New microemulsions for oxidative decontamination of mustard gas analogues and polymer-thickened half-mustard

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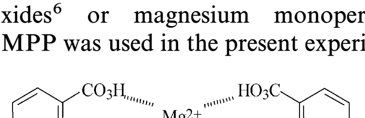
Chemical decontamination of toxic compounds (warfare agents and pesticides) is of increasing importance. In this study, we report the oxidation of mustard gas analogues in microemulsion media. A first formulation, very well-suited for stock-pile destruction, allows a fast, quantitative and chemoselective oxidation of the analogues. In a second formulation, the choice of microemulsion components used allowed us to study the oxidation of a polymer-thickened half-mustard (2-chloroethylphenyl sulfide), opening the field of application of these microemulsions to on-site decontamination. These results confirm both the efficiency and potential of microemulsions for mustard gas destruction/decontamination in essentially aqueous systems.

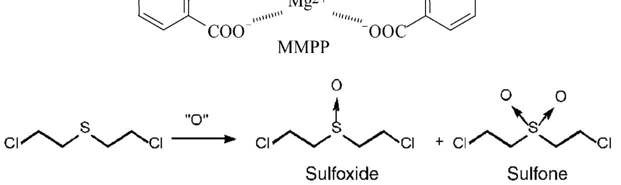
Formulation de nouvelles microémulsions pour la décontamination par oxydation d'analogues soufrés de l'ypérite et d'un demi-moutarde adsorbé sur polymère. La décontamination chimique de composés toxiques (pesticides ou toxiques de guerre) est d'une importance croissante. Dans cette étude, nous décrivons l'oxydation de composés soufrés modèles de l'ypérite en milieu microémulsion. Dans un premier temps, une formulation particulièrement bien adaptée à la destruction de stocks d'ypérite est décrite: celle ci permet une oxydation rapide, quantitative et chimiosélective des modèles du toxique. Une deuxième formulation nous a ensuite permis de réaliser l'oxydation d'un modèle très proche de l'ypérite (le demi-moutarde 2-chloroéthylphényl sulfure) formulé sur polymère, ouvrant ainsi le champ d'application de nos systèmes à la décontamination sur site. Ces résultats démontrent encore une fois l'efficacité et le potentiel des microémulsions pour la destruction de l'ypérite en mileu majoritairement aqueux.

Bis(2-chloroethyl) sulfide, known as mustard gas or yperite, is a chemical warfare agent first used in World War I. Large amounts of this compound are still stockpiled throughout the world. The compound attacks mucous membranes, skin, eyes and the respiratory tract and is an alkylating agent that is lethal even at low doses.[1] Until the 1980's, yperite was mainly destroyed by incineration. However, this incurs the additional hazard of transportation to the incineration site and release of toxic compounds during the process. Safer methods are required for the *in situ* destruction of the compound. Since the corresponding sulfoxide (Scheme 1) is relatively harmless, we studied here its degradation by oxidation. However, oxidation may also give rise to the sulfone, which is somewhat toxic.[2]

A method for rapid detoxification that favours production of the sulfoxide is thus required. Oxidation in a basic reaction medium can also allow the detoxification of mustard gas: elimination of HCl by the chlorosulfoxide and/or the chlorosulfone leads to the corresponding vinyl sulfoxide and/or vinyl sulfone, which are harmless compounds. Various oxidising agents have been used for this decontamination reaction, including hypochlorites,[3] peracids of the oxone type,[4] oxaziridines,[5] peroxides[6] or magnesium monoperoxyphthalate (MMPP).[7] MMPP was used in the present experiments.



MMPP



Scheme 1 Oxidation products of yperite.

