

Supplementary material

Derivation of eqn. (6) of the main text

The integrated second order rate equation for a substrate **S** reacting with **1** is

$$\begin{aligned} \{1/([\mathbf{1}]_0 - [\mathbf{S}]_0)\} \ln \{[\mathbf{S}]_0([\mathbf{1}]_0 - [\mathbf{P}]_t) / \{[\mathbf{1}]_0([\mathbf{S}]_0 - [\mathbf{P}]_t)\}\} &= k_2 t, \text{ therefore} \\ \{[\mathbf{S}]_0([\mathbf{1}]_0 - [\mathbf{P}]_t) / \{[\mathbf{1}]_0([\mathbf{S}]_0 - [\mathbf{P}]_t)\}\} &= \exp\{([\mathbf{1}]_0 - [\mathbf{S}]_0)k_2 t\} \text{ and} \\ \{[\mathbf{S}]_0([\mathbf{1}]_0 - [\mathbf{P}]_t)\} &= [\mathbf{1}]_0([\mathbf{S}]_0 - [\mathbf{P}]_t)\exp\{([\mathbf{1}]_0 - [\mathbf{S}]_0)k_2 t\} \end{aligned} \quad (\text{S1})$$

Expansion of eqn. (S1) and collection of terms gives eqn. (S2),

$$[\mathbf{P}]_t = [\mathbf{S}]_0[\mathbf{1}]_0 \{ \exp\{([\mathbf{1}]_0 - [\mathbf{S}]_0)k_2 t\} - 1 \} / [\mathbf{1}]_0 \{ \exp\{([\mathbf{1}]_0 - [\mathbf{S}]_0)k_2 t\} - [\mathbf{S}]_0 \} \quad (\text{S2})$$

Cf. main text eqn. (5). $[\mathbf{P}]_t = [\mathbf{S}]_0 - [\mathbf{S}]_t$ therefore,

$$\begin{aligned} [\mathbf{S}]_t &= [\mathbf{S}]_0 - [\mathbf{S}]_0[\mathbf{1}]_0 \{ \exp\{([\mathbf{1}]_0 - [\mathbf{S}]_0)k_2 t\} - 1 \} / [\mathbf{1}]_0 \{ \exp\{([\mathbf{1}]_0 - [\mathbf{S}]_0)k_2 t\} - [\mathbf{S}]_0 \} \\ &= ([\mathbf{S}]_0[\mathbf{1}]_0 - [\mathbf{S}]_0^2) / [\mathbf{1}]_0 \{ \exp\{([\mathbf{1}]_0 - [\mathbf{S}]_0)k_2 t\} - [\mathbf{S}]_0 \} \end{aligned}$$

Division throughout by $[\mathbf{S}]_0$ gives,

$$[\mathbf{S}]_t = ([\mathbf{1}]_0 - [\mathbf{S}]_0) / ([\mathbf{1}]_0 / [\mathbf{S}]_0) \exp\{([\mathbf{1}]_0 - [\mathbf{S}]_0)k_2 t\} - 1 \quad (\text{S3})$$

Cf. main text eqn (6).

Table S1: The absorption coefficients for methyl 4-nitrophenyl sulfide and sulfoxide at 350 nm in acetone and acetone-co-solvent mixtures.

Acetone ^a	Co-solvent ^a	4-O ₂ NC ₆ H ₄ SMe $\epsilon/\text{m}^2 \text{mol}^{-1b}$	4-O ₂ NC ₆ H ₄ S(O)Me $\epsilon/\text{m}^2 \text{mol}^{-1b}$
100		1144 ± 10	62.6 ± 2.8
	Hexane		
75	25	1123 ± 22	58.8 ± 1.4
50	50	1091 ± 34	56.5 ± 0.42
10	90	856.0 ± 15.8	38.0 ± 16.7
	Acetonitrile		
50	50	1185 ± 34	57.1 ± 1.4
	Water		
98	2	1208 ± 16	56.9 ± 2.3
95	5	1268 ± 46	56.7 ± 2.9
90	10	1307 ± 25	53.6 ± 2.5
85	15	1426 ± 26	47.2 ± 5.4
80	20	1582 ± 52	50.2 ± 2.7
75	25	1466 ± 29	47.6 ± 3.1
	Methanol		
99	1	1139 ± 14	60.3 ± 1.1
90	10	1139 ± 14	58.4 ± 1.5
80	20	1167 ± 61	52.6 ± 1.2
70	30	1232 ± 37	49.2 ± 0.72
50	50	1210 ± 41	44.9 ± 0.39

^a All as (% v/v). ^bUncertainties are 95% confidence intervals

Table S2: The absorption coefficients for methyl 4-nitrophenyl sulfoxide and sulfone at 330 nm in acetone and acetone-co-solvent mixtures.

