Activation of hydrogen peroxide *via* bicarbonate, sulfate, phosphate and urea in the oxidation of methyl phenyl sulfide

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ABSTRACT

The presence of bicarbonate had a strong effect on the rate of oxidation of methyl phenyl sulfide (MPS) by hydrogen peroxide. At different concentrations of bicarbonate and hydrogen peroxide, we have observed different proportional amounts of methyl phenyl sulfoxide (MPSO) and methyl phenyl sulfone (MPSO$_2$). With equimolar amounts of hydrogen peroxide, bicarbonate and methyl phenyl sulfide, the two oxidation products coexisted, and it was very difficult to isolate methyl phenyl sulfoxide. With a large excess of hydrogen peroxide and bicarbonate ion (10-fold), methyl phenyl sulfone appeared as the sole oxidation product, and we never observed methyl phenyl sulfoxide. Other possible activating agents such as H$_2$PO$_4{}^-$, HSO$_4{}^-$ and urea have also been used. It has been observed that comparative values of k_1 and k_2 for bicarbonate in H$_2$O were similar and very high, whereas they were distant from one another and lower for other potential activating agents. The same method using H$_2$O/EtOH (50:50) produced methyl phenyl sulfoxide as the sole reaction product after 2 h at RT.

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1. Introduction

Selective oxidation of sulfides to sulfoxide and sulfone under adjusted reaction conditions is an important process in the decontamination of sulfur mustard (a chemical warfare agent) [1–5] and production of organosulfurous compounds of medicinal importance [6].

The decontamination products of HD (hydrogen mustard: S(CH$_2$CH$_2$Cl)$_2$) *via* oxidation are sulfoxide (HDO) and sulfone (HDO$_2$). The sulfoxide is nonvesicant and quite stable toward hydrolysis, whereas the sulfone still retains appreciable vesicant activity and is prone to slow hydrolysis. Thus, HD can be rendered nonvesicant *via* selective oxidation to the sulfoxide [7].

Due to the toxic nature of mustard gas, the less toxic but structurally similar analogue 2-chloroethyl sulfide or methyl phenyl sulfide are commonly used to study this reaction [7].

Hydrogen peroxide is an ideal waste-avoiding oxidant for decontamination of chemical warfare agents, since water is the only theoretical by-product of the reaction. Additionally, hydrogen peroxide is very attractive as an oxidant for liquid-phase reactions due to its solubility in water and many organic solvents. Moreover, aqueous hydrogen peroxide solution is safe

in storage, operation and transportation, and it is easily available and relatively cheap. Hydrogen peroxide alone, without any organic solvent or catalyst, however, has to be used in a controlled manner due to the possibility of an over-oxidation reaction. Thus, oxidation of an organosulfurous compound (RR′S) by hydrogen peroxide can produce two oxidation products, sulfoxide (RR′SO) and sulfone (RR′SO$_2$), under different reaction conditions [8].

Hydrogen peroxide is a widely used oxidant with high active oxygen but with slow oxidising properties in the absence of activators. Many catalysts have been developed for hydrogen peroxide [9–18] in the oxidation of sulfides. A novel method for the activation of H$_2$O$_2$ by bicarbonate ion (BAP: bicarbonate-activated peroxide) was described in the oxidation of chemical warfare agents and stimulant sulfides in a mixed alcohol/water solvent [19–22]. The conditions of the BAP system are mild, with the pH around neutral, and the components of the system are inexpensive and environmentally friendly, including a broad spectrum decontamination solution ("Decon Green").

The active oxidant in the catalytic pathway was recognised as peroxymonocarbonate ion (HCO$_4{}^-$) formed by a reaction between bicarbonate ion and H$_2$O$_2$. The use of an alcohol cosolvent provided organic substrate solubility and favoured formation of peroxymonocarbonate.

In this study, we have investigated the role of the nature and the concentration of different activating agent (such as bicarbonate, hydrogen sulfate, dihydrogen phosphate and urea), surfactant, and

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cosolvent in the oxidation rate of methyl phenyl sulfide (a hydrogen mustard stimulant) *via* hydrogen peroxide.

2. Experimental

2.1. General

Electron ionization GC–MS spectra were recorded on a Varian (SATURN 4D) spectrometer using an ionization current of 8 μA with a capillary column (DB-5MS, 0.1 μm, 30 m $\times$ 0.250 mm). Only *m/z* values having intensities of more than 10% are given. Gas chromatograms were recorded on a Varian (STAR 3400cX) with a packed column (10% OV-101 CWHP 80/100, 2 m $\times$ 1.8″). Retention times for GC–MS and GC were reported using temperature programming (100–250 °C, 5 °C/min) with He flow rate of 10 mL/min.