In a recent review of the hydrolysis of toxic organophosphorus compounds,[8] we described the advantages of organised molecular systems as reaction media. There appear to have been few studies on the use of such media for the degradation of sulfur-containing compounds, although they appear to offer considerable advantages for rapid and chemoselective reactions. Drago *et al.* reported the advantages of phase transfer for oxidation of sulfur compounds with sodium hypochlorite,[9] while Lion and colleagues employed MMPP successfully both with and without surfactant.[7] Menger and Elrington employed a microemulsion to form the sulfoxide of the half-mustard Cl-CH_2CH_2-S-CH_2CH_3 with sodium hypochlorite.[10] Menger and Rourk later described the formulation of microemulsions able to simultaneously destroy, *via* oxidative and hydrolytic mechanisms, simulants of three chemical warfare agents.[11]

We have recently shown that micellar or mixed micellar media (water + structured polar solvent) are well-suited for the hydrolysis of toxic organophosphorus compounds.[12] Glycerol was used for the hydrolysis reaction. In another study on the oxidation of mustard gas analogues,[13] we selected formamide, which we had previously used to produce colloidal media.[14] In this respect, Chen and Reymond demonstrated the high reactivity of a mixture of hydrogen peroxide and formamide for the oxidation of alkenes.[15] They postulated the formation of small amounts of performic acid, which is used up as it is generated *in situ.*

In an analogous system, we replaced the rather unstable hydrogen peroxide with MMPP. A micellar medium consisting of a cetylpyridinium chloride and water–formamide binary system (50 : 50 v/v) allowed the quantitative oxidation of the half-mustard 2-chloroethyl sulfide by MMPP with 99% sulfoxide production.[16] These examples indicate the suitability of

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organised aqueous media for the decontamination of mustard gas.

However, mustard gas is often "thickened" by mixing with 5–10% of a polymer thickener.[3] The thickened agent is more viscous and adheres better to surfaces than the neat agent, making it more difficult to remove. The possible presence of a thickener in the poison adds a significant constraint to the design of a decontamination medium.

We report here the development of new decontaminant microemulsions. A microemulsion is an isotropic and optically transparent dispersion of oil in water (O/W) or water in oil (W/O), where the "oil" is a hydrocarbon (or an organic solvent). Such chemical systems form spontaneously when water (a structured polar solvent) or a mixture of structured polar solvents, a surfactant (noted TA), a cosurfactant (noted coTA, generally a low molecular weight alcohol) and a hydrocarbon are mixed in specific proportions. Microemulsions, with dispersed droplets averaging 50–500 Å in diameter, remain clear indefinitely. Microemulsions allow greater oil solubilisation than micellar solutions, and thus a better solubilisation of the toxin. Furthermore, the presence of an organic solvent in these systems could permit the solubilisation of the thickened agent.

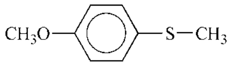
Two types of microemulsions were developed: one very well-suited to stock-pile destruction (formulation A), and a second, in which the choice of components used allowed us to study the oxidation of a polymer-thickened half-mustard, opening the field of application of this microemulsion to on-site decontamination (formulation B).

Results and discussion

Formulation A: microemulsion for stock-pile destruction

First let us describe the constituents of the microemulsion. The continuous phase of microemulsion A was water or the binary system water–formamide (50 : 50 v/v). We used cetylpyridinium chloride (CPCl) as surfactant (we had already used it in micellar solutions) because it promotes localisation of both MMPP and formamide (the oxidising system) at the micellar interface *via* the following mechanisms: by exchange of the counter-ion Cl^- and the perphthalate ion for MMPP, and for formamide, by preferential solvation (with respect to water) of the pyridinium head.[17] Butanone was used as cosurfactant; no oxidation of this compound by MMPP can occur under the conditions used.

