Oxidation of thioanisole by hydrogen peroxide: activation by nitriles

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ABSTRACT: The oxidation of thioanisole (PhSMe) by H_2O_2 is activated by acetonitrile (MeCN) and propionitrile (EtCN) and involves the formation of a transient peroxyimidate, **1**, by reaction of HO_2^- and RCN, and **1** can be rapidly trapped by PhSMe. The rate of oxidation of PhSMe is then independent of the concentrations of PhSMe and of H_2O_2, but varies linearly with $[HO_2^-]$ and [RCN]. In very dilute PhSMe it and H_2O_2 compete in reacting with **1**, and the rate then depends on [PhSMe]. The initial reaction gives PhSOMe, and subsequent formation of $PhSO_2Me$ is slow. The rates of oxidation are slightly higher than that expected from the MeCN-activated decomposition of H_2O_2, which involves a second molecule of H_2O_2 in conversion of the peroxyimidate into amide and oxygen. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: sulfide oxidation; thioanisole; nitriles; peroxyimidates; zero-order kinetics

INTRODUCTION

Decontamination of chemical weapons under mild conditions is complicated, because although nucleophiles react rapidly with phosphonofluoridate nerve agents, decomposition of the chlorosulfide blister agent HD (Mustard), involves oxidation, or the use of strong bases in aprotic media.[1] The hydroperoxide ion, HO_2^-, formed by deprotonation of H_2O_2, is a very reactive nucleophile,[2] but H_2O_2 is a weak oxidant towards sulfides and has to be activated, for example, by conversion into a peroxy acid. Hydrogencarbonate ion and H_2O_2 generate a peroxocarbonate which is an effective oxidant at a pH where HO_2^- is a nucleophile.[3] Molybdate ion and H_2O_2 generate a variety of peroxomolybdates,[4] and the tetraperoxomolybdate dianion rapidly oxidizes sulfides at pH $\approx$ 10 where HO_2^- reacts nucleophilically.[5,6] Decomposition of peroxomolybdates, especially the triperoxomolybdate dianion, also generates singlet oxygen, which reacts rapidly with many organic compounds, including sulfides.[7]

The reaction of HO_2^- with nitriles generates short-lived peroxyimidates which convert alkenes into epoxides and oxidize sulfides to sulfoxides and sulfones.[8–10] Mixtures of H_2O_2 and nitriles are preparatively useful as alternatives to peroxy acids in oxidations of alkenes and sulfides.[9,10]

Oxidations of arylmethyl sulfides by acetonitrile–H_2O_2 have been examined in methanol–K_2CO_3 and the results were interpreted in terms of competition between the sulfide and H_2O_2 for the short-lived intermediate, **1**,[10a] which we show as a peroxyimidate, although we do not know the extent of its protonation (Scheme 1).
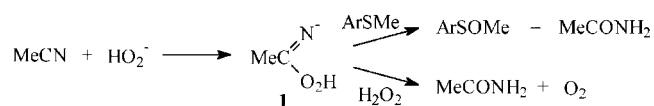
Scheme 1

Competitive trapping in a mixture of sulfides was favored by electron-donating substituents in MeOH–K_2CO_3, although there was no such effect on trapping by the less reactive sulfoxides and other reactions might have intervened.[10a] For example, organic solvents promote formation of peroxocarbonates from HCO_3^- and H_2O_2,[3] and the reaction of **1** with H_2O_2 could generate singlet oxygen, which would react rapidly with sulfides.[7,11]

We therefore examined the kinetics of oxidation of thioanisole by nitrile-activated H_2O_2 in water with $[H_2O_2] \gg [NaOH]$ to avoid possible catalysis by carbonate or hydrogencarbonate ion.[3] Under these conditions $[HO_2^-]$ is approximately equal to [NaOH]. The postulated mechanism of activation indicates that reactions should be zeroth order in [PhSMe] provided that it is at a sufficient concentration to compete effectively with H_2O_2 for **1**. Reaction products were identified by their ^{1}H NMR spectra.

EXPERIMENTAL

Materials. Hydrogen peroxide, 30% or 50%, stabilized or unstabilized, was used as in earlier work,[5] and the results

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were the same with the different samples. Thioanisole was material used earlier,[5] acetonitrile (MeCN) and propionitrile (EtCN) (Aldrich) were of spectrophotometric grade and benzonitrile was obtained from ACROS. Solutions were prepared in redistilled, deionized, water and reactions were followed at 25.0°C.

