 minutes, the uptake measurements started by moving the
123 injector stepwise (steps of 2 cm), exposing the ATD surface for 10 minutes. The injector was then
124 reset to position 0 for another 10 minutes. The procedure was repeated until the entire length of the
125 coated tube was exposed, which is equivalent to 10 positions of 2 cm each.

126 The decay of gas phase butanol obeyed first order kinetics according to:

127

$$\ln \frac{C(0)}{C(t)} = k_{obs}t \quad [1]$$

128

129 C(0) and C(t) are the inlet and outlet concentrations of butanol after a reaction time (t), and k_{obs} is
130 the measured first order rate constant. The uptake coefficient can then be calculated according to:
131

$$\gamma = \frac{4 k_{obs}}{\langle v \rangle} \frac{V}{S_{surf}} \quad [2]$$

132
133 where V is the total volume of the reactor, S_{surf} is the surface area exposed to the gas, and $\langle v \rangle$ is
134 average molecular velocity. For a cylindrical flow tube, the geometric uptake coefficient is given
135 by:
136

$$\gamma_{geo} = \frac{2r}{\langle v \rangle} k_{obs} \quad [3]$$

137
138 where r is the radius ($r_{tube} = 0.55$ cm).

139 It is worth noting that the uptake coefficients reported here are at steady state, reached after
140 10 minutes of exposure, and not the initial uptake coefficients usually reported in the literature.⁴

141
142 Diffusion correction

143
144 Uptake was corrected for diffusion effects that may form axial and radial concentration profiles along
145 the reactor, limiting the reaction rate. The method used, proposed by Cooney-Kim-Davis and derived
146 by Murphy and co-workers,³⁰ assumes that in the boundary condition the analyte is adsorbed or reacts
147 with some characteristic probability on each wall collision, which is the corrected uptake coefficient.
148 We solved the differential equation numerically, as proposed by Li et al.,³¹ where the corrected uptake
149 coefficient is given as function of the transmittance (C/C₀).

3 – Results and Discussion

Butanol Uptake Kinetics

For a solid film, the reactive surface area may be larger than the geometric surface area due to the presence of multiple layers of particles and/or because of the existence of pores. In the case of a fully accessible internal surface, the specific surface area can be used for the uptake calculations. Therefore, butanol uptake coefficients were measured as a function of dust film mass (Figure S3a). For these measurements, different fresh films of ATD were tested while other conditions were kept constant. The uptake coefficient increased linearly with the mass of the film, indicating that the entire inner surface is participating in the uptake process.⁴ Therefore, mass-dependent γ_{geo} uptake coefficients were corrected by the BET surface area of the samples according to:

$$\gamma_{BET} = \gamma_{Geo} \frac{S_{surf}}{S_{BET} m_{film}} \quad [4]$$

where S_{BET} is the BET surface area and m_{film} is the mass coated in the sample holder tube. The BET-corrected uptake coefficients, reported below, were observed to be independent of the actual mass of the film (Figure S3b).

Uptake rates were measured for different initial (inlet) concentrations of butanol and were observed to decrease from 5.3×10^{-7} to 2.2×10^{-7} when the concentration increases from 20 to 55 ppb (Figure S4). For an initial concentration of 800 ppb (± 160 ppb) of butanol, uptake could not be detected, due to very rapid surface saturation. Initial uptake coefficients tend to be independent of concentration when all active sites on the fresh surface are available for adsorption/reaction.^{7,32} El Zein et al.²⁰ reported no concentration dependence for the initial uptake coefficient, whereas an inverse dependence on initial H_2O_2 concentration was observed for steady state uptake. Nicolas et al.,¹⁶ using a similar experimental apparatus, also reported that both dark and irradiated uptake kinetics on titanium dioxide decreased inversely to initial ozone mixing ratio.

