

Electronic Supplementary Information

for

**Sulfoxidation with Hydrogen Peroxide Catalyzed by
[SeO₄{WO(O₂)₂}₂]²⁻ and The Mechanism**

Keigo Kamata^{a,b} Tomohisa Hirano,^a Ryo Ishimoto,^a and Noritaka Mizuno^{*.a,b}

^a*Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan. E-mail: tmizuno@mail.ecc.u-tokyo.ac.jp; Fax: +81 3 5841 7220; Tel: +81 3 5841 7272*

^b*Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan.*

Synthesis and Characterization of [(n-C₄H₉)₄N]₂[SeO₄{WO(O₂)₂}₂] (I). The tetra-*n*-butylammonium salt derivative of [SeO₄{WO(O₂)₂}₂]²⁻ was synthesized according to the literature procedure.^{S1} In 15% aqueous H₂O₂ (9.25 mL, 42 mmol), H₂WO₄ (1.75 g, 7 mmol) was suspended and the resulting suspension was stirred at 305 K for 30 min. The pale yellow solution was filtered to remove insoluble materials followed by addition of 80% H₂SeO₄ (2.1 mL, 28 mmol). The solution was stirred at 273 K for 60 min and an excess amount of [(n-C₄H₉)₄N](NO₃) (3.05 g, 10 mmol) was added in a single step. The solution was stirred at 273 K for 30 min and the white precipitate (1.07 g) was collected by the filtration followed by the washing with an excess amount of H₂O and diethyl ether. The precipitate was evacuated to dryness. A portion of the product (0.2 g) was dissolved in the acetonitrile solution (1 mL) containing a drop of H₂O₂ at 298 K and the solution was cooled to 277 K. The colorless plate-like crystalline solid was obtained by vapor diffusion of diethyl ether into the acetonitrile solution. Yield: 0.11 g (55% based on the crude product). ¹⁸³W NMR (11.20 MHz, CD₃CN, 298 K, Na₂WO₄): δ = -569.2 (Δν_{1/2} = 3.9 Hz); ⁷⁷Se NMR (51.30 MHz, CD₃CN, 298 K, (CH₃)₂Se): δ = 1168.9 (Δν_{1/2} = 3.7 Hz); UV/Vis (CH₃CN) □_{max} (ε) 259 nm (1258 (mol of W)⁻¹dm³cm⁻¹); IR (KCl): 972, 915, 884, 864, 847, 831, 779, 739, 698, 654, 593, 576, 520, 463, 393, 371 cm⁻¹; Raman: ν = 987, 974, 922, 884, 868, 838, 783, 599, 583, 542, 398, 336, 306, 264 cm⁻¹; positive ion MS (CSI, CH₃CN): *m/z*: 1398 [{(n-C₄H₉)₄N]₃SeO₄{WO(O₂)₂}₂]⁺; 2554 [{(n-C₄H₉)₄N]₅{SeO₄{WO(O₂)₂}₂}₂]⁺; 3709 [{(n-C₄H₉)₄N]₇{SeO₄{WO(O₂)₂}₂}₃]⁺; elemental analysis calcd (%) for C₃₂H₇₂N₂O₁₄SeW₂ [(n-C₄H₉)₄N]₂[SeO₄{WO(O₂)₂}₂]: C 33.26, H 6.28, N 2.42, Se 6.83, W 31.82; found: C 33.21, H 6.30, N 2.48, Se 6.53, W 31.21.

Synthesis and Characterization of [(n-C₆H₁₃)₄N]₃[AsO₄{WO(O₂)₂}₄]. The tetra-*n*-hexylammonium salt derivative of [AsO₄{WO(O₂)₂}₄]³⁻ was synthesized according to the literature procedure.^{S2} Yield: 2.41 g (43%). ¹⁸³W NMR (11.20 MHz, CD₃CN, 298 K,

Na₂WO₄): $\delta = -567.5$ ($\Delta\nu_{1/2} = 5.0$ Hz); UV/Vis (CH₃CN) λ_{\max} (ϵ) 255.2 nm (1184 (mol of W)⁻¹dm³cm⁻¹); IR (KCl): 978, 917, 892, 876, 845, 756, 729, 647, 590, 574, 520, 485, 435 cm⁻¹; Raman: $\nu = 990, 924, 900, 862, 843, 653, 597, 580, 534, 386, 336, 328, 303, 232$ cm⁻¹; positive ion MS (CSI, CH₃CN): m/z : 2613 [$\{(n\text{-C}_6\text{H}_{13})_4\text{N}\}_4\text{AsO}_4\{\text{WO}(\text{O}_2)_2\}_4\}^+$; elemental analysis calcd (%) for C₇₂H₁₅₆N₃O₂₄AsW₄ ($[(n\text{-C}_6\text{H}_{13})_4\text{N}]_3[\text{AsO}_4\{\text{WO}(\text{O}_2)_2\}_4]$): C 38.29, H 6.96, N 1.86, As 3.32, W 32.56; found: C 38.06, H 6.99, N 1.80, As 3.13, W 32.39.

Synthesis and Characterization of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{SO}_4\{\text{WO}(\text{O}_2)_2\}_2]$: The tetra-*n*-butylammonium salt derivative of $[\text{SO}_4\{\text{WO}(\text{O}_2)_2\}_2]^{2-}$ was synthesized according to the literature procedure.^{S3} Yield: 1.39 g (54%). ¹⁸³W NMR (11.20 MHz, CD₃CN, 298 K, Na₂WO₄): $\delta = -587.2$ ($\Delta\nu_{1/2} = 2.6$ Hz); UV/Vis (CH₃CN) λ_{\max} (ϵ) 254.1 nm (1270 (mol of W)⁻¹dm³cm⁻¹); IR (KCl): 988, 974, 962, 922, 887, 858, 850, 739, 679, 655, 646, 599, 594, 575, 540, 526, 487 cm⁻¹; Raman: $\nu = 994, 970, 915, 883, 865, 806, 750, 662, 600, 582, 547, 409, 336, 311, 289, 266$ cm⁻¹; positive ion MS (CSI, CH₃CN): m/z : 1351 [$\{(n\text{-C}_4\text{H}_9)_4\text{N}\}_3\text{SO}_4\{\text{WO}(\text{O}_2)_2\}_2\}^+$; elemental analysis calcd (%) for C₃₂H₇₂N₂O₁₄SW₂ ($[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{SO}_4\{\text{WO}(\text{O}_2)_2\}_2]$): C 34.67, H 6.55, N 2.53, W 33.16; found: C 34.69, H 6.59, N 2.44, W 34.16.

Synthesis and Characterization of $[(n\text{-C}_6\text{H}_{13})_4\text{N}]_3[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]$. The tetra-*n*-hexylammonium salt derivative of $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]^{3-}$ was synthesized according to the literature procedure.^{S4} Yield: 1.39 g (50%). ³¹P NMR (109.25 MHz, CD₃CN, 298 K, H₃PO₄): $\delta = 4.5$ ($^2J_{\text{W-P}} = 18.5$ Hz); ¹⁸³W NMR (11.20 MHz, CD₃CN, 298 K, Na₂WO₄): $\delta = -588.2$ ($^2J_{\text{W-P}} = 18.4$ Hz, $\Delta\nu_{1/2} = 7.3$ Hz); UV/Vis (CH₃CN) λ_{\max} (ϵ) 254.2 nm (1268 (mol of W)⁻¹dm³cm⁻¹); IR (KCl): 977, 853, 843, 797, 757, 728, 660, 649, 603, 591, 573, 549, 525, 444 cm⁻¹; Raman: $\nu = 990, 864, 821, 655, 597, 580, 543, 391, 333, 305, 266, 237$ cm⁻¹; positive ion MS (CSI, CH₃CN): m/z : 2569 [$\{(n\text{-C}_6\text{H}_{13})_4\text{N}\}_4\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4\}^+$; elemental analysis calcd (%) for C₇₂H₁₅₆N₃O₂₄PW₄ ($[(n\text{-C}_6\text{H}_{13})_4\text{N}]_3[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]$): C 39.05, H 7.10, N 1.90, P 1.40, W 32.22; found: C 38.82, H 6.97, N 1.36, P 1.36, W 33.28.

