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Microemulsions as reaction media. Self-organizing assemblies in an environmental cleanup problem

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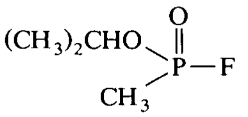
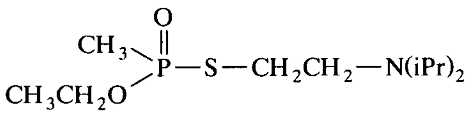
Abstract. A microemulsion system has been developed that simultaneously destroys three environmental contaminants by combined oxidative/hydrolytic pathways. The method is rapid, cheap, and mild. No special equipment (stirrer, heater, photolyzer, etc.) is required. Self-organization converts a seemingly intractable 8-component mixture into a useful system, a tactic discovered by living cells long ago.

Introduction

On January 15, 1993 more than 130 countries signed the International Convention on Prohibition of the Development, Production, Stockpiling, and Use of Chemical Weapons and on their Destruction (known as the Chemical Weapons Convention[1]). The agreement states that stockpiled chemical warfare agents are to be destroyed in an "essentially irreversible manner" by the end of the year 2004. This will be no small task. United States alone possesses about 25000 tons of chemical warfare agents (primarily mustard and the nerve agents GB and VX). Although the Convention did not specify a particular disposal technology, it is clear that, to ensure public acceptability, the waste stream created by any chemical demilitarization system must be environmentally innocuous.



GB



VX

$(ClCH_2CH_2)_2S$

mustard

Despite the planned mass disposal, there will always remain a risk that individuals of ill intent will obtain or synthesize various amounts of these chemicals for their own purposes. The overall problem has, therefore, two rather different aspects to it: (*a*) destruction of bulk material and (*b*) rapid deactivation in cases of actual use.

Since the chemical warfare agents are lethal in minute quantities, and since the agents are difficult to detect without a direct search, the value of (*b*) to the public security is obvious.

Various methods have already been tested for bulk destruction. United States has mixed GB with caustic (aqueous NaOH), but some batches required weeks to arrive at a zero GB assay. Incineration of GB, VX, and mustard works well (> 99.99999% efficiency), but it has been hard to pursuade the citizenry that local incinerators will never go awry. Canada has used lime at 95°C to hydrolyze mustards (the hydrolysis products being incinerated or spread on prairie land for further degradation). The former Soviet Union has neutralized chemical warfare agents by batch treatment with aqueous ethanolamine at 100°C for 30–45 minutes. The U.N. at Al Muthanna, Iraq destroyed mustards by incineration (1100°C for 3–4 seconds) and nerve agents by batch hydrolysis (excess aqueous NaOH in a recirculating reactor). None of these procedures is, of course, germane to the need for possesing a rapid detoxification method in cases of threatened or actual use.

Ingenious new technologies have been tested with regard to chemical weapons destruction. These include ^{60}Co gamma irradiation, wet-air oxidation, supercritical-water oxidation, plasma-arc processes, molten-salt oxidation, and enzyme-based detoxification. (It has even been proposed to transport all the chemical weapons to an isolated spot and then A-bombing the site: one technological horror being used to counter another). Nothing yet has come of these alternative methods, but it may be hoped that one or more of them will, ultimately, achieve success not only with chemical weapons but with environmental pollutants in general.

Our interest has been solely on chemical detoxification processes in situations where personnel or equipment have become, accidentally or deliberately, exposed to the chemical agents. The following list of specifications reveals the magnitude of the challenge:

(*a*) *Speed.* To be truly effective, the detoxification reactions must be completed in less than a minute (and, ideally, much less than a minute).

(*b*) *Generality*. The detoxification regime should simultaneously encompass both major groups of chemical warfare agents, namely mustards and phosphorus(V) compounds.

(*c*) *Capacity*. The detoxification reactions must operate on realistically high levels of chemical agent. This is an important stipulation because typical conditions for most kinetic studies (10^{-5} to 10^{-3} M substrate) are inappropriate for use in the field.

(*d*) *Conditions*. Burdensome paraphernalia (*e.g.* photolysis lamps, stirring motors, heating devices, etc.) should be avoided. Caustic media, such as used in the bulk destruction, are valueless because skin, computer boards, and other sensitive surfaces may require decontamination. Aqueous systems are preferred over the more toxic and flammable organic solvents.

(*e*) *Efficiency*. Catalytic processes are, of course, ideal. But an agent could also be advantageously destroyed with a decontaminant via a 1:1 stoichiometric reaction provided the molecular weight of the decontaminant is not too great. High-molecular weight decontaminants require a great deal of material and are inefficient in this respect.