175 When the temperature increased from 283 to 298 K, the uptake coefficient decreased from 1.2
176 $\times 10^{-6}$ to 1.8×10^{-7} , which is approximately one order of magnitude (Figure S5). The reactive uptake
177 coefficient reported herein represents the overall kinetics of the heterogeneous process, and therefore
178 encompasses both chemical reactions and physical adsorption. Adsorption is an exothermic
179 phenomenon favored by a decrease in temperature.³³ Thereby, the temperature dependence suggests
180 the importance of adsorption/desorption in the butanol uptake mechanism, even under reactive
181 conditions. A similar dependence was previously reported for other VOCs.^{32, 34}

182 Humidity also has a strong influence on the uptake kinetics of butanol onto ATD (Figure S6).
183 At 10% relative humidity, the uptake coefficient is 6% of the value measured under dry conditions,
184 suggesting that water and butanol compete for available sites on the surface of ATD. To better
185 understand the influence of relative humidity on butanol uptake, an ATD film was successively
186 exposed to different relative humidity levels under dark conditions. First, the tube was exposed to air
187 and butanol (20 ppb) under dry conditions, and the disappearance of butanol was recorded. Then,
188 butanol flow was turned off and the tube was left under air until butanol was not detected. Thereafter,
189 butanol flow was resumed and the sample was exposed to the VOC with 2%, 5%, and 10% moisture.
190 Between each relative humidity level, the sample was left under dry air flow for evacuation. The
191 presence of water vapor in the feed stream significantly reduced butanol surface adsorption capacities
192 (Figure S7). Surface saturation was faster at higher water vapor contents, up to 10% relative humidity,
193 no change in butanol concentration was observed.

194 The uptake of water onto mineral particles has been studied by several authors and recently
195 reviewed.³⁵ However few studies have focused on the competitive uptake of water and other trace
196 gases, particularly under irradiation. For pure TiO_2 , relative humidity has a positive effect up to about
197 30% relative humidity, as observed by Sassine et al.,³⁶ who reported that the uptake of formaldehyde
198 increased from 6% to 30% relative humidity, and decreased at higher humidities. The influence of
199 humidity seems to vary depending on the combination of trace gas and mineral studied, and results
200 are often controversial. Under dark conditions using ATD and other realistic dust, regardless of the

201 trace gas studied, relative humidity has been found to have a negative influence on gas uptake.^{19, 32,}
202 ^{37, 38} Our results show that the presence of light did not change this negative trend for butanol uptake.

203 In terms of competition between butanol and water for available surface sites, water molecules
204 are smaller and faster, giving them an advantage over butanol molecules. Regarding the affinity
205 between the mineral surface and water molecules, Gustafson and coworkers³⁹ noted a difference
206 between ATD and CaCO₃ isotherms in the sub-monolayer range, demonstrating stronger water-ATD
207 interactions compared to CaCO₃. They proposed that the difference might be due to the higher
208 electronegativity of Si which increases the polarity of the –OH group, resulting in a stronger H-bond
209 in the ATD. Furthermore, water adsorption capacity is related to other characteristics such as the
210 mineral composition, cation hydration energies, presence of swellable clay minerals, porosity, etc.⁴⁰

211 Interestingly, the system shows a hysteresis. When the ATD film was exposed to decreasing
212 levels of relative humidity under irradiation, butanol uptake increased more rapidly than was observed
213 for a freshly humidified surface (Figure 1). That is, water condensation may first reduce
214 heterogeneous processing, but its evaporation may afterwards change the surface characteristics to
215 enhance its reactivity. Water uptake measurements on ATD have shown that one monolayer of water
216 is developed at about 11% relative humidity.³⁹ In going from dry to slightly humid conditions,
217 adsorbed water molecules dissociate leaving OH groups on the surface. By increasing relative
218 humidity, once surface is fully hydroxylated, extra water molecules will be accommodated in outer
219 layers via hydrogen bonds.⁴¹ Those surface OH groups can form OH radicals under dry conditions
220 and illumination, providing an additional pathway for butanol oxidation.

221

Figure 1: Decreasing relative humidity (RH) and successively exposing the sample surface to butanol and H₂O vapor. For butanol initial concentration of 20 ppb, temperature = 20 °C, 7 lamps, mass of ATD = 69 mg.

