

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

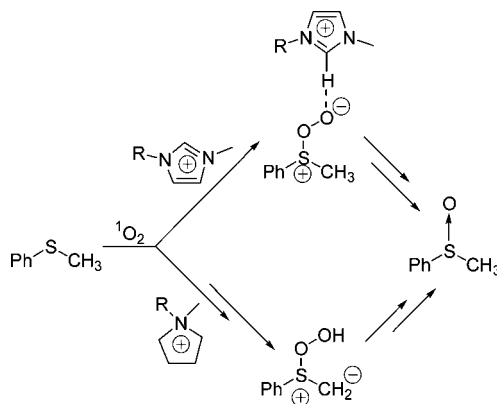
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## ABSTRACT



A study of the reaction of thioanisole with singlet oxygen in pyrrolidinium- and imidazolium-based ionic liquids has been carried out. In these solvents, thioanisole shows a strongly enhanced reactivity with respect to molecular aprotic solvents, probably due to a stabilization of the persulfonate intermediate in the ionic medium. Product isotope effects suggest a mechanistic change ongoing from pyrrolidinium to imidazolium solvents.

Room-temperature ionic liquids (ILs) continue to deserve great attention as solvents for a large variety of applications as a result of the fact that the great number of combinations of anions and cations make them flexible and tunable media for inorganic and organic reactions, catalysis, and electrochemical studies.<sup>1</sup> Although in recent years the possible use of ILs in photochemical reactions has been explored,<sup>2</sup> very few studies concerning the

reactivity of singlet oxygen (<sup>1</sup>O<sub>2</sub>) in ILs have been carried out.<sup>3</sup> To investigate <sup>1</sup>O<sub>2</sub> chemistry in ILs, we felt it worthwhile to

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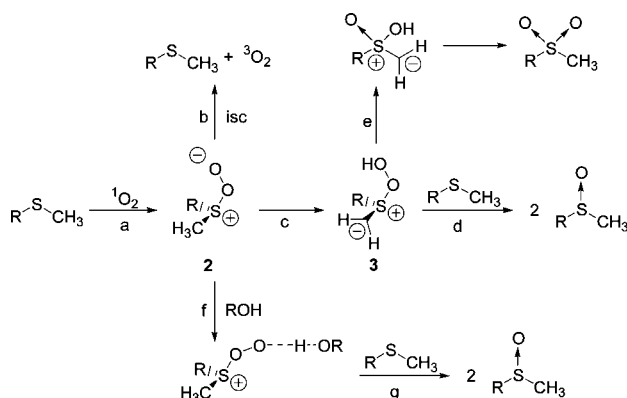
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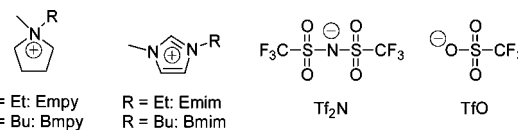
focus our attention on its reactivity with sulfides, since this class of reactions exhibits quite a complex mechanism where the solvent exerts a major role by influencing the fate of the persulfoxide intermediate (2).<sup>4</sup> Thus, as shown in Scheme 1,

**Scheme 1.** General Mechanisms for the Reaction of Singlet Oxygen with Sulfides in Aprotic and Protic Solvents



in aprotic solvents (e.g., benzene, acetonitrile) the persulfoxide intermediate (a nucleophilic species unreactive toward sulfides) can undergo both intersystem crossing, to give  $^3\text{O}_2$  and the sulfide (path b), or when  $\alpha$ -hydrogen atoms are present, a rearrangement to a hydroperoxysulfonium ylide (3) via an intramolecular hydrogen atom abstraction (path c). This second intermediate can then react with the sulfide to give two molecules of sulfoxide (path d) or rearrange to give sulfone (path e). The key point in this process is represented by the competition between the hydroperoxysulfonium ylide formation (path c) and the unproductive intersystem crossing (path b). A different situation holds instead in protic solvents or in the presence of protic additives.<sup>5</sup> In this case the intersystem crossing process (path b) is significantly reduced by the persulfoxide stabilization by hydrogen bond formation (path f). The complex thus formed is then able to react with the sulfide substrate to give two molecules of sulfoxide (path g) without involving the formation of the hydroperoxysulfonium ylide.

We have carried out a detailed investigation of the singlet oxygen promoted oxidation of thioanisole (1) in a series of imidazolium- and pyrrolidinium-containing ILs<sup>6</sup> (Figure 1) and present evidence showing that the ILs can be very convenient solvents for this reaction, in contrast with aprotic solvents where thioanisole is practically unreactive. More-



**Figure 1.** Structures of the ions forming the ionic liquids under investigation.

over, very interestingly, our results also show that the solvent-induced mechanistic dichotomy illustrated above also holds in ILs.

