

Isolation and characterization of charge-tagged phenylperoxyl radicals in the gas phase: direct evidence for products and pathways in low temperature benzene oxidation.

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Supplementary Information

Synthesis and characterization of materials

N,N,N-trimethyl-4-((2-thioxopyridin-1(2*H*))-yloxy)benzenaminium iodide

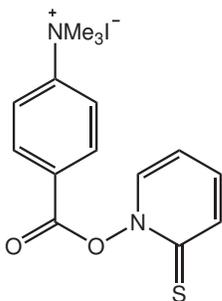
The reaction and product purification were conducted under minimal lighting in order to minimize decomposition of the photolabile Barton ester. In a 10 mL reaction vial were placed 4-carboxy-*N,N,N*-trimethylbenzenaminium iodide (1.000 g, 3.256 mmol) and *N*-hydroxypyridine-2-thione (0.4550 g, 3.578 mmol) and 6 mL of dry DMF was added. The mixture was magnetically stirred

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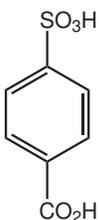
until the solids dissolved, then *N,N'*-dicyclohexylcarbodiimide (0.7494 g, 3.632 mmol) was added in one portion, followed by a few crystals of 4,4-dimethylaminopyridine. The vial was capped to exclude moisture and the mixture was stirred in the dark for 15 hours, then quenched with the addition of 0.2 mL of water. After a further 15 minutes, more water (20 mL) was added and the mixture was filtered and the precipitate washed several times with water (total volume 50 mL). Solvents were evaporated from the filtrate first by rotary evaporation (bath temperature 40°C), then under high vacuum to give a crude product of mass 1.5339 g. Recrystallisation from MeOH/hexane (three crops) afforded a higher quality product of mass 0.9797 g (72.3%). An analytical sample was obtained by dissolving 100 mg in 10 mL H₂O, washing three times with CH₂Cl₂, then filtering and evaporation of solvent under reduced pressure to give a crop of pale yellow crystals of mass 91.91 mg.



¹H NMR (500 MHz, *d*₆-DMSO): δ 3.73 (s, 9H, Me₃ x 3 (9k)), 7.01 (t, 1H, d), 7.52 (t, 1H, c), 7.62 (d, 1H, e), 8.30 (d, 2H, i), 8.38 (d, 2H, h), 8.55 (d, 1H, b). ¹³C NMR (125 MHz, *d*₆-DMSO): δ 56.4 (3k), 113.5 (d), 122.0 (2i), 127.2 (g), 131.8 (2h), 135.5 (c), 135.7 (b), 139.6 (e), 151.6 (j), 160.8 (f), 174.3 (a). FTIR (neat): 3423 m, 1768 s, 1711 w, 1606 m, 1529 m, 1447 s, 1412 m, 1281 w, 1256 s, 1227 w, 1202 w, 1169 m, 1139 m, 1085 m, 1029 vs, 940 w, 845 asym, 821 w, 761 m, 740 w. ESI-MS (-ve): 127.0. ESI-MS (+ve): 289.2. HRESI-MS (+ve): C₁₅H₁₇N₂O₂S⁺ requires 289.1011. Found 289.0999.

4-Sulfobenzoic acid

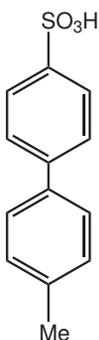
4-Toluenesulfonyl chloride (1.009 g, 5.292 mmol) was dissolved in 10 mL water and KMnO_4 (1.658 g, 10.49 mmol) and KOH (0.319 g, 5.69 mmol) were added. The mixture was stirred and heated at 90°C overnight, then cooled, filtered and the precipitate rinsed with a few mL of water. The filtrate was rotary-evaporated to dryness, taken up in 3 mL water and the resultant suspension filtered to remove the precipitate. After diluting the filtrate with a few more mL water, 2 mL of concentrated H_2SO_4 was added and the mixture heated until all solid dissolved. Crystallisation occurred upon cooling and the white crystals of the product were collected by filtration and washed with a few mL of cold, dilute H_2SO_4 . Drying under vacuum afforded 0.577 g (2.85 mmol, 54%) of 4-sulfobenzoic acid.