Synthesis and Characterization of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{HAsO}_4\{\text{WO}(\text{O}_2)_2\}_2]$. The tetra-*n*-butylammonium salt derivative of $[\text{HAsO}_4\{\text{WO}(\text{O}_2)_2\}_2]^{2-}$ was synthesized according to the literature procedure.^{S5} Yield: 2.60 g (49%). ¹⁸³W NMR (11.20 MHz, CD₃CN, 298 K, Na₂WO₄): $\delta = -603.9$ ($\Delta\nu_{1/2} = 5.0$ Hz); UV/Vis (CH₃CN) λ_{\max} (ϵ) 252.1 nm (1330 (mol of W)⁻¹dm³cm⁻¹); IR (KCl): $\nu = 968, 932, 871, 843, 814, 777, 739, 664, 584, 575, 569, 527, 512, 495, 457, 385, 366$ cm⁻¹; Raman: $\nu = 983, 914, 889, 859, 821, 651, 580, 531, 464, 391, 315, 264, 237$ cm⁻¹; positive ion MS (CSI, CH₃CN): m/z : 1395 [$\{(n\text{-C}_4\text{H}_9)_4\text{N}\}_3\text{HAsO}_4\{\text{WO}(\text{O}_2)_2\}_2\}^+$, 2548 [$\{(n\text{-C}_4\text{H}_9)_4\text{N}\}_5\{\text{HAsO}_4\{\text{WO}(\text{O}_2)_2\}_2\}_2\}^+$; elemental analysis calcd (%) for C₃₂H₇₃N₂O₁₄AsW₂ ($[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{HAsO}_4\{\text{WO}(\text{O}_2)_2\}_2]$): C 33.35, H 6.38, N 2.43, As 6.50, W 31.90; found: C 33.08 H 6.33, N 2.39, As 6.35, W 31.44.

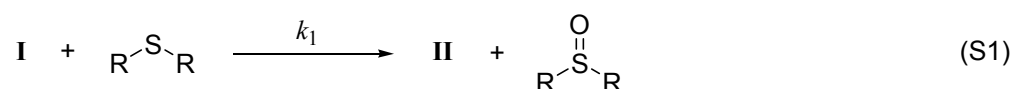
Synthesis and Characterization of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{HPO}_4\{\text{WO}(\text{O}_2)_2\}_2]$. The tetra-*n*-butylammonium salt derivative of $[\text{HPO}_4\{\text{WO}(\text{O}_2)_2\}_2]^{2-}$ was synthesized according to the literature procedure.^{S6} Yield: 1.70 g (60%). ³¹P NMR (109.25 MHz, CD₃CN, 298 K, H₃PO₄): $\delta = 2.8$ ($^2J_{\text{W-P}} = 17.3$ Hz); ¹⁸³W NMR (11.20 MHz, CD₃CN, 298 K, Na₂WO₄): $\delta = -626.4$ ($^2J_{\text{W-P}} = 17.1$ Hz, $\Delta\nu_{1/2} = 5.8$ Hz); UV/Vis (CH₃CN) λ_{\max} (ϵ) 251.5 nm (1294 (mol of W)⁻¹dm³cm⁻¹); IR (KCl): 1019, 996, 963, 882, 853, 843, 800, 737, 646, 625, 584, 569, 538, 487 cm⁻¹; Raman: $\nu = 977, 915, 887, 862, 807, 652, 582, 536, 335, 319, 300, 262, 239$ cm⁻¹; positive ion MS (CSI, CH₃CN): m/z : 1351 [$(\text{TBA})_3\text{HPO}_4\{\text{WO}(\text{O}_2)_2\}_2\}^+$; elemental analysis calcd (%) for C₃₂H₇₃N₂O₁₄PW₂ ($[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{HPO}_4\{\text{WO}(\text{O}_2)_2\}_2]$): C 34.67, H 6.64, N 2.53, P 2.79, W 33.17; found: C 34.50, H 6.54, N 2.33, P 2.75, W 33.48.

Synthesis and Characterization of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Ph}_2\text{SiO}_2\{\text{WO}(\text{O}_2)_2\}_2]$. The tetra-*n*-butylammonium salt derivative of $[\text{Ph}_2\text{SiO}_2\{\text{WO}(\text{O}_2)_2\}_2]^{2-}$ was synthesized by the modification of the reported method; tetraphenylphosphonium was replaced by

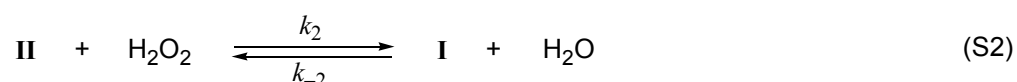
tetra-*n*-butylammonium.^{S7} Yield: 1.70 g (40%). ¹H NMR (270 MHz, CD₃CN, 298 K, TMS): δ = 7.77 (m, 4H, *m*-), 7.36 (m, 6H, *o*-, *p*-); ¹³C NMR (67.80 MHz, ClCD₂CD₂Cl, 298 K, TMS): δ = 135.5, 130.0, 128.3; ²⁹Si NMR (53.45 MHz, CD₃CN, 298 K, TMS): δ = -34.6 (²*J*_{Si-P} = 2.9 Hz, Δ*v*_{1/2} = 1.0 Hz); ¹⁸³W NMR (11.20 MHz, CD₃CN, 298 K, Na₂WO₄): δ = -651.6 (Δ*v*_{1/2} = 3.9 Hz); IR (KCl): ν = 974, 965, 933, 881, 850, 840, 746, 712, 701, 638, 582, 563, 505, 480, 437 cm⁻¹; Raman: ν = 1006, 983, 940, 915, 886, 858, 646, 626, 588, 573, 531, 518, 403, 341, 325, 306, 262, 204 cm⁻¹; positive ion MS (CSI, CH₃CN): *m/z*: 1469 [{(*n*-C₄H₉)₄N}₃PhSiO₂{WO(O₂)₂}₂]⁺; elemental analysis calcd (%) for C₄₄H₈₂N₂O₁₂SiW₂ [(*n*-C₄H₉)₄N]₂[Ph₂SiO₂{WO(O₂)₂}₂]: C 43.07, H 6.74, N 2.28, Si 2.29, W 29.97; found: C 43.00, H 6.89, N 2.08, Si 2.00, W 27.28.

