

Supporting Information:

**Laser flash photolysis of titanium dioxide suspensions for the
evaluation of solvent-mediated radical reactions**

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Materials and Instrumentation:

All reagents used were purchased from Sigma Aldrich and used as received, with the exception of 97% 1,1-diphenylethylene. 1,1-diphenylethylene was purified using a Silica column with pentane as the mobile phase to allow for removal of all traces of benzophenone. TiO₂ P25 was purchased from Univar Canada.

All laser flash photolysis experiments were performed using a Surelite Nd-YAG laser with wavelength of 355 nm (18 mJ pulse⁻¹) in a customized LFP-111 laser flash photolysis system (Luzchem Inc., Ottawa, Canada) and 0.7 cm² x 0.7 cm² cuvettes from Luzchem. Samples had an absorbance of ~ 0.3 at the laser wavelength, with some variation when selecting for TiO₂ concentration.

Experimental methodology:

Sample Preparation: Stock solutions of 0.4 g/l TiO₂ P25 were made with each of the 3 solvents (1,3-dioxolane, acetonitrile, and 1,4-dioxane), with 20 min sonication so suspend the mixture (repeated before each use). Typical sample preparation involved the addition 25 μL of 0.4 g/L TiO₂ suspension diluted to 2 ml with additional solvent, for a final TiO₂ concentration of 5 mg/L inside 0.7 cm x 0.7 cm cuvettes with stir rods. Samples were purged with argon for 10 min, and sonicated for 10 min to insure consistent suspension of the TiO₂. 1,1-diphenylethylene (DPE) was added via syringe between LFP experiments to allow direct comparison between the same sample with and without DPE.

Laser flash photolysis: Sample cuvettes were placed in a temperature controlled holder at 25°C with stirring. Samples were also lightly shaken beforehand to insure suspension. Transient absorbance decays were collected at 330 nm and 580 nm at various time scales (1 μs – 10 ms), time scale referring to the maximum time measured in the decay. The resolution was 625 evenly separated points per decay, with the first 20% (first 2 divisions) being pre-trigger before the laser pulse. Decays were averaged in the software from 10 shots. Transient absorption spectra were taken using decays in the 1 ms time scale, with absorbances averaged over time-ranges in the decays.

Data Analysis: For each transient absorbance decay, the first 20% was removed and the rest shifted to start at zero to align with the laser pulse timing. The unaltered graphs can be observed in the insets below (Figure S1), alongside the shifted decay curves. If each decay was plotted together in a double logarithmic scale, they showed strong overlap. To obtain a continuous set of data over the entire range of analysis, data points present in prior timescales were removed in subsequent timescales. This allowed for each time-scale to give data in the ranges that they are most accurate in measuring, and have a continuous connected data-set that could be easily plotted (See figure 1a).