^1H NMR (500 MHz, d_6 -DMSO): δ 2.51 (s, 1H, SO_3H), 7.72 (d, 2H, 2b), 7.92 (d, 2H, 2c). ^{13}C NMR (125 MHz, d_6 -DMSO): δ 125.9 (2b), 129.2 (2c), 130.9 (d), 152.0 (a), 167.1 (CO_2H).

4'-Methylbiphenyl-4-sulfonic acid

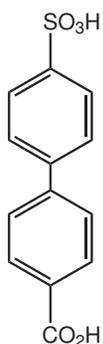
A stirred solution of 4-phenyltoluene (100 mg, 0.594 mmol) in 0.2 mL CH_2Cl_2 was placed under nitrogen and cooled to -10°C . Chlorosulfonic acid (3.0 mL of a 0.614 M solution in CH_2Cl_2 , 1.8 mmol) was added dropwise over 3 min, then the solvent was removed under vacuum. The resulting white solid was taken up in a small amount of 0.1 M KOH solution, filtered to remove any precipitate, then reacidified with concentrate H_2SO_4 . Upon cooling, a white precipitate was formed, which was filtered off and washed with a small amount of cold, dilute H_2SO_4 . After drying under vacuum, the yield of 4'-methylbiphenyl-4-sulfonic acid was 50.03 mg (0.202 mmol, 34%).



^1H NMR (500 MHz, D_2O): δ 2.43 (s, 3H, CH_3), 7.41 (d, 2H, 2d), 7.67 (d, 2H, 2c), 7.81 (d, 2H, 2b), 7.90 (d, 2H, 2a).

4'-Sulfobiphenyl-4-carboxylic acid

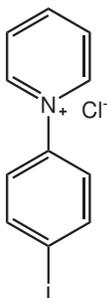
A solution of 4'-methylbiphenyl-4-sulfonic acid (50.0 mg, 0.202 mmol) in 2 mL H₂O was treated with KMnO₄ (67.3 mg, 0.426 mmol) and heated at reflux overnight. After cooling, 2 mL H₂O and KOH (65mg, 1.2mmol) were added and the resulting suspension was filtered through Celite, rinsing the precipitate with a few mL H₂O. The filtrate was acidified with 2 mL concentrated H₂SO₄ and the volume reduced under vacuum to approximately 6 mL. Cooling of the mixture afforded white crystals of the product which were filtered and washed with 1 mL cold H₂O. Drying under vacuum gave the desired product in a yield of 48.3 mg (0.174 mmol, 86%).



¹H NMR (500 MHz, *d*₆-DMSO): δ 2.53 (s, 1H, SO₃H), 7.74 (m, 4H, 2b&2c), 7.83 (d, 2H, 2f), 8.04 (d, 2H, 2g). ¹³C NMR (125 MHz, *d*₆-DMSO): δ 126.5 (2C), 126.7 (2C), 127.2 (2C), 129.9, 130.3 (2C), 139.5, 144.1, 147.8, 167.5 (CO₂H).

***N*-(4-iodophenyl)pyridinium chloride**

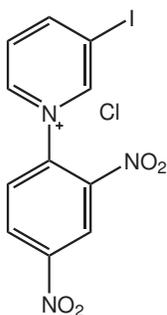
Prepared from *N*-(2,4-dinitrophenyl)pyridinium chloride and 4-iodoaniline as described by Zhao *et al.*¹



¹H NMR (500 MHz, *d*₆-DMSO): δ 8.61 (b, 1H), 8.45 (d, 7.3 Hz, 2H), 7.78 (d, 7.9 Hz, 2H), 7.31 (d, 7.9 Hz, 2H), 6.42 (t, 12 Hz, 1H). ¹³C NMR (500 Mhz, *d*₆-DMSO) δ 89.9, 110.04, 119.7, 128.0, 138.3, 138.7, 155.3.

3-iodo-*N*-(2,4-dinitrophenyl)pyridinium chloride

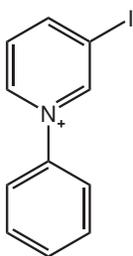
A stirred solution of 3-iodopyridine (1.002 g, 4.89 mmol) and 1-chloro-2,4-dinitrobenzene (0.999 g, 4.93 mmol) in acetone (5 mL) was heated at reflux for 24 hours. The reaction mixture was cooled and the resulting precipitate filtered, then washed with petroleum ether, to yield a pale brown powder. The resulting filtrate was placed under vacuum to remove solvent, then a further 5 mL acetone added and the reaction and workup repeated to yield further product (0.561 g, 28 %).