The success of chemical decontamination in micellar solutions was found to depend largely on the lipophilicity of the model compounds (evaluated by the log P parameter) and their corresponding sulfoxides. The reactivity and selectivity of the reaction were related to the localisation of the different substrates in the microheterogeneous medium. *p*-Methoxyphenyl methyl sulfide (**1**), thioanisole (**2**) and the half mustard 2-chloroethyl phenyl sulfide (**3**) (log $P < 3$ for these three compounds) appeared to be suitable compounds to model the degradation of yperite.[16] So, we used these compounds as simulants in the oxidation reaction in microemulsions where they acted as the oil of the system. Indeed, according to the "molecular economy principle", postulated by our laboratory,[14a] we chose to retain compounds having several functions: here, the model substrate to be oxidised constituted the microemulsion oil.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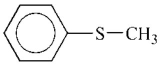
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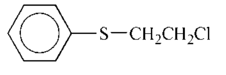
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In order to obtain a pseudo-ternary phase diagram, we retained a cosurfactant : surfactant weight ratio of 2; the microemulsion oil chosen was thioanisole, and the third constituent was the binary solvent system (water–formamide; 50 : 50, v/v). The resulting pseudo-ternary phase diagram is presented in Fig. 1.

The microemulsion zone is sufficiently large to be used for the oxidation process. Moreover, solubilisation of more than 20% oil can be achieved in a homogeneous medium. So, large quantities of the toxin (or its model compound) can be neutralised, limiting the volume of microemulsion required.

We retained the following formulation for the oxidation tests: 60% of the pseudo-constituent (coTA–TA) with a weight ratio of 2; 30% of the binary system water–formamide (50 : 50 v/v); 10% of the model compound. This formulation is visualised by point A on the phase diagram.

The three model substrates were oxidised in the formulation described above. MMPP was used stoichiometrically with regard to the model substrate (the molar ratio sulfide : MMPP was kept constant and equal to 0.55; MMPP is a di-oxidant, so 1.1 equiv. were used for 1 equiv. of the analogue). The experimental conditions of stock-pile destruction allow us to control the relative stoichiometry of the oxidising agent and of the mustard gas; in contrast, the amounts and the concentrations of the toxin are unknown in battlefield decontamination. In this case, the problem is more difficult to resolve: decontaminant solutions are often used in excess, so over-oxidation can occur. Our results are summarised in Table 1.

The analysis of these results shows that the three model substrates are oxidised quantitatively (or nearly quantitatively), whatever the microemulsion used (aqueous or binary solvent system): minimal observed conversion is 98%. The selectivity in favour of sulfoxide is excellent: no more than 6% sulfone is produced, and only 1% sulfone is formed

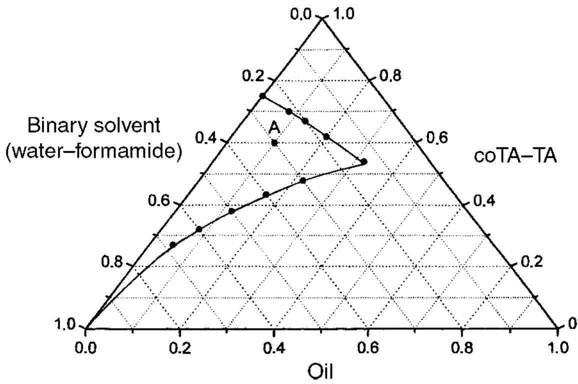

Fig. 1 Pseudo-ternary phase diagram of the CPCl–butanone–thioanisole–binary solvent (water–formamide, 50 : 50 v/v) system.

Table 1 Oxidation of the model substrates in microemulsion medium by MMPP[a]

Model substrates	Microemulsion			
	Aqueous		Binary system[b]	
	Yield/%[c]	Select.[c]	Yields/%[c]	Select.[c]
p-CH_3O-C_6H_4-SCH_3	100	95 : 5	99	94 : 6
C_6H_5-SCH_3	100	96 : 4	100	99 : 1
C_6H_5-SCH_2CH_2Cl	98	96 : 4	98	95 : 5

[a] All reactions were carried out at 25 °C for 1 h. The molar ratio MMPP : substrate was kept constant and equal to 0.55. [b] Water–formamide (50 : 50 v/v). [c] Yields and selectivity (molar ratio sulfoxide : sulfone) were determined by HPLC after calibration using an internal standard. The uncertainty of the results is evaluated at ±2%.

in the oxidation of thioanisole by the binary solvent system microemulsion.

