

Supporting Information

Confirming lack of CO photo-evolution of butyrophenone on oxidized TiO₂(110)

We observed CO photo-evolution (m/z 28) from the sample holder on clean titania so it is necessary to use ¹⁸O₂ to confirm the absence of butyrophenone induced carbonyl photo-desorption. We prepared an ¹⁸O-enriched surface of reduced TiO₂(110) by annealing the crystal in 10⁻⁴ mbar ¹⁸O₂ and then vacuum annealing to produce a reduced surface. We observe m/z 107 in the butyrophenone monolayer (α_2) desorption peak, which suggests that mixing occurs between butyrophenone and lattice oxygen. Mixing also occurs in the monolayer (α_2) and complexed state (α_3) when ¹⁸O₂ is used to prepare oxidized TiO₂(110) (Figure 2). Since we observe limited ¹⁸O mixing in the monolayer state and more mixing once photolyzed, the lack of mass 30, which would be due to C¹⁸O, indicates that carbonyl photo-desorption is not a significant process. The lack of mass 30 PSD signal indicates that mass 28 is probably due to CO desorption from the sample holder and alkyl chain cracking (C₂H₄). Further, the lack of mass 31 signal indicates that the mass 29 peak observed is not from HCO.

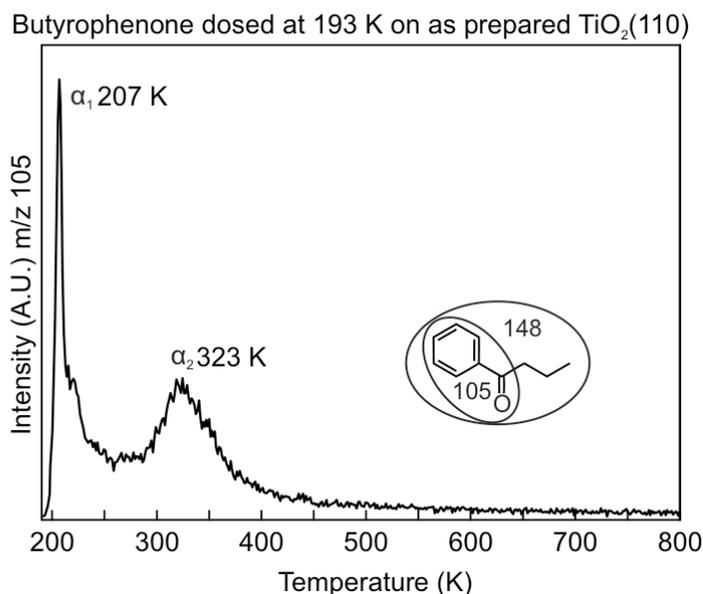


Figure S1. Temperature programmed reaction spectra of a multilayer coverage of butyrophenone on TiO₂(110): multilayer, α_1 , and monolayer, α_2 , of butyrophenone on as-prepared r-TiO₂(110) dosed at 192K. The heating rate used was 2 K s⁻¹.

m/z	NIST Database	r-TiO ₂ (110) Multilayer	r-TiO ₂ (110) Monolayer	o-TiO ₂ (110) Multilayer	o-TiO ₂ (110) Monolayer	o-TiO ₂ (110) Butyrophenone-O Complex	o-TiO ₂ (110) Monolayer after UV Irradiation
148	0.16	0.16	0.12	0.21	0.16	0.07	---
120	0.99	0.08	0.08	0.08	0.08	0.05	---
105	1.00	1.00	1.00	1.00	1.00	1.00	1.00
78	0.05	0.08	0.08	0.06	0.06	0.07	0.05
77	0.49	0.63	0.66	0.56	0.63	0.65	0.56
51	0.15	0.37	0.34	0.26	0.31	0.34	---
43	0.02	0.06	0.05	0.04	0.07	0.06	0.07
27	0.04	0.27	0.24	0.14	0.18	0.25	0.13

Table S1. Mass spectrometer fragments of butyrophenone desorbing from different desorption states on r-TiO₂(110) and o-TiO₂(110). All intensities are with respect to the most intense fragment, m/z 105. Fragments have been corrected for their transmission coefficient, multiplier gain, and ionization efficiency.