^1H NMR (500 MHz, d_6 -DMSO): δ 9.79 (s, 1H), 9.42 (d, 5.9 Hz, 1H), 9.29 (d, 7.8 Hz, 1H), 9.11 (s, 1H), 8.95 (d, 8.8 Hz, 1H), 8.42 (d, 8.3 Hz, 1H), 8.20 (t, 7.1 Hz, 1H). ^{13}C NMR (500 Mhz, d_6 -DMSO) δ 156.1, 150.7, 149.2, 144.9, 142.8, 137.9, 131.9, 130.0, 128.2, 121.3, 96.1. ESI-MS (+ve): 372.

3-iodo-*N*-phenylpyridinium chloride

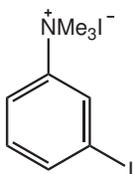
A stirred solution of 3-iodo-*N*-(2,4-dinitrophenyl)pyridinium chloride (101 mg, 0.248 mmol) and aniline (freshly distilled, 30 μ L, 0.315 mmol) in 80 % EtOH (1.5 mL) was heated at reflux for 16 hours. The reaction mixture was cooled and filtered. Solvent was removed from the resulting filtrate to yield a deliquescent dark red powder. Product was used by dilution of reaction mixture in methanol, without further isolation. For characterisation, the product was isolated on filter paper and heater under vacuum for 8 hours, then, while under nitrogen, d_6 -DMSO was added and NMR measurements performed.



^1H NMR (500 MHz, d_6 -DMSO): δ 9.66 (s, H), 9.34 (d, 5.9 Hz, H), 9.13 (d, 7.8 Hz, H), 8.55 (t, 7.9 Hz, H), 7.89 (m, 2H), 7.74 (m, 2H). ^{13}C NMR (500 MHz, d_6 -DMSO) δ 154.0, 149.7, 144.0, 142.2, 131.4, 130.1, 128.5, 125.0, 96.8. ESI-MS (+ve): 282.

3-iodo-*N,N,N*-trimethylbenzenaminium iodide

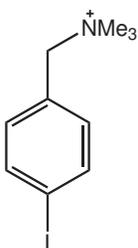
To a reaction vial was added 3-iodoaniline (132 mg, 0.603 mmol), K_2CO_3 (84 mg, 0.608 mmol) and 5 mL of dry MeOH. Methyl iodide (376 μ L, 6.04 mmol) was added and the vial capped and stirred at 50 °C for 18 hours. The solvent was then removed *in vacuo* to yield an orange powder. The crude material was dissolved in hot acetonitrile, filtered, then precipitated by addition of copious diethyl ether. The precipitate was filtered, then washed with diethyl ether and air dried to yield 180 mg (0.463 mmol, 77 %) of an off-white powder.



1H NMR (500 MHz, d_6 -DMSO): δ 8.30 (s, H), 7.99 (d, 7.9 Hz, H), 7.94 (d, 7.3 Hz, H), 7.40 (t, 7.9 Hz, H), 3.60 (s, 9H). ^{13}C NMR (300 MHz, d_6 -DMSO) δ 148.0, 138.9, 131.73, 128.8, 120.1, 96.4, 56.4. ESI-MS (-ve): 127. ESI-MS (+ve): 262.

***N*-(4-iodobenzyl)-*N,N,N*-trimethylammonium iodide**

To a reaction vial was added 4-iodobenzylamine.HCl (115 mg, 0.427 mmol), K₂CO₃ (61.8 mg, 0.447 mmol) and 5 mL of dry MeOH. Methyl iodide (270 μL, 4.34 mmol) was added and the vial capped and stirred at 50 °C for 4 days. The solvent was then removed *in vacuo* to yield an orange powder. The crude material was dissolved in hot acetonitrile, filtered, then precipitated by addition of copious diethyl ether. The precipitate was filtered, then washed with diethyl ether and air dried to yield 97.2 mg (0.241 mmol, 56.5%) of a light yellow powder.



¹H NMR (300 MHz, *d*₆-DMSO): δ 7.88 (d, 8.2 Hz, 2H), 7.33 (d, 8.2 Hz, 2H), 4.49 (s, 2H), 3.01 (s, 9H). ¹³C NMR (300 Mhz, *d*₆-DMSO) δ 138.0, 135.0, 128.0, 98.3, 67.2, 52.0. ESI-MS (-ve): 127. ESI-MS (+ve): 276.

