

Electronic Supplementary Information

Photooxygenation of alkanes by dioxygen with *p*-benzoquinone derivatives with high quantum yields

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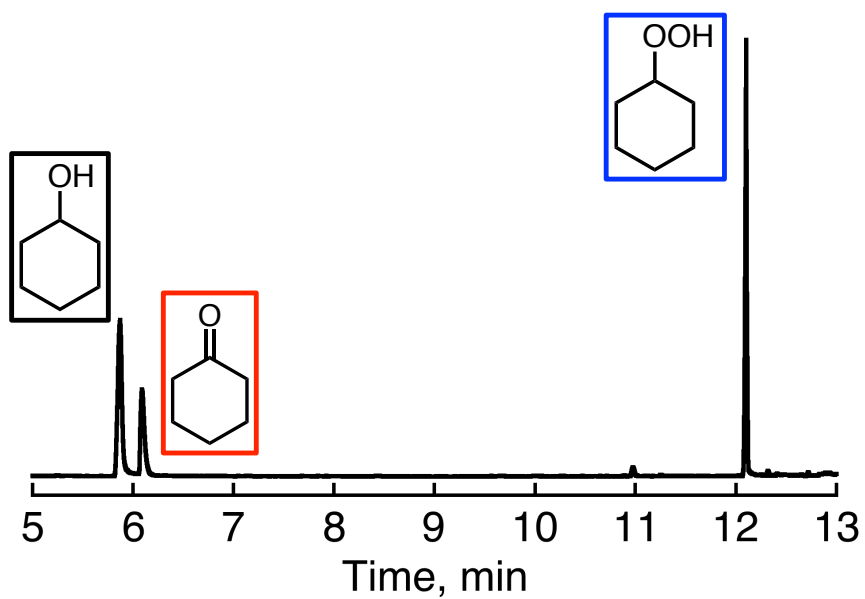


Fig. S1 GC chart of an oxygen-saturated cyclohexane solution containing PXQ (2.0 mM) under photoirradiation by use of a xenon lamp (500 W; $\lambda > 390$ nm) at 298 K for 26 h.

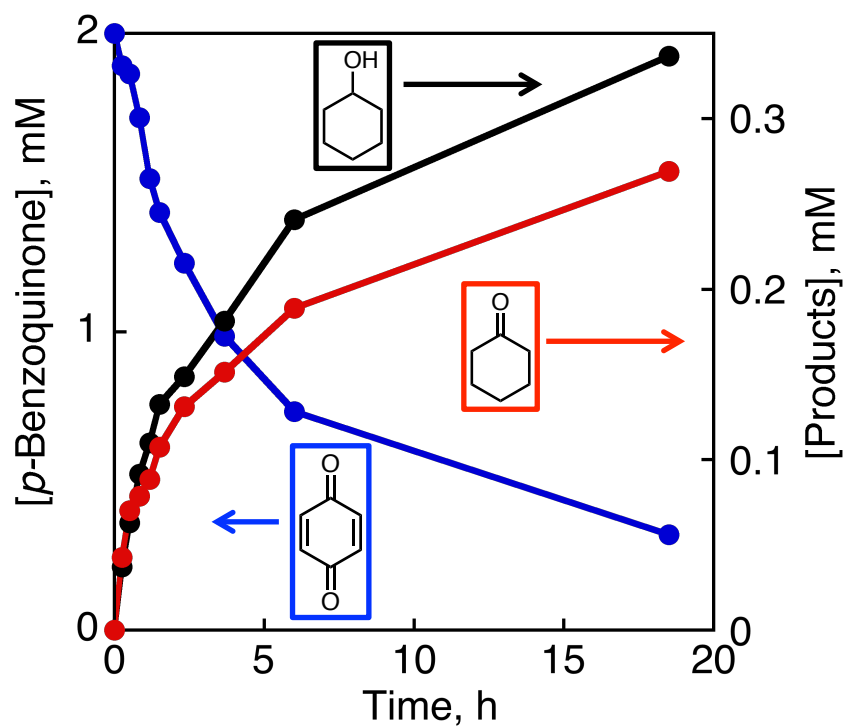


Fig. S2 Reaction time profiles for formation of cyclohexanol (black) and cyclohexanone (red) in the photooxygenation of an oxygen-saturated cyclohexane solution containing *p*-benzoquinone (Q) (2.0 mM) under visible light irradiation by use of a xenon lamp (500 W; $\lambda > 390$ nm) at 298 K. MeCN (2%) was used as a co-solvent to dissolve Q.