Kinetics. Reactions with MeCN or EtCN were followed spectrophotometrically on an HP 8451A spectrometer by measuring the decrease in absorbance as PhSMe is oxidized.[12] The wavelength was varied between 270 and 300 nm, depending upon [PhSMe] and [H_2O_2]. The absorbance change during reaction increases with decreasing wavelength, but the absorbance of H_2O_2 at low wavelengths is such that we followed the reaction with 1 M H_2O_2 at 290 and 300 nm.

Plots of absorbance against time were linear for up to over 90% reaction with dilute H_2O_2 and higher [PhSMe], but the extent of linearity decreased as [H_2O_2] was increased and [PhSMe] decreased. However, the number of data points in the linear region (30–70) was adequate for calculation of the slopes. The slopes were converted into reaction rates, i.e. zeroth-order rate constants, k_0 l mol^{-1} s^{-1}, by extrapolating absorbance back to the time of mixing and equating the decrease of absorbance in the course of reaction with the initial concentration of PhSMe. The reaction was started by adding PhSMe in a small volume of MeCN or EtCN to the stirred reaction mixture with a spring-loaded Hamilton syringe.

Formation of bubbles due to decomposition of peroxides is a problem when reactions are followed spectrophotometrically.[5] We did not have this problem in the present work provided that PhSMe is trapping all the peroxyimidate, but there is bubbling once PhSMe has reacted, and absorbance at complete reaction of PhSMe was estimated after tapping the cuvette and using a gentle vacuum to remove bubbles. However, we could not follow the reaction with [H_2O_2] > 1 M.

In all experiments H_2O_2 and nitrile were in large excess over PhSMe and their concentrations did not change significantly during reaction. As a control, absorbance was monitored in the absence of PhSMe and the decrease was small relative to that with PhSMe. The reference solution contained acetamide and NaOH, although their absorbances should be negligible at 270–280 nm.

The decomposition of H_2O_2 by reaction with MeCN was monitored titrimetrically following the general procedure of Wiberg.[8] Aliquots were removed and the reaction was quenched by 3 M H_2SO_4, KI was added and I_2 was titrated against $Na_2S_2O_3$, after addition of 0.001 M Na_2MoO_4. In one experiment samples were analyzed immediately after the acid quench, but generally analysis was made after removal of all the samples. Reactions were followed for up to 40% in dilute H_2O_2 and ~10% in more concentrated H_2O_2, to limit the depletion of MeCN.

NMR spectroscopy. Products of reaction in 5 vol.% MeCN were identified by their ^1H NMR spectra in a Varian Inova (Unity) instrument (400 MHz for ^1H), with suppression of the signal of ^1H_2O.[5a] Chemical shifts were referred to external sodium 3-(trimethylsilyl) propionate (TSP) in D_2O, and are: PhSOMe, 7.70 (3H), 7.79 (2H) and CH$_3$, 2.94 ppm; PhSO$_2$Me, o-H, 8.02 (d), m-H, 7.75 (t), p-H, 7.85 (t) and CH$_3$, 3.32 ppm; PhSMe, 7.42 (4H, multiplet), 7.28 (1H, t) and CH$_3$, 2.55 ppm. Signals of the amides were: acetamide, CH$_3$, 2.04 (s) ppm, and for propionamide: ^1H, 1.12 ppm (t), $J = 8$ Hz and 2.88 ppm (q); ^{13}C, 12.19 (CH_3CH_2-) and 31.26 (CH_3CH_2-) ppm. The product of the reaction in the presence of PhCN was identified as PhSOMe, by its CH$_3$ signal.

RESULTS AND DISCUSSION

Kinetics

Both H_2O_2 and HO_2^- absorb at up to 320 nm,[13] but except with high [H_2O_2] we followed the oxidations at 270 and 280 nm. Very little sulfone was formed, and it was identified by its ^1H NMR spectrum, which was taken 10–15 min after initiation of the reaction and was never more than 5% of PhSOMe.

With H_2O_2 in large excess over NaOH, [HO_2^-] ≈ [NaOH], but we made the (small) correction[13] by taking the base dissociation constant $K_b = 3 \times 10^{-3}$, and using the equation

$$[HO_2^-] = \frac{[NaOH]}{1 + K_b/[H_2O_2]} \qquad (1)$$

We assume that K_b will not be significantly affected by dilute MeCN or EtCN and H_2O_2 acts as its own buffer.[2c]

All the reactions give good linear plots of absorbance against time for much of the reaction, but there is uncertainty in the absorbance after complete reaction of PhSMe, in part because of bubbling, but also because of the continuing decomposition of H_2O_2, which should be relatively unimportant (Experimental). For reaction in 5 vol.% MeCN, 0.1 M H_2O_2 and 0.001 M NaOH, oxidation of PhSMe is complete within ca 100 s, and in that time with no PhSMe the absorbance decreases by 0.001 and 0.0006 at 270 and 280 nm, respectively. Decreases in absorbance due to oxidation of PhSMe shown in Fig. 1 are very much larger than those due to decomposition of H_2O_2, and some of the data points have been omitted for clarity. These figures also illustrate how the extents of linearity in plots of absorbance against time depend on reactant concentrations.