Our experimental setup allowed switching between 0 and 7 lamps in different geometrically symmetrical configurations. Each lamp emits UV-A radiation in the wavelength range from 300 to 420 nm, with a maximum around 350 nm. Figure S8 shows the systematic increase of the uptake coefficient as a function of UV light irradiance. The dark uptake coefficient is 5 times less than the light uptake coefficient for irradiation with 7 lamps. This gives clear evidence of the photochemical nature of the interactions between butanol (which does not absorb within this wavelength region) and ATD (which semiconductor content is activated by light). This is in agreement with previous studies which also observed photo-enhanced uptake for inorganic compounds over different mineral dust proxies.^{16-20, 37, 38} However, few similar studies on organic compounds are available.²¹

237

238 The uptake (loss) of butanol was accompanied by the formation of a variety of gas phase products
239 (Figure 2). Major products were observed at m/z 45.033 ($\text{C}_2\text{H}_5\text{O}^+$), 31.017 (CH_3O^+), 59.049 ($\text{C}_3\text{H}_7\text{O}^+$),
240 33.033 (CH_5O^+), 69.069 (C_5H_9^+), 115.111 ($\text{C}_7\text{H}_{15}\text{O}^+$), and five other minor products were detected at
241 very low concentrations (below 0.1 ppb) at 83.085 ($\text{C}_6\text{H}_{11}^+$), 87.080 ($\text{C}_5\text{H}_{11}\text{O}^+$), 97.101 ($\text{C}_7\text{H}_{13}^+$),
242 111.116 ($\text{C}_8\text{H}_{15}^+$), and 129.127 ($\text{C}_8\text{H}_{17}\text{O}^+$). Products identification is detailed in Table 1. It is
243 interesting to note that fragments with m/z greater than butanol were also detected (for instance m/z
244 69.069 and m/z 115.111), indicating the possibility of dimerization or recombination of intermediates.
245 It should be noted that m/z 31.017 is here assigned to formaldehyde, although other compounds may
246 interfere at this m/z, as discussed by Schirpp et al. and Inomata et al.^{42, 43}. No product formation was
247 observed in the dark.

248

Table 1: Product identification and m/z to molecules assignments.

Major Products			Minor Products		
m/z	Formula	Compound	m/z	Formula	Compound
45.033	$\text{C}_2\text{H}_5\text{O}^+$	Acetaldehyde	83.085	$\text{C}_6\text{H}_{11}^+$	fragment Hexanal
31.017	CH_3O^+	Formaldehyde / fragment Propanal	87.080	$\text{C}_5\text{H}_{11}\text{O}^+$	Pentanal
59.049	$\text{C}_3\text{H}_7\text{O}^+$	Propanal/ Acetone	97.101	$\text{C}_7\text{H}_{13}^+$	fragment Heptanal
33.033	CH_4O^+	Metanol	111.116	$\text{C}_8\text{H}_{15}^+$	fragment Octanal
69.069	C_5H_9^+	fragment Octanal / Pentanal	129.127	$\text{C}_8\text{H}_{17}\text{O}^+$	Octanal
115.111	$\text{C}_7\text{H}_{15}\text{O}^+$	Heptanal			

249

Figure 2: Product concentration profile for each position/residence time along the reactor. For initial butanol concentration of 20 ppb, dry conditions, $T = 20\text{ }^{\circ}\text{C}$, 7 lamps, mass of ATD = 110 mg.

To explore whether these products are arising from “freshly” up taken butanol or from adsorbed molecules, a film was exposed to gas phase butanol in the dark until surface saturation (i.e., constant butanol signal). Maintaining the butanol flow throughout the reactor, the lights were then switched on and off in the following sequence: 1) 30 minutes two lamps on; 2) 30 minutes four lamps on; 3) 1 hour all lamps off; 4) 30 minutes 6 lamps on. We observed (see Figure 3) production of different compounds (CH_3O^+ , $\text{C}_2\text{H}_5\text{O}^+$, $\text{C}_3\text{H}_7\text{O}^+$, C_5H_9^+ , and $\text{C}_7\text{H}_{15}\text{O}^+$) immediately after the lights were turned on, with increasing intensity at higher light fluxes. Nevertheless, there was no drop in the gas phase butanol concentration, suggesting that products were formed from butanol already adsorbed on the surface. Product formation was quantified (subtracting the background value from the concentration during irradiation) for each round of illumination (number of lamps switched on; Figure 4). Although only major products are shown in Figure 3 and Figure 4, the same minor products listed in Table S3 were also present. Figure 4 clearly demonstrates that irradiation enhanced product formation. It is known that photocatalytic reaction rates are proportional to the radiant flux for low/moderate illumination intensities.⁴⁴ Chapuis et al.⁴⁵ also observed lower product concentrations at lower light intensities, other factors being equal, for the photocatalytic oxidation (PCO) of n-

269 butanol.