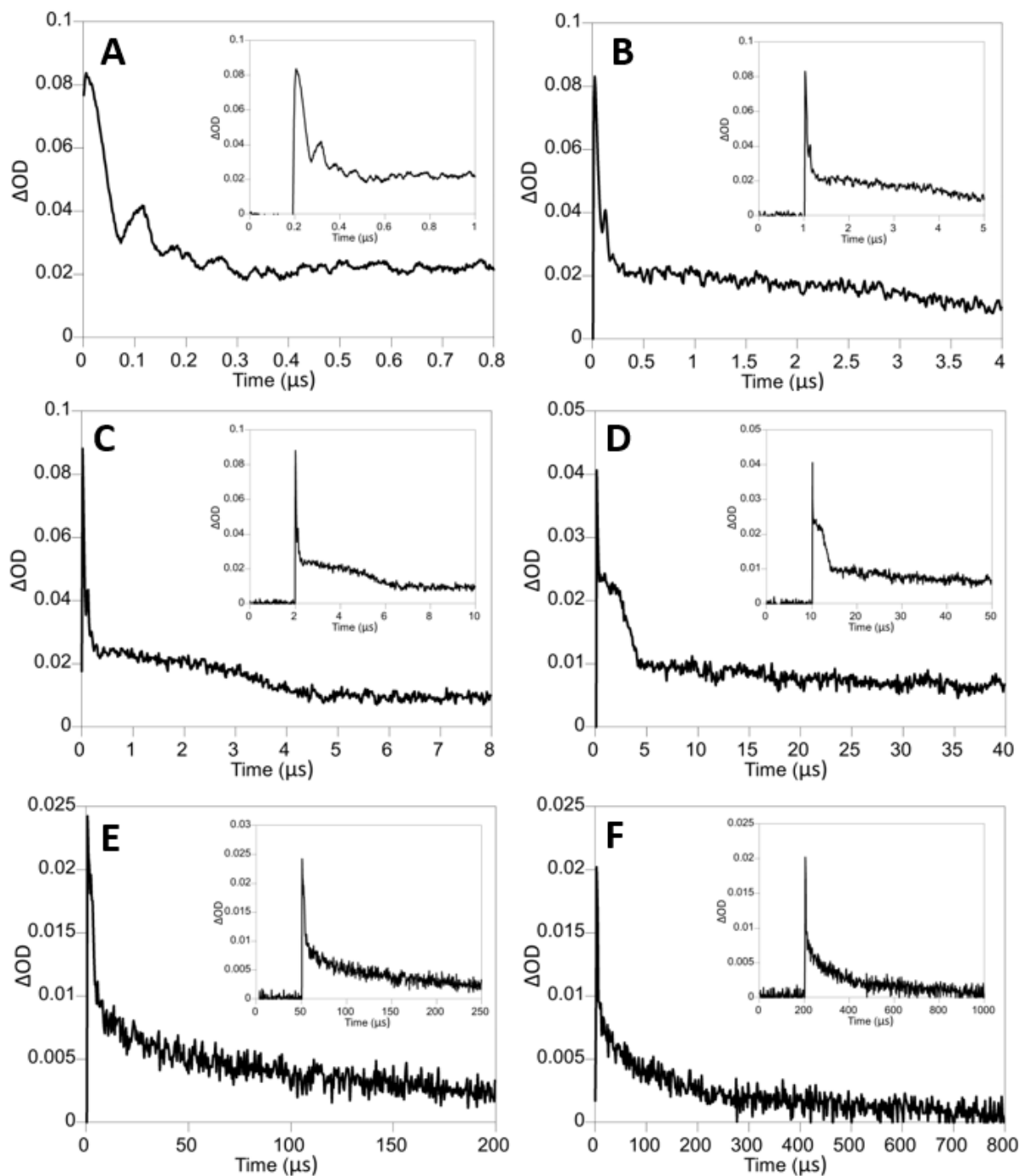


Figure S1. Time shifted (to eliminate pre-trigger data) transient absorbance decays ($\lambda_{\text{ex}} = 355 \text{ nm}$) at 330 nm for 5 mg/L TiO_2 in 1,3-Dioxolane, with corresponding unaltered decays (inset), at a) 1 μs time scale b) 5 μs time scale c) 10 μs time scale d) 50 μs time scale e) 250 μs time scale f) 1 ms time scale.

