

Harnessing Applied Potential to Oxidation in Water

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Supplementary Material

General Experimental Detail

All infrared spectra were obtained using a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer; thin film spectra were acquired using sodium chloride plates.

All ¹H and ¹³C NMR spectra were measured at 400.13 and 100.62 MHz using a Bruker DPX 400 MHz spectrometer. The solvent used for NMR spectroscopy was CDCl₃ (unless stated otherwise) using TMS (tetramethylsilane) as the internal reference.

All chromatographic manipulations used silica gel as the adsorbent. Reactions were monitored using thin layer chromatography (TLC) on aluminium backed plates with Merck Kieselgel 60 F254 silica gel. TLC visualised by UV radiation at a wavelength of 254 nm, or stained by exposure to an ethanolic solution of phosphomolybdic acid (acidified with concentrated sulphuric acid), followed by charring where appropriate. Purification by column chromatography used Merck Kieselgel 60 H silica adsorbent.

Electrolyses were carried out with a ISO-TECH IPSO1603D power source in a three-neck round bottom flask (100 mL) with embedded BDD disc electrode (3.0 cm² Diafilm, Windsor Scientific) and a platinum wire counter electrode (1 mm diameter, approximately 0.2 cm²). An ultra-turrax high shear mixer (6500 rpm) was used for agitation.

General Procedure for Oxidation of Sulfides with *ex situ* Electrochemically-Generated Hypochlorite

In an undivided 100 mL-round-bottom-flask cell fitted with a boron-doped diamond anode as the working electrode and a platinum wire cathode as the counter electrode, aqueous 1.0 M Na₂CO₃·10 H₂O (100 mL) was stirred (6500 rpm, ultra-turrax) while being cooled to 0 °C in an ice bath. A fixed potential of 10.0 V was applied for 1 h, which resulted in a constant current of approximately 0.3 A (ca. 30% current efficiency corresponding to approximately 1.5 mmol oxidant being generated). After this time, the solution was brought to pH 6 by careful addition of aq. HCl (5 M).

The sulphide substrate (1.0 mmol) was added, and the reaction mixture stirred at room temperature. Extraction was carried out with ethyl acetate (3 x 50 mL), and the combined organic solutions washed with brine (50 mL), dried (MgSO₄), filtered and the solvents removed under reduced pressure. The products were approximately 95% pure by LC/MS analysis. Analytically pure samples could be obtained by column chromatography eluting with light petroleum:ethyl acetate (20:1).

Sulfoxide from thioanisole¹

Yellow oil; ν_{\max} (cm⁻¹) 3054, 2996, 2911, 1657, 1581, 1038, 956; ¹H NMR (400 MHz, CDCl₃): δ_{H} 2.71 (3 H, s), 7.48-7.54 (3 H, m), 6.64 (2 H, dd, *J* 10.4, 9.6 Hz) ppm; ¹³C NMR (100 MHz, CDCl₃): δ_{C} 43.89, 123.4, 129.3, 133.6, 145.6.

Sulfoxide from 4-fluorothioanisole²

Yellow oil; ν_{\max} (cm⁻¹) 3096, 3062, 2996, 1655, 1641, 1046 (S=O), 958, 834 (C-F); ¹H NMR (400 MHz, CDCl₃): δ_{H} 2.73 (3 H, s), 7.21-7.26 (2 H, m), 7.66-7.69 (2 H, m) ppm; ¹³C NMR (100 MHz, CDCl₃): δ_{C} 44.0, 117.0, 125.5, 130.1, 141.2.

Sulfoxide from 2-methoxythioanisole³

Yellow oil; ν_{\max} (cm⁻¹) 3009, 2941, 2918, 2841, 1161, 1037, 960, 758; ¹H NMR (400 MHz, CDCl₃): δ_{H} 2.76 (3 H, t, *J* 2.12 Hz), 3.87 (3 H, t, *J* 2.12 Hz), 6.92 (1 H, dd, *J* 0.8, 8.4 Hz), 7.16 (1 H, ddd, *J* 0.8, 7.6, 14.8 Hz), 7.44 (1 H, ddd, *J* 2.0, 8.4, 16.0 Hz), 7.80 (1 H, dd, *J* 1.6, 7.6 Hz) ppm; ¹³C NMR (100 MHz, CDCl₃): δ_{C} 41.1, 55.6, 110.6, 121.5, 124.3, 131.9, 132.9, 154.7.

