Electronic Supplementary Information

Probing the photoreactivity of aryl chlorides with oxygen

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Experimental details:

Equipment

HPLC. The analyses by HPLC were made using a Merck-Hitachi 655A-11 liquid chromatograph equipped with 655A-22 UV (detection at 220 nm, 254 nm or 275 nm) and Shimadzu SPD-M6A photodiode array detectors. A Merck LiChroCART 125-4 (12.5 cm length, 4 mm internal diameter, RP-18, 5 µm) column and a gradient elution of water and acetonitrile was employed.

GC-MS. The analyses by GC-MS were performed on a Agilent Technologies 6890N gas chromatograph with a 5973 inert mass selective detector (E.I. 70 eV). A J&W Scientific DB-35MS (30 m length, 0.25 mm I.D. and 0.25 µm film thickness) capillary column was used. The initial temperature, 50 ºC or 70 ºC, was maintained during 5 min and then a heating rate of 10 ºC/min was used until a final temperature of 270 ºC was reached.

LC-MS. The LC-MS system is an Agilent Technologies 1200 Series LC coulpled to a Bruker Daltonics HCT *ultra* (ion trap detector). The ionization modes are ESI (positive/negative) and APCI. A Purospher STAR (Merck) LiChroCART 125-2 (12.5 cm length, 2 mm internal diameter, RP-18, 5 µm) column stabilized at 30 ºC was used.

Quantum Yields

The average photodegradation rate of a given compound *A* is proportional to the absorbed radiation and to its reaction quantum yield. If the absorption is lower than 0.02 at a excitation wavelength λ, the integration of the rate equation leads to

$$\ln([A]/[A]_0)_\lambda = -2.303\phi_\lambda I_{0\lambda}\varepsilon_{A\lambda} b\, t\,,$$

where $[A]_0$ is the initial concentration, $[A]$ is the concentration a time *t*, ϕ_λ is the photodegradation quantum yield, $I_{0\lambda}$ the intensity of the incident radiation, ε_λ is the absorption coefficient and *b* is the optical path. Thus, the ϕ_λ of an unknown compound *A* can be obtained from the ratio between the degradation rate constants of *A* and a reference compound, when irradiated in the same conditions.

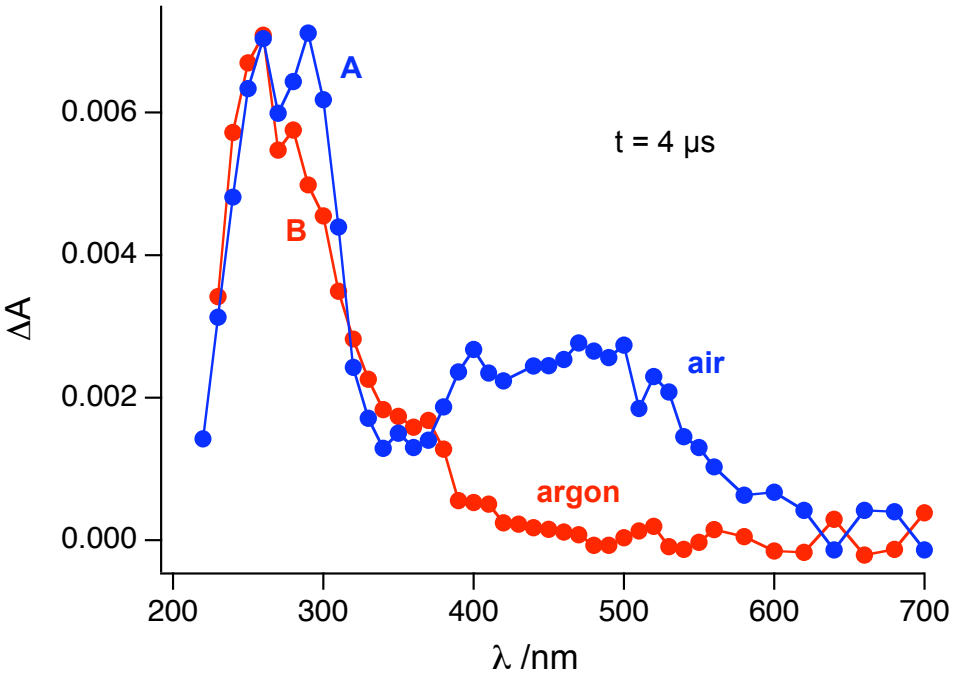

Figure S1: Transient absorption spectra of chlorobenzene (**1**) in ethanol, with (A, blue) and without (B, red) oxygen, observed 4 µs after the laser pulse (266 nm).

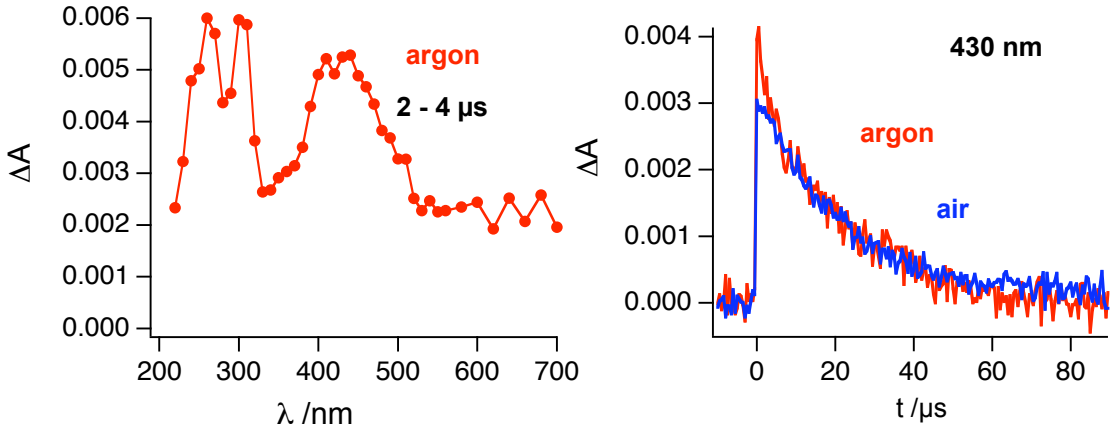

Figure S2: Left: Transient absorption spectrum of 4-chloroanisole (**2**) in ethanol in the absence of oxygen (argon saturated) observed 2- 4 µs after the laser pulse (266 nm). Right: decay traces at 430 nm in air (blue) and argon (red) saturated solutions.