Synthesis and Characterization of [(*n*-C₄H₉)₄N]₂{WO(O₂)₂}₂(μ-O)]. The tetra-*n*-butylammonium salt derivative of [{WO(O₂)₂}₂(μ-O)]²⁻ was synthesized according to the literature procedure.^{S8} Yield: 0.2 g (12%). ¹⁸³W NMR (11.20 MHz, CD₃CN, 298 K, Na₂WO₄): δ = -587.5 (Δ*v*_{1/2} = 24.3 Hz); IR (KCl): ν = 962, 955, 848, 835, 655, 631, 615, 571, 554, 543, 524 cm⁻¹; Raman: ν = 970, 961, 858, 844, 801, 786, 662, 624, 597, 572, 470, 328, 308, 275, 259 cm⁻¹; positive ion MS (CSI, CH₃CN): *m/z*: 1270.3 [{(*n*-C₄H₉)₄N}₃{WO(O₂)₂}₂(μ-O)]⁺; elemental analysis calcd (%) for C₃₂H₇₂N₂O₁₁W₂ [(*n*-C₄H₉)₄N]₂{WO(O₂)₂}₂(μ-O)]: C 37.37, H 7.06, N 2.72, W 35.75; found: C 37.24, H 7.13, N 2.69, W 35.28.

Kinetic Derivation. The selenium-containing dinuclear peroxotungstate **I** reacts with a sulfide, leading to a sulfoxide and the subsequent peroxo species **II** (eqn (S1)):



Then, **I** is regenerated by the reaction of **II** with an H₂O₂ (eqn (S2)):



From the steady-state approximation on **I** and **II** (eqns (S3) and (S4)) and the mass balance (eqn (S5)), the rate of the formation of sulfoxide can be expressed by (eqn (S6)):

$$\frac{d[\text{I}]}{dt} = -k_1[\text{sulfide}][\text{I}] + k_2[\text{II}][\text{H}_2\text{O}_2] - k_{-2}[\text{I}][\text{H}_2\text{O}] = 0 \quad (\text{S3})$$

$$\frac{d[\text{II}]}{dt} = k_1[\text{sulfide}][\text{I}] - k_2[\text{II}][\text{H}_2\text{O}_2] + k_{-2}[\text{I}][\text{H}_2\text{O}] = 0 \quad (\text{S4})$$

$$[\text{I}]_t = [\text{I}] + [\text{II}] \quad (\text{S5})$$

$$R_0 = \frac{d[\text{sulfoxide}]}{dt} = \frac{k_1 k_2 [\text{I}]_t [\text{sulfide}] [\text{H}_2\text{O}_2]}{k_1 [\text{sulfide}] + k_2 [\text{H}_2\text{O}_2] + k_{-2} [\text{H}_2\text{O}]} \quad (\text{S6})$$

When the *k*₁, *k*₂, and *k*₋₂ values in eqn (S6) are 9.3, 2.6, and 2.0 × 10⁻¹ M⁻¹s⁻¹, respectively, the experimental data in Figures 4 and 5 could be fitted with a simulation curve calculated using eqn (S6). All the kinetic data were fitted with the Igor Pro ver. 5.05 program.

Data of Products

Methyl phenyl sulfoxide: ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 2.64 (s, 3H), 7.51–7.55 (m, 3H), 7.61–7.64 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 44.2, 124.3, 130.1, 131.6, 147.6; MS (70 eV, EI): m/z (%): 140 (100) [M^+], 125 (100), 124 (25), 109 (13), 97 (62), 94 (18), 91 (14), 78 (15), 77 (51), 65 (16), 51 (45), 50 (19), 45 (11).

Methyl phenyl sulfone: ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 3.04 (s, 3H), 7.59–7.70 (m, 3H), 7.91–7.93 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 44.4, 128.0, 130.2, 134.5, 141.9; MS (70 eV, EI): m/z (%): 156 (36) [M^+], 141 (33), 94 (42), 77 (100), 51 (28).

Methyl *p*-methoxyphenyl sulfoxide: ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 2.63 (s, 3H), 3.82 (s, 3H), 7.04–7.09 (m, 2H), 7.55–7.60 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 50.0, 58.7, 121.0, 129.2, 139.3, 165.3; MS (70 eV, EI): m/z (%): 170 (21) [M^+], 155 (100), 154 (12), 139 (16), 123 (11).

Methyl *p*-methylphenyl sulfoxide: ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 2.36 (s, 3H), 2.62 (s, 3H), 7.32–7.35 (m, 2H), 7.48–7.52 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 21.0, 43.4, 124.3, 130.6, 142.4, 124.8; MS (70 eV, EI): m/z (%): 154 (66) [M^+], 139 (100), 138 (19), 111 (12), 91 (36), 77 (28), 67 (13), 65 (20), 63 (11).

***p*-Fluorophenyl methyl sulfoxide:** ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 2.66 (s, 3H), 7.23–7.33 (m, 2H), 7.65–7.71 (m, 2H); MS (70 eV, EI): m/z (%): 158 (58) [M^+], 143 (100), 142 (18), 127 (16), 115 (41), 112 (14), 95 (27), 83 (19), 75 (23).

***p*-Chlorophenyl methyl sulfoxide:** ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 2.64 (s, 3H), 7.48–7.52 (m, 2H), 7.55–7.60 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 43.5, 126.1, 130.1, 137.1, 144.9; MS (70 eV, EI): m/z (%): 176 (17), 175 (11), 174 (48) [M^+], 161 (34), 160 (28), 159 (100), 158 (54), 145 (12), 143 (39), 131 (36), 128 (18), 127 (12), 125 (12), 112 (15), 111 (22), 108 (32), 76 (11), 75 (35), 74 (17), 69 (14), 63 (11), 50 (24), 45 (32).

***p*-Bromophenyl methyl sulfoxide:** ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 2.63 (s, 3H), 7.48–7.53 (m, 2H), 7.63–7.68 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 43.4, 125.4, 126.3, 133.0, 145.5; MS (70 eV, EI): m/z (%): 281 (19), 220 (62) [M^+], 218 (67), 205 (98), 204 (100), 203 (92), 202 (77), 189 (28), 187 (28), 177 (26), 175 (20), 171 (24), 131 (23), 122 (20), 108 (72), 96 (46), 86 (11), 82 (21), 77 (29), 76 (47), 75 (27), 74 (34), 69 (25), 63 (23), 59 (10), 58 (18), 56 (21), 51 (28), 50 (56), 45 (14), 43 (15).

4-(Methylsulfinyl)-acetophenone: ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 2.57 (s, 3H), 2.70 (s, 3H), 7.69–7.73 (m, 2H), 8.05–8.08 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 26.8, 43.2, 124.5, 129.6, 139.5, 151.1, 198.7; MS (70 eV, EI): m/z (%): 182, (63) [M^+], 168 (10), 167 (100), 152 (73), 151 (12), 139 (22), 124 (12), 121 (13), 76 (12), 50 (13).

4-Methyl sulfinyl benzonitrile: ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 2.68 (s, 3H), 7.52–7.59 (m, 2H), 7.81–7.86 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 43.1, 114.5, 118.5, 125.0, 133.7, 151.7; MS (70 eV, EI): m/z (%): 165 (89) [M^+], 150 (100), 149 (24), 122 (60), 119 (18), 116 (13), 102 (29), 90 (11), 76 (16), 75 (26), 51 (14), 50 (13), 45 (10).

***p*-Nitrophenyl methyl sulfoxides:** ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 2.73 (s, 3H), 7.84 (d, J = 8.1 Hz, 2H), 8.34 (d, J = 7.7 Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 43.8, 125.1, 125.8, 150.1, 152.8, 150.3, 154.5; MS (70 eV, EI): m/z (%): 185 (100) [M^+], 170 (45), 140 (22), 124 (12), 112 (14), 96 (10), 92 (10), 84 (10), 76 (17), 75 (11), 63 (14).