Sulfoxide from ethyl vinyl sulfide⁴

Yellow oil; ν_{\max} (cm⁻¹) 2950, 2891, 1657, 1438, 1019, 743; ¹H NMR (400 MHz, CDCl₃): δ_{H} 1.29 (3 H, t, *J* 7.2 Hz), 2.65 (1 H, dq, *J* 7.4 Hz), 2.85 (1 H, dq, *J* 7.4 Hz), 5.99 (1 H, d, *J* 10.0 Hz), 6.10 (1 H, d, *J* 16.8 Hz), 6.58 (1 H, dd, *J* 10.0 & 16.8 Hz) ppm; ¹³C NMR (100 MHz, CDCl₃): δ_{C} 5.6, 46.5, 48.6, 122.6, 139.8.

Sulfoxide from furfuryl methyl sulfide⁵

Yellow oil; ν_{\max} (cm⁻¹) 2972, 2916, 1423, 1033, 933, 744; ¹H NMR (400 MHz, CDCl₃): δ_{H} 2.52 (3 H, s), 4.06 (2 H, q, *J* 13.92 Hz), 6.40 (2 H, m), 7.39 (1 H, dd, *J* 2.0 Hz) ppm; ¹³C NMR (100 MHz, CDCl₃): δ_{C} 37.9, 52.2, 111.2, 143.5, 143.9.

General Procedure for Epoxidation of Olefins with *in situ* Electrochemically-Generated Hypochlorite

A solution of 1.0 M Na₂CO₃·10H₂O was brought to pH 6 by careful addition of aq. HCl (5 M), and placed into an undivided cell fitted with a boron-doped diamond anode as the working electrode, and a platinum wire cathode as the counter electrode. Olefin (1.0 mmol) was added, and the mixture stirred (6500 rpm, ultra-turrax) and cooled to 0 °C. A fixed potential of 10.0 V was applied (approximately 0.3 A current) until complete conversion to epoxide was observed by TLC. Extraction was carried out with ethyl acetate (3 x 50 mL), and the combined organic layers washed with brine (50 mL), dried (MgSO₄), filtered, and the solvents removed under reduced pressure. The products were approximately 95% pure by LC/MS analysis. Analytically pure samples could be obtained by column chromatography, eluting with light petroleum:ethyl acetate (20:1).

1-Phenylcyclohexene oxide⁶

Colourless oil; ν_{\max} (cm⁻¹) 3084, 1602, 1495, 1446, 1359, 1249, 1173, 1132, 1079, 1030, 993, 974; ¹H NMR (400 MHz, CDCl₃): δ_{H} 1.62-1.66 (2 H, m), 1.73-1.77 (2 H, m), 2.19 (2 H, d, *J* 2.4 Hz), 2.39 (2 H, d, *J* 2.0 Hz), 3.97 (1 H, s), 7.13-7.16 (1 H, m), 7.25-7.29 (2 H, m), 7.34-7.36 (2 H, m) ppm; ¹³C NMR (100 MHz, CDCl₃): δ_{C} 19.8, 20.1, 24.7, 28.2, 60.1, 61.8, 125.3, 127.1, 128.2, 142.8.

trans-Stilbene oxide⁶

Colourless solid; m.p. 66-67 °C; ν_{\max} (film)/cm⁻¹ 3020, 2924, 1658, 1597, 1450, 1381, 1273, 1172, 1072, 1126; ¹H NMR (400 MHz, CDCl₃): δ_{H} 3.84 (2 H, s), 7.28-7.37 (10 H, m) ppm; ¹³C NMR (100 MHz, CDCl₃): δ_{C} 62.94, 125.61, 128.56, 128.66, 137.19.

trans- α -Methylstilbene oxide⁶

Colourless oil; ν_{\max} (cm⁻¹) 3061, 1602, 1495, 1449, 1381, 1279, 1157, 1118, 1065, 1027, 980; ¹H NMR (400 MHz, CDCl₃): δ_{H} 1.46 (3 H, s), 3.96 (1 H, s), 7.23-7.46 (10 H, m) ppm; ¹³C NMR (100 MHz, CDCl₃): δ_{C} 16.67, 63.05, 67.09, 125.66, 126.88, 127.80, 127.90, 128.44, 129.02, 135.88, 142.28.