Values of k_0 for reaction in MeCN–H_2O are in given Table 1 and those for reaction mediated by EtCN in Table 2, with [EtCN] equivalent to [MeCN] in 5 vol.% MeCN.
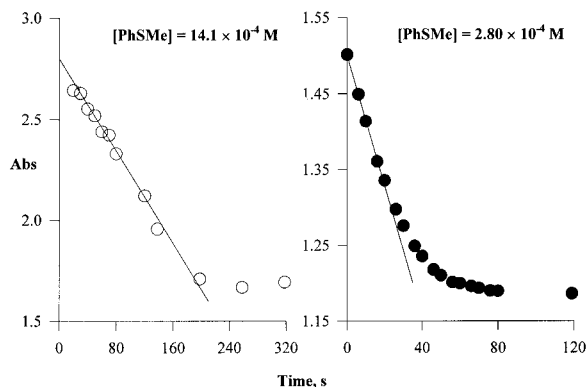
Figure 1. Variation of absorbance at 270 nm with time for reaction of thioanisole at 25.0°C, 0.1 M H_2O_2, 0.001 M NaOH in H_2O–MeCN (95:5, v/v) for 14.1×10^{-4} (○) and 2.80×10^{-4} (●) M PhSMe

The data in Table 1 show that k_0 increases with increasing [MeCN] and [HO_2^-] and, except for a few outlying points, values of k_0/[MeCN][HO_2^-] are not very sensitive to [H_2O_2] or [PhSMe]. There are uncertainties in k_0 due to experimental limitations in following the reaction spectrometrically, and difficulties in estimating absorbances after complete oxidation of PhSMe (Experimental). We assume that MeCN and EtCN are not exerting significant kinetic solvent effects, and it is difficult to decide whether effects of an increase in [PhSMe] on values of k_0 and k_0/[MeCN][HO_2^-] are real or due to experimental error, because there are differences in k_0 from experiments at different wavelengths. However, with a few exceptions, values of k_0/[MeCN][HO_2^-] are within 10% of the mean value of 7.8×10^{-4} l mol^{-1} s^{-1} (Table 1).

Slow reactions with and without NaOH

There is a slow oxidation of PhSMe by H_2O_2 in H_2O–MeCN in the absence of NaOH, which gives only sulf-

Table 2. Reaction with propionitrile[a]

10^4[PhSMe] (M)	2.81	4.50	16.5
$10^6 k_0$ (l mol^{-1} s^{-1})	9.07 (10.3)	10.50 (9.88)	11.5

[a] At 25°C, 6.83 vol.% EtCN, 0.1 M H_2O_2 and 0.001 M NaOH. Rates were measured at 280 nm (270 nm in parentheses).

Table 3. Products without and with NaOH[a]

Time (min)	PhSMe	PhSOMe	$PhSO_2Me$	$MeCONH_2$
5[b]	87	13		
20[b]	60	40		
10		65	35	188 (135)
15		27	73	333 (173)
35			100	1060 (200)

[a] Mole % of reactants and products, at 25°C, 5 vol.% MeCN, 0.1 M H_2O_2, 0.001 M PhSMe and 0.001 M NaOH.
[b] Without NaOH.

oxide, and was monitored by ^{1}H NMR spectroscopy (Table 3). The extent of reaction is in the range expected from data for reaction in H_2O–t-BuOH[5a] and the rate constant extrapolated from data for the acid-catalyzed oxidation of 4-nitrothioanisole.[14]

The reaction was started in a neutral solution where oxidation of PhSMe is slow and no $MeCO \cdot NH_2$ is formed. After 5 min, 0.001 M NaOH was added to one portion. All the PhSMe had been oxidized within 5 min after addition of NaOH, the time required for acquisition of the NMR spectrum, and with time PhSOMe was converted into $PhSO_2Me$ (Table 3), although this reaction does not necessarily involve the peroxyimidate.[15] Acetamide is formed after addition of NaOH to an extent greater than that expected in terms of oxidations of sulfide and sulfoxide due to reaction of **1** with H_2O_2[8] (Table 3). The amounts of acetamide in parentheses are calculated on the assumption that the overall formation of PhSOMe generates 1 equiv. and of $PhSO_2Me$ 2 equiv. of $MeCONH_2$. The excess $MeCONH_2$ increases sharply