Ethyl phenyl sulfoxide: ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 1.08 (t, J = 7.3 Hz, 3H), 2.66–2.97 (m, 2H), 7.51–7.62 (m, 5H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 5.8, 50.1, 124.8, 130.0, 131.7, 143.5; MS (70 eV, EI): m/z (%): 154 (26) [M^+], 126 (64), 125 (17), 97 (12), 78 (100), 77 (21), 51 (22).

Benzyl methyl sulfoxide: ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ 2.40 (t, J = 7.3 Hz, 3H), 3.8–4.0 (m, 2H), 7.2–7.4 (m, 5H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 37.3, 59.4, 128.7, 129.2, 130.8, 131.3; MS (70 eV, EI): m/z (%): 154 (1) [M^+], 106 (1), 105 (2), 92 (8), 91 (100), 89 (2), 78 (1), 77 (7), 65 (10), 63 (2), 51 (5).

Diphenyl sulfoxide: ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 7.43–7.53 (m, 6H), 7.65–7.65 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 125.1, 130.3, 132.0, 147.3; MS (70 eV, EI): m/z (%): 203 (15) [$M^+ + 1$], 202 (100) [M^+], 186 (14), 185 (22), 174 (15), 173 (21), 155 (11), 154 (83), 153 (23), 152 (12), 141 (13), 125 (11), 109 (84), 97 (36), 77 (48), 65 (33).

Diphenyl sulfone: ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 7.54–7.65 (m, 6H), 7.93–7.95 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 128.3, 130.5, 134.4, 142.5; MS (70 eV, EI): m/z (%): 218 (28) [M^+], 153 (4), 152 (6), 127 (5), 126 (8), 125 (100), 97 (17), 77 (35), 51 (25).

Methyl *n*-octyl sulfoxide: ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 0.97 (t, J = 7.3 Hz, 3H), 1.60–1.69 (m, 12H), 2.40 (s, 3H), 2.61–2.68 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 14.1, 22.9, 23.0, 29.0, 29.4, 29.5, 32.2, 38.1, 52.3; MS (70 eV, EI): m/z (%): 177 (10) [$M^+ + 1$], 112 (11), 107 (17), 94 (13), 91 (13), 85 (11), 84 (17), 83 (27), 82 (13), 81 (100), 80 (25), 79 (11), 77 (10), 71 (41), 70 (20), 69 (24), 57 (63), 56 (29), 55 (30), 53 (10), 43 (48), 42 (10), 41 (50).

Methyl *n*-octyl sulfone: ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 0.86 (t, J = 5.9 Hz, 3H), 1.27–1.78 (m, 12H), 2.83 (s, 3H), 2.96–3.02 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 14.1, 22.9, 23.0, 28.7, 29.4, 29.5, 32.2, 40.5, 54.8; MS (70 eV, EI): m/z (%): 193 (3) [$M^+ + 1$], 177 (6), 175 (4), 112 (11), 107 (11), 84 (12), 83 (21), 81 (100), 80 (24), 71 (49), 70 (17), 69 (21), 57 (64), 56 (23), 55 (34).

Ethyl *n*-propyl sulfoxide: ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 1.03 (t, J = 7.4 Hz, 3H), 1.22 (t, J = 7.5 Hz, 3H), 1.63–1.78 (m, 2H), 2.56–2.74 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 6.7, 13.2, 16.6, 45.4, 53.2; MS (70 eV, EI): m/z (%): 120 (43) [M^+], 103 (13), 78 (100), 77 (12), 63 (51), 50 (21), 43 (82), 41 (58).

Diallyl sulfoxide: ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 3.32–3.54 (m, 4H), 5.31–5.40 (m, 4H), 5.77–5.92 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 54.6, 123.6, 127.1; MS (70 eV, EI): m/z (%): 130 (16) [M^+], 113 (5), 100 (12), 89 (8), 82 (16), 81 (100), 80 (23), 79 (14), 73 (12), 68 (33), 67 (12).

Diallyl sulfones: ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 3.74 (d, J = 7.0 Hz 2H), 5.39–5.47 (m, 2H), 5.79–5.95 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 56.6, 124.9, 125.8; MS (70 eV, EI): m/z (%): 146 (0.1) [M^+], 105 (6), 97(2), 82 (2), 81 (20), 79 (2), 68 (6), 67 (100), 54 (49).

Di(2-hydroxyethyl) sulfoxide: ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 2.93–3.09 (m, 2H), 3.89 (t, J = 4.9 Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 55.2, 123.4, 127.7; MS (70 eV, EI): m/z (%): 138 (3) [M^+], 104 (3), 96 (4), 94 (70), 91 (3), 76 (100), 63 (44), 61 (14).

Phenyl vinyl sulfoxide: ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 5.83 (d, J = 4.7 Hz, 1H), 6.09 (d, J = 8.1 Hz, 1H), 6.73 (d, J = 4.9, 8.2 Hz, 1H), 7.36–7.62 (m, 5H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 120.7, 125.2, 130.4, 132.0, 144.3, 144.7; MS (70 eV,

EI): m/z (%): 152 (19) [M^+], 136 (8), 124 (13), 123 (16), 109 (31), 104 (100), 97 (14), 91 (11), 78 (42), 77 (31), 65 (15), 51 (32), 50 (11).

Phenyl vinyl sulfone: ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 6.10 (d, J = 5.0 Hz, 1H), 6.37 (d, J = 8.2 Hz, 1H), 6.80 (d, J = 5.0, 8.2 Hz, 1H), 7.62–7.73 (m, 2H), 7.85–7.89 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 128.3, 129.0, 130.3, 134.6, 139.2, 140.5; MS (70 eV, EI): m/z (%): 168 (21) [M^+], 125 (100), 97 (13), 78 (11), 77 (100), 65 (12), 51 (35).

Tetrahydrothiophene sulfoxide: ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 1.91–2.22 (m, 4H), 2.7–2.90 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 25.9, 54.9; MS (70 eV, EI): m/z (%): 104 (61) [M^+], 87 (5), 76 (3), 63 (29), 60 (4), 59 (4), 56 (7), 55 (100).

2-Mehyltetrahydrothiophene 1-oxide: $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): *cis*-isomer: δ = 11.6, 25.3, 32.9, 55.3, 58.9; *trans*-isomer: δ = 15.0, 25.2, 34.5, 53.0, 65.1; MS (70 eV, EI): m/z (%): 118 (83) [M^+], 101, (19), 87 (8), 69 (100), 68 (24), 67 (23), 63 (74), 59 (12), 56 (30), 55 (32).

Tetrahydrothiopyran 1-oxide: ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 1.48–1.66 (m, 4 H), 2.00–2.17 (m, 2 H), 2.60–2.87 (m, 4 H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 19.4, 25.0, 52.4; MS (70 eV, EI): m/z (%): 118 (77) [M^+], 101 (24), 90 (19), 69 (100), 68 (22), 67 (22), 63 (68), 56 (21), 55 (32).

Dibenzothiophene 5,5-dioxide: ^1H NMR (270 MHz, CDCl_3 , 298 K, TMS): δ = 7.81 (d, 2H, J = 8.1 Hz), 7.78 (d, 2H, J = 8.9 Hz), 7.62 (dt, 2H, J = 7.4 and 0.8 Hz), 7.51 (dt, 2H, J = 7.6 and 0.5 Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CDCl_3 , 298 K, TMS): δ = 122.1, 122.7, 130.9, 132.1, 134.4, 138.3; MS (70 eV, EI): m/z (%): 217 (15), 216 (100), 188 (10), 187 (36), 171 (13), 168 (32), 160 (27), 150 (14), 144 (17), 139 (25), 136 (31), 115 (18), 104 (15), 79 (16), 75 (10), 63 (12).

