Supporting Information for:

Reaction of Singlet Oxygen with Thioanisole in Ionic Liquids: A Solvent Induced Mechanistic Dichotomy

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Experimental details.

Materials and methods. The photochemical reactions were carried out in a Helios Italquartz Photochemical Multirays Reactor equipped with ten fluorescence lamps (400-600 nm, 14 W each) and thermostated using a Haake F3 water circulating apparatus. GC analyses were performed on an Agilent 6850 Series II gas chromatograph equipped with an Agilent OV1 capillary column (methyl siloxane, 30 m length, ID 0.32 mm, film 0.25 \(\mu\)m) using the following temperature gradient: 70 °C (5 min), 250 °C (10 °C min\(^{-1}\)). GC-MS analyses were performed on an Agilent 6890N gas chromatograph equipped with an Agilent 5973Network mass selective detector and an Agilent OV5 (5 % phenyl methyl siloxane, 30 m length, ID 0.25 mm, film 0.25 \(\mu\)m) using the following temperature gradient: 70 °C (5 min), 250 °C (10 °C min\(^{-1}\)). HPLC analyses were performed on an Agilent 1100 series apparatus equipped with an Alltima C\(_{18}\) (5\(\mu\), 250 mm length) using the following solvent gradient: 0 min, MeCN/H\(_2\)O 65:35, 1 mL min\(^{-1}\) flow; 5 min, MeCN/H\(_2\)O 65:35, 1 mL min\(^{-1}\) flow; 20 min, MeCN, 2 mL min\(^{-1}\) flow (UV detector, \(\lambda = 263\) nm). \(^1\)H NMR and \(^{13}\)C NMR spectra were recorded on a Brucker AC-300P spectrometer operating at 300 MHz and 75 MHz, respectively. The measurements were carried out using the standard pulse-sequences. The \(^1\)H NMR and \(^{13}\)C NMR spectra of the ionic liquids were recorded using pure compounds with an internal deuterium lock (C\(_6\)D\(_{12}\)). The identity of all the oxidation products was confirmed by GC-MS analyses on authentic commercial specimens. Thioanisole, phenyl sulfide, methyl phenyl sulfoxide and methyl phenyl sulfone were commercial products of the highest available purity and were used as supplied. The commercially available benzoquinone was purified by sublimation before use. With the exception of the commercially available [Emim][TfO], the ionic liquids illustrated in Chart 1, ie. [Bmpy][Tf\(_2\)N],\(^{S1}\) [Empy][Tf\(_2\)N],\(^{S2}\) [Bmim][Tf\(_2\)N]\(^{S1}\) and [Emim][Tf\(_2\)N],\(^{S1}\) were prepared according to literature procedures.\(^{S1}\) They were washed extensively with water to remove halides impurities, which were expected to be below 25 ppm based on AgNO\(_3\) tests, and were dried under vacuum at room temperature overnight followed by drying at 70 °C for more than 24 h prior characterization by NMR (the identity was confirmed after comparison with previously reported data).\(^{S1,S2}\) In order to remove traces of adventitious acid species, the ionic liquids were diluted with methylene chloride, washed saturated aqueous sodium carbonate and dried over anhydrous magnesium sulphate followed by solvent evaporation.\(^{S3}\) The ILs thus obtained were dried under vacuum at 70 °C for more than 24 h prior use. Acetonitrile (HPLC-plus grade) was first refluxed and then distilled over calcium hydride before use.

Preparation of trideuteromethyl phenyl sulfide (\(1-d_3\)). A suspension of thiophenol (2.0 g, 18.2 mmol) and sodium carbonate (2.0 g, 18.9 mmol) in ethanol (100 mL) was stirred for 30 min under Ar
atmosphere at room temperature after which iodomethane-$d_3$ (99.5 atom % D, 2.9 g, 20 mmol) was slowly added. The mixture was stirred under reflux for 5 h and then cooled. After partial solvent evaporation, the mixture was poured into water (100 mL) and extracted with three portions of dichloromethane (50 mL each). The combined organic layers were washed with water and brine and dried over anhydrous Na$_2$SO$_4$. After filtration and solvent evaporation, the mixture was purified by flash chromatography (silica gel, hexane/ethyl acetate 9:1) to afford 1.7 g (73.5 % yield) of a colorless oil.

70 eV EI mass spectrum: $m/z$ (rel. intensity) 65 (10), 79 (24), 93 (19), 109 (41), 127 (M$^{+}$*, 100).

$^1$H-NMR (300 MHz, CD$_3$Cl): $\delta$: 7.3-7.1 (m, aromatic H).

$^{13}$C-NMR (75 MHz, CD$_3$Cl): $\delta$: 138.3 (aromatic C1), 128.8 (aromatic meta-C), 126.6 (aromatic ortho-C), 125.0 (aromatic para-C).

