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SENSITIZED PHOTO-OXIDATION OF THIOPHENOLATES
A SINGLET OXYGEN REACTION

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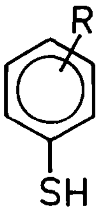
Abstract: Tetraphenylporphyrin-sensitized photo-oxidation of thiophenolates leads to the corresponding benzenesulfonates. The reaction proceeds via attack of singlet oxygen on the thiophenolate anion. A reaction mechanism is proposed.

In view of the results of our investigations concerning the photo-oxidation of primary aromatic amines [1] we considered it worth while to study the reactivity of thiophenols and thiophenolates towards singlet oxygen.

The sensitized photo-oxidation of organic sulfur compounds has received little attention. It has been demonstrated by Murray et al. [2] that dialkyldisulfides can be photo-oxidized by singlet oxygen to thiolsulfinates (RSOSR') or thiolsulfonates (RSO_2SR') - depending on the reaction conditions - via a persulfoxide intermediate. Foote et al. [3] have shown that sulfides react in a similar way with singlet oxygen, yielding sulfoxides or sulfones. In both cases diaryl compounds proved to be inert, although they could be co-oxidized with dialkyl compounds.

We have subjected the following substituted thiophenols to sensitized photo-oxidation (sensitizer: meso-tetraphenylporphyrin, TPP; $\lambda > 360$ nm) in various solvents:



R = H	1		
m-NO_2	2	p-NO_2	6
m-Cl	3	p-Cl	7
m-CH_3	4	p-CH_3	8
m-OCH_3	5	p-OCH_3	9

Surprisingly, no oxidation could be detected in either of the solvents used (t-BuOH, CH_3OH, CH_3CN), although singlet oxygen was present in the solutions as was demonstrated by the fact that 1,3-diphenylisobenzofuran (DBPF, a well-known scavenger of singlet oxygen [4]) was rapidly photo-oxidized under our conditions.

The thiolate anions proved to be far more reactive. In solution, thiophenolates are slowly oxidized by ground state oxygen [5,6,7]. This reaction, which leads to disulfides and/or higher oxidation products, depending mainly on the solvent used, was avoided by carrying out the experiments in protic media which stabilize the anions by hydrogen bonding.

When the thiophenols mentioned above were subjected to TPP-sensitized photo-oxidation in the presence of an equimolar amount of base (t-BuOK), a rapid reaction ensued which could be monitored by the decreasing UV-absorption (260 - 300 nm) of the thiolate anion and a simultaneous increase (ca. 230 nm) of the absorption at lower wavelengths. In all cases the wavelength maximum of the resulting absorption spectrum coincided with the maximum of the corresponding sulfonate.

Irradiations on a preparative scale in t-BuOH/EtOH (9 : 1) (immersion well reactor; Hanau TQ 81 mercury lamp; $Fe_2(SO_4)_3/H_2SO_4$-filter cutting off at 360 nm; TPP (λ_{max} = 420 nm) 1.5 x 10^{-6} M; temperature 15 °C) yielded sulfonates as major products accompanied by varying amounts of disulfide. These compounds were identified by NMR spectrometry and by comparison with authentic samples. No other products could be detected. The procedure for work-up was as follows: evaporation of the solvent, extraction of the residue with CH_3OH, filtration, evaporation to dryness. The disulfide was separated from the sulfonate by extraction with ether. Some relevant experimental data are presented in Table I.

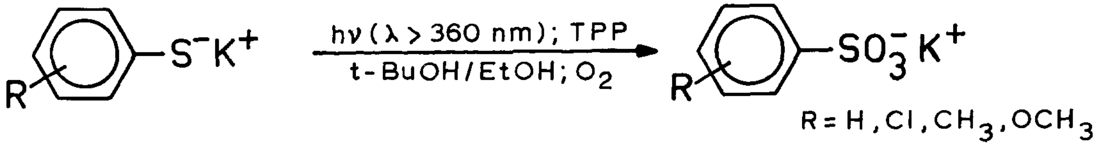


Table I

substrate $RC_6H_4S^-K^+$		weight (mg)	concentration (mM)	time (min)	yield (%) $RC_6H_4SO_3K$	yield (%) $(RC_6H_4S)_2$
1	R = H	128	2.3	6	51	28
7	R = p-Cl	130	2.9	8	90	--
8	R = p-CH_3	141	2.9	7	65	10
		100	0.5	7	45	20
9	R = p-OCH_3	123	2.3	6	71	13

Determination of reaction rates in various solvents and with variously substituted thiophenolates gave the following results (the rate of disappearance of the thiophenolate was determined by ultraviolet absorption spectrophotometry):

1) The reaction rate decreases with increasing ability of the solvent to form hydrogen bonds with the thiophenolate anion. The rate decreases in the following order:
benzene (with 18-crown-6) ≈ CH_3CN > CH_3CN/t-BuOH > t-BuOH > MeOH > t-BuOH/H_2O (8:1, v/v) > H_2O.

