

Supplementary Information:

Room temperature sonochemical initiation of thiol-ene reactions

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Materials and Analytical Methods:

All chemicals used were purchased from Sigma Aldrich and used as received (with the exception of 2,2-diphenyl-1-picrylhydrazyl which was purchased from Fluka). Absorption spectra were recorded using an Agilent 8453 UV-Visible Spectrophotometer with a 1.0 cm quartz cuvette. Fluorescence spectra were recorded using a Gilden Photonics FluoroSENS fluorimeter with a 1.0 cm polystyrene cuvette. The ultrasound source was a Sonic Systems Sonic Processor L500-20 generator fitted with a 20 kHz Horn attachment. A Bruker Avance 250 NMR was used to collect the ¹H-NMR spectra. Samples for GC and GC-MS analysis were prepared by taking a 300 μL sample from the reaction and making up to 1500 μL with methanol.

GC method: Samples were analysed for % conversion on an Agilent 6890N Network GC System using the following method: Injection volume: 1.0 μL, N₂ carrier gas, Split Ratio: 50.0, Flow rate: 2 mL/min, FID detector temperature: 300 °C, Column: Agilent 19091J-413 HP-5 5% Phenyl Methyl Siloxane 300 m x 320 μm x 0.25 μm, Temperature program: starting temperature; 50 °C, ramp: 40 °C/min to 70 °C (hold for 0.25 min), ramp: 60 °C/min to 85 °C, ramp 15 °C/min to 100 °C, ramp 100 °C/min to 300 °C (hold for 4 min).

GC-MS method: Thioether products were identified by comparison with Library chromatograms for GC-MS analysis using an EI-MS Agilent 5975C inert MSD Triple Axis Detector coupled to an Agilent 7890A GC System with a HP 5MS 30 m x 25 mm x 0.25 μm column: carrier gas: He, flow rate: 2 mL/min, split ratio: 10:1, inlet temperature: 300 °C, oven temperature ramp: 20 °C/min from 70 °C to 230 °C, FID: 300 °C, MS Source 230 °C, MS Quad 150 °C.

Experimental procedures:

DPPH Dosimetry:

Radical production was quantified using a 0.08 mM solution of 2,2-diphenyl-1-picrylhydrazyl (DPPH) in toluene. In the sonochemical case the glassware was assembled as in the protocol below. 90 mL of DPPH solution and the prescribed amount of AIBN charged to the flask. The solution was purged with nitrogen for 45 minutes at a moderate flow. The nitrogen flow was then reduced to a slow flow in order to maintain a positive pressure of nitrogen in the flask. The solution was sonicated for 20-60 minutes at an intensity of 17 W cm⁻². Samples were taken at time intervals and the absorbance was measured at a wavelength of 520 nm.

In the thermal case the glassware was assembled as in the protocol detailed below. 25 mL of DPPH solution was charged to the flask and the solution was purged with nitrogen for 15 minutes. The solution was then heated to

50 °C and 0.05 g AIBN was added as a solution in 5 mL of toluene. Samples were taken periodically over a 10 minute period and the absorbance measured.

Terephthalic Acid Dosimetry: Radical induced production of fluorescent 2-hydroxyterephthalic acid (HTA) from an aqueous solution of terephthalic acid (TA) was used to measure the relative rates of radical production in thermal and sonochemical systems. HTA production, and therefore, the change in solution fluorescence is directly proportional to radical production in a given system. Comparison of the rate of change of fluorescence in different systems can be used as a means to compare the radical production in those systems.

85 mL of a 0.0002 M solution of TA in pH 8 phosphate buffer and 0.04 g (0.15 mmol, 1.75 mM) of potassium persulfate were charged to the glassware/horn assembly described below. The solution was cooled to 24 °C with a constant water flow. The solution was sonicated for 60 minutes at an intensity of 17 W cm⁻². Samples were taken at periodic time intervals and fluorescence was measured using an excitation frequency of 310 nm and an emission range of 350-550 nm.

The thermal dosimetry was conducted in a similar manner using the apparatus described below. 20 mL of 0.0002 M TA solution in pH 8 phosphate buffer was heated to 45 °C and 0.012 g (0.04 mmol, 1.75 mM) of potassium persulfate in 5 mL of TA solution was then charged to the flask. Samples were taken periodically over a 60 minute time period and the fluorescence of each sample was measured as above.