**Photooxidation general procedure.** Photooxidation reactions were carried out in a photoreactor equipped with 10 fluorescence lamps (400-600 nm; 14 W each). A stirred 1 mL solution containing the sulfide ($5 \times 10^{-2}$ M) and methylene blue ($5 \times 10^{-4}$ M) in O$_2$-saturated (at least 15 min O$_2$ bubbling) dry IL was irradiated for 1 h, under O$_2$ atmosphere, in a rubber cap-sealed jacketed tube thermostated at 20 °C by a water circulating apparatus. An internal standard (4-methylbenzophenone) was added and the mixture was extracted with four portions of diethyl ether (2 mL each). The collected ethereal phases were then analyzed by GC, GC-MS and HPLC (comparison with authentic specimens). Photooxidations of thioanisole were also carried out in the presence of benzoquinone ($5 \times 10^{-3}$ M) in [Bmpy][Tf$_2$N] and [Emim][Tf$_2$N] or in the presence of Ph$_2$S (0.25 M) in [Bmpy][Tf$_2$N]. In no case products were observed when the experiments were carried out in the absence of methylene blue or in a deoxygenated solution.

**Determination of kinetic isotope effect.** From an equimolar mixture of 1 and 1-d$_3$ ($2.5 \times 10^{-2}$ M each) and methylene blue ($5 \times 10^{-4}$ M) in O$_2$-saturated dry IL (1.5 mL) a 0.5 mL portion was taken and extracted with four portions of diethyl ether (1 mL each). The collected ethereal phases were analyzed by GC-MS (single ion monitoring mode) to check the initial 1/1-d$_3$ molar ratio (ratio of the intensity of molecular peaks $m/z = 124, 127$). The other 1 mL was reacted as described above but limiting the irradiation time in order to keep the sulfide conversion under 15 %. After usual workup, the 4/4-d$_3$ and 5/5-d$_3$ values were determined by GC-MS analysis (single ion monitoring mode) by the ratio of the intensity of molecular peaks $m/z = 140, 143$ and 156, 159 respectively.

**Determination of $^{1}$O$_2$ quenching rate constants ($k_T$) for 1 and Ph$_2$S.** $^{1}$O$_2$ was produced in the ILs or MeCN by energy transfer to O$_2$ from the triplet state of phenazine (ca. $5 \times 10^{-5}$ M), generated by excitation at 355 nm from a Nd:YAG laser (pulse width ca. 7 ns and energy < 3 mJ per pulse). The
phosphorescence emission of $^1\text{O}_2$ (1270 nm) emerging from the cuvette passed through a cut-off filter at 1050 nm and three pieces of gelatin cut-off filter at 870 nm and was detected by a germanium diode detector (5 mm diameter). After amplification with a two-stage home-made amplifier (ca. 100 MHz bandwidth, 14 dB), the output of the diode was fed into a digital signal analyzer and computer stored and analyzed. Rate constants for the quenching of $^1\text{O}_2$ ($k_T$) were determined from the decrease of $^1\text{O}_2$ emission lifetime in O$_2$-saturated solvent, in the presence of various amounts of substrates (0-0.8 M). All measurements were carried out at 22 ± 2 °C.

Figure S1. Dependence of $k_{\text{obs}}$ on concentration of thioanisole in [Bmim][Tf$_2$N] (■), [Emim][Tf$_2$N] (△) and [Bmpy][Tf$_2$N] (▼).

Figure S2. Dependence of $k_{\text{obs}}$ on concentration of diphenyl sulfide in [Emim][Tf$_2$N] (△) and [Bmpy][Tf$_2$N] (▼).
Mechanism of sulfone formation in the $^1$O$_2$ promoted oxidation of thioanisole in pyrrolidinium ILs.

**Table S1.** Product isotope effect for sulfoxide (4) and sulfone (5) formation in the singlet oxygen promoted oxidation of equimolar amounts of 1 and 1-d$_3$ in pyrrolidinium ILs.

<table>
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<th>Solvent</th>
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<td>[Bmpy][Tf$_2$N]</td>
<td>1.33 ± 0.8</td>
<td>1.3 ± 0.1</td>
</tr>
<tr>
<td>[Empy][Tf$_2$N]</td>
<td>1.25 ± 0.03</td>
<td>1.22 ± 0.05</td>
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a) PhSOCH$_3$/PhSOCD$_3$ and PhSO$_2$CH$_3$/PhSO$_2$CD$_3$ molar ratios determined in the oxidation of an equimolar mixture of 1 and 1-d$_3$ keeping the substrate conversion under 15%. The values were determined by GC-MS analysis (single ion monitoring mode) by the ratio of the intensity of molecular peaks m/z = 140, 143 and 156, 159 respectively. The values are the average of at least three independent determinations. b) 10 % (v/v) MeCN.

Scheme S1
Once stated that in pyrrolidinium ILs the $^{1}$O$_2$ promoted sulfoxidation of 1 follows the same mechanism as in aprotic solvents, the mechanistic scenario for a 1 and 1-$d_3$ mixture is reported in Scheme S1.