Table 1. Reactions with MeCN[a]

MeCN (vol.%)	[NaOH] (M)	[H_2O_2] (M)	10^4[PhSMe] (M)	$10^6 k_0$ (l mol^{-1} s^{-1})	$10^4 k_0$/[MeCN][HO_2^-] (l mol^{-1} s^{-1})
2.5	0.001	0.1	3.10	3.14 (3.24)	6.9
			4.90	3.40 (3.25)	7.2
			15.5	3.84 (3.44)	7.8
5.0	0.001	0.01	4.50	6.69 (7.11)	7.4
			14.1	8.49 (7.87)	9.5
		0.1	2.80	7.03 (7.42)	7.8
			4.50	8.50 (8.67)	9.2
			14.1	8.00 (7.61)	8.4
	0.002	0.1	2.80	11.3 (12.1)	6.3
			4.50	13.4 (13.6)	7.3
			14.1	17.2 (15.5)	9.0
	0.001	0.5	15.5	7.54 (7.29)[b]	7.8
		1.0	15.5	7.18 (6.29)[b]	7.1
10.0		0.1	15.5	15.6 (14.3)	7.8

[a] Initial zero-order rate constants, l mol^{-1} s^{-1}, followed at 280 nm (270 nm in parentheses unless specified otherwise).
[b] Followed at 300 nm (290 nm in parentheses).

towards the end of the reaction, which is the MeCN-promoted decomposition of H_2O_2.[8]

Kinetic form

The linearity of the plots of absorbance against time (Fig. 1), provided that [PhSMe] is sufficient for quantitative trapping of intermediate **1**, is as expected for the reactions in Scheme 1, and is inconsistent with significant contributions by other reactions.

Decomposition of peroxyimidate, **1**, by reaction with H_2O_2 should generate $^1O_2$, which should rapidly oxidize PhSMe,[7,11] but there is also unproductive conversion of $^1O_2$ into $^3O_2$, and partitioning should depend on [PhSMe], which would preclude the observation of zeroth-order kinetics and the rate of formation of $^1O_2$ would depend on $[H_2O_2]$. We conclude that this reaction path could, at most, make only a minor contribution to the oxidation of PhSMe. The direct oxidation of PhSMe by H_2O_2, or formation of a peroxyimidic species from non-ionic H_2O_2 and MeCN, appear to be much slower than the reactions at higher pH (Tables 1 and 3). However, reaction of H_2O_2 with PhSMe (Table 3) should be first order rather than zeroth-order in [PhSMe], and might make a minor contribution at higher [PhSMe], although the rate would also depend significantly on $[H_2O_2]$ and we see no such effect (Table 1).

Decomposition of H_2O_2

In agreement with existing evidence, the rate of decomposition of H_2O_2, v l mol^{-1} s^{-1}, depends on [MeCN] and $[HO_2^-]$, but not on $[H_2O_2]$, and similar values are obtained titrimetrically and spectrophotometrically (Table 4).

Provided that PhSMe traps peroxyimidate, **1**, quantitatively, the rate of oxidation, k_0 (Table 1), should be half the rate, v, in the absence of PhSMe (Table 4), but the relative values are 1.6:1, based on a mean value of $v/[MeCN][HO_2^-] = 12.4 \times 10^{-4}$ l mol^{-1} s^{-1} as compared with $k_0/[MeCN][HO_2^-] = 7.8 \times 10^{-4}$ l mol^{-1} s^{-1}. Several factors may account for this discrepancy, by making

oxidation faster or decomposition of H_2O_2 slower than expected from the reactions shown in Scheme 1.

There is a direct reaction of H_2O_2 with PhSMe, which from other data we expect to be of minor importance except with the highest [PhSMe], and if we exclude these values (Table 1) the ratio increases to 1.8:1, which is almost within the scatter of the data.

Another possibility is that we are underestimating the rate of the reaction of HO_2^- with MeCN in the absence of PhSMe, and two factors could be involved. First, the formation of peroxyimidate, **1**, may be reversible, but its trapping by PhSMe is generally faster than reversion to HO_2^- and MeCN, and decomposition by attack of H_2O_2 is not fast enough to prevent some return in the absence of PhSMe. Second, the decomposition of peroxy acids involves attack of a peroxy anion on the peroxy acid, e.g. reaction of H_2O_2 with anionic peroxyimidate,[15] but in the absence of PhSMe, [peroxyimidate] may be such that decomposition involves reaction of peroxyimidic acid and peroxyimidate. In that event, the rate of decomposition of H_2O_2 would be the rate of formation of peroxyimidate, **1**, rather than twice that rate as in the classical reaction in the absence of PhSMe.[8]

We cannot distinguish between these explanations and in view of the uncertainties in the rate data (Table 1) the discrepancies between the two sets of data may not be real.