Sonochemical and thermal protocols in toluene with AIBN:

Sonochemical Protocol: 85 mL of toluene and 0.3 g (18 mmol., 0.03 molar eq.) of 2,2'-Azobis(2-methylpropionitrile) (AIBN) were charged to a 3 necked pear shaped jacketed flask which fitted the ultrasound horn assembly. The flask was fitted with a thermocouple the jacket was cooled to 24 °C with a constant water flow. The flask was covered to protect it from ambient UV light. The flask was sealed and purged with nitrogen for 45 minutes on a moderate flow rate. After purging a slow flow of nitrogen was maintained. 55 mmol (limiting reagent) of alkene and 9 mL (83 mmol, 1.5 molar eq.) of 1-butanethiol were charged to the reaction flask by injection. The reaction was then sonicated at an intensity of 17 Wcm⁻² for 4 hours. Regular samples were taken during the reaction time and analysed by GC and GC-MS (see details above). Control reactions were carried out according to this procedure but omitting the AIBN.

Optimised sonochemical reaction conditions for Butyl-vinyl-ether: The reaction was conducted according to the protocol described above, but with a higher ultrasound intensity (21 Wcm⁻²) and the following reagent charges: 7.2 mL (55 mmol, limiting reagent) of butyl vinyl ether, 30 mL (278 mmol, 5 molar eq.) of 1-butanethiol, 0.9 g (54 mmol, 0.09 molar eq.) of AIBN and 50 mL of toluene.

Thermal Protocol: 25 mL of toluene was charged to a 2 necked 50 mL round bottomed flask fitted with a thermometer and a magnetic stirrer hot plate assembly. The flask was covered to protect it from ambient UV light, sealed and purged with nitrogen for 15 minutes on a moderate flow rate. After purging, a slow flow of nitrogen was maintained and the flask was heated to 50 °C. 6.6 mmol (limiting reagent) of alkene and 9.9 mmol (1.5 molar eq.) of 1-butanethiol were charged to the flask. The reaction was started by charging 0.025 g (0.15 mmol, 0.02 molar eq.) of AIBN in 5 mL of toluene to the reaction. The reaction was allowed to proceed for 2 hours. Samples were taken during the reaction and analysed by GC and GC-MS. Control reactions were carried out according to this procedure but omitting the AIBN.

Sonochemical and thermal protocols in water with potassium persulfate:

Sonochemical Protocol: 85 mL of deionised water, 6.6 mmol (limiting reagent) of alkene, 0.04 g (0.15 mmol., 0.02 molar eq.) of potassium persulfate ($K_2S_2O_8$) and 3.75 g (33 mmol., 5 molar eq.) of cysteamine HCl were charged to a 3 necked pear shaped jacketed flask which fitted the ultrasound horn assembly. The flask was fitted with a thermocouple and the jacket cooled to 24 °C with a constant water flow. The flask was covered to protect it from ambient UV light. The reaction was then sonicated at an intensity of 17 Wcm^{-2} for 2 hours. Samples were taken during the reaction time, quenched into 2 wt% hydroquinone solution in D_2O to prevent any further reaction and analysed for conversion by 1H -NMR. Control reactions were carried out according to this procedure but omitting the potassium persulfate.

Thermal Protocol: 25 mL of deionised water, 1.95 mmol. (limiting reagent) of alkene, 1.12 g (9.86 mmol., 5 molar eq.) of cysteamine HCl and 0.012 g (0.04 mmol 0.02 molar eq.) of $K_2S_2O_8$ was charged to a 2 necked 50 mL round bottomed flask fitted with a thermometer and a magnetic stirrer hot plate assembly. The flask was covered to protect it from ambient UV light. The flask was heated to 45 °C. The reaction was allowed to proceed for 2 hours. Samples were taken during the reaction time, quenched into 2 wt% hydroquinone solution in D_2O to prevent any further reaction and analysed for conversion by 1H -NMR. Control reactions were carried out according to this procedure but omitting the $K_2S_2O_8$.