Supplementary Mass Spectra

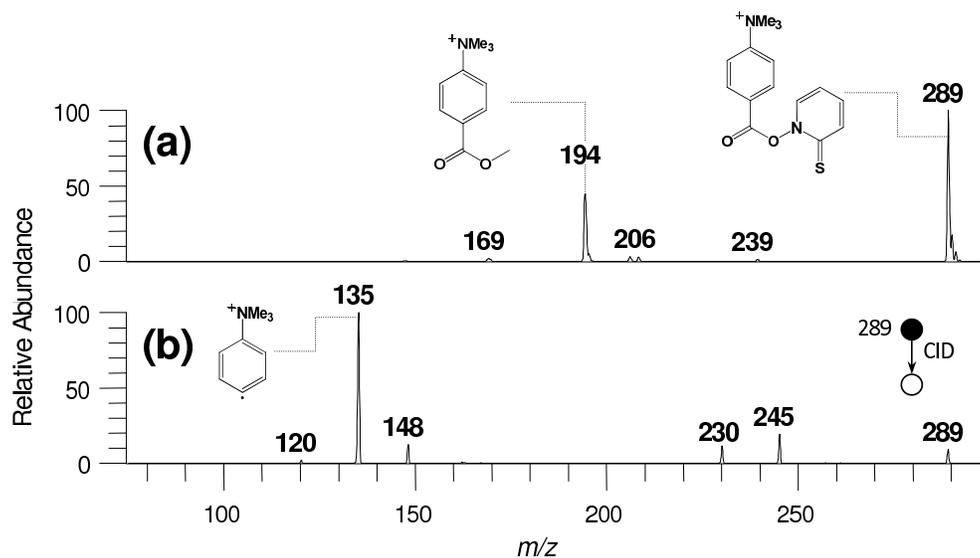


Figure S1: (a) ESI-MS spectrum of N,N,N -trimethyl-4-((2-thioxopyridin- N -yloxy)carbonyl)benzaminium cation in $H_2O/MeOH$ during positive mode electrospray resulting in an M^+ ion at m/z 289. (b) Isolation of M^+ and subsequent CID of m/z 289.

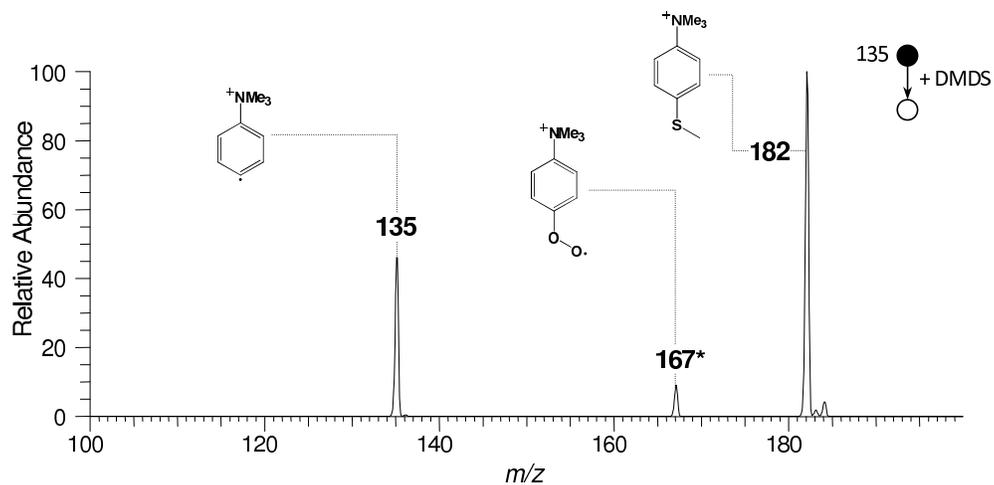


Figure S2: Isolation of the 4-(*N,N,N*-trimethylammonium)phenyl radical cation in the presence of 1,2-dimethyldisulfide.