Reactivity of peroxyimidates

Peroxyimidates react rapidly with alkenes and sulfides[9,10] and the observation of zeroth-order kinetics in the oxidation of PhSMe shows that peroxyimidates, or the imidic acids, are considerably more reactive than typical peroxy acids. Sulfide oxidations by peroxycarboxylic acids and by peroxymonosulfate ion are first order in sulfide and can be followed by conventional methods.[1,12,16,17] For example, oxidations by the peroxocarbonate ion are first order in sulfide and can be followed readily at room temperature,[3] and for oxidation of PhSMe by 10^{-4} M HSO_5^-, $t_{0.5} \approx 11$ s at 25.0°C and the reaction is first order in sulfide.[17]

Table 4. Acetonitrile-mediated decomposition of H_2O_2[a]

MeCN (vol.%)	10^3[NaOH] (M)	$10^3[HO_2^-]$ (M)	$10^6 v$ (l mol^{-1} s^{-1})	$10^4 v/[MeCN][HO_2^-]$ (l mol^{-1} s^{-1})
5	1.0	0.97	12.0, 10.7[b]	12.9, 11.5[b]
5	2.0	1.94	21.0	11.8
5	1.0	0.99	11.7[c]	12.6
10	1.0	0.97	22.6	12.1
10	2.0	1.94	48.2	12.7

[a] At 25°C and 0.1 M H_2O_2 unless specified otherwise.
[b] Calculated from four points and immediate titration, rates are measured spectrometrically are 12.5 (± 0.1) $\times 10^{-6}$ l mol^{-1} s^{-1} at 270 and 280 nm.
[c] In 0.5 M H_2O_2, initial rate determined spectrometrically is 12.8 (± 0.02) $\times 10^{-6}$ l mol^{-1} s^{-1} at 270 and 280 nm.

Competition between substituted thioanisoles is favored by electron-donating substituents with $\rho = 1.0$,[10a] showing that oxidation by the peroxyimidate is activated and therefore much slower than a diffusion-controlled reaction.

The high reactivity of peroxyimidate, relative to other peroxy acids, also applies to alkene epoxidation.[9] We do not know the source of the high reactivity, but the hydroperoxy group loses a hydrogen ion in the course of reaction and may be favored by the imidic nitrogen.

Our kinetic data are consistent with the preparative results,[10b] and Payne *et al.*[9] have noted the desirability of avoiding high pH in these nitrile-mediated reactions with alkenes. Various groups have successfully used K_2CO_3 to control the pH in epoxidations and sulfide oxidations,[10] although here there may have been a contribution of reaction with peroxocarbonate, especially in organic solvents.[3] The problem with using high pH may be that alkali promotes decomposition of H_2O_2 rather than affecting formation and reaction of the peroxyimidate.

Reaction with benzonitrile

The oxidation of 0.001 M PhSMe and 0.01 M H_2O_2 was examined in an aqueous mixture with 0.04 M PhCN. With no NaOH the mixture remained turbid for up to 4 h at room temperature, but with 0.001 M NaOH it clarified within 3 min and we saw ^1H NMR signals of the CH_3 group of PhSOMe and $PhSO_2Me$ within the time (10 min) required for signal acquisition. The reaction occurs readily, despite the heterogeneous conditions, and Payne *et al.*[9] had noted that epoxidation of cyclohexene in MeOH is faster with PhCN than with MeCN. We could not use absorption spectroscopy to follow this reaction and ^1H NMR signals of the products in the aromatic region are obscured by those of PhCN.

CONCLUSIONS

Reactions of HO_2^- with nitriles generates peroxyimidates, which are rapidly trapped by PhSMe forming sulfoxide and subsequently sulfone. In aqueous solutions of MeCN or EtCN formation of sulfoxide is significantly faster than the competing reaction of H_2O_2 with peroxyimidate. Except with very dilute PhSMe, the rate of oxidation is that of formation of peroxyimidate, but as [PhSMe] decreases trapping is no longer quantitative and the rate of oxidation is no longer independent of [PhSMe].

The rate of reaction of HO_2^- and MeCN in the absence of PhSMe, giving $O_2 + MeCONH_2$, is higher than that with PhSMe by a factor of 1.6, although a factor of 2 would be expected, and there may be minor contributions from other oxidative reactions.

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