1,4-Oxathiane 4-oxide: ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 2.51–2.65 (m, 2H), 2.88–2.98 (m, 2H), 3.68–3.76 (m, 2H), 4.15–4.24 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 59.9, 47.0; MS (70 eV, EI): m/z (%): 120 (40) [M^+], 104 (2), 94 (5), 93 (3), 92 (100), 77 (27), 76 (21), 63 (15), 62 (5), 61 (4), 60 (3), 59 (24), 58 (3), 57 (3), 50 (8).

1,3-Dithiolane 1-oxide: ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 2.75–2.81 (m, 1H), 3.35–3.45 (m, 2H), 3.69–3.92 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 55.4, 57.5, 78.9; MS (70 eV, EI): m/z (%): 124 (10), 123 (6), 122 (100) [M^+], 94 (8), 78 (8), 77 (5), 76 (11), 74 (6), 73 (29), 63 (8), 60 (33), 59 (17), 58 (5).

1,3-Dithiane 1-oxide: ^1H NMR (270 MHz, CD_3CN , 298 K, TMS): δ = 2.00–2.14 (m, 1H), 2.40–2.67 (m, 4H), 3.16–3.25 (m, 1H), 3.64 (d, J = 12.7 Hz, 1H), 3.97 (d, J = 12.7 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CD_3CN , 298 K, TMS): δ = 52.8, 50.1, 28.3, 27.4; MS (70 eV, EI): m/z (%): 138 (9), 137 (8), 136 (100) [M^+], 119 (12), 106 (25), 90 (50), 89 (6), 87 (50), 74 (11), 73 (39), 72 (8), 63 (9), 62 (5), 61 (31), 60 (27), 59 (14), 57 (5).

Thianthrene 5-oxide (SSO): ^1H NMR (270 MHz, CDCl_3 , 298 K, TMS): δ 7.44 (dt, 2H, J = 1.2, 7.6 Hz), 7.54 (dt, 2H, J = 1.2, 7.6 Hz), 7.62 (dd, 2H, J = 1.2, 7.6 Hz), 7.92 (dd, 2H, J = 1.2, 7.6 Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CDCl_3 , 298 K, TMS): δ = 124.3, 128.2, 128.8, 129.7, 141.2; elemental analysis calcd (%) for $\text{C}_{12}\text{H}_8\text{OS}_2$: C 62.04, H 3.47; found: C 61.92, H 3.65.

Thianthrene 5,5-dioxide (SSO₂): ^1H NMR (270 MHz, CDCl_3 , 298 K, TMS): δ = 7.50–7.59 (m, 4H), 7.63–7.68 (m, 2H), 8.19–8.25 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CDCl_3 , 298 K, TMS): δ = 125.5, 127.7, 128.7, 132.0, 135.1, 135.3.

***cis*-Thianthrene 5,10-dioxide (*cis*-SOSO):** ^1H NMR (270 MHz, CDCl_3 , 298 K, TMS): δ = 7.69–7.76 (m, 4H), 8.04–8.11 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.5 MHz, CDCl_3 , 298 K, TMS): δ = 123.7, 130.8, 138.4.

trans-Thianthrene 5,10-dioxide (trans-SOSO): ^1H NMR (270 MHz, CDCl_3 , 298 K, TMS): $\delta = 7.63\text{--}7.70$ (m, 4H), $8.08\text{--}8.14$ (m, 4H); ^{13}C $\{^1\text{H}\}$ NMR (67.5 MHz, CDCl_3 , 298 K, TMS): $\delta = 127.8, 131.4, 142.8$.

Thianthrene 5,5,10-trioxide (SOSO₂): ^1H NMR (270 MHz, CDCl_3 , 298 K, TMS): $\delta = 7.67\text{--}7.73$ (m, 2H), $7.73\text{--}7.84$ (m, 2H), $8.12\text{--}8.21$ (m, 4H); ^{13}C $\{^1\text{H}\}$ NMR (67.5 MHz, CDCl_3 , 298 K, TMS): $\delta = 125.0, 126.1, 130.7, 133.0, 134.1, 147.8$.

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Table S1 Effect of catalysts on oxidation of thioanisole with H₂O₂^a

entry	catalyst	yield (%)	selectivity (%)		<i>R</i> ₀ (mM min ⁻¹)
			sulfoxide	sulfone	
1	I	90	95	5	25.0
2	without	<1	–	–	–
3 ^b	H ₂ SeO ₄	1	99	1	<0.1
4 ^c	SeO ₂	12	93	7	0.4
5	H ₂ WO ₄	1	44	56	<0.1
6	H ₂ SeO ₄ + H ₂ WO ₄	4	92	8	0.2
7	(TBA) ₂ [{WO(O ₂) ₂ } ₂ (μ-O)]	45	87	13	3.1
8	(TBA) ₂ [SO ₄ {WO(O ₂) ₂ } ₂]	73	92	8	16.0
9 ^d	(THA) ₃ [AsO ₄ {WO(O ₂) ₂ } ₄]	83	92	8	15.8
10 ^d	(THA) ₃ [PO ₄ {WO(O ₂) ₂ } ₄]	61	92	8	7.7
11	(TBA) ₂ [HAsO ₄ {WO(O ₂) ₂ } ₂]	61	87	13	4.1
12	(TBA) ₂ [HPO ₄ {WO(O ₂) ₂ } ₂]	52	89	11	3.7
13	(TBA) ₂ [Ph ₂ SiO ₂ {WO(O ₂) ₂ } ₂]	11	86	14	0.5

^a Reaction conditions: Catalyst (W: 0.2 mol% relative to thioanisole and H₂O₂), thioanisole (1 mmol), 30% aqueous H₂O₂ (1 mmol), CH₃CN (6 mL), 293 K, 30 min. Yield was determined by GC. *R*₀ values were determined from the reaction profiles at low conversions (≤20%) of both thioanisole and H₂O₂. ^b H₂SeO₄ (0.1 mol%). ^c SeO₂ (0.1 mol%). ^d THA = [(*n*-C₆H₁₃)₄N]⁺.

Table S2 Oxidation of various acyclic sulfides with 30% aqueous H₂O₂ catalyzed by **I**^a

$$\begin{array}{c}
 \text{R}_1-\text{S}-\text{R}_2 + \text{H}_2\text{O}_2 \xrightarrow[\text{CH}_3\text{CN, 293 K}]{\text{I}} \text{R}_1-\overset{\text{O}}{\parallel}{\text{S}}-\text{R}_2 + \text{H}_2\text{O}
 \end{array}$$

entry	substrate		time (min)	yield (%)	selectivity to sulfoxide(%)	H ₂ O ₂ efficiency (%)
	R ₁	R ₂				
1	Ph	Me	120	99	90	99
2 ^b	Ph	Me	240	98	95	98
3	4-CH ₃ OC ₆ H ₄	Me	120	>99	90	>99
4	4-CH ₃ C ₆ H ₄	Me	120	98	93	98
5	4-FC ₆ H ₄	Me	120	>99	88	>99
6	4-ClC ₆ H ₄	Me	120	99	87	99
7	4-BrC ₆ H ₄	Me	120	99	87	99
8	4-COMeC ₆ H ₄	Me	120	99	85	99
9	4-CNC ₆ H ₄	Me	200	>99	81	>99
10	4-NO ₂ C ₆ H ₄	Me	210	>99	78	>99
11 ^b	4-NO ₂ C ₆ H ₄	Me	800	96	99	96
12	Ph	Et	100	>99	82	>99
13 ^b	Ph	Et	100	98	96	98
14	Bn	Me	120	>99	94	>99
15	Ph	Ph	210	97	81	97
16 ^c	Ph	Ph	720	98	85	98
17 ^d	Ph	Ph	120	>99	98	>99
18	<i>n</i> -C ₈ H ₁₇	Me	120	96	94	96
19 ^d	<i>n</i> -C ₃ H ₇	Et	120	98	95	98
20	<i>n</i> -C ₃ H ₇	Et	60	97	90	97
21	allyl	allyl	120	>99	86	>99
22 ^b	allyl	allyl	150	>99	94	>99
23 ^d	allyl	allyl	90	99	99	99
24	HOC ₂ H ₄	HOC ₂ H ₄	60	95	99	95
25	Ph	vinyl	240	95	86	95
26 ^d	Ph	vinyl	330	97	95	97