In a typical reaction, a 1 mL oxygen-saturated solution of **1** ( $5 \times 10^{-2}$  M) and methylene blue ( $5 \times 10^{-4}$  M) in anhydrous ionic liquid was irradiated for 1 h (400–600 nm) at 20 °C. After extraction with diethyl ether, the mixture was analyzed by GC, GC-MS, and HPLC (comparison with authentic specimens). Under the same conditions, some experiments were also carried out with diphenyl sulfide as the substrate and, for comparison, in MeCN. Blank experiments, carried out under the same reaction conditions but in the absence of methylene blue or oxygen, showed the absence of a significant amount of products. In all cases, the mass balance was >95%. Moreover, laser flash photolysis experiments allowed us to measure the  $^1\text{O}_2$  self-decay rate constant ( $k_0$ ) as well as the  $^1\text{O}_2$  total quenching rate constant by **1** and diphenyl sulfide ( $k_T$ ) in the solvents examined. All results are reported in Table 1.

**Table 1.** Self Decay and Quenching Rate Constants of Singlet Oxygen, Products and Yields in the Oxidation of Thioanisole and Diphenyl Sulfide in ILs

entry	solvent	$k_0$ (s <sup>-1</sup> )	$k_T$ (M <sup>-1</sup> s <sup>-1</sup> )	yields (%) <sup>a</sup>	
				SO	SO <sub>2</sub>
Thioanisole					
1	[Bmpy][Tf <sub>2</sub> N]	$2.1 \times 10^4$	$3.8 \times 10^6$	32	3.5
2	[Empy][Tf <sub>2</sub> N] <sup>c</sup>			53	2.3
3	[Emim][Tf <sub>2</sub> N]	$3.6 \times 10^4$	$5.7 \times 10^6$	>98	<i>b</i>
4	[Bmim][Tf <sub>2</sub> N]	$9.8 \times 10^4$	$9.0 \times 10^6$	15	<i>b</i>
5	[Emim][TfO]			12	<i>b</i>
6	MeCN	$2.0 \times 10^4$	$4.7 \times 10^6$	<i>b</i>	<i>b</i>
7	[Bmpy][Tf <sub>2</sub> N] <sup>d</sup>			26	2.4
8	[Emim][Tf <sub>2</sub> N] <sup>d</sup>			>98	<i>b</i>
Diphenyl Sulfide					
9	[Bmpy][Tf <sub>2</sub> N]	$2.1 \times 10^4$	$7.4 \times 10^4$	<i>b</i>	<i>b</i>
10	[Emim][Tf <sub>2</sub> N]	$3.6 \times 10^4$	$1.0 \times 10^5$	6	<i>b</i>

<sup>a</sup> Referred versus the initial amount of substrate and determined by GC analysis with the exception of methyl phenyl sulfone in [Bmpy][Tf<sub>2</sub>N], which was quantified by HPLC analysis because of peak overlapping due to traces of IL present in the ethereal phase. <sup>b</sup> Not detected. <sup>c</sup> 10% (v/v) MeCN. <sup>d</sup> In the presence of benzoquinone ( $5 \times 10^{-3}$  M). Benzoquinone was recovered unreacted.

Looking first at the  $k_0$  and  $k_T$  values reported in Table 1, it appears clear that both of these constants are quite close to those observed in MeCN as well as in other aprotic molecular solvents<sup>7</sup> and that, under our reaction conditions ( $[\mathbf{1}] = 5 \times 10^{-2}$  M), in all cases most of the  $^1\text{O}_2$  generated is intercepted by **1**. It can also be observed that, whereas

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(6) Because [Empy][Tf<sub>2</sub>N] is solid at room temperature, 10% (v/v) dry MeCN was added to obtain a liquid mixture.

thioanisole is unreactive in MeCN (entry 6),<sup>8</sup> the yields of sulfoxide (**4**) in ILs range from appreciable to excellent, the latter situation being observed in [Emim][Tf<sub>2</sub>N] (entry 3) where the conversion into sulfoxide is practically quantitative. Small amounts of sulfone (**5**) were formed in pyrrolidinium-based ILs, whereas **4** is the exclusive reaction product in imidazolium-based ILs (entries 3–5). Moreover, the efficiency of the reactions in both [Bmpy][Tf<sub>2</sub>N] and [Emim][Tf<sub>2</sub>N] was not suppressed by the presence of benzoquinone, a very efficient O<sub>2</sub><sup>••</sup> trapping agent (entries 7 and 8),<sup>9</sup> thus allowing us to exclude the occurrence of a photooxygenation mechanism not involving singlet oxygen but an initial electron transfer oxidation of **1** by the excited sensitizer, followed by the reaction of **1**<sup>•+</sup> with O<sub>2</sub><sup>••</sup> formed by reaction of the reduced sensitizer with O<sub>2</sub>.<sup>10</sup>