2.2. Oxidation of methyl phenyl sulfide with activated H$_2$O$_2$

Methyl phenyl sulfide, H$_2$O$_2$ (30%) and Triton X-405 (octylphenol ethoxylate (non-ionic surfactant)) were obtained from Merck Company. Methyl phenyl sulfoxide and methyl phenyl sulfone were prepared in our laboratory [23,24] and were characterised by GC and GC–MS. The oxidation reaction was initiated by the addition of methyl phenyl sulfide to a stirred aqueous solution of H$_2$O$_2$ and activating agent (sodium bicarbonate, sodium dihydrogen phosphate, sodium hydrogen sulfate and urea) and Triton X-405 (as surfactant). The reaction was monitored, and the percentage of sulfides in the reaction mixture was determined *via* GC.

2.3. Preparation of methyl phenyl sulfoxide

Methyl phenyl sulfide (0.001 mol, 0.1 mL), H$_2$O$_2$ (0.001 mol, 0.1 mL of 35% solution), sodium bicarbonate (0.005 mol, 0.042 g), Triton X-405 (4%, 0.4 g) and H$_2$O/EtOH 50:50 (10 mL) were placed in a 50 mL, one-necked flask equipped with a mechanical stirrer. The solution was stirred at RT for 100 min. Extraction with chloroform, drying and evaporation of solvent have afforded methyl phenyl sulfoxide as an white solid. GC: retention time: 16.5 min. GC–MS: retention time: 6.9 min; *m/z* (intensity (%)): 41(17), 43(10), 45(25), 50(36), 51(68), 53(23), 55(12), 65(19), 77(50), 81(11), 94(24), 97(87), 124(20), 125(83), 140(100), 141(24).

2.4. Preparation of methyl phenyl sulfone

Methyl phenyl sulfide (0.001 mol, 0.1 mL), H$_2$O$_2$ (0.01 mol, 1 mL of 35% solution), sodium bicarbonate (0.005 mol, 0.042 g), Triton X-405 (4%, 0.4 g) and H$_2$O (10 mL) were placed in a 50 mL, one-necked flask equipped with a mechanical stirrer. The solution was stirred at RT for 50 min. Extraction with chloroform, drying and evaporation of solvent have afforded methyl phenyl sulfone as an white solid. GC: retention time: 17.6 min. GC–MS: retention time: 8.1 min; *m/z* (intensity (%)): 50(22), 51(47), 65(16), 77(100), 93(12), 94(51), 141(29), 156(31).

3. Results and discussion

Oxidation of methyl phenyl sulfide was performed after admixture of methyl phenyl sulfide with the aqueous solution of H$_2$O$_2$, activating agent and Triton X-405 surfactant, and the composition of the reaction mixture was followed by GC. The retention times of MPS, MPSO and MPSO$_2$ were 10.3, 16.5 and 17.6 min, respectively, in GC and 3.8, 6.9 and 8.1 min, respectively, in GC–MS.

The presence of bicarbonate had a strong effect on the oxidation rate of methyl phenyl sulfide by hydrogen peroxide. At different concentrations of bicarbonate and hydrogen peroxide, we have
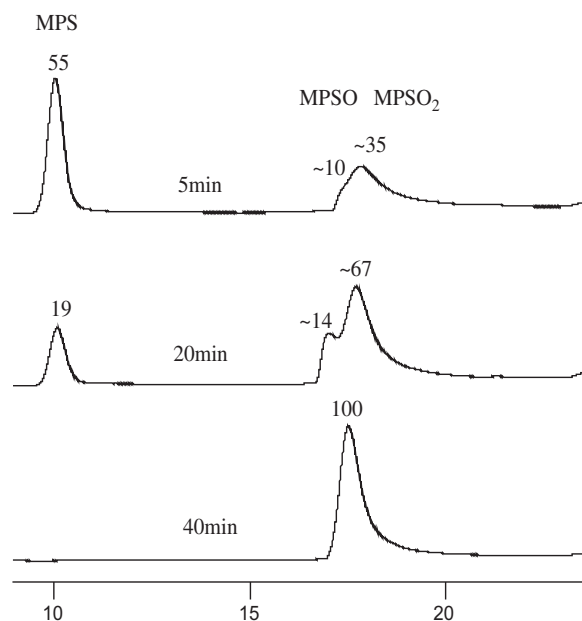