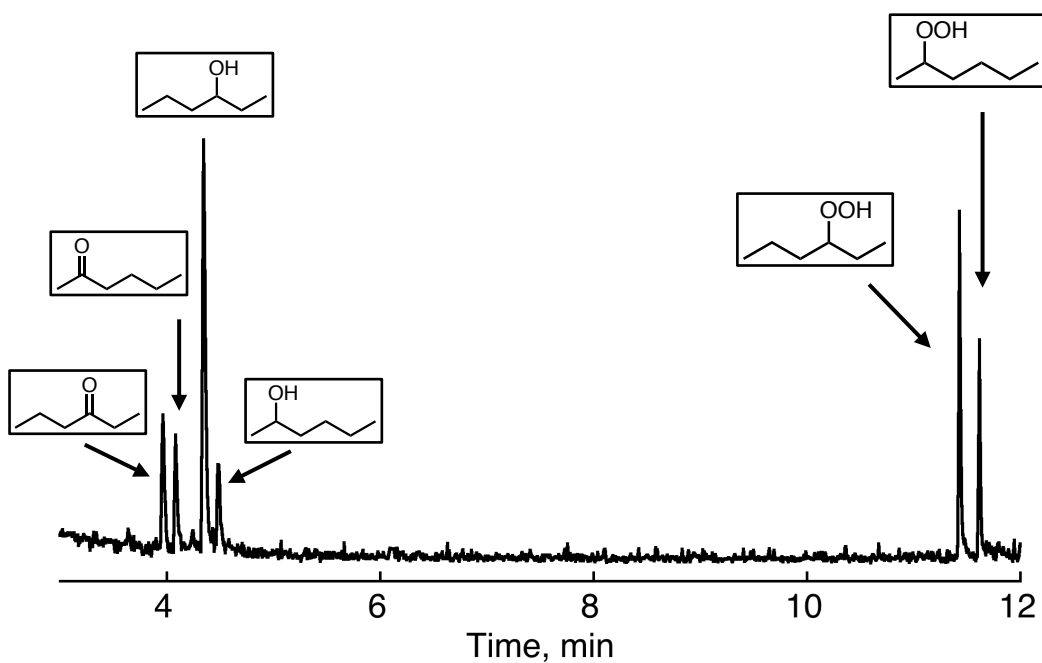


Fig. S3 GC chart of an oxygen-saturated hexane solution containing PXQ (2.0 mM) under photoirradiation by use of a xenon lamp (500 W; $\lambda > 390$ nm) at 298 K for 26 h.

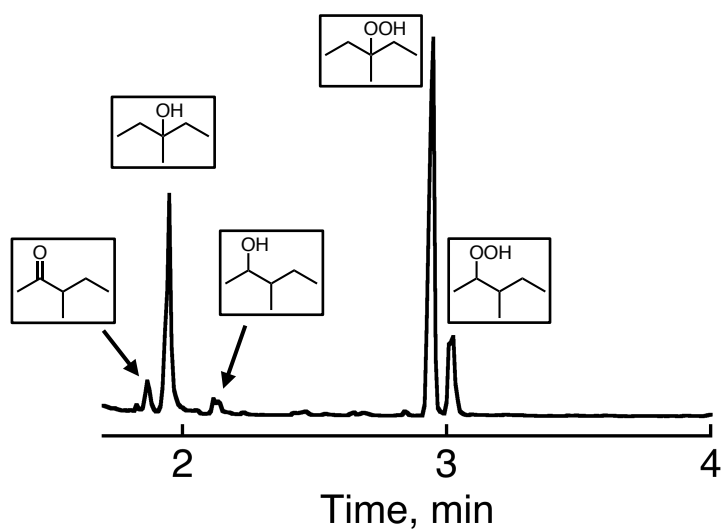


Fig. S4 GC chart of an oxygen-saturated 3-methylpentane solution containing PXQ (2.0 mM) after photoirradiation by use of a xenon lamp (500 W; $\lambda > 390$ nm) at 298 K for 26 h.