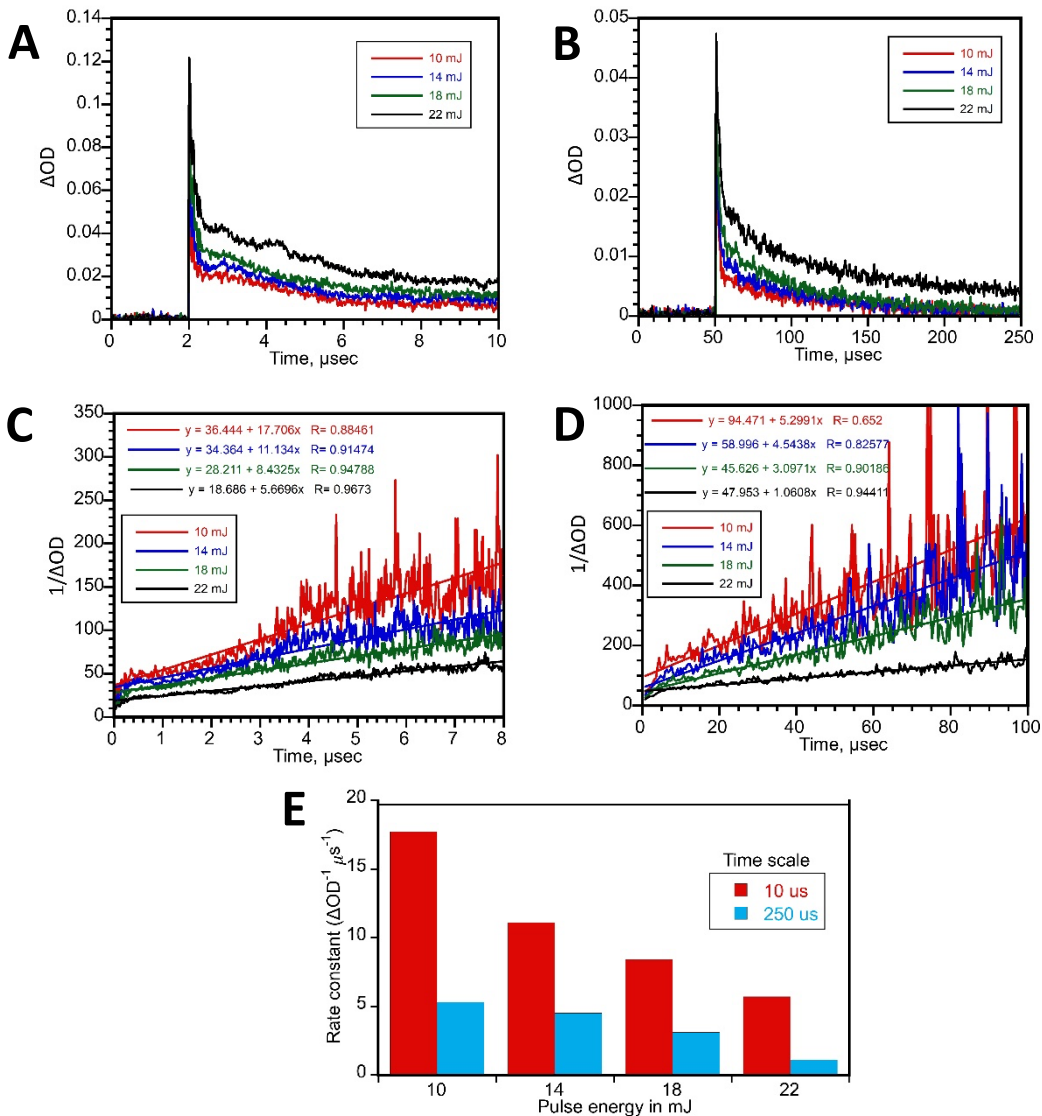


Figure S2. Transient absorbance decays ($\lambda_{ex} = 355 \text{ nm}$) at 330 nm for 5 mg/L TiO_2 in 1,3-Dioxolane, with various laser excitation intensities for a) $10 \mu\text{s}$ time scale, b) $250 \mu\text{s}$ time scale, c,d) the respective reciprocal plots for 2^{nd} order analysis, and e) a comparison of the calculated 2^{nd} order rate constants. While the kinetics are not strictly 2^{nd} order, within a single time scale you can reasonably fit a 2^{nd} order trend. However, at higher time scales the found 2^{nd} order rate constant becomes much smaller. Also, changing the pulse energy of the laser leads to a trend that does not fit expectations for a 2^{nd} order relationship. The rate constant should not decrease with increasing pulse energy as observed. Overall this shows that 2^{nd} order is not adequate in describing the transient absorbance decay of TiO_2 suspensions.

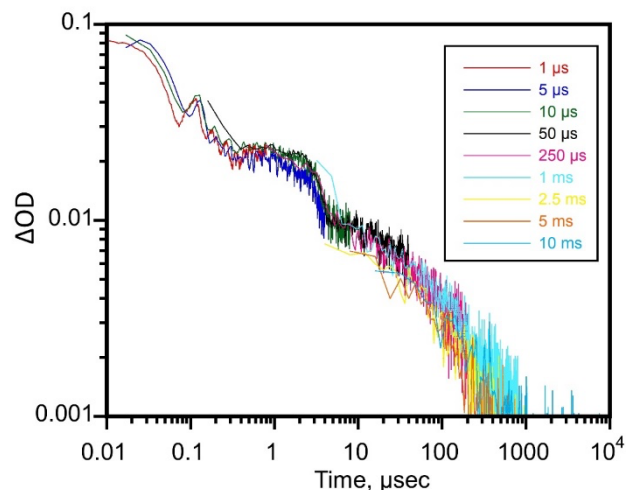


Figure S3. Transient absorbance decays ($\lambda_{\text{ex}} = 355 \text{ nm}$) at 330 nm for 5 mg/l TiO_2 in 1,3-Dioxolane with various time scales overlaid. Logarithmic scaling was done in both axis to better show the full range of the data, and it showed strong overlap in all regions of the decay can be observed. The lower y-axis limit was set to 0.001 due to inconsistent detection for absorbances below this value.