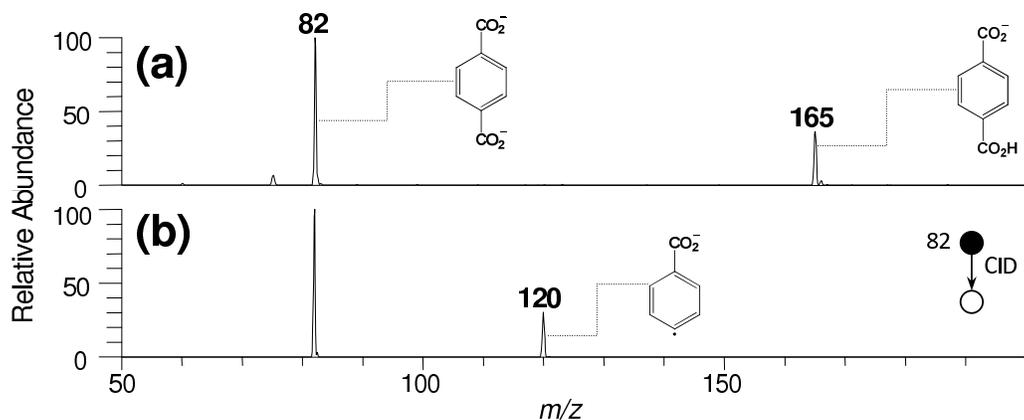


Figure S3: (a) ESI-MS of terephthalic acid in MeOH:NH₄OH during negative mode electrospray resulting in an [M - H]⁻ ion at *m/z* 165 and [M - 2H]²⁻ ion at *m/z* 82. (b) Isolation of [M - 2H]²⁻ and subsequent CID of *m/z* 82.

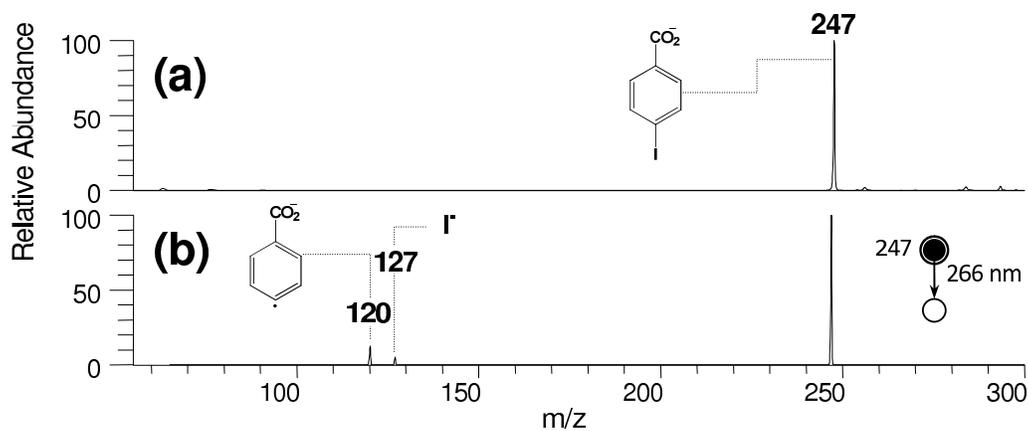


Figure S4: (a) ESI-MS of 4-iodobenzoic acid in MeOH:NH₄OH during negative mode electro-spray resulting in an $[M - H]^-$ ion at m/z 247. (b) Isolation of the $[M - H]^{1-}$ ion and subsequent laser pulse at 266 nm results in formation of 4-carboxylatophenyl radical anion (**2**) at m/z 120.

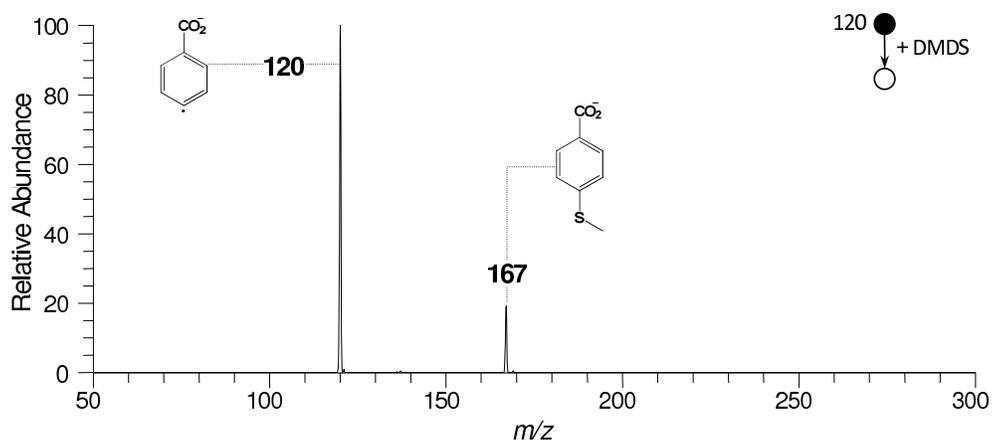


Figure S5: Isolation of the 4-carboxylatophenyl radical anion in the presence of 1,2-dimethyldisulfide.