DPPH Dosimetry Results:

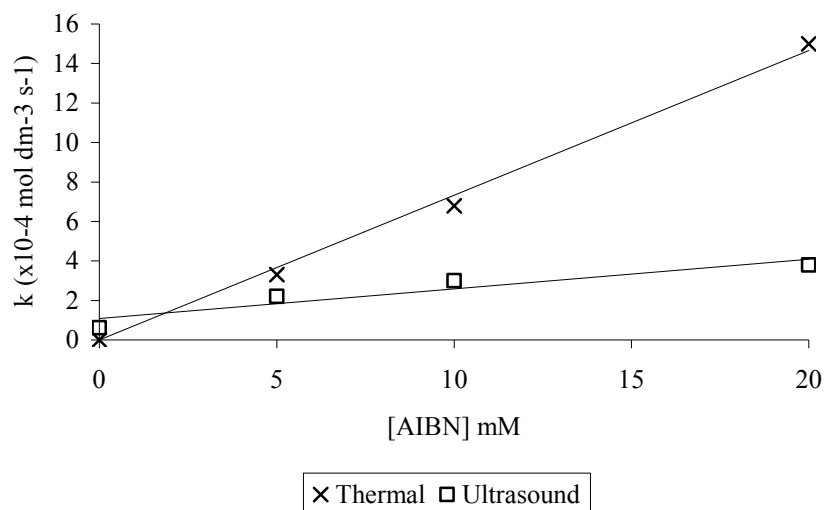


Figure S 1: Rate constants for radical production in 0.08 mM DPPH solution using ultrasound and thermal initiation.

TA Dosimetry:

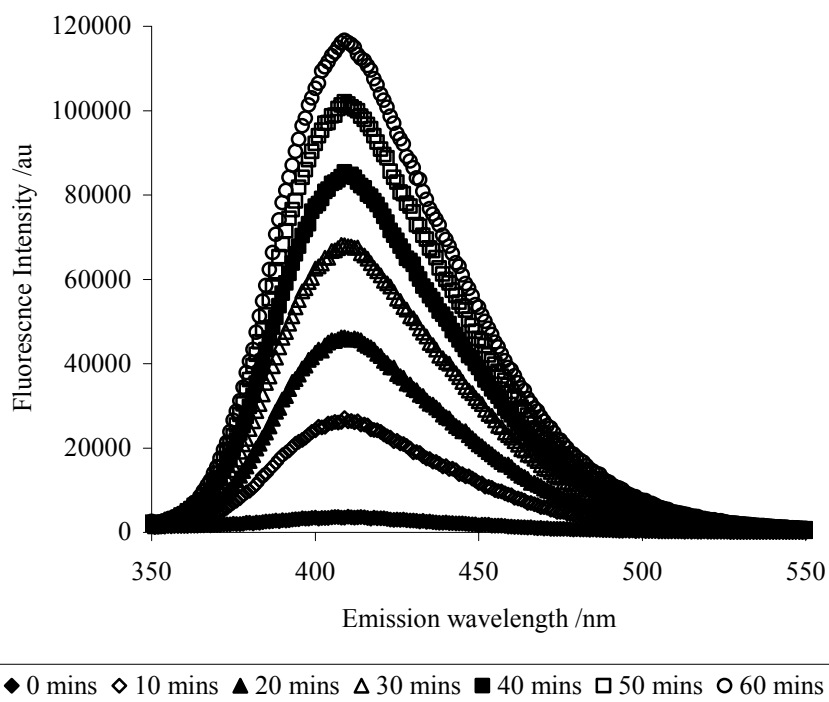



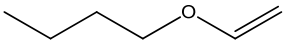
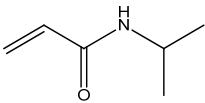
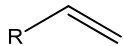
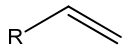
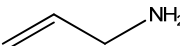
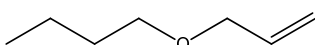
Figure S 2: Typical series of fluorescence spectra taken during the sonication of a 0.0002 M aqueous solution of terephthalic acid with $K_2S_2O_8$.