^a Reaction conditions: **I** (0.1 mol% relative to substrate and H₂O₂), sulfide (1 mmol), 30% aqueous H₂O₂ (1 mmol), CH₃CN (6 mL), 293 K. Yield and selectivity were determined by GC and NMR. Remaining H₂O₂ after reaction was estimated by potential difference titration of Ce³⁺/Ce⁴⁺ (0.1 M of aqueous Ce(NH₄)₄(SO₄)₄·2H₂O). Yield (%) = (sulfoxide (mol) + sulfone (mol) × 2)/H₂O₂ used (mol) × 100. H₂O₂ efficiency (%) = (sulfoxide (mol) + sulfone (mol) × 2)/consumed H₂O₂ (mol) × 100. ^b **I** (0.01 mol%), CH₃CN (1 mL). ^c **I** (0.02 mol%), CH₃CN (1 mL). ^d 30% aqueous H₂O₂ (2 mmol), 323 K.

Table S3 Cartesian coordinates (in Å) of the calculated structures

atom	x (Å)	y (Å)	z (Å)
O	-1.18529	-0.50772	-0.62061
O	-3.09479	0.564621	1.17572
O	-2.46755	1.710327	-1.40224
O	-2.43366	2.841782	-0.44725
O	-0.92539	2.291931	1.719559
O	-0.24229	0.993698	1.678619
O	1.317535	-0.81384	0.423508
O	3.245773	1.009048	-0.56622
O	2.6232	0.666016	2.23494
O	2.606995	2.128464	2.00177
O	1.100357	2.795883	-0.13286
O	0.400436	1.671921	-0.76569
O	0.569595	-2.19058	-1.86636
Se	0.059036	-1.6969	-0.38524
W	-1.744	1.206207	0.332855
W	1.899857	1.139587	0.491348
O	-0.46275	-2.87543	0.633026

Charge = -2; $E = -1197.99074$ hartree.

Table S3 (Continued)

B

atom	x (Å)	y (Å)	z (Å)
O	0.004868	-0.087006	2.656113
O	0.004868	2.796204	2.656113
O	-2.523773	1.127975	2.656113
O	-2.572662	2.189880	1.600571
O	-0.021255	1.495209	0.181183
O	1.104782	-1.068832	0.321472
O	-0.510773	-2.079575	-1.768738
O	1.191132	0.214996	-2.098953
O	-0.123077	0.609268	-2.656128
O	-2.153442	0.062851	-0.903564
O	-1.684479	-0.500168	0.369278
O	0.377579	-2.796204	2.387146
Se	1.062851	-1.349579	2.024643
W	-0.783691	1.527939	1.786942
W	-0.307587	-0.515839	-1.085632
O	2.572662	-1.088455	2.617554

Charge = -2; $E = -1122.83923274$ hartree.

Table S3 (Continued)

TS1

atom	x (Å)	y (Å)	z (Å)	displacement vector of the imaginary frequency mode atom		
				x	y	z
O	2.410932	0.522364	0.018467	-0.05	-0.01	0.05
O	1.658988	2.786097	-1.255406	0.00	0.01	0.00
O	1.147585	2.510844	1.555270	0.00	-0.02	0.00
O	-0.118853	3.010265	0.973979	0.01	-0.01	0.00
O	-0.891264	1.640146	-1.212806	0.02	-0.01	0.00
O	-0.083987	0.448653	-1.517136	0.02	-0.03	0.06
O	1.166511	-1.876033	-0.425450	0.00	0.05	0.04
O	-1.042322	-2.722839	1.164591	0.02	-0.01	-0.01
O	-1.015812	-2.325989	-1.721182	0.00	0.00	0.02
O	-2.255664	-1.709423	-1.229990	-0.01	0.01	0.03
O	-0.087400	0.014877	1.047932	-0.22	0.14	0.18
O	2.824954	-1.564681	1.819551	-0.01	0.00	0.00
Se	2.628983	-1.187023	0.231888	0.02	-0.01	0.00
W	0.775364	1.748297	-0.203852	0.01	0.02	-0.01
W	-0.782226	-1.457556	0.031120	-0.01	-0.04	-0.03
O	3.851153	-1.656266	-0.764979	0.00	0.01	0.00
O	-1.930923	-0.025467	0.840844	0.81	0.06	0.11
C	-3.843077	1.728738	1.443915	0.01	0.00	-0.01
Se	-3.989254	0.162575	0.533153	-0.31	0.03	-0.02
C	-3.967935	0.789275	-1.174586	-0.06	0.03	-0.01
H	-3.859607	1.483902	2.508123	-0.01	0.00	0.00
H	-4.676188	2.396229	1.200633	0.11	0.15	0.07
H	-2.874601	2.172858	1.197200	0.05	-0.07	0.03
H	-3.951208	-0.086663	-1.824516	-0.09	0.04	-0.02
H	-3.036972	1.344423	-1.319171	-0.01	-0.05	0.01
H	-4.856102	1.403556	-1.360231	0.04	0.12	-0.17

Charge = -2; E = -1675.9902245 hartree.

Table S3 (Continued)
TS2

atom	x (Å)	y (Å)	z (Å)	displacement vector of the imaginary frequency		
				mode atom		
				x	y	z
O	2.705419	0.517712	-0.269942	-0.05	-0.01	0.05
O	1.801397	2.438047	-1.946321	0.00	0.01	-0.01
O	1.439550	2.749359	0.887151	0.00	-0.02	0.00
O	0.126819	3.075674	0.284802	0.01	-0.01	0.00
O	-0.695502	1.243291	-1.511269	0.02	-0.01	0.00
O	0.150319	0.042588	-1.603332	0.02	-0.01	0.06
O	1.546104	-1.956460	-0.072610	0.00	0.06	0.03
O	-0.593413	-2.489273	1.733217	0.02	-0.02	-0.01
O	-0.647269	-2.725306	-1.170312	0.00	0.00	0.02
O	-1.893348	-2.047391	-0.791534	-0.01	0.01	0.04
O	0.288995	0.176063	0.990976	-0.22	0.17	0.15
O	3.271370	-1.064030	1.956594	-0.01	0.00	0.00
Se	3.002446	-1.084405	0.335834	0.02	0.00	0.00
W	1.016625	1.618241	-0.652945	0.00	0.02	-0.02
W	-0.399162	-1.493951	0.347002	0.00	-0.05	-0.02
O	4.203836	-1.737559	-0.577826	0.00	0.00	-0.01
O	-1.559294	0.064345	0.872738	0.83	0.07	0.07
C	-4.942273	-1.922755	-1.967923	-0.01	-0.01	-0.02
C	-5.047575	-0.659948	-1.534784	-0.01	0.00	-0.02
C	-3.868802	0.194818	-1.177430	-0.05	0.02	0.00
S	-3.625393	0.249857	0.661983	-0.31	0.05	0.00
O	-3.319045	2.058783	0.898861	0.03	-0.01	-0.02
O	-3.197077	2.398571	2.353656	0.01	-0.01	-0.01
O	-2.028415	2.698629	2.932088	-0.01	0.01	0.02
H	-5.826658	-2.510901	-2.204924	-0.01	-0.03	0.02
H	-3.968644	-2.398313	-2.058534	-0.01	0.00	-0.04
H	-6.034825	-0.213156	-1.401099	-0.02	-0.03	0.03
H	-4.001420	1.230350	-1.504883	-0.10	0.01	-0.05
H	-2.933767	-0.192789	-1.585344	-0.05	0.06	-0.02
H	-4.162475	2.583350	0.432842	0.13	0.15	-0.02
H	-2.387871	2.267531	0.365695	0.07	-0.05	0.05
H	-4.115650	2.372250	2.943194	0.00	-0.04	-0.02
H	-1.977785	2.932808	3.993665	-0.03	0.00	0.02
H	-1.100818	2.698411	2.363606	-0.01	0.05	0.04