The microemulsion medium has a marked influence on the oxidation reaction: first, it allows total solubilisation of the model substrates (as opposed to micellar solutions, where the model substrates form emulsions in the aqueous or binary system continuous phase); then, the preferential location at the interface of the oxidising agent (MMPP and formamide) and of the model substrates leads to a better contact between the reactants that favours the first oxidation (leading to sulfoxide); finally, the more hydrophilic sulfoxide is expelled into the continuous phase, preventing further oxidation. Note here that the microemulsion allows fast reaction times: in 3.5 min (time required to dissolve MMPP in the reaction medium), thioanisole oxidation is complete; the results (yield and selectivity) were unchanged after 1 h reaction.

Formulation A is therefore very efficient: it allows fast and quantitative oxidation of various mustard gas analogues, with strong sulfoxide selectivity. We can also add that all the reagents used are cheap, available on the laboratory and the industrial scales and do not require particular conditions for their utilisation.

We then modified the formulation: our goal being a system to permit on-site detoxification of mustard gas (and not stockpile destruction), and more particularly destruction of polymer-thickened mustard gas.

Formulation B: microemulsion for decontamination of polymer-thickened agent

Mustard gas and Soman (3,3-dimethyl-2-butylmethylphosphonofluoridate) are often formulated with 5 to 10% (by weight) of an organic polymer. For example, Paraloid K125, a methylethylbutyl methacrylate copolymer of high molecular weight, developed by Rohm & Haas, is used to thicken such toxic agents.[3] We thus used K125 in order to prepare the model substrate (10% by weight with regard to the half-mustard).

The polymer has multiple roles: (*i*) it controls the rheology of toxin scattered by the weapon's explosion; (*ii*) its higher viscosity makes it adhere better to surfaces, so the toxin is more difficult to remove, extending its action; (*iii*) finally, because of its organic nature, the polymer prevents solubilisation of the toxin in most aqueous decontaminant solutions. It was observed that upon contact with water, a polymer film can form at the interface between the thickened agent and water: this prevents the thickened agent from dissolving into the decontaminant solution.[3] The presence of a thickener in the poison adds constraints to the conception of an efficient decontamination medium.

The choice of mustard gas analogue was critical: indeed, the model must present a lipophilicity near that of yperite, and must also allow similar solubilisation of the polymer (Paraloid K125). The rheology and the behaviour of the couple polymer/model substrate must be as near as possible to those of the thickened mustard gas. With *p*-methoxyphenyl methyl sulfide and thioanisole, the polymer does not present the same solubilisation characteristics, being insufficiently soluble. In contrast, the half-mustard 2-chloroethyl phenyl sulfide seems to mimic the thickened mustard gas satisfactorily: the polymer first expands, then dissolves.

The relative proportion of polymer with regard to the half-mustard was set at 10% by weight: in these proportions only part of the polymer was solubilised, the rest being present in an elastic and very viscous form.

In order to be efficient, the microemulsion must contain two essential components: an organic solvent able to solubilise both toxin and polymer, and a decontaminating agent that reacts with the toxin and neutralises it. MMPP was again used.

The previous results (formulation A) being more than satisfactory, we chose to conserve, as well as possible the best formulation studied, but adapted to battlefield conditions:
(*i*) cetylpyridinium chloride as surfactant;
(*ii*) butan-1-ol as cosurfactant; this compound leads to a larger (compared to butanone) microemulsion zone in the phase diagram;
(*iii*) water as continuous phase; no formamide was used because of its toxicity;
(*iv*) benzyl chloride as oil; this solvent dissolves the polymer efficiently (up to 5.8% weight), has a low freezing point (−43 to −39 °C), which is an advantage for low-temperature use, has low toxicity and has previously been used by Bartram and colleagues as a substitute for *N*-cyclohexyl-2-pyrrolidone in the U.S. Army D.A.M. (decontamination agent multipurpose) formulation.[18] Benzyl chloride is, however, a reactive material, so only war equipment and materials can be detoxified on the battlefield by the microemulsions described here (it cannot be used for skin decontamination).