1,2-Dihydronaphthalene oxide⁶

Colourless oil; ν_{\max} (film)/cm⁻¹ 3052, 3022, 2931, 2849, 1655, 1495, 1315, 1127, 936; ¹H NMR (400 MHz, CDCl₃): δ_{H} 1.66-1.75 (1 H, m), 2.32-2.39 (1 H, m), 2.47-2.52 (1 H, m), 2.70-2.79 (1 H, m), 3.68 (1 H, t, *J* 4.0 Hz), 3.80 (1 H, d, *J* 4.0 Hz), 7.05 (1 H, d, *J* 7.2 Hz), 7.13-7.24 (2 H, m), 7.33-

7.37 (1 H, dd, J 16.0, 7.2 Hz) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 21.73, 24.16, 53.44, 55.06, 126.05, 128.14, 129.73, 132.45, 136.60.

Styrene oxide⁷

Colourless oil; ν_{max} (film)/ cm^{-1} 3034, 2916, 1600, 1494, 1452, 1390, 1255, 1199, 875, 699; ^1H NMR (400 MHz, CDCl_3): δ_{H} 2.78 (1 H, dd, J 2.8, 5.6 Hz), 3.12 (1 H, dd, J 4.0, 5.6 Hz), 3.84 (1 H, dd, J 2.4, 4.0 Hz), 7.25-7.35 (5 H, m) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 51.20, 52.39, 125.48, 127.92, 129.75, 137.49.

4-Chlorostyrene oxide⁸

Colourless oil; ν_{max} (film)/ cm^{-1} 3034, 2916, 1600, 1494, 1452, 1390, 1255, 1199, 1072, 875, 757, 699; ^1H NMR (400 MHz, CDCl_3): δ_{H} 2.74 (1 H, dd, J 2.8, 5.6 Hz), 3.13 (1 H, dd, J 4.0, 5.2 Hz), 3.82 (1 H, dd, J 4.0, 6.8 Hz), 7.19 (2 H, d, J 8.4 Hz), 7.30 (2 H, d, J 8.4 Hz) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 51.24, 51.78, 127.38, 128.86, 130.90, 136.17.

4-Fluorostyrene oxide⁸

Colourless oil; ν_{max} (film)/ cm^{-1} 3034, 2916, 1601, 1494, 1453, 1391, 1256, 1200, 1072, 876, 756, 699; ^1H NMR (400 MHz, CDCl_3): δ_{H} 2.75 (1 H, dd, J 2.4, 5.2 Hz), 3.13 (1 H, dd, J 4.0, 5.6 Hz), 3.84 (1 H, dd, J 2.8, 3.6 Hz), 7.03 (2 H, dd, J 2.0, 8.8 Hz), 7.24 (2 H, dd, J 2.0, 8.8 Hz) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 51.18, 51.56, 115.38, 115.59, 127.16, 127.24, 163.93, 164.79.

2-Chlorostyrene oxide⁹

Colourless oil; ν_{max} (film)/ cm^{-1} 3061, 2997, 1698, 1593, 1475, 1437, 1153, 1250, 1125, 1055, 1033, 879, 750; ^1H NMR (400 MHz, CDCl_3): δ_{H} 2.66 (1 H, dd, J 2.4, 5.6 Hz), 3.19 (1 H, dd, J 4.4, 5.6 Hz), 4.21 (1 H, dd, J 2.4, 4.0 Hz), 7.15-7.30 (4 H, m) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 50.08, 50.74, 125.68, 126.42, 133.84, 135.56.

trans-4-Octene oxide¹⁰

Colourless Oil; ν_{max} (film)/ cm^{-1} 2958, 1771, 4463, 1215, 910; ^1H NMR (400 MHz, CDCl_3): δ_{H} 0.86-0.90 (6 H, m), 1.41-1.55 (8 H, m), 2.63-2.67 (2 H, m) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 13.97, 19.37, 34.20, 58.48.