Dosimetry Results:

Initiation	[K ₂ S ₂ O ₄] /mM	T /°C	Rate of change of fluorescence at 410 nm (au/min)
Thermal	1.75	45±2	2383 ± 724
	0		No rxn
20 kHz Ultrasound	1.75	24 ± 2	1763 ± 113
	0		1296 ± 74

Analytical Data: toluene Series:

GCMS Data:

Alkene	Alkene structure	Alkene M _r (g mol ⁻¹)	Alkene RT (min)	Product M _r (g mol ⁻¹)	Product RT (min)
Norbornene		94	2.7	184	9.8
Butyl vinyl ether		100	2.4	190	9.4
N-isopropylacrylamide		113	6.3-6.7	203	11.1
1-heptene		98	2.3	188	9.58
1-pentene		70	n/a	160	8.1
Allyl amine		57	1.65	147	n/a
Allyl butyl ether		114	3.7	204	10.0

GC Data:

Alkene	Alkene RT (min)	Product RT (min)
Norbornene	2.17	5.32
Butyl vinyl ether	2.07	5.12
N-isopropylacrylamide	3.34	5.89
1-heptene	2.05	5.21
1-pentene	1.78	4.42
Allyl amine	1.82	n/a
Allyl butyl ether	2.38	5.45

GC Analysis for % conversion:

$$\%conversion = \frac{(A_p)}{(A_{SM} + A_p)} \times 100\%$$

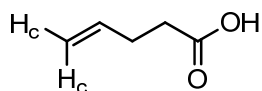
A_p = Area under product peak, A_{SM} = Area under starting material peak

Analytical Data: Aqueous Series:

¹H-NMR Spectra were analysed using Bruker Topspin Software (version 2.1).

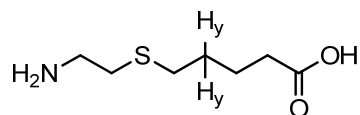
4-pentenoic acid:

$$\%conversion = \frac{(I_{H_y}/2)}{((I_{H_y}/2) + (I_{H_c}/2))} \times 100\%$$



H_y: 1.5 ppm (2H, m)

H_c: 5.8 ppm (2H, m)

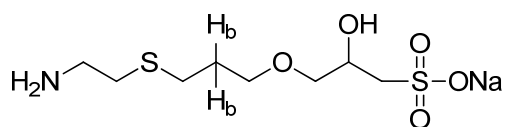
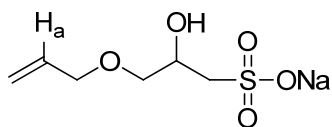


3-allyloxy-2-hydroxy-1-propanesulfonic acid:

$$\%conversion = \frac{(I_{H_b}/2)}{((I_{H_a}) + (I_{H_b}/2))} \times 100\%$$

H_a: 5.9 ppm (1H, dd)

H_b: 1.8 ppm (2H, m)



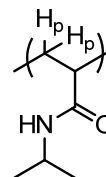
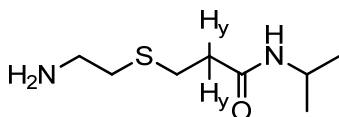
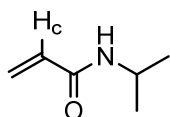
NIPAm:

$$\%conversion = \frac{(I_{H_y}/2)}{((I_{H_y}/2) + H_c + (I_{H_p}/2))} \times 100\%$$

H_y: 2.4 ppm (2H, t)

H_c: 5.6 ppm (1H, dd)

H_p: 1.6 ppm (2H, br m)

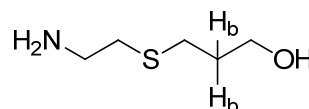
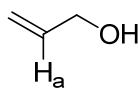


Allyl Alcohol:

$$\%conversion = \frac{(I_{H_b}/2)}{((I_{H_a}) + (I_{H_b}/2))} \times 100\%$$

H_a: 5.9 ppm (1H, dd)

H_b: 1.8 ppm (2H, m)



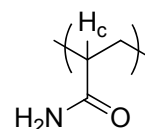
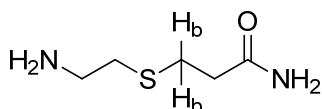
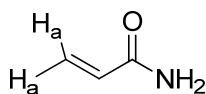
Acrylamide:

$$\%conversion = \frac{(I_{H_b}/2)}{((I_{H_b}/2) + (I_{H_a}/2) + I_{H_c})} \times 100\%$$

H_a: 6.2 ppm (2H, d)

H_b: 2.5 ppm (2H, t)

H_c: 2.2 ppm (1 H, br m)



Allyl amine:

$$\%conversion = \frac{(I_{H_x}/2)}{((I_{H_x}/2) + (I_{H_c}/2))} \times 100\%$$

H_x: 3.2 ppm (2H, t)

H_c: 5.8 ppm (2H, m)