To obtain mechanistic information, we have also investigated the reaction of an equimolar mixture of PhSCH<sub>3</sub> and PhSCD<sub>3</sub> (**1-d**<sub>3</sub>). The results, displayed in Table 2, show that the pyrrolidinium ILs exhibit a significant product isotope effect (ranging from 1.2 and 1.3) on sulfoxide formation (i.e., product ratio **4/4-d**<sub>3</sub>). Such an isotope effect is instead absent in imidazolium ILs where **1** and **1-d**<sub>3</sub> are oxidized at the same rate, the **4/4-d**<sub>3</sub> product ratio being unity within experimental error (Table 2). The same result was obtained for the reaction in MeOH that was studied for comparison.

**Table 2.** Product Isotope Effect in the Singlet Oxygen-Promoted Oxidation of Thioanisole in ILs

solvent	<b>4/4-d</b> <sub>3</sub> <sup>a</sup>	solvent	<b>4/4-d</b> <sub>3</sub> <sup>a</sup>
[Bmpy][Tf <sub>2</sub> N]	1.33(8)	[Bmim][Tf <sub>2</sub> N]	1.04(1)
[Empy][Tf <sub>2</sub> N] <sup>b</sup>	1.25(3)	[Emim][TfO]	0.98(1)
[Emim][Tf <sub>2</sub> N]	1.02(2)	MeOH	1.03(1)

<sup>a</sup> **4/4-d**<sub>3</sub> molar ratio determined in the oxidation of an equimolar mixture of **1** and **1-d**<sub>3</sub> under the same reaction conditions described above but 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 and 143. The values are the average of at least three independent determinations. The error (standard deviation) in the last significant digit is given in parentheses. <sup>b</sup> 10% (v/v) MeCN.

Another important difference between pyrrolidinium and imidazolium ILs was found with respect to the oxidation of Ph<sub>2</sub>S. Whereas Ph<sub>2</sub>S was unreactive in [Bmpy][Tf<sub>2</sub>N] as observed in molecular aprotic solvents (it lacks an α-C-H bond), it exhibited an appreciable reactivity in [Emim][Tf<sub>2</sub>N], affording phenyl sulfoxide as the exclusive product in 6%

yield.<sup>11</sup> However, when the reaction of **1** in [Bmpy][Tf<sub>2</sub>N] was carried out in the presence of Ph<sub>2</sub>S the additive was cooxidized to give Ph<sub>2</sub>SO.<sup>12</sup>

**Reactivity.** Even though the simple comparison of the yields does not strictly represent a quantitative comparison of the singlet oxygen chemical reactivity toward thioanisole in the different solvents given the differences in the <sup>1</sup>O<sub>2</sub> lifetime as well as in the rate constant of total quenching by thioanisole, there is no question that all ILs examined exhibit a very strong enhancing effect on the chemical reactivity of <sup>1</sup>O<sub>2</sub> toward thioanisole when compared with MeCN. A reasonable rationalization is that in ILs the thioanisole persulfoxide intermediate may be better stabilized than in aprotic solvents by a more efficient coordination exerted by the ionic solvent, which may interact with the negatively charged peroxy appendage of the persulfoxide as well as with the positively charged sulfur atom. Thus, with respect to molecular aprotic solvents, in ILs the unproductive inter-system crossing step (path b in Scheme 1) should be significantly slowed down relative to the chemical path.<sup>13,14</sup> On the other hand, the good coordinating power of ILs is clearly indicated by their *E*<sub>T</sub><sup>N</sup> values which are higher than those for polar aprotic solvents.<sup>15</sup> Moreover, it should also be considered that imidazolium-type solvents have a relatively acidic C–H bond,<sup>16</sup> thus in these solvents the coordination might also assume the character of a hydrogen bond (see below).