270

271

Figure 3: Saturation experiment: Concentration profiles for butanol (right scale) and main products over butanol-saturated ATD surface for different irradiation intensities (2, 4, and 6 lamps, indicated by bars above the graph). Experimental conditions were: Air flow rate 200 ml/min, dry conditions, $T = 20\text{ }^{\circ}\text{C}$, mass of ATD = 35 mg.

272

273 Concerning the study of alcohols under atmospheric simulated conditions onto different
274 mineral proxies, mainly small aldehydes, ketones, and carboxylic acids were reported as products.
275 Styler and Donaldson²¹ studied the photooxidation of isopropanol and n-propanol over TiO_2 films in
276 a Knudsen cell, operated at much lower pressure than in the current investigation, and identified
277 acetone and propionaldehyde, respectively, as main products. The same authors, Styler, Myers, and
278 Donaldson,⁴⁶ studied the photooxidation of fluorotelomer alcohols onto Mauritanian sand and
279 volcanic ashes and found aldehydic products in the gas phase and perfluorinated carboxylic acids as
280 sorbed products. Recently, Romanias and coworkers³² also studied the photochemistry of isopropanol
281 on Gobi natural dust under pure air, reporting the formation of acetone, formaldehyde, acetic acid,
282 and acetaldehyde as products when the dust was illuminated.

284

Figure 4: Net product formation of major products for different light intensities during the saturation experiment (Figure 3). The number of lamps is represented by bar color as indicated in the legend.

285

286 Most of the available literature for alcohols, and specifically butanol, investigates
287 photocatalytic oxidation (PCO) on TiO₂, with the goal of optimizing conditions to mineralize the
288 organic compound. Yao and Feilberg⁴⁷ quantified product formation for the photocatalytic
289 degradation of 52 ppb of n-butanol through TiO₂-coated ceramic filters, reporting acetaldehyde,
290 butyraldehyde, propionaldehyde/acetone, ethanol, formic acid, acetic acid, and formaldehyde as
291 potential byproducts. They pointed out, however, that the observed products accounted for only a
292 fraction of the reactant consumption, suggesting that butanol could be directly degraded producing
293 CO₂ and water.

294 In our case, the total yield (sum of the yield of all detected products) is around 30 – 40%,
295 implying that either all of the adsorbed butanol is not converted into products, or some butanol is
296 converted into non-volatile products that accumulate on the surface or yet is mineralized to CO₂ and
297 water. Butanal can be expected to be one of the first intermediates from the butanol oxidation, it is

therefore interesting to note that we did not detect it. It was however detected in studies investigating the oxidation on pure TiO₂ at much higher concentrations than ours.⁴⁷⁻⁵¹ In addition to butanal, propionaldehyde, acetaldehyde, 1-propanol, and ethanol were also found by those authors. It is worthwhile to note that all of these studies investigated oxidation on pure TiO₂ at much higher concentrations than used in this study. Nevertheless, this study generally agrees with previous reports that, mineral dust (ATD containing 2.0 – 5.0 wt% Fe₂O₃ and 0.5 – 1 wt% TiO₂) can promote photooxidation of an organic compound on its surface similar to pure semiconductors such as TiO₂.

Gas phase products give some insight into the butanol degradation mechanism under our experimental conditions. We propose that during photooxidation adsorbed butanol is first directly oxidized to an aldehyde by photo-generated holes or OH radicals from residual water on the surface.

The process then continues via a series of complex reactions, which are expected to be similar to those proposed by other authors,^{48, 52, 53} with aldehydes being converted to shorter chain aldehydes and/or alcohols.