The resulting pseudo-ternary phase diagram is presented in Fig. 2. It shows a large microemulsion zone, which could allow us to work in direct microemulsion (water as continuous phase; left part of the diagram) or inverse microemulsion (benzyl chloride as continuous phase; right part of the diagram). The main advantage resides in the quantity of oil that can be dissolved in water-rich formulations: for example, 15% benzyl chloride dissolves in a formulation containing 50% water. However, the decontaminating system must be essentially aqueous, because large quantities of organic solvent are susceptible to damage painted surfaces, plastics, rubbers, *etc.*

Finally, a useful formulation must be largely aqueous, and be able to accept the addition of 10% by weight of the substrate without phase separation, in order to be efficient in the battlefield (this constraint is necessary to preserve a microemulsion at the time of the application of our system on the polymer-thickened toxin). Table 2 shows the behaviour of many phase diagram points before and after addition of 10% (by weight) half-mustard.

We have therefore performed the oxidation tests at points E, H and K. In a comparative way, we used a stoichiometric amount of MMPP with regard to the half-mustard, as previously described for formulation A. The oxidation reaction being stoichiometric, large weights of peracid must be used in battlefield decontamination. However, the water-rich microemulsions described here (minimum 40% by weight of water) allow solubilisation of large amounts of MMPP. We can also compare the effect of an increasing quantity of oil on the oxidation of thickened half-mustard, the amount of water remaining between 40 and 50% by weight. Half-mustard and polymer-thickened half-mustard were oxidised in the formulations described above. The results obtained are listed for comparison in Table 3.

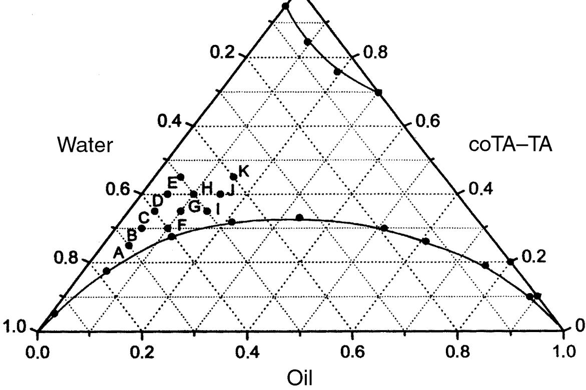

Fig. 2 Pseudo-ternary phase diagram of the CPCl–butan-1-ol–benzyl chloride–water system.

Table 2 Behaviour of some phase diagram formulations after addition of 10% (by weight) of the half-mustard 2-chloroethyl phenyl sulfide

Points	Composition [coTA–TA]–oil–water	Physical state after half-mustard addition
A	25 : 5 : 70	Phase separation
B	30 : 5 : 65	Phase separation
C	35 : 5 : 60	Phase separation
D	40 : 5 : 55	Microemulsion
E	45 : 5 : 50	Microemulsion
F	30 : 10 : 60	Phase separation
G	35 : 10 : 55	Phase separation
H	40 : 10 : 50	Microemulsion
I	35 : 15 : 50	Phase separation
J	40 : 15 : 45	Microemulsion
K	45 : 15 : 40	Microemulsion

[a] By weight with a fixed cosurfactant–surfactant ratio of 2 (also by weight).

For half-mustard oxidation, the same results were obtained as with the previously described microemulsion (formulation A). Yields were over 95% and selectivity in favour of the sulfoxide remained important (less than 10% sulfone produced). These results therefore confirm the efficiency of microemulsions as reaction media for mustard gas analogue oxidation.