Acetone ^a	Co-solvent ^a	O ₂ NC ₆ H ₄ S(O)Me $\epsilon/\text{m}^2 \text{mol}^{-1\text{b}}$	O ₂ NC ₆ H ₄ S(O) ₂ Me $\epsilon/\text{m}^2 \text{mol}^{-1\text{b}}$
100		195.3 ± 9.1	22.6 ± 3.2
	Acetonitrile		
50	50	195.3 ± 4.2	21.1 ± 0.60
	Water		
98	2	181.9 ± 6.8	23.7 ± 1.2
95	5	177.4 ± 9.3	26.5 ± 0.46
90	10	168.9 ± 6.3	25.6 ± 1.4
85	15	145.0 ± 1.6	26.1 ± 1.2
80	20	155.2 ± 8.8	26.3 ± 0.57
75	25	146.4 ± 7.7	27.9 ± 1.9

^a All as (% v/v). ^bUncertainties are 95% confidence intervals

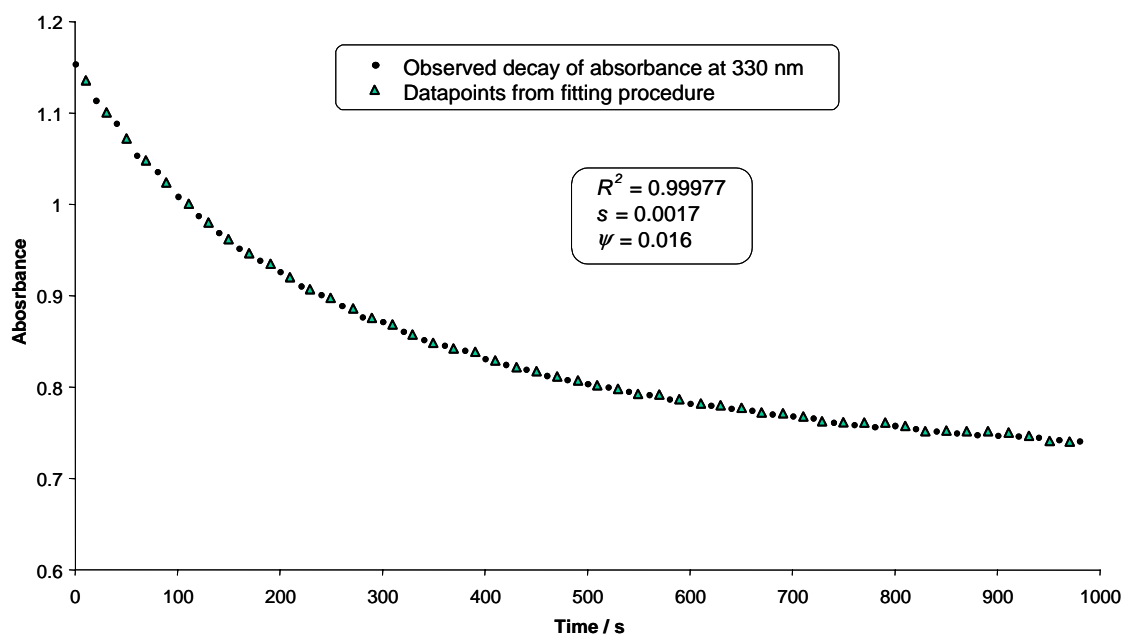


Fig. S1: Δ , Decrease in absorption (330 nm) with time of the reaction of methyl 4-nitrophenyl sulfoxide with 0.4 molar equivalents of dimethyldioxirane in acetone, at 20.0 °C; \bullet and the decay profile fitted with Eqn. (8)