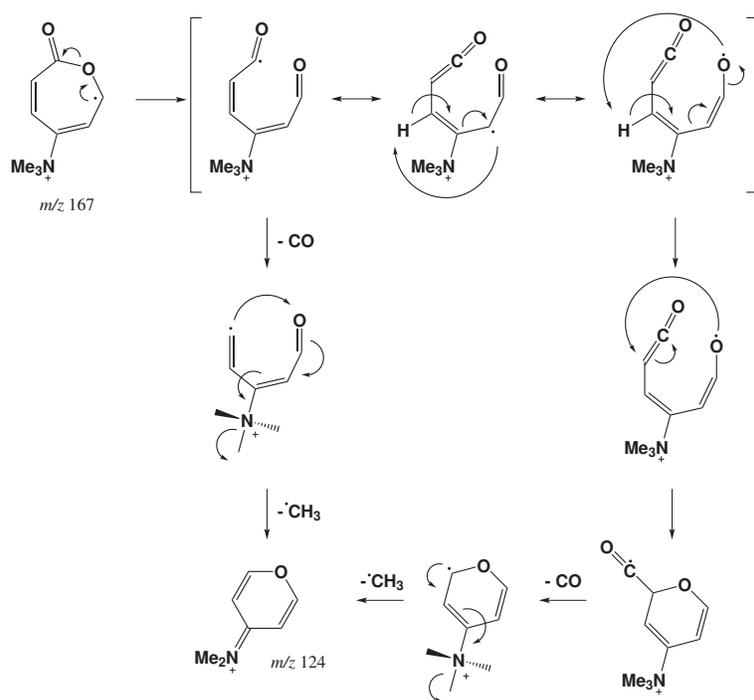


Figure S6: Putative mechanism for loss of 43 Da from the 4-(N,N,N-trimethylammonium)phenylperoxyl radical (**1-OO**).