For oxidation of the polymer-thickened half-mustard, we note that sulfide conversion decreased by 10 to 15%, and the proportion of sulfoxide obtained decreased by 10 to 15%, with a corresponding increase in sulfone production. These results can be interpreted by considering the physical state of the half-mustard: one part, accessible, is incorporated in the microemulsion oil droplets, and then converted into the corresponding sulfoxide. Another part of the sulfide, however, is trapped in the polymer. Competition occurs between the oxidation of the sulfoxide already formed and the less available sulfide fraction: the proportion of sulfone produced then increases.

The MMPP consumed for sulfoxide oxidation is lacking at the end of the reaction, no longer permitting quantitative oxidation of the sulfide, as observed in the absence of thickener.

We can also note that the percentage of oil used in the microemulsion weakly influences the yield and selectivity of the reaction. So, 5% (and even better 10%) could be sufficient to allow extraction of half-mustard from the polymeric phase into the microemulsion phase.

Another effect can decrease solvation of the K125 polymer by benzyl chloride; it is assumed that sulfur mustard restricts the mobility of polymeric chains by acting as an antiplasticising agent. Antiplasticisation results from one or both of the following effects: (*i*) a decrease in free volume upon addition of the toxin, the toxin acting as a diluent that fills the excess volume of the polymer, or (*ii*) polymer-toxin interactions, which create steric hindrance and decrease the segmental mobility of the polymer.[19] Similar behaviour could be postulated for the half-mustard 2-chloroethyl phenyl sulfide, which has a structure resembling that of yperite.

Table 3 Oxidation of half-mustard and polymer-thickened half-mustard in various microemulsion formulations[a]

Formulation	Half-mustard	Polymer-thickened	half-mustard
E	Yield %[b]	96	81
(5% OIL)	Select.[b]	95 : 5	80 : 20
H	Yield %[b]	95	86
(10% OIL)	Select.[b]	90 : 10	84 : 16
K	Yield %[b]	97	84
(15% OIL)	Select.[b]	97 : 3	87 : 13

[a] All reactions were carried out at 25 °C for 1 h. The molar ratio MMPP : substrate was kept constant and equal to 0.55. [b] Yields and selectivity (molar ratio sulfoxide : sulfone) were determined by HPLC after calibration using an internal standard. The uncertainty of the results is evaluated at ±2%.

These results show that microemulsions are well-suited for the oxidative destruction of polymer-thickened half-mustard. Despite difficult experimental conditions: 10% by weight of polymer with regard to the toxin, whereas 3 to 5% only are generally used, and a small quantity of decontaminant microemulsion was used with regard to the thickened-polymer half-mustard (weight of microemulsion used only 10 times the weight of thickened half-mustard, whereas large amounts are used in on-site decontamination), the microemulsion developed remained efficient: with 10% oil formulation, more than 85% of the model substrate was oxidised, of which 85% was in the form of the sulfoxide.

Conclusion

In this study, we developed new decontaminant microemulsions. The systems were shown to be well-suited for selective oxidation of mustard gas analogues.

Firstly, we formulated systems where the model substrate was also the microemulsion oil: this strategy could be applied to the oxidation of stock-piled mustard gas. Indeed, the oxidation of the simulants in microemulsion media is fast (oxidation of thioanisole was complete in 3.5 min), quantitative and highly chemoselective (sulfoxide production of up to 99%). Total solubilisation of the simulants, preferential location at the micellar interface of both oxidising agent and model substrates and expulsion of the sulfoxide produced into the continuous phase explain the efficiency observed.