(*f*) *Economics*. It is desirable that the cost of the detoxification regime be kept to a minimum. A decontaminant requiring, for example, a 20-step synthesis would probably not warrant consideration no matter how clever its design.

Such were the constraints imposed upon us in the search for a remedy to chemical warfare agents. As will be seen, we have chosen a self-organizing assembly, the microemulsion, as a vehicle for attacking the problem[2]. The microemulsion-based method is rapid, simple, cheap, mild, and selective. These features arise from the fact that microemulsions represent a community of molecules that function only by virtue of cooperative action. Each of the eight initial components (water, hydrocarbon, surfactant, cosurfactant, mustard simulant, GB and VX simulants, and decontaminant) has its own particular residence site and its own particular role in the reaction. Without self-assembly, *there would have been an intractable jumble* of reagents. With the self-assembly inherent to microemulsions, there is formed a system organized to discharge its purpose usefully and efficiently. Cellular systems discovered the tactic long ago.

One final thought by way of introduction. Applied research teaches basic scientists, like ourselves, a valuable lesson: It is more difficult to solve a problem with external constraints than to solve a problem where any rate, any temperature, any pH, any reaction scale, or any cost will do. The difference here lies in searching for a result that is *needed vs.* obtaining a result that is *publishable*. This is not to deny the desirability of both forms of success. But it does seem true that no scientific discipline remains vibrant for long unless, ultimately, the discipline enhances the welfare of the person in the street. Thus, the opportunity and challenge of investigating a problem with an applied component should be welcomed by basic scientists.

Results and discussion

A microemulsion is a 3- or 4-component self-organizing assembly[3]. To prepare a microemulsion, one need only mix the proper ratio of water, hydrocarbon ("oil"), surfactant, and cosurfactant (generally a low molecular weight alcohol). The result is a single, clear phase in which hydrocarbon droplets are suspended in water (O/W type) or else water droplets are suspended in hydrocarbon (W/O type). In either case, the droplets are small (50–500 Å), accounting for the fact that microemulsions are thermodynamically stable and that they remain clear indefinitely. It is amazing to observe substantial amounts of heptane "dissolve" in an aqueous solution of surfactant and cosurfactant.

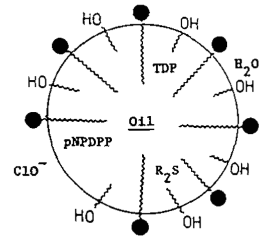


Figure 1. The 8-component oil-in-water microemulsion used in this study. NPDPP, TDP, and R_2S are three contaminants in the oil droplet (see text) which are destroyed by hypochlorite in the aqueous phase. Surfactant (heavy dots with tails) and cosurfactant (alcohol) stabilize the oil droplet.

The presence of cosurfactant (typically butanol or pentanol) is required to impart a near-zero surface tension between the droplet and continuous phase. With surfactant alone, a mixture of water and hydrocarbon is a milky and unstable suspension. Figure 1, depicting the structure of an O/W microemulsion, shows how both the surfactant and cosurfactant gravitate to the oil/water interface. This interface, incidentally, is enormous (estimated at 10^9 cm^2/l)[4] owing to the large amount of oil in the water and to the small droplet size.

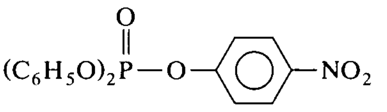
An almost infinite number of recipes for microemulsions are possible. Two that we have investigated in the past[2] are given here for illustration purposes: (*a*) 69% water, 11% dodecane, 11% sodium dodecyl sulfate, and 9% 1-pentanol; (*b*) 5% water, 80% cyclohexane, 5% sodium dodecyl sulfate, and 10% 1-butanol. The former microemulsion is of the O/W type, the latter of the W/O type.

Microemulsion formulations can be procured from the literature, but we found it just as simple to prepare them *ad hoc*. Thus, a hydrocarbon, surfactant, and cosurfactant can be mixed into a smooth white paste. Water is then added with mild agitation to achieve clarity. Alternatively, a mixture of water, surfactant, and cosurfactant is added to a hydrocarbon until a clear microemulsion is obtained. All formulations reported herein are given in weight-percent.