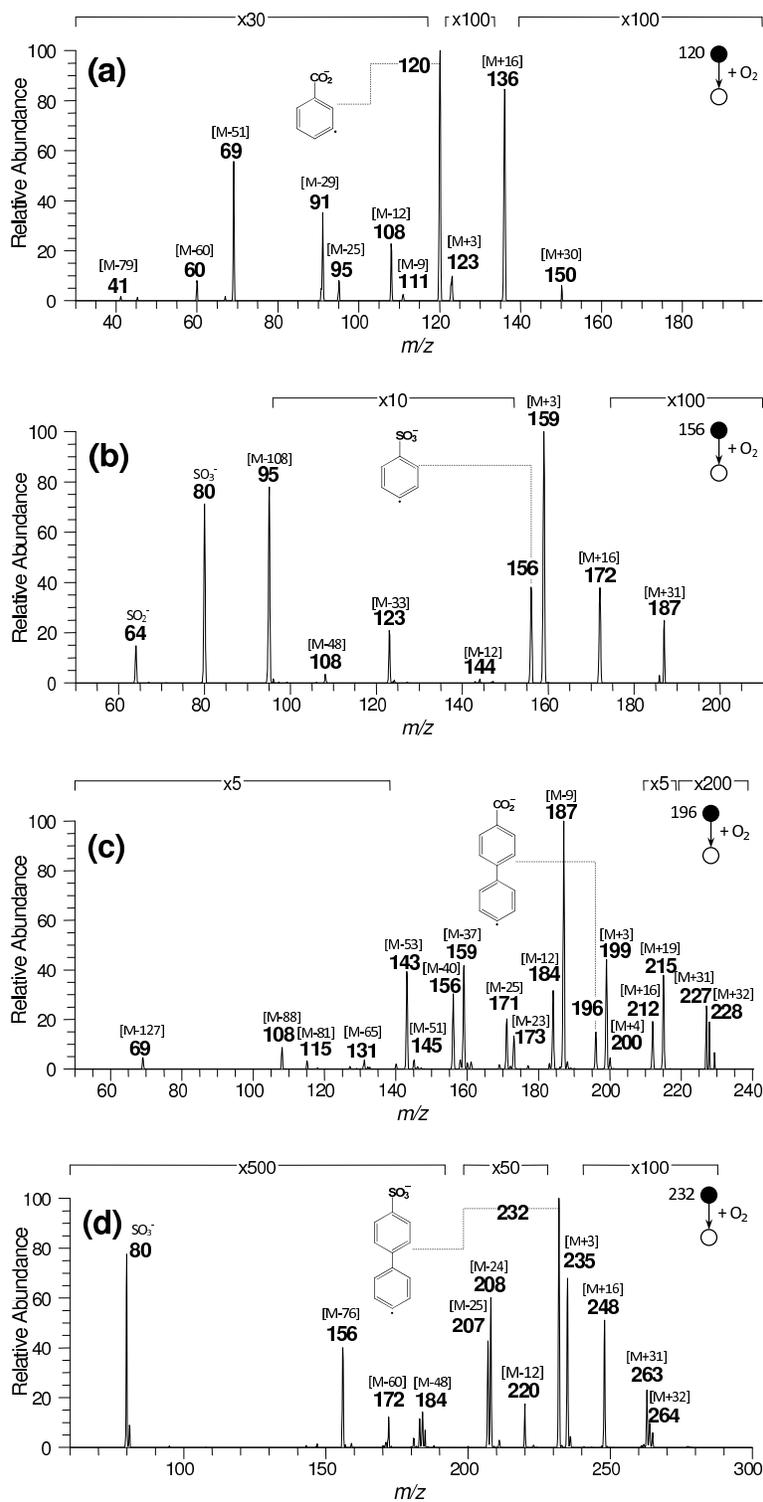


Figure S7: Isolation of the (a) 3-carboxylatophenyl, (b) 4-sulfonatophenyl, (c) 4-carboxylatobiphenyl, and (d) 4-sulfonatobiphenyl radical anions in the presence of O_2 .