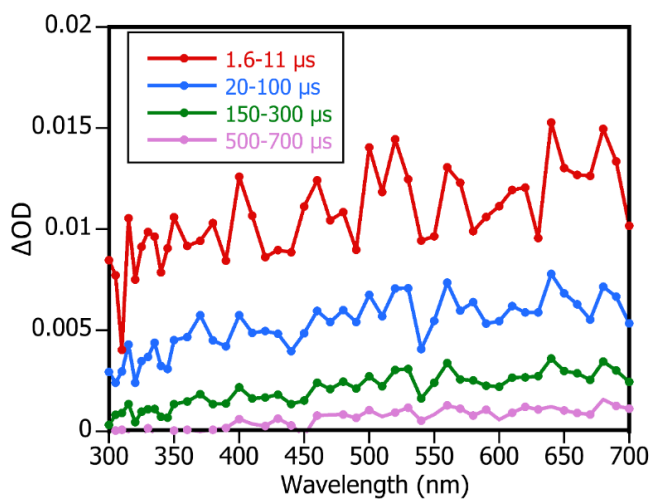


Figure S4. Transient absorbance spectra of 5 mg/l TiO_2 in 1,3-Dioxolane ($\lambda_{\text{ex}} = 355 \text{ nm}$) at various averaged ranges. There is little shape to the spectra, with only a slightly sloping down to the left, and the signal decreases at a similar rate over the whole spectrum down to almost zero by the 500-700 range.

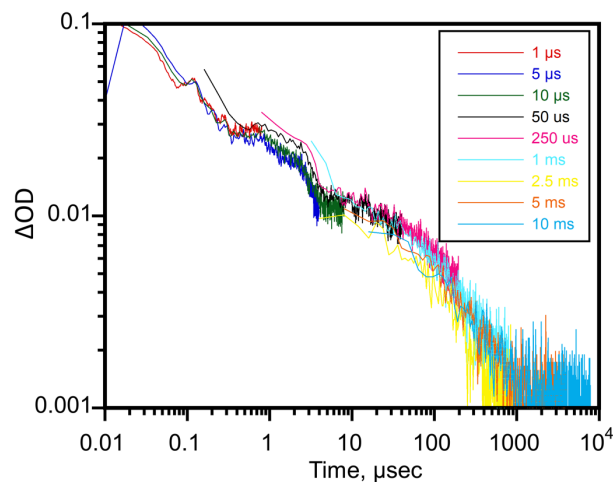


Figure S5. Transient absorbance decays ($\lambda_{\text{ex}} = 355 \text{ nm}$) at 580 nm for 5 mg/l TiO_2 in 1,3-Dioxolane with various time scales overlaid. Similarly to Figure S2, a logarithmic scaling was used, and strong overlap is present over the entire range. Relatively similar decay in comparison to decay at 330 nm, with a marginal enhancement at very long time-scales.