Interestingly, a dramatic enhanced reactivity was also observed by Clennan and co-workers in the reaction of aromatic sulfides with <sup>1</sup>O<sub>2</sub> carried out in zeolites.<sup>17</sup> In this case too, the authors attributed such a behavior to the stabilization of the persulfoxide exerted by the zeolite countercation. This similarity might lend support to the suggestion that zeolites may be in some way considered the solid counterparts of ionic liquids.<sup>18</sup>

**Reaction Mechanisms.** The different behaviors observed in pyrrolidinium and imidazolium ILs (product isotope effect and reactivity of Ph<sub>2</sub>S) suggest that in these two classes of ILs the reaction should follow two different mechanisms. In pyrrolidinium ILs, the product isotope effect observed on sulfoxide formation (Table 2) clearly indicates that an

(11) This low sulfoxide yield (with respect to that of **1**) is somewhat expected from the *k*<sub>0</sub> and *k*<sub>T</sub> values reported in Table 1. Accordingly, under our conditions (initial sulfide concentration of 5 × 10<sup>−2</sup> M) in [Emim][Tf<sub>2</sub>N], 89% of <sup>1</sup>O<sub>2</sub> is intercepted by thioanisole, whereas only 12% is by Ph<sub>2</sub>S.

(12) In [Bmpy][Tf<sub>2</sub>N], the reaction of **1** (0.05 M) in the presence of Ph<sub>2</sub>S (0.25 M) under usual reaction conditions afforded methyl phenyl sulfoxide (11 mmol) and diphenyl sulfoxide (8.5 mmol).

(13) As *k*<sub>T</sub> does not change very much in ILs with respect to molecular solvents, the strong increase in reactivity observed in the former solvents should be mainly associated with a decrease in the intersystem crossing rate.

(14) Preliminary experiments indicate that the rate enhancement effect observed with thioanisole is not present with dibutyl sulfide. A possibility is that the persulfoxide of dialkyl sulfide is stable enough also in aprotic solvents (lone pair on sulfur not delocalized as in an aromatic sulfide) that the larger coordinating effect of ILs may be practically not felt. However, it might also be that in the dibutyl persulfoxide the relatively long alkyl chains hamper the coordination by the IL solvent. In this respect, it may be noted that steric effects might rationalize the finding that the reactivity of thioanisole in [Bmim][Tf<sub>2</sub>N] is much lower than in [Emim][Tf<sub>2</sub>N] (Table 1). Clearly, further detailed study is necessary to understand how the structure of the sulfide influence the IL coordination in the persulfoxide.

(7) In benzene: *k*<sub>0</sub> = 3.3 × 10<sup>4</sup> s<sup>−1</sup>, *k*<sub>T</sub> = 8.0 × 10<sup>5</sup> M<sup>−1</sup>s<sup>−1</sup>. In methanol: *k*<sub>0</sub> = 1.0 × 10<sup>5</sup> s<sup>−1</sup>, *k*<sub>T</sub> = 2.0 × 10<sup>6</sup> M<sup>−1</sup>s<sup>−1</sup>. Wilkinson, F.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1995**, *24*, 663.

(8) This observation is not surprising since Sawaki and co-workers observed that the conversion of **1** into products was 0.48% after 8 h irradiation in benzene and 0.8% after 2 h irradiation in MeCN. Ishiguro, K.; Hayashi, M.; Sawaki, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7265.

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$\alpha$ -hydrogen atom abstraction step should take place during the oxidation process, as predicted by the mechanism proposed for the reaction in aprotic solvents in which an  $\alpha$ -hydrogen is removed during the product determining step to form the hydroperoxysulfonium ylide and ultimately the sulfoxide product (Scheme 1, path c).<sup>19</sup> Moreover, it is noteworthy that the KIE values observed in our experiments are very close to those observed by Clennan in the reaction of  $^1\text{O}_2$  with 2,2,8,8-tetradeuterio-1,5-dithiacyclooctane (1.21)<sup>19a</sup> or with a series of 1,3-dithianes (1.31–1.62).<sup>19b</sup> In both cases, the observation of a product isotope effect was considered strong support for the mechanism via hydroperoxysulfonium ylide (Scheme 1, path c). Additional important evidence in this respect is that whereas diphenyl sulfide is not directly oxidized by singlet oxygen in pyrrolidinium solvents (which is expected because, as stated before, it lacks  $\alpha$ -hydrogens and cannot form the ylide), its oxidation to diphenyl sulfoxide takes place when it is reacted with singlet oxygen in the presence of **1**. In this case it is the ylide formed from thioanisole persulfoxide that can oxidize the diphenyl sulfide as it oxidizes the thioanisole itself.<sup>20</sup> In conclusion, both the presence of a product isotope effect and the co-oxidation of  $\text{Ph}_2\text{S}$  strongly support the hypothesis that the reaction of  $^1\text{O}_2$  with **1** in pyrrolidinium ILs follows the mechanism observed in aprotic solvents (Scheme 1, path c).<sup>21</sup>