As presented by Ye et al.,⁵³ aldehydes are oxidized via two pathways, either through the C(n) acid, or by direct conversion to the C(n-1) aldehyde. No acids were detected here, which may be due to their lower volatility or their high affinity for the dust surface (and tubing). Alcohols such as propanol and ethanol can also remain adsorbed on dust surface.⁴⁵ A global mechanism is suggested in Figure 5. In general, we can say:

324

325 Some studies highlight the contribution of superoxide radical and other radical species derived from
 326 oxygen.^{52, 54} The superoxide radical may contribute, for instance, to charge separation (between e_{cb}^-
 327 and h_{vb}^+). Molecular O_2 is also very important, as it can directly oxidize the aldehyde to an acid⁴⁸ or
 328 react with alkyl radicals,⁵² forming a hydroxylated peroxy radical and $HOO^\bullet$ radicals. In anhydrous
 329 systems, O_2 is the active oxidizing species, and its ionosorbates are the only negatively charged
 330 species able to react with holes.³³

334

335 Additionally, intermediary reactions in the oxidation mechanism may lead to the formation of radicals,
 336 resulting in the propagation of chain reactions⁵² involving O_2 .⁵⁴ Recombination of radicals is then
 337 likely to occur, resulting in products of higher molar mass than the initial compound.

338

339

Figure 5: Suggested mechanism for butanol photooxidation on ATD's surface.

340

341 Carbonyl compounds were the predominant products observed in the gas phase. Aldehydes and
 342 ketones absorb at UV-Vis wavelengths (>290 nm), acting as radical precursors for further
 343 photochemical reactions. On the other hand, alcohols, including butanol, do not absorb light at these

wavelengths and therefore generally have longer lifetimes in the troposphere.⁵⁵ We emphasize that mineral dust plays an important role not only acting as a scavenger for alcohol molecules, but also in converting them into more reactive species.

Atmospheric Implications

We presented the effect of ambient conditions such as temperature, relative humidity, and light intensity on an oxygenated organic compound uptake on realistic mineral dust particles. Uptake was maximized at low temperature and low humidity.

We estimated the lifetime of butanol due to its heterogeneous photooxidation on mineral dust surfaces. The calculation used the first order rate constant under atmospheric conditions i.e., with the uptake coefficient measured at 20 ppbv of butanol, for dry conditions, at 20° C under a real UV-A (315-400 nm) irradiance, determined using the Quick TUV model, for latitude of 40° North at noon during equinox day, or solar zenith angle of 40° . For very high dust loadings (surface area density of 0.052 m² m⁻³), the butanol lifetime was found to be 1.48 days whereas for regular clean days (surface area density of 1x10⁻⁴ m² m⁻³) it was 770 days. By comparison, the butanol lifetime due to OH radical reaction is estimated as 1.4 days.⁵⁵ As a consequence, this butanol removal pathway can only be effective in a dust plume.

More importantly, the photochemistry described here occurs on illuminated mineral dust, with adsorbed organic compounds typically being oxidized to shorter and more volatile products. Butanol, for instance, will produce aldehydes such as formaldehyde, acetaldehyde, and propionaldehyde which are potential sources of atmospheric radicals. More complex products (e.g., dimers of reaction intermediates) were also formed in small amounts. In other words, mineral dust can be regarded as a reservoir for such compounds, transporting pollution for source regions to remote places and may transport, where tens of pptv of aldehydes may be a significant contribution to their actual concentrations. Overall, mineral dust is not inert and opens new photochemical pathways that so far

370 have not been considered in current atmospheric models.

371

372

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376

377 **Supporting Information**

378 Lamp calibrations (total irradiance for different configuration of lamps) are presented in Figures S1
379 and Table S1. A schematic overview of the experimental setup is given in Figure S2. Dependence of
380 geometric uptake coefficient on butanol and the BET uptake coefficients are shown in Figure S3a and
381 S3b, respectively. BET uptake coefficients as a function of butanol concentration, reactor temperature,
382 relative humidity, and number of lamps are shown in Figure S4, S5, and S6, S8. Butanol loss upon
383 exposing an ATD film to different relative humidity levels under dark conditions is presented in
384 Figure S7. Details about product identification and PTR-MS standards are also given in the SI in
385 Figure S9 and Tables S2 and S3.

386

387

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