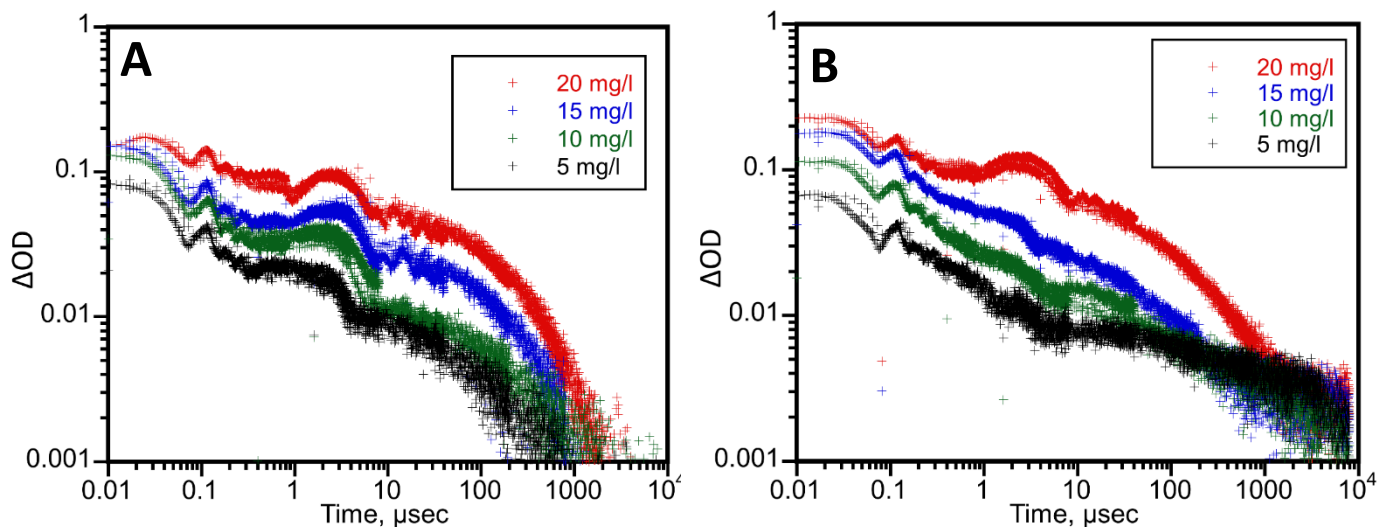


Figure S6. Combined transient absorbance decays ($\lambda_{\text{ex}} = 355 \text{ nm}$) at 330 nm of 1,3-Dioxolane with various concentrations of TiO_2 a) without any DPE, b) and with 50 mM DPE. Changing TiO_2 concentration has a strong effect on both the initial strength of the transient signal, as well as the overall shape of the decay. Interestingly, there is little effect on the amount of the DPE-solvent adduct transient signal, and increase TiO_2 concentration appears to mask the signal from the adduct radical.

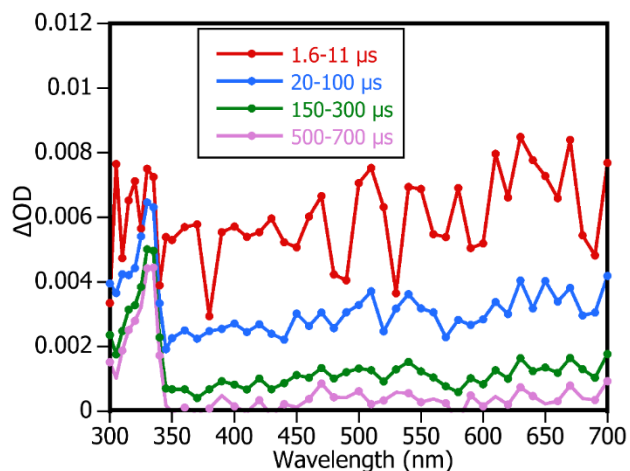


Figure S7. Transient absorbance spectra of 50 mM DPE and 5 mg/l TiO_2 in 1,3-Dioxolane ($\lambda_{\text{ex}} = 355 \text{ nm}$) at various averaged time ranges. The signal from the DPE-solvent adduct transient is mostly covered by the signal from the TiO_2 at 1.6-11 μs , before being quite obvious at longer time-scales. At 500-700 μs , the peak from the adduct radical is the only significant signal remaining.

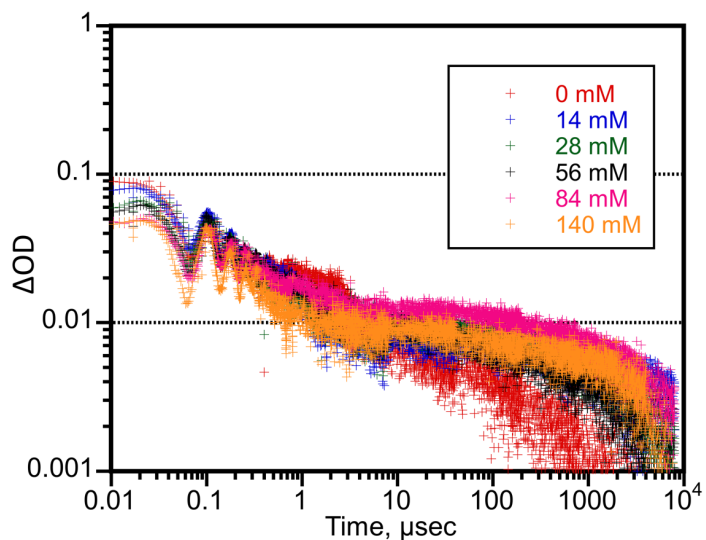


Figure S8. Combined transient absorbance decays ($\lambda_{\text{ex}} = 355 \text{ nm}$) at 330 nm of 1,3-Dioxolane with 5 mg/l TiO_2 and various concentrations of DPE.