Charge = -2; E = -1830.786619 hartree.

Table S3 (Continued)
TS3

atom	x (Å)	y (Å)	z (Å)	displacement vector of the imaginary frequency		
				mode atom		
				x	y	z
O	3.162309	0.489702	-0.197616	-0.04	-0.01	-0.02
O	3.629778	-1.893904	1.056583	0.00	0.00	0.00
O	2.855387	-1.814118	-1.712462	-0.01	0.01	0.00
O	2.004031	-2.854438	-1.093400	0.00	0.01	0.00
O	0.821474	-2.003393	1.179673	0.01	0.01	0.00
O	1.050856	-0.588073	1.506114	0.00	0.01	-0.04
O	1.022151	2.056737	0.453366	0.02	-0.03	-0.03
O	-1.512580	1.798497	-0.813851	0.02	0.02	0.02
O	-0.927937	1.411030	2.012431	0.00	0.00	-0.02
O	-1.783406	0.291789	1.604531	-0.01	-0.01	-0.01
O	-1.032372	-0.991805	-0.702853	0.68	0.35	-0.14
O	0.592422	-0.192548	-1.008700	-0.14	-0.17	-0.14
O	2.400407	2.524075	-1.944340	0.00	-0.01	0.00
Se	2.569280	2.110179	-0.364327	0.01	0.01	0.00
W	2.308406	-1.354466	0.098309	0.01	-0.01	0.01
W	-0.539153	0.790543	0.185350	-0.02	0.02	0.02
O	3.532358	3.090976	0.536226	0.00	0.00	0.00
C	-2.139250	-2.221840	0.127105	-0.41	-0.25	0.08
C	-3.090622	-1.691949	-0.719873	-0.10	-0.15	0.08
C	-4.003386	-0.567651	-0.365413	-0.02	-0.03	0.00
S	-5.774978	-1.157118	-0.365536	-0.01	0.01	0.00
C	-6.615010	0.475172	-0.136945	-0.01	0.00	0.00
C	-8.049957	0.387385	-0.554217	0.00	0.01	0.00
C	-9.097307	0.544272	0.264859	0.00	0.00	0.00
H	-1.581014	-3.106753	-0.152969	0.00	0.06	-0.08
H	-2.086935	-1.928802	1.170309	-0.11	-0.03	0.00
H	-3.150704	-2.069577	-1.737977	-0.03	-0.04	0.03
H	-3.934961	0.232924	-1.109779	0.03	-0.05	-0.01
H	-3.759824	-0.157983	0.616559	-0.03	-0.02	0.00
H	-6.080581	1.197818	-0.765194	-0.01	0.00	0.00
H	-6.526637	0.796914	0.905484	-0.01	0.01	0.00
H	-8.222908	0.164235	-1.607380	0.00	0.00	0.00
H	-10.119472	0.468690	-0.097320	-0.01	-0.01	0.00
H	-8.963372	0.752109	1.324426	0.00	0.00	0.00

Charge = -2; E = -1830.777874 hartree.

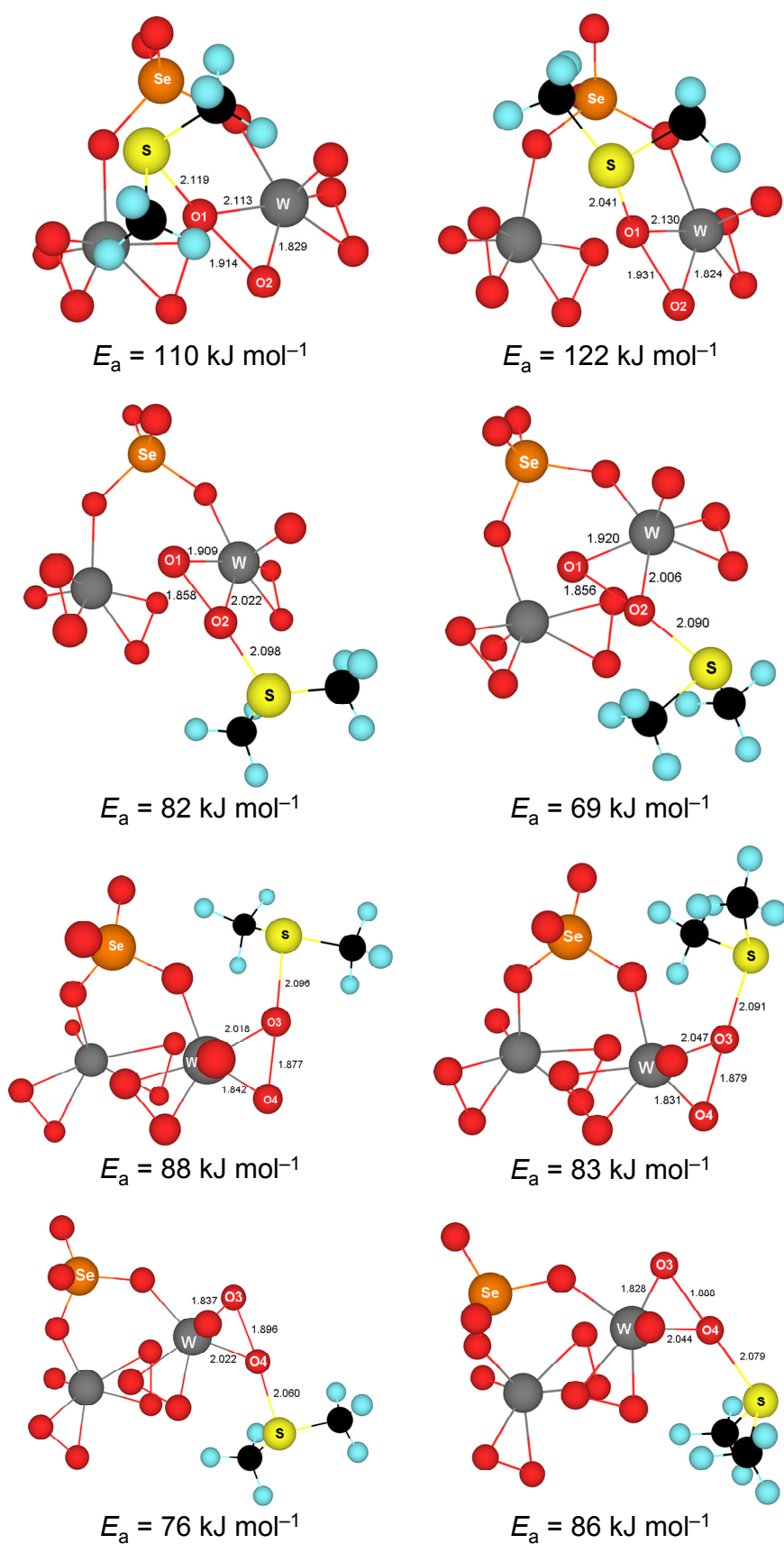


Figure S1 Transition-state structures and the corresponding activation barriers for the oxidation of dimethyl sulfide (bond lengths in Å). Orange, gray, red, black, and light blue balls represent selenium, tungsten, oxygen, carbon, and hydrogen atoms, respectively.