Fig. 1. GC analysis of the reaction mixture of methyl phenyl sulfide (0.001 mol) in aqueous solution (10 mL) of Triton X-405 (4%) in the presence of a 10-fold excess amount of H$_2$O$_2$ and sodium bicarbonate (activating agent).

observed different proportional amounts of methyl phenyl sulfoxide (MPSO) and methyl phenyl sulfone (MPSO$_2$). The optimised conditions for causing each of the two compounds to predominate were determined. With equimolar amounts of hydrogen peroxide, bicarbonate ion and methyl phenyl sulfide, two oxidation products coexisted, and it was very difficult to isolate methyl phenyl sulfoxide. Using H$_2$O/EtOH (50:50) as the solvent medium in the same conditions produced MPSO as the sole reaction product after 2 h at RT. On the other hand, with excess amounts of hydrogen peroxide and bicarbonate ion (10-fold), methyl phenyl sulfone appeared as the sole oxidation product after 40 min at RT, and we never observed methyl phenyl sulfoxide (Fig. 1, Table 1, entry 5). Other possible activating compounds such as H$_2$PO$_4^-$, HSO$_4^-$ and urea have been used for oxidation of methyl phenyl sulfoxide by H$_2$O$_2$ (Fig. 2, Table 1, entries 2–4).

The activating properties of these compounds were lower than that of bicarbonate, but selective oxidation to MPSO was easier to accomplish. With NaHPO$_4$, oxidation of MPS at RT with excess amounts of H$_2$O$_2$ and bicarbonate produced 100% of MPSO after 6 h (Fig. 2a, Table 1, entry 2). The same method using urea (CO(NH$_2$)$_2$) was performed with a duration of 180 min (Fig. 2c, Table 1, entry 4). KHSO$_4$ activated oxidation of MPS by H$_2$O$_2$, but selective oxidation to MPSO was not possible with this compound (Fig. 2b, Table 1, entry 3).

Table 1
Reaction times and proportional amounts of oxidation product of methyl phenyl sulfide (0.001 mol) in the presence of 10-fold excess of H$_2$O$_2$ and different activating agents in an aqueous solution (10 mL) of Triton X-405 surfactant (4%).

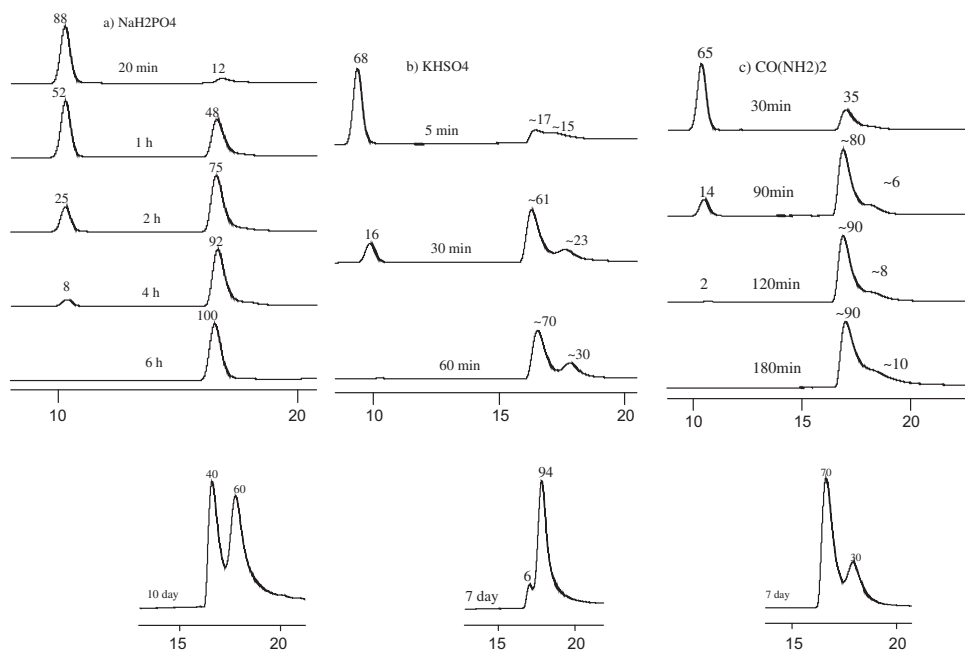| Entry	Activating agent	Sulfide (MPS) (%)	Sulfoxide (MPSO) (%)	Sulfone (MPSO2) (%)	Time
1	–	28	45	27	90 min
		5	–	95	12 h
2	NaH$_2$PO$_4$	–	100	–	6 h
		–	40	60	10 days
3	KHSO$_4$	–	70	30	60 min
		–	6	94	7 days
4	CO(NH$_2$)$_2$	–	100	–	180 min
		–	60	40	7 days
5	NaHCO$_3$	–	–	100	40 min