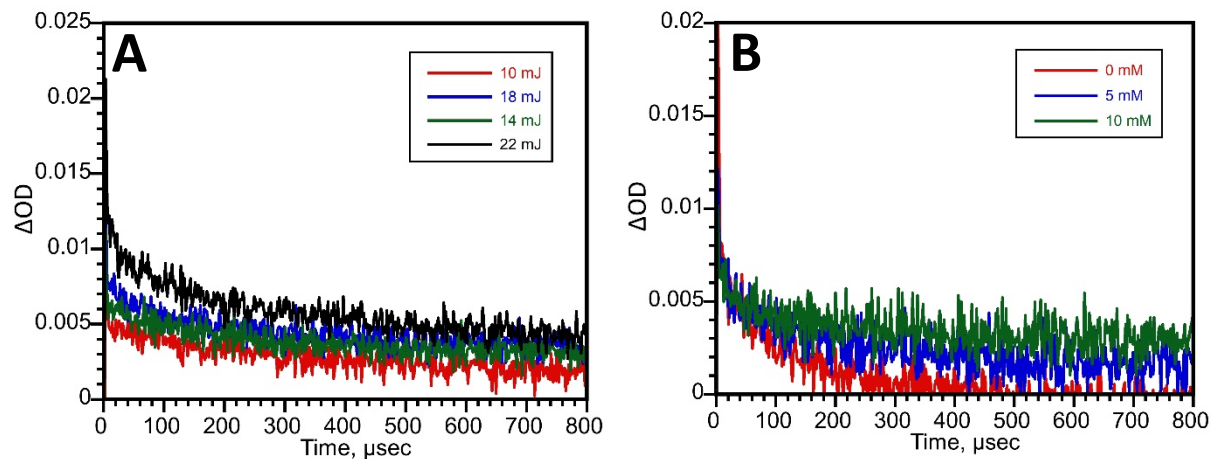


Figure S9. 1 ms time scale transient absorbance decays ($\lambda_{\text{ex}} = 355 \text{ nm}$) at 330 nm of 1,3-Dioxolane with 5 mg/l TiO_2 with a) various low concentrations of DPE, and b) 50 mM DPE with various laser-excitation powers.

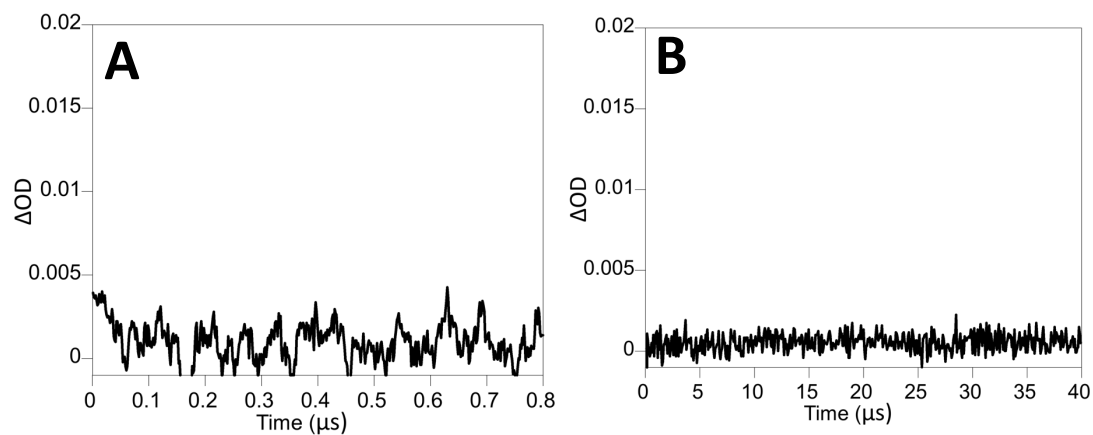


Figure S10. Transient absorbance decays ($\lambda_{\text{ex}} = 355 \text{ nm}$) at 330 nm of 1,3-Dioxolane with no TiO_2 and 50 mM DPE at a) 1 μs time scale and b) 50 μs time scale. There is no significant signal without TiO_2 , as the signal is oscillating above and below zero. Therefore DPE alone will not give detectable transients without TiO_2 .