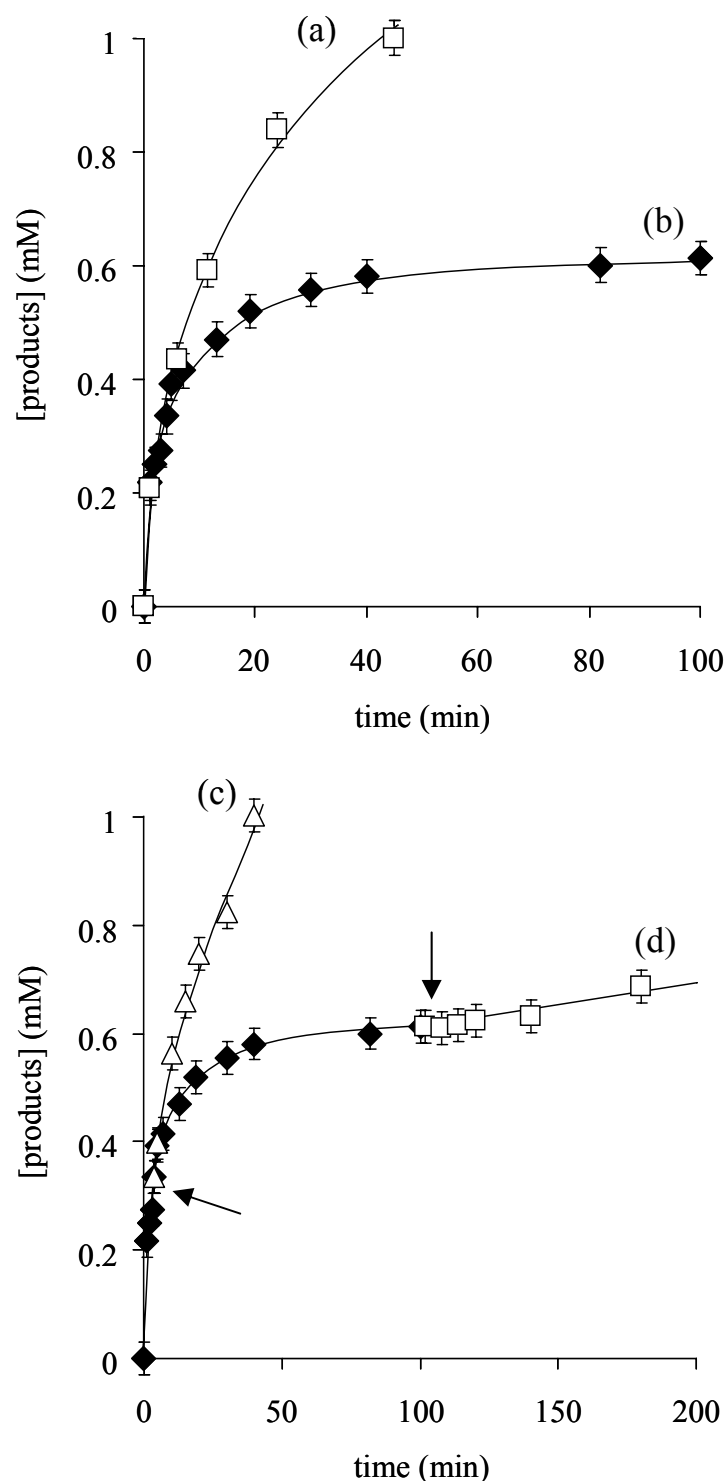


Figure S2 Reaction profiles for the (a) catalytic and (b, c, and d) stoichiometric oxidation of diphenyl sulfide by **I**. (a) Reaction conditions: **I** (0.31 mM), diphenyl sulfide (3.12 mM), 30% aqueous H₂O₂ (3.12 mM) CH₃CN (3.2 mL), 233 K. (b) Reaction conditions: **I** (0.31 mM), diphenyl sulfide (3.12 mM), CH₃CN (3.2 mL), 233 K. (c) After 4 min (i.e., one equivalent of the active oxygen with respect to **I** was transferred), 30% aqueous H₂O₂ (3.12 mM) was added as indicated by an arrow. (d) After 100 min (i.e., two equivalents of the active oxygen with respect to **I** were transferred), 30% aqueous H₂O₂ (3.12 mM) was added as indicated by an arrow. Yield and selectivity were determined by LC. [Products] (mM) = ([sulfoxide] + 2×[sulfone]) (mM).

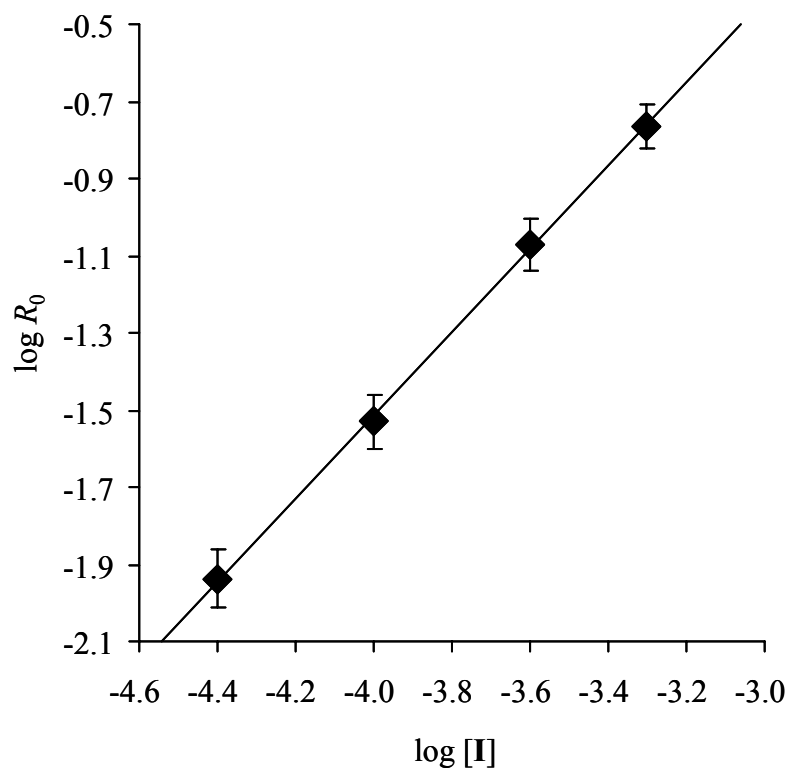


Figure S3 Dependence of the reaction rate on the concentration of **I**: **I** (0.04–0.50 mM), thioanisole (50 mM), H₂O₂ (50 mM), H₂O (250 mM), CH₃CN (6 mL), 273 K. R_0 values were determined from the reaction profiles at low conversions (<20%) of both thioanisole and H₂O₂. Slope = 1.08 ($R^2 = 0.99$).