4-Bromobutene oxide¹¹

Colourless oil; ν_{max} (film)/ cm^{-1} 3052, 2994, 1725, 1431, 1262, 1217, 1073, 909; ^1H NMR (400

MHz, CDCl_3): δ_{H} 2.00-2.10 (1 H, m), 2.10-2.21 (1 H, m), 2.61 (1 H, dd, J 2.8, 4.8 Hz), 2.85 (1 H, m), 3.08-3.12 (1 H, m), 3.52 (2 H, dd, J 6.0, 7.2 Hz) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 28.99, 35.68, 47.08, 50.76.

4-Methoxystyrene oxide¹²

Colourless oil; ν_{max} (film)/ cm^{-1} 3002, 2956, 1611, 1461, 1248, 872, 835, 738, 702; ^1H NMR (400 MHz, CDCl_3): δ_{H} 3.65 (1 H, dd, J 3.6, 11.2 Hz), 3.69 (1 H, dd, J 3.6, 11.2 Hz), 3.80 (3 H, s), 4.84 (1 H, dd, J 3.6, 8.8 Hz), 6.90 (2 H, d, J 8.8 Hz), 7.30 (2 H, d, J 8.8 Hz) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 50.88, 55.31, 73.71, 114.04, 127.33, 132.04, 159.66.

trans- β -Methylstyrene oxide¹³

Colourless oil; ν_{max} (film)/ cm^{-1} 3062, 2984, 1600, 1496, 1459, 1250, 1020, 952, 858, 743, 697; ^1H NMR (400 MHz, CDCl_3): δ_{H} 1.44 (3 H, d, J 4.2 Hz), 3.03 (1 H, dq, J 2.0, 4.8 Hz), 3.57 (1 H, d, J 2.0 Hz), 7.17-7.33 (5 H, m) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 17.90, 59.02, 59.51, 125.54, 128.26, 128.45, 137.74.

Voltammetry

Further investigation of the hypochlorite formation was possible by voltammetric detection of the electrolysis product at the platinum wire electrode (see Figure 1, data obtained under ultra-turrax agitation with 6500 rpm) and comparison with the current for hypochlorite reduction for a commercial calibration standard. It can be seen that typically 1.5 mmol hypochlorite in 100 mL solution are produced after 1h electrolysis with 0.3 A current (current efficiency approximately 30% after one hour). Note that current yield is better in the early stages of the electrolysis with approx. 1 mmol hypochlorite produced in 20 minutes.

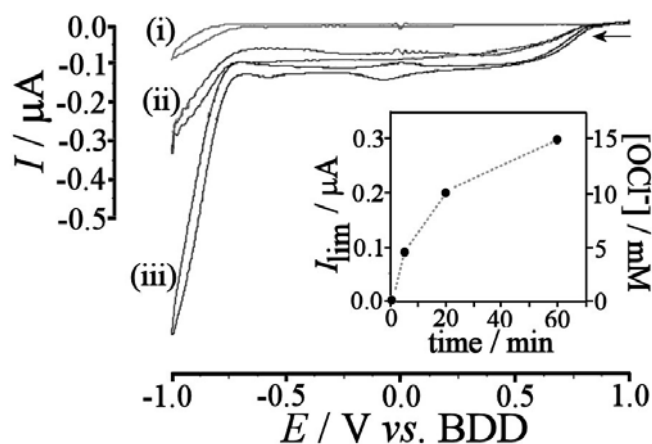


Figure 1. Voltammetric determination (scan rate 0.1 Vs^{-1} , temperature 0°C) of hypochlorite in aqueous 1 M Na_2CO_3 (pH adjusted to 6 with 5 M HCl) employing hypochlorite reduction at a

platinum wire electrode (approximately 0.2 cm²) with ultra-turrax agitation (6500 rpm): (i) before electrolysis, (ii) 5 minute electrolysis, (iii) 5 mM hypochlorite, inset shows plot of the observed limiting current (and the corresponding hypochlorite concentration) versus electrolysis time.

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