Secondly, we developed a microemulsion for on-site decontamination, and particularly for oxidation of polymer-thickened half-mustard. The formulation was efficient: despite the difficult experimental conditions we imposed (10% polymer with regard to the toxin, low amount of microemulsion used), oxidation of 2-chloroethylphenyl sulfide occurred with 85% conversion and suitable chemoselectivity (no more than 15% of sulfone was produced). The relative speeds of simulant solubilisation (which requires sufficient solvation of the polymer, and which is thus a slow phenomenon) and oxidation (relatively faster) are responsible for the lower yields and selectivity: a fraction of the MMPP being used for oxidation of the freshly produced sulfoxide rather than for oxidation of the polymer-trapped sulfide.

Nevertheless, these results demonstrate both the efficiency and potential of microemulsions for mustard-gas destruction/decontamination in essentially aqueous systems.

Materials and methods

Chemicals

p-Methoxyphenyl methyl sulfide (97%), thioanisole (99%), 2-chloroethyl phenyl sulfide (98%) and MMPP (monoperoxyphthalic acid, magnesium salt hexahydrate, 80%) were purchased from Aldrich. Cetylpyridinium chloride monohydrate (99%) and formamide (99.5%) were obtained from Acros. Butanone (>99.5%) and benzyl chloride (99.5%) were purchased from Fluka. Butan-1-ol (>99.5%) was purchased from Prolabo. We thank Rohm & Haas (France) for a sample of Paraloid K125.

Pseudo-ternary phase diagrams

Formulation A. We used thioanisole as oil to plot the phase diagram, and the weight ratio cosurfactant–surfactant (pseudo-constituent) was 2. The pseudo-ternary phase diagram was obtained by titrating several mixtures of pseudo-constituent and oil with the binary solvent system (water–formamide, 50 : 50, v/v) until transparency, as described previously.[20]

For the other model substrates (*p*-methoxyphenyl methyl sulfide and 2-chloroethyl phenyl sulfide), we only checked that the microemulsions were obtained in the retained formulation by substituting thioanisole with the other mustard-gas simulants.

Formulation B. The same procedure was used, except that the surfactant–cosurfactant–oil (benzyl chloride) mixture was titrated with water.

Oxidation in formulation A

The procedure used is illustrated by thioanisole oxidation: a mixture of 0.703 g (5.67×10^{-3} mol; 1 equiv.) of thioanisole, 2.812 g of butanone, 1.406 g of CPCl and 2.109 g of the binary solvent system (water–formamide; 50 : 50, v/v) was stirred magnetically in a round-bottom flask. This mixture is homogeneous, in accordance with the phase diagram. Then, 1.928 g (3.90×10^{-3} mol; 0.55 equiv.) of 80% MMPP is introduced rapidly. One hour later, residual MMPP is neutralised by excess $NaHCO_3$; the mixture is extracted with chloroform (3 × 50 mL) and the solvent evaporated under reduced pressure. The residue is taken up in 50 mL chloroform in a graduated flask. One milliliter of this solution is added to a 25 mL graduated flask along with 1 mL standard stock solution of benzophenone and made up to the mark with chloroform. The resulting solution is then analysed by HPLC as previously described.[16] Sulfoxides, sulfones and starting sulfides (eventually) only were detected by HPLC. No evidence for vinyl sulfoxide and/or vinyl sulfone production was found. The microemulsion's pH was not determined: it might be slightly acidic (because of the influence of the MMPP). However, microemulsions being microheterogeneous (continuous phase, interface, micellar core), it is always difficult to determine exactly the pH parameter.

Oxidation in formulation B

A mixture of 0.489 g of 2-chloroethyl phenyl sulfide (2.835×10^{-3} mol; 1 equiv.) and 0.049 g of K125 polymer (10% by weight with respect to the toxic) is introduced in a round-bottom flask; 10 min later (time for optimum solvation of the polymer by the simulant), 5.380 g of previously prepared microemulsion (0.717 g CPCl; 1.434 g butan-1-ol; 0.538 g benzyl chloride and 2.690 g water; formulation H) and 0.964 g of 80% MMPP (1.95×10^{-3} mol; 0.55 equiv.) were added. One hour later, the reaction medium was treated and analysed in the same way as formulation A.

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