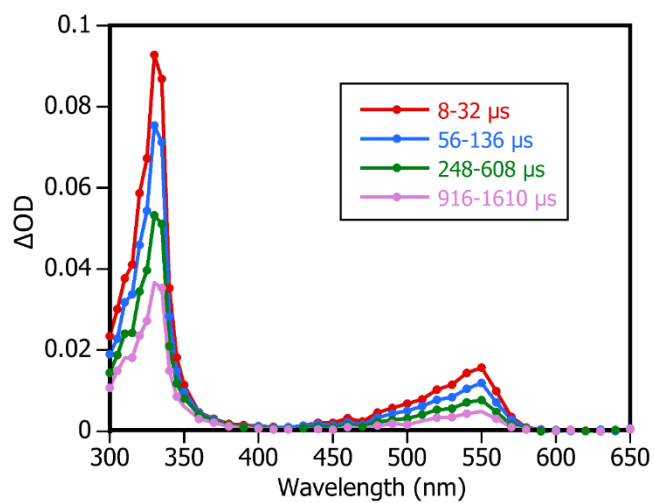


Figure S11. Transient absorbance spectra of 5 mM benzophenone in 1,3-Dioxolane ($\lambda_{ex} = 355$ nm) at various averaged time ranges. The spectra of the benzophenone radical transient is similar to that of the DPE-solvent adduct, however with a more noticeable peak at 550 nm.

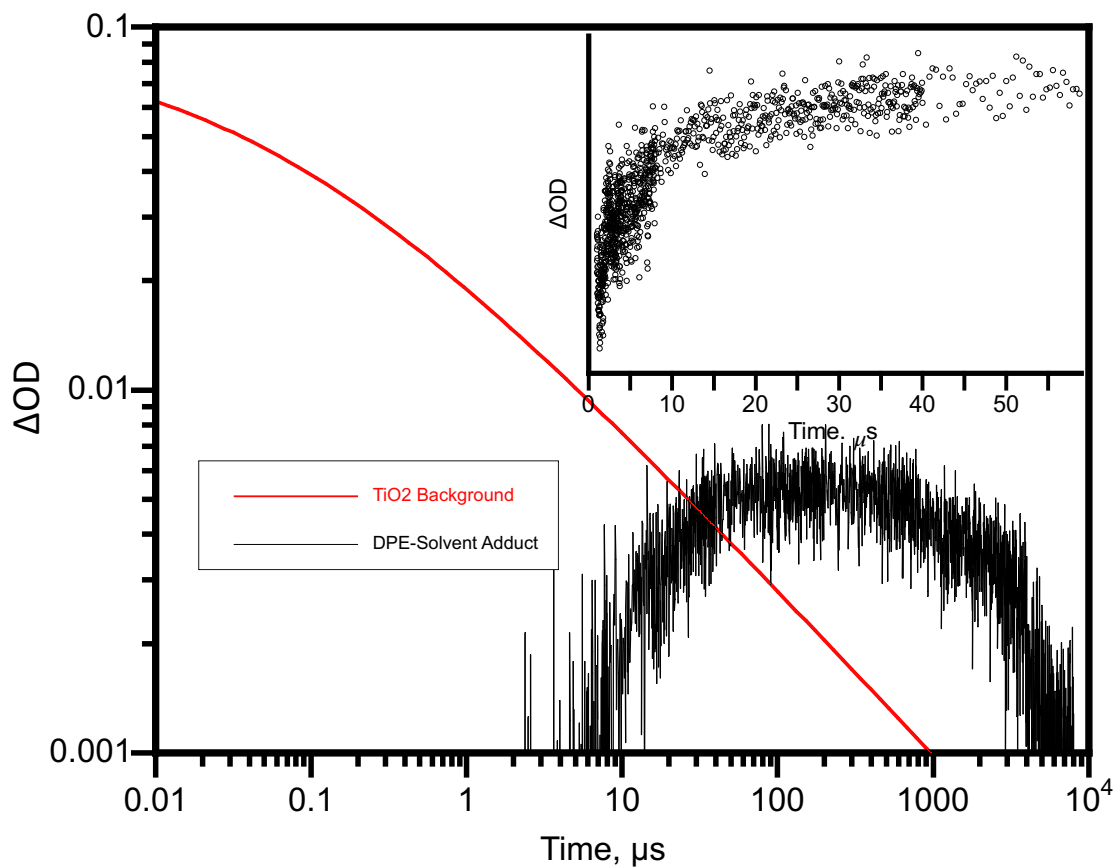


Figure S12. Separated contributions from TiO_2 and DPE-Solvent adduct from the combined transient absorbance decay ($\lambda_{\text{ex}} = 355 \text{ nm}$) at 330 nm for 1,3-Dioxolane with 5 mg/l TiO_2 and 50 mM DPE . We note that the fitting for the TiO_2 decay was used as the background to obtain slightly less noise for the data in the presence of DPE. However, a clear growth and decay of the DPE-Solvent adduct is observed. The inset shows a linear representation of the first $60 \mu\text{s}$ following laser excitation. Unfortunately, the signal-to-noise ratio makes evaluation of the rate of formation between different concentrations impossible.