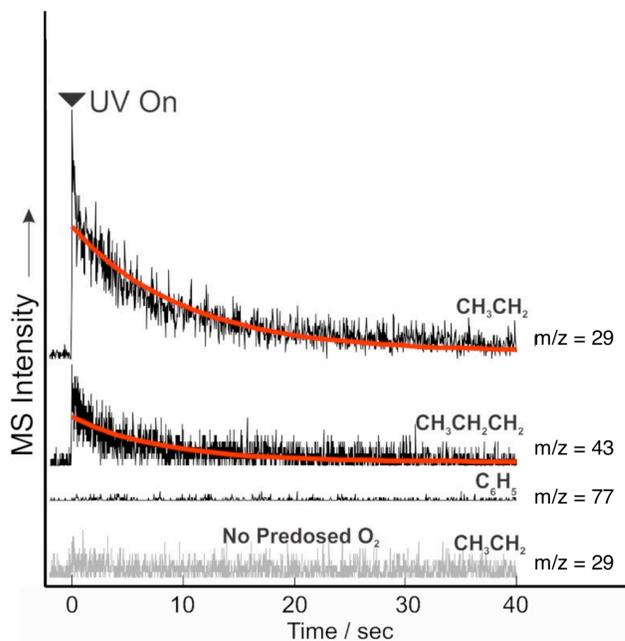


Figure S2. Photon-stimulated desorption (PSD) measurements of m/z 29, 43, and 77 from butyrophenone on O_2 -predosed $TiO_2(110)$ as well as the PSD of m/z 29 from butyrophenone on as-prepared $TiO_2(110)$ surface (grey). The triangle marks the start of a 5-minute UV-light irradiation performed at 300 K. (Only the first 40 seconds are shown here.) Mass 43 and 29, characteristic of a propyl fragment, are observed to desorb from oxidized $TiO_2(110)$ surface when irradiated while mass 77, characteristic of benzoate, does not. The decay of m/z 29 and 43 on the pre-oxidized surface were fit to a single exponential and the fit parameters are shown in Table S1.

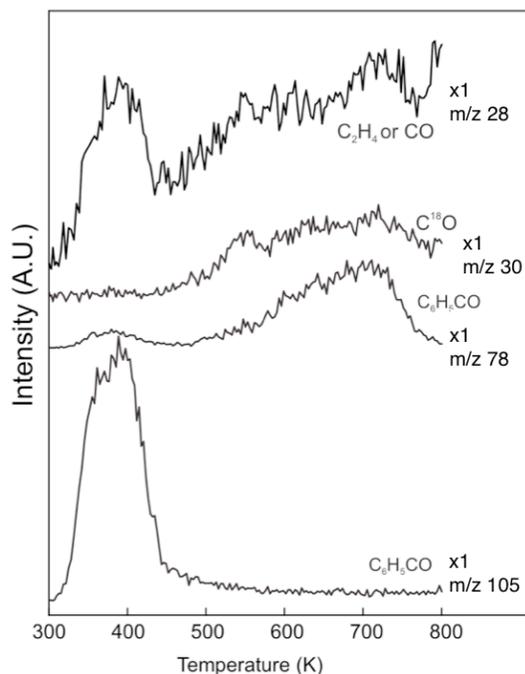


Figure S3. Temperature programmed reaction spectra of butyrophenone dosed on $^{18}O_2$ -predosed surface at 300 K after 5 minutes UV photolysis. m/z 30 evolves with m/z 28 and 78, implying that mixing has occurred. There is no m/z 30 for the same experiment on the $^{16}O_2$ -predosed surface. The heating rate used was 2 K s^{-1} . For this experiment, we used a Xe lamp with a bandwidth filter of 200–400 nm (92 mW/cm^2 total flux).