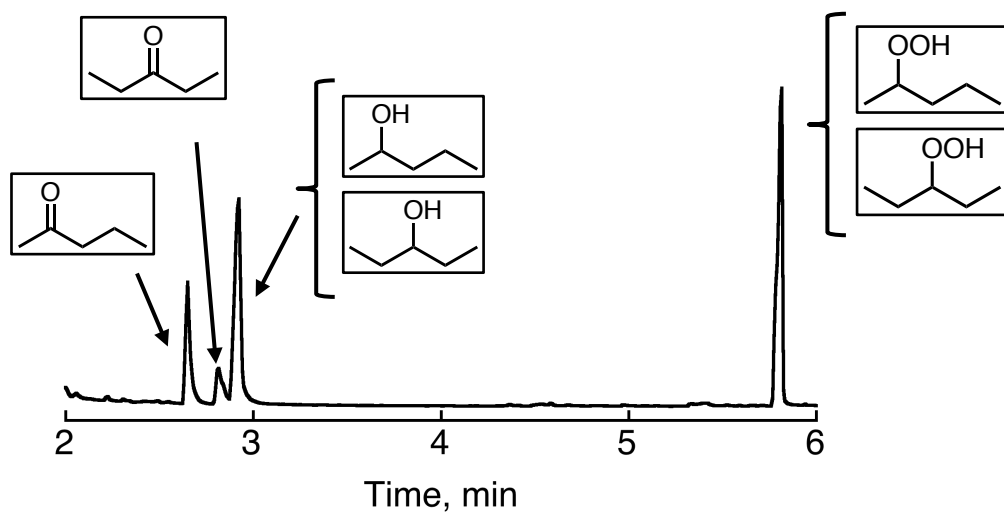


Fig. S5 GC chart of an oxygen-saturated pentane solution containing PXQ (2.0 mM) under photoirradiation by use of a xenon lamp (500 W; $\lambda > 390$ nm) at 298 K for 26 h.

Experimental section

Materials. Chemicals were purchased from commercial source and used without purification, unless otherwise noted. Potassium ferrioxalate used as an actinometer to determine the quantum yield was prepared according to the literature and purified by recrystallization from hot water.^{S1} Deuterated [²H₁₂]cyclohexane (C₆D₁₂) was obtained from Euri SO-TOP, CEA, France, and used as received.

Reaction procedures. The photooxygenation of saturated hydrocarbons with PXQ was carried out by the following procedure. Typically, a cyclohexane solution (3.0 cm³) containing PXQ (2.0 mM) in a square quartz cuvette (10 mm i.d.) with a silicon septum was saturated with oxygen by bubbling oxygen through a stainless tube for 5 min. When DDQ was used instead of PXQ, acetonitrile (0.05 cm³) was added to the solution as a co-solvent. The solution was then irradiated with a 500 W xenon lamp (Ushio Optical Module X SX-UID 500XAMQ) through a color filter glass (Asahi Techno Glass Y43) transmitting $\lambda > 390$ nm at room temperature. After photoirradiation, the corresponding oxygenated products were identified and quantified by comparison of the GC retention time and the MS spectra (Shimadzu QP-5000) in comparison with those of authentic samples.

The amounts of hydroperoxides were determined by titration by iodide ion as follows. The photoirradiated solution was titrated with excess amount of NaI (0.1 M). The amount of I₃⁻ formed was then determined from the UV-vis spectrum ($\lambda_{\text{max}} = 361$ nm, $\epsilon_{361} = 2.5 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$).^{S2}

Quantum yield determination. A standard actinometer (potassium ferrioxalate) was used for the quantum yield determination of the photooxygenation of cyclohexane with PXQ. Typically, a square quartz cuvette (10 mm i.d.), which contained an O₂-saturated cyclohexane solution (3.0 cm³) of PXQ (2.0 mM) was irradiated with monochromatised

light ($\lambda = 420$ nm) from a Shimadzu RF-5300PC fluorescence spectrophotometer. Under the conditions of actinometry experiments, PXQ absorbed essentially 35% incident light of $\lambda = 420$ nm. The light intensity of monochromatised light of $\lambda = 420$ nm was determined as 1.5×10^{-9} einstein s^{-1} . The photochemical reaction was monitored using a Shimadzu GC-17A gas chromatograph and Shimadzu MS-QP5000 mass spectrometer. Triphenylphosphine (4 mM) was added to the reaction solution (5.0×10^{-5} cm³) to reduce hydroperoxides to alcohols before each measurement.^{S3} The quantum yields were determined from increase of total amount of products.

Laser flash photolysis measurements. The measurements of nanosecond transient absorption spectra in the photochemical reactions of PXQ with saturated hydrocarbons were performed according to the following procedures. Typically, a nitrogen saturated acetonitrile solution containing cyclohexane (0 – 9.2 M) and PXQ (10 mM) was excited by a Nd:YAG laser (Continuum, SLII-10, 4-6 ns fwhm) at $\lambda = 355$ nm with the power of 8 mJ/pulse. Photoinduced events were estimated by use of a continuous Xe lamp (150 W) and an InGaAs-PIN photodiode (Hamamatsu 2949) as a probe light and a detector, respectively. The output from the photodiodes and a photomultiplier tube was recorded with a digitizing oscilloscope (Tektronix, TDS3032, 300 MHz). The transient spectra were recorded for fresh solutions in each laser excitation. All experiments were performed at 298 K.

Reference for ESI

- (S1) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, 1956, **235**, 518.
- (S2) S. Fukuzumi, S. Kuroda and T. Tanaka, *J. Am. Chem. Soc.*, 1985, **107**, 3020.
- (S3) B. P. C. Hereijgers and B. M. Weckhuysen, *J. Catal.*, 2010, **270**, 16.