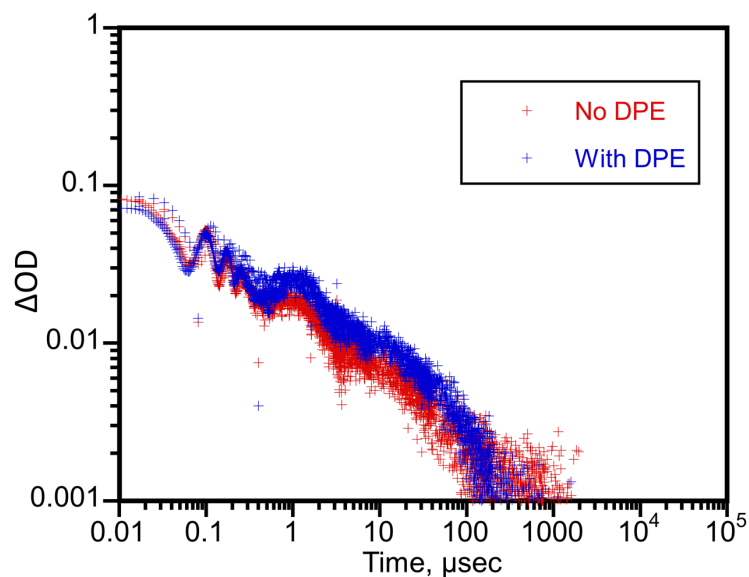


Figure S13. Combined transient absorbance decays ($\lambda_{\text{ex}} = 355 \text{ nm}$) at 330 nm for acetonitrile with 5 mg/l TiO_2 , with and without DPE. The decay without DPE is similar to the decay using 1,3-dioxolane as a solvent, but slightly faster in comparison. There is no noticeable difference in decay rate with and without DPE, implying no significant formation of transients from a DPE-solvent adduct transient.

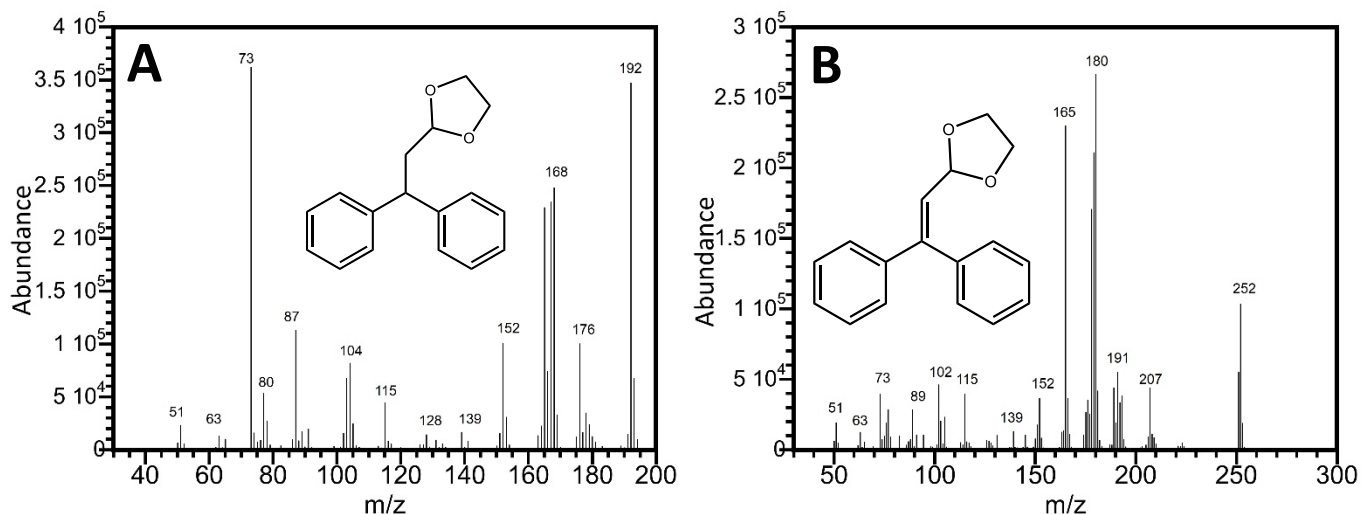


Figure S14. Mass Spectrometry fragmentation patterns (GC-MS) for the two expected final products from the DPE-Solvent Adduct Radical. The two products depend on if the radical gains a hydrogen to form a double bond (B), or loses another hydrogen to form a single bond (A). Due to raising acidity in the system, the single bond is expected to be favored.