If all the sulfone derives from the ylide 3 and assuming that the rates the ylide electrophilic attack on the sulfide are independent on isotopic substitution (i.e. $k^S_H = k^S_D = k^{SD}_D = k^{SD}_H$), the [5]/[5-$d_3$] molar ratio is given by eq. S1.

\[
\frac{[5]}{[5-d_3]} = \frac{k_{SO}[3]}{k_{SO}^D[3-d_3]} \quad \text{(S1)}
\]

Since the $k_{SO}/k_{SO}^D$ ratio may be larger than 1, S5 S2 should hold.

\[
\frac{[5]}{[5-d_3]} \geq \frac{[3]}{[3-d_3]} \quad \text{(S2)}
\]

Now, always on the basis of Scheme S1 and assuming the pathway leading from the ylide to sulfone (minor product) to be negligible with respect to that leading to sulfoxide (largely major product), eqs. S3 and S4 can be derived:

\[
\frac{d[4]}{dt} = 2k^u_{S}[3][1+d_3] + k^u_{SO}[3-d_3][1] = [3] \left( 2k^u_{S}[1] + k^u_{SO}[1-d_3] \right) + k^u_{SO}[3-d_3][1] \quad \text{(S3)}
\]

\[
\frac{d[4-d_3]}{dt} = 2k^o_{SO}[3-d_3][1-d_3] + k^u_{SO}[3-d_3][1] + k^u_{SO}[3][1-d_3] = [3-d_3] \left( 2k^o_{SO}[1-d_3] + k^u_{SO}[1] \right) + k^u_{SO}[3][1-d_3] \quad \text{(S4)}
\]

From eqs S3 and S4, eq S5 is then obtained.

\[
\frac{[4]}{[4-d_3]} = \frac{[3] \left( 2k^u_{S}[1] + k^o_{SO}[1-d_3] \right) + k^u_{SO}[3-d_3][1]}{[3-d_3] \left( 2k^o_{SO}[1-d_3] + k^u_{SO}[1] \right) + k^u_{SO}[3][1-d_3]} \quad \text{(S5)}
\]

In our case (equimolecular mixture of 1 and 1-$d_3$) and under the assumption made above (i.e. $k^S_H = k^S_D = k^{SD}_H = k^{SD}_D$), eqs. S5 is simplified to eq. S6.
\[
\frac{[4]}{[4-d_3]} = \frac{3[3]+[3-d_1]}{3[3-d_1]+[3]} = \frac{3}{3-d_1} + \frac{1}{3} \quad \text{(S6)}
\]

Thus, on the basis of eq. S6 and from the \([4]/[4-d_3]\) values determined in the experiments with equimolar amounts of \(1\) and \(1-d_3\) (Table S1), it can be calculated that \([3]/[3-d_3] = 1.8\) ([Bmpy][Tf2N]) and 1.6 ([Empy][Tf2N]). These values are significantly higher than those actually found for the \([5]/[5-d_3]\) molar ratio (Table S1) hence, on the basis of eq. S2, sulfone cannot exclusively derive from the ylide. Since \([5]/[5-d_3]\) is found to be, within experimental errors, equal to \([4]/[4-d_3]\) (Table S1) it is reasonable to suggest that the sulfone derives from sulfoxide overoxidation.
References.


Figure S3. GC-MS analysis of the $^1\text{O}_2$ promoted oxidation of 1 in [Emim][Tf$_2$N].

Figure S4. GC analysis of the $^1\text{O}_2$ promoted oxidation of 1 in [Emim][Tf$_2$N].
Figure S5. GC-MS analysis of the $^1$O$_2$ promoted oxidation of 1 in [Bmpy][Tf$_2$N].
Figure S6. HPLC analysis of the $^1\text{O}_2$ promoted oxidation of 1 in [Bmpy][Tf$_2$N].

Figure S7. GC analysis of the $^1\text{O}_2$ promoted oxidation of 1 in [Bmpy][Tf$_2$N].
Figure S8. $^1$H NMR and $^{13}$C spectra of 1-d$_3$ (300 MHz and 75 MHz respectively, CDCl$_3$ + TMS)
Figure S9. EI (70 eV) mass spectrum of 1-d$_3$. 
Figure S10. $^1$H NMR and $^{13}$C NMR spectra of [Bmim][Tf$_2$N] (300 MHz and 75 MHz respectively, pure compound with C$_6$D$_{12}$ as internal deuterium lock).
Figure S11. $^1$H NMR and $^{13}$C NMR spectra of [Emim][Tf$_2$N] (300 MHz and 75 MHz respectively, pure compound with C$_6$D$_{12}$ as internal deuterium lock).
Figure S12. $^1$H NMR and $^{13}$C NMR spectra of [Bmpy][Tf$_2$N] (300 MHz and 75 MHz respectively, pure compound with C$_6$D$_{12}$ as internal deuterium lock).
Figure S12. $^1$H NMR and $^{13}$C NMR spectra of [Empy][Tf$_2$N] (300 MHz and 75 MHz respectively, CD$_3$CN).