Fig. 2. GC analyses of the reaction mixture of methyl phenyl sulfide (0.001 mol) in aqueous solution (10 mL) of Triton X-405 (4%) in the presence of 10-fold excess amount of H_2O_2 and activating agent: (a) sodium dihydrogen phosphate; (b) sodium hydrogen sulfate and (c) urea.

Triton X-405 (non-ionic surfactant) act as a MPS dissolving agent in aqueous solution The presence of Triton X-405 (as surfactant) produces a slight increase in the oxidation rate of MPS to MPSO and $MPSO_2$ until 4%, after which it decreases the oxidation rate (Table 2). It seems that 4% is the critical micelle concentration (cmc) of Triton X-405 in H_2O. Considering the proportional amounts of MPS, MPSO and $MPSO_2$ in the reaction mixture, it seems that the formation of $MPSO_2$ is more influenced by surfactant concentration.

We constructed differential equations concerning the variation of concentrations of MPS, MPSO and $MPSO_2$ over time, following a two step consecutive oxidation reaction mechanism (Scheme 1) and with an excess amount of H_2O_2 as oxidation reactant (imposing). The solution of these differential equations and the concentrations of MPS, MPSO and $MPSO_2$ (with $C_0 = [MPS]_0$; initial concentration of methyl phenyl sulfide) over time can be expressed by the following equations [25].

$$[MPS] = C_\circ e^{-k'_1 t} \tag{1}$$

$$[MPSO] = \frac{k'_1 C_\circ}{k'_2 - k'_1}(e^{-k'_1 t} - e^{-k'_2 t}) \tag{2}$$

$$[MPSO_2] = C_\circ \left(1 - \frac{k'_2 e^{-k'_1 t}}{k'_2 - k'_1} + \frac{k'_1 e^{-k'_2 t}}{k'_2 - k'_1}\right) \tag{3}$$

Experimental results concerning the variation of concentrations of MPS, MPSO and $MPSO_2$ over time match well with these equations derived from a two steps consecutive oxidation mechanism.

In the conditions in which $k'_1 > k'_2$, Eq. (3) become

$$[MPSO_2] = C_\circ(1 - e^{-k'_2 t}) \tag{4}$$

The values of k_1, k_2 and their proportional values (k_1/k_2) for different activating agents are evaluated from Eqs. (1) and (4) and our experimental investigations (Table 3).

Thus the comparative values of the rate constants can be expressed as

$$k_1(HCO_3^-) > k_1(HSO_4^-) > k_1(Urea) > k_1(H_2PO_4^-)$$

$$k_2(HCO_3^-) > k_2(HSO_4^-) > k_2(H_2PO_4^-) > k_2(Urea)$$

and the comparative proportional values of k_1 and k_2 (k_2/k_1) for different activating agents can be expressed as

$$\frac{k_1}{k_2}(Urea) > \frac{k_1}{k_2}(HSO_4^-) > \frac{k_1}{k_2}(H_2PO_4^-) > \frac{k_1}{k_2}(HCO_3^-)$$

We can concluded that in excess amounts of H_2O_2 and activating agent in H_2O, the comparative values of k_1 and k_2 for bicarbonate were very high and approximately equal, whereas they were lower and distant from one another for other potential activating agents. Thus, complete separation of each step in the oxidation of methyl phenyl sulfide was impossible with bicarbonate, but it was possible in certain circumstances with other activated agents.

In the presence of co-solvent, the oxidation rates (k_1 and k_2) decreased (with a stronger effect on k_2), and in these conditions, separation of the two steps was possible.

Table 2
Proportional amounts of MPS, MPSO and $MPSO_2$ in the reaction mixture of MPS (0.001 mol), H_2O_2 (0.01 mol) and sodium bicarbonate (0.005 mol) in the presence of different concentrations of Triton X-405 surfactant in 10 mL H_2O after 40 min at RT.