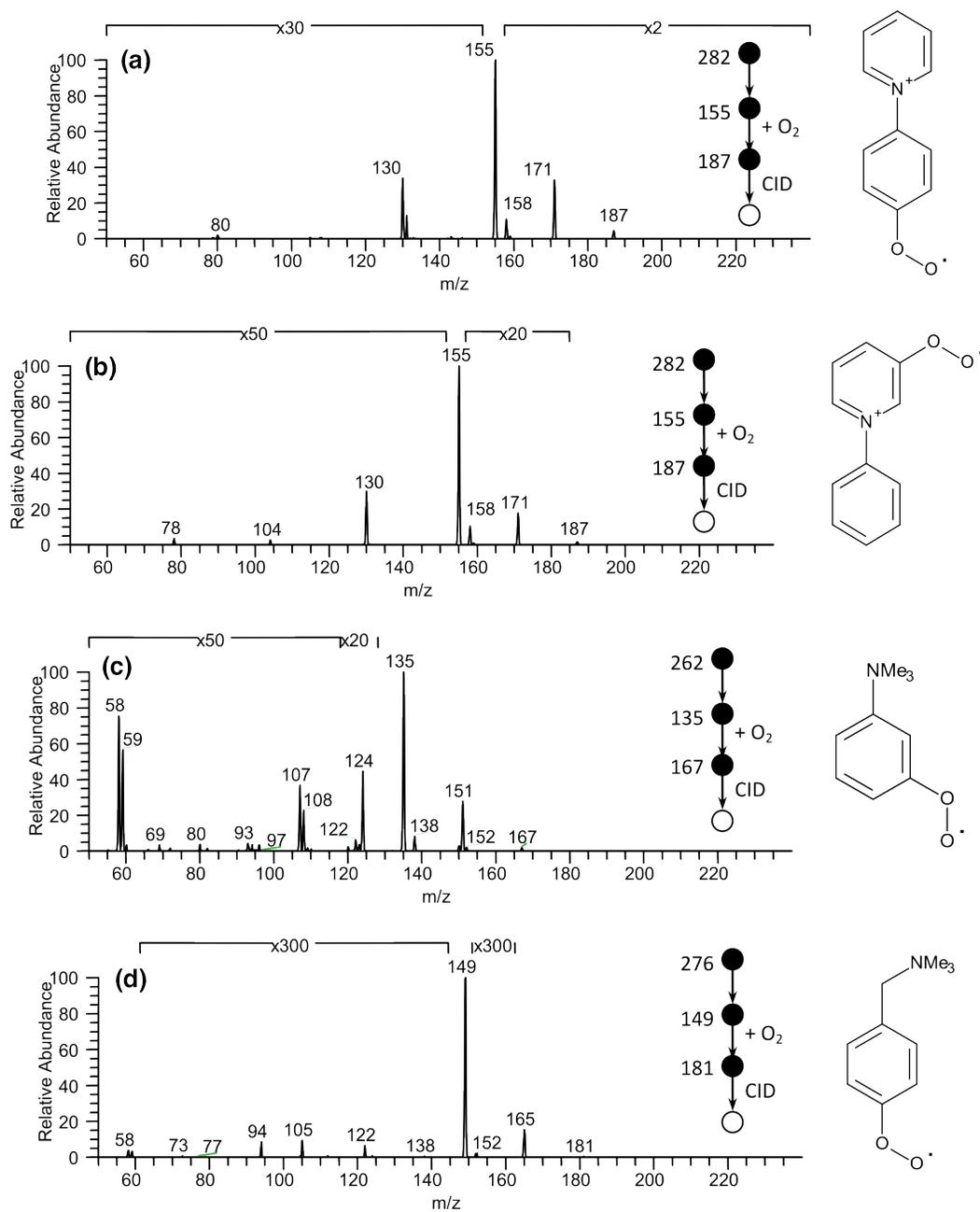


Figure S8: Representative CID spectra of a) *N*-(4-phenylperoxyl)pyridinium, b) *N*-phenylpyridinium-3-ylperoxyl c) 3-(*N,N,N*-trimethylammonium)phenylperoxyl and d) 4-(*N,N,N*-trimethylammoniummethyl)phenylperoxyl radical cations.

Table S1: Comparison of energies calculated at the B3LYP/6-311++G(d,p) level between O-O bond cleavage and attack by the peroxy moiety at the *ipso*-carbon.

	ΔH_{peroxy} (kcal mol ⁻¹)	$\Delta H_{\text{ipso}}^{\ddagger}$ (kcal mol ⁻¹)	$\Delta H_{\text{O-Ocleave}}^{\ddagger}$ (kcal mol ⁻¹)	$\Delta H_{\text{O-Ocleave}}$ (kcal mol ⁻¹)
H	-42.4	-15.3 (27.1)	-8.8 (33.6)	-6.4 (36.0)
CO ₂ ⁻	-48.7	-25.9 (22.8)	-22.4 (26.3)	-16.5 (32.2)
SO ₃ ⁻	-47.4	-23.5 (23.9)	-19.8 (27.6)	-14.4 (33.0)
⁻ O ₃ SC ₆ H ₄	-46.1	-23.3 (22.8)	-19.0 (27.1)	-14.9 (31.2)
⁺ NMe ₃	-38.7	-9.0 (29.7)	-0.93 (37.8)	0.2 (39.0)

Table S2: Comparison of free energies calculated at the B3LYP/6-311++G(d,p) level between O-O bond cleavage and attack by the peroxy moiety at the *ipso*-carbon.

	ΔG_{peroxy} (kcal mol ⁻¹)	$\Delta G_{\text{ipso}}^{\ddagger}$ (kcal mol ⁻¹)	$\Delta G_{\text{O-Ocleave}}^{\ddagger}$ (kcal mol ⁻¹)	$\Delta G_{\text{O-Ocleave}}$ (kcal mol ⁻¹)
H	-32.4	-4.95 (27.5)	0.78 (33.2)	-4.2 (28.2)
CO ₂ ⁻	-38.8	-15.6 (23.2)	-13.0 (25.8)	-14.8 (24.0)
SO ₃ ⁻	-36.5	-13.0 (23.5)	-9.5 (27.0)	-11.9 (24.6)
⁻ O ₃ SC ₆ H ₄	-35.4	-12.4 (23.0)	-9.0 (26.4)	-12.7 (22.7)
⁺ NMe ₃	-28.2	1.84 (30.0)	7.5 (35.7)	2.5 (30.7)

References

- (1) Zhao, S.; Xu, X.; Zheng, L.; Liu, H. *Ultrason. Sonochem.* **2010**, *17*, 685–689.