Different behaviors are instead observed with imidazolium ionic liquids. In this case the product isotope effects were unity within experimental error (Table 2), thus showing that the mechanism involving hydroperoxysulfonium ylide formation is not operating in these solvents. Moreover, in the imidazolium solvent [Emim][Tf<sub>2</sub>N] diphenyl sulfide is oxidized to diphenyl sulfoxide even in the absence of thioanisole. These results thus suggest that the mechanism of the singlet-oxygen-promoted sulfoxxygenation of thioanisole is very likely the same as that observed in protic solvents (path f in Scheme 1). This mechanistic hypothesis is

consistent with our finding that the sulfoxidation of thioanisole promoted by  $^1\text{O}_2$  in MeOH (Table 2) does not exhibit a product isotope effect as well as with the observation that  $\text{Ph}_2\text{S}$  can be sulfoxidated in this solvent.<sup>22</sup>

The reason for the mechanistic change ongoing from pyrrolidinium to imidazolium solvents is probably related to the fact that, as mentioned before, imidazolium solvents have an acidic C–H bond and may be able to coordinate the persulfoxide oxygen by hydrogen bonds. Accordingly, in the scale of hydrogen bond acidity (Kamlet–Taft  $\alpha$  parameters) the imidazolium ILs show an  $\alpha$  value moderately high (0.659 and 0.625, respectively, for [Emim][Tf<sub>2</sub>N] and [Bmim][Tf<sub>2</sub>N])<sup>23,24</sup> comparable to that of *tert*-butanol ( $\alpha$  = 0.68).<sup>25</sup> If this interpretation is correct, it may be that, as occurs in protic solvents, the nucleophilicity of persulfoxide is significantly reduced,<sup>26</sup> thus allowing it to react with the sulfide substrate to give the sulfoxide (Scheme 1, path g) but inhibiting its reaction with a molecule of sulfoxide to give the sulfone,<sup>27</sup> as actually observed in imidazolium ILs where sulfone formation was not detected.

In conclusion, we have found that ionic liquids are good solvents for the sulfoxxygenation of thioanisole by singlet oxygen. Particularly, the reaction in [Emim][Tf<sub>2</sub>N] may have synthetic interest as it provides complete conversion into sulfoxide without any overoxidation to sulfone. Probably, this is due to a stabilizing effect by the IL on the persulfoxide intermediate, which relatively slows down the intersystem crossing pathway with respect to chemical reactions. Moreover, through the study of product isotope effect and the reaction of diphenyl sulfide, it has been discovered that in ILs there is the same mechanistic dichotomy observed in molecular solvents. Accordingly, in pyrrolidinium-type solvents the persulfoxide is converted to a hydroperoxysulfonium ylide intermediate as it occurs in conventional aprotic solvents. With imidazolium-type solvents, which possess an acidic C–H bond, a hydrogen-bonded persulfoxide is probably formed and the reaction proceeds through this species without involving the intermediacy of the hydroperoxysulfonium ylide intermediate.

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**Supporting Information Available:** Experimental details, isotope effects, and product analyses. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(15) (a) The  $E_N^\ddagger$  values for [Emim][Tf<sub>2</sub>N] (0.644) and [Bmpy][Tf<sub>2</sub>N] (0.544)<sup>15b</sup> are in the range associated to those of aliphatic alcohols (0.654 and 0.546 for ethanol and 2-propanol, respectively)<sup>15c</sup> and higher than that of MeCN (0.460).<sup>15c</sup> (b) Crowhurst, L.; Mawdsley, P. R.; Perez-Arlandis, L. M.; Salter, P. A.; Welton, T. *Phys. Chem. Chem. Phys.* **2003**, *5*, 2790. (c) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319.

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(21) Rearrangement of the ylide might be taken as the origin of the small amounts of sulfone observed in the pyrrolidinium solvents (Scheme 1, path e). However, we have observed that the formation of sulfone is subject to the same products KIE observed with the sulfoxide (Supporting Information). This observation is in line with a sulfone generation from partial oxidation of the formed sulfoxide, presumably by the persulfoxide,<sup>20</sup> whereas a higher isotope effect should have been expected in the sulfone formation via ylide rearrangement (see Supporting Information for details).

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(24) Moreover, these values are higher than those of pyrrolidinium ILs ( $\alpha$  = 0.427 for [Bmpy][Tf<sub>2</sub>N]).<sup>15b</sup>

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