Entry	Surfactant Triton X-405	Sulfide (MPS) (%)	Sulfoxide (MPSO) (%)	Sulfone (MPSO₂)
1	–	17	0	83
2	1%	5	0	95
3	4%	0	0	100
4	8%	11	50	39

Table 3
Rate constants (k_1, k_2) and their proportional values (k_1/k_2) in the oxidation of methyl phenyl sulfide (0.001 mol) in the presence of 10-fold excess of H_2O_2 and different activating agents in an aqueous solution (10 mL) of Triton X-405 surfactant (4%).

Rate constant	Activating agents			
	NaHCO₃	NaH₂PO₄	KHSO₄	CO(NH₂)₂
k_1 (mol⁻¹ min⁻¹)	0.11	11×10^{-3}	72×10^{-3}	25×10^{-3}
k_2 (mol⁻¹ min⁻¹)	0.12	0.65×10^{-4}	1.5×10^{-4}	0.35×10^{-4}
k_1/k_2	~1	169	480	714
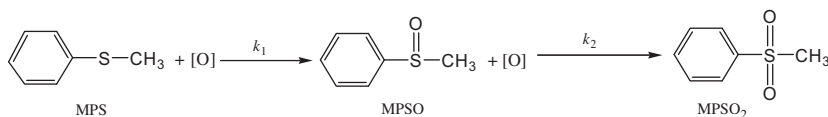
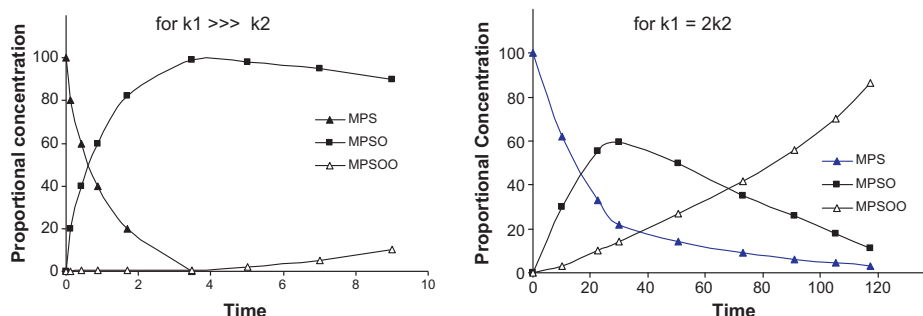**Scheme 1.** Two steps oxidation of methyl phenyl sulfide.

Fig. 3. Variation of proportional amounts of methyl phenyl sulfide (MPS), methyl phenyl sulfoxide (MPSO) and methyl phenyl sulfone (MPSO$_2$) with time, for different comparative values of k_1 and k_2.

The time at which the maximum amount of MPSO is present is obtained by differentiating Eq. (2) and resolving the following equation:

$$\frac{d[\text{MPSO}]}{dt} = \frac{-k_1' C_\circ (k_1' e^{-k_1' t} - k_2' e^{-k_2' t})}{k_2' - k_1'} = 0 \tag{5}$$

and is expressed by

$$t = \frac{1}{k_1' - k_2'} \ln \frac{k_1'}{k_2'} \tag{6}$$

from which was extracted the equation expressing the maximum amount of MPSO in terms of k_1' and k_2'.

$$\text{MPSO}_{\text{max}} = C_\circ \left(\frac{k_1'}{k_2'} \right)^{(k_2'/k_2' - k_1')} \tag{7}$$

Considering different proportional values of k_1 and k_2 ($k_1' \gg k_2'$ and $k_1' \sim k_2'$) and using these equations, we can evaluate the mixture composition over time (Fig. 3). For $k_1' = 100k_2'$, separation of the two steps and formation of MPSO (avoiding formation of MPSO$_2$) is possible, and $[\text{MPSO}]_{\text{max}} \approx C_0$. On the other hand, when $k_1' = 2k_2'$, separation of the two steps is impossible, and MPSO is rapidly transformed to MPSO$_2$. The maximum concentration of MPSO attainable in these conditions and at a favourable time is $0.5C_0$.

4. Conclusion

In this study, the influence of different activating agents on the rate and selective oxidation of MPS to MPSO and MPSO$_2$ was investigated. In the presence of excess amounts of H$_2$O$_2$ and bicarbonate, $k_1' \sim k_2'$; separation of the two oxidation steps was impossible; and methyl phenyl sulfone was the sole final oxidation product. In the presence of excess amounts of urea, dihydrogen phosphate and hydrogen sulfate, $k_1 > k_2$. In these cases, separation of the two steps was possible, and by controlling the reaction time, each oxidation product (sulfoxide or sulfone) was obtained.

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