2) The reaction rate becomes higher when electron donating substituents are present and it is lowered by electron withdrawing substituents. Within the para-series this effect is more pronounced than within the meta-series.

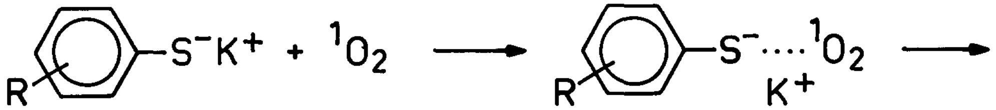
The presumed intermediacy of singlet oxygen was confirmed by the following observations:

1) The solvent deuterium isotope effect on photo-oxygenation reactions is a virtually unambiguous test for the involvement of singlet oxygen in a reaction [8]. We have studied the rate of reaction of para-methoxythiophenolate in CD_3OD and in CH_3OH under otherwise identical conditions. The rate of disappearance proved to be nine times higher in CD_3OD (the lifetimes of singlet oxygen in CH_3OH and in CD_3OD are 7×10^{-6} s and ca. 68×10^{-6} s, respectively [9]).

2) Singlet oxygen generated by a microwave discharge (2450 Mc) in an O_2/N_2 mixture was capable of oxidizing para-thiocresolate. The spectral features of this process closely resemble those of the photochemical experiments in all respects.

3) The well-known singlet oxygen quencher 1,4-diazabicyclo[2.2.2]octane [10] (DABCO) when present in a concentration of 10^{-3} M induced a twofold reduction in the rate of photo-oxidation. At 10^{-2} M a ninefold reduction of the rate was observed.

The above findings are consistent with a mechanism in which the first step is attack of singlet oxygen on the thiophenolate anion:



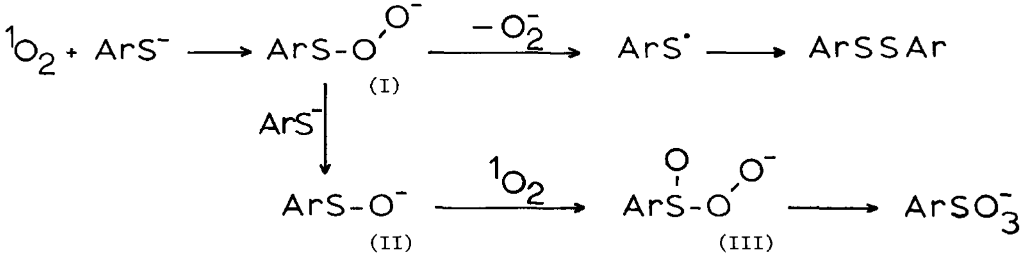
In constructing a more detailed reaction mechanism the following experimental observations are relevant:

1) Since benzenesulfinates may occur as intermediates we have subjected these salts separately to our photo-oxidation conditions. They proved to be completely unreactive.

2) On increasing the starting concentration of the thiophenolate a decrease of the relative amount of disulfide was observed.

3) From the literature [6] it is known that thiyl radicals have a strong tendency to dimerize to disulfides. They are not further oxidized by oxygen [6]. Aromatic disulfides are inert to singlet oxygen, as was mentioned earlier [2]. Sulfenates (RSO^-M^+) are possible intermediates in our photo-oxidation. Only one type of sulfenic acid has been isolated thus far: anthraquinone-1-sulfenic acid [11,12]. This compound is unstable in alkaline solution. It is converted to sulfinate by ground state oxygen [11] (decay time ca. 1 minute in t-BuOH [7]).

The following hypothetical reaction scheme accounts for the facts:



As product of the reaction between thiophenolate and singlet oxygen a peroxysulfenate (I) is proposed. This intermediate either can lose superoxide-anion with formation of the thiyl radical, which subsequently dimerizes to disulfide, or can react with thiophenolate, which results in the formation of sulfenate (II). Intramolecular rearrangement of (I) leading to sulfinate is improbable; in that case sulfinate would be a major product, contrary to what has been observed. High thiophenolate concentrations enhance the rate of the process leading to sulfonate, thus decreasing the relative amount of disulfide.

It is unlikely that the formation of sulfonate results from thermal oxidation of sulfenate (II). Oxidation of sulfenate by ground state oxygen is known to produce sulfinate [7,11] which has not been detected in our reaction mixtures. We therefore tentatively propose a second photochemical step in which the sulfenate is oxidized by singlet oxygen. The peroxysulfinate (III) thus produced is expected to rearrange to sulfonate. This rearrangement is comparable to the rearrangement of peroxysulfides and peroxydisulfides to sulfones and thiolsulfonates, respectively [2,3].

The reaction produces medium to high yields of sulfonates which can be easily isolated and purified. It thus provides a useful mild oxidation method. Further experiments to establish the mechanism and to extend the synthetic scope of the reaction are in progress.

References and Notes

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