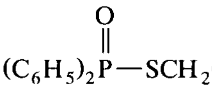
Although microemulsions can be prepared from cationic, anionic, and neutral surfactants, we used exclusively a cationic material, cetyltrimethylammonium chloride (CTAC, cetyl = hexadecyl). The corresponding bromide salt was avoided because under our oxidizing conditions (described below), bromide was converted into bromine, and the microemulsions turned yellow. A cationic surfactant was preferred over the alternative charge types because it gave the fastest rates of detoxification. An oxidation-resistant alcohol, *tert*-butanol, served as the cosurfactant.

$C_{16}H_{33}\overset{+}{N}(CH_3)_3\,Cl^-$ $(CH_3)_3COH$
CTAC, surfactant cosurfactant

Since, for safety and licensing reasons, direct examination of GB, VX, and mustard was not possible, three "simulants" were used instead: 4-nitrophenyl diphenyl phosphate (NPDPP), *S*-ethyl diphenyl phosphothioate (EDP), and dibutyl sulfide (DBS). NPDPP and EDP resemble in reactivity GB and VX, respectively. Actually, NPDPP is somewhat less reactive toward hydrolysis than GB, so that any hydrolytic scheme developed for NPDPP is likely to be also useful for the "real thing"[5]. Mustard and its simulant DBS are conveniently destroyed via oxidation to the sulfoxide[6]. Accordingly, any microemulsion must contain both hydrolytic and oxidative capabilities if it is to meet our need to deactivate a combination of nerve agents and mustard[7].



NPDPP



$(C_6H_5)_2P(=O)-SCH_2CH_3$

EDP

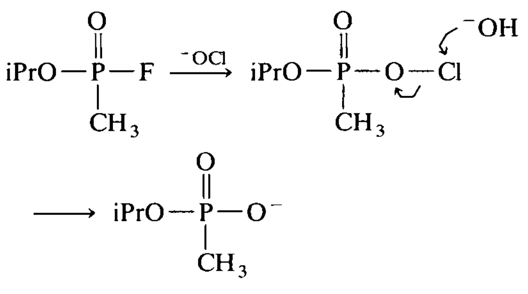
$(C_4H_9)_2S$

DBS

Deciding upon the decontamination agent, a necessary ingredient of the microemulsion system, was not difficult. We had already demonstrated that sulfides are oxidized at remarkably fast rates (< 15 sec, 23°C) when dissolved in an oil-in-water microemulsion containing a 2-fold excess of hypochlorite[2]. Sulfoxide is formed exclusively and quantitatively (Eqn. 1). The process is much faster than phase-transfer catalysis[8] and requires no stirring since microemulsions are homogeneous. If a hypochlorite-bearing microemulsion could be formulated to, additionally, hydrolyze GB and VX simulants, then a generally applicable preparation would be in hand.

$$R_2S \xrightarrow{^-OCl} R_2SO \tag{1}$$

Concomitant hypochlorite-induced oxidation of DBS and hydrolysis of NPDPP and EDP was a reasonable expectation. Thus, hypochlorite has been shown to be a better nucleophile than hydroxylamine and hydroxide ion toward tetraethyl pyrophosphate in water[9]. In its reaction with 4-nitrophenyl acetate, hypochlorite displays a nucleophilic reactivity three orders of magnitude greater than expected from its pK_a of 7.3 (owing in part, no doubt, to the so-called "α effect")[10]. Hypochlorite is also an efficient catalyst in the hydrolysis of GB[11]. Although the reaction is first-order in substrate and hypochlorite, the latter is not consumed. A reasonable mechanism for this "turnover" behavior is given in Eqn. 2. Nucleophilic attack on the Cl of the intermediate is seen to regenerate hypochlorite.



(2)

Whatever the exact mechanistic details, it is clear that hypochlorite can serve our dual objective: oxidize sulfides to sulfoxides and promote hydrolysis of phosphorus(V) compounds.

Common household bleach (5.25% phosphate-free sodium hypochlorite purchased at a local grocery store) provided the decontaminant. Bleach is cheap and, as mentioned, economy was a prime consideration. Hypochlorite also met our needs in that it has a low molecular weight and a "little goes a long way". Since more than 30% of hypochlorite is oxygen, the "wasted" portion of the molecule is kept to a minimum during sulfide oxidation. And, of course, if the mechanism in Eqn. 2 is operative, then the hydrolytic phase of the decontamination consumes no hypochlorite at all. In summary, hypochlorite furnishes a potentially low-cost, high-efficiency solution to the problem.

Table I Composition by weight-percent of nineteen O/W microemulsions [a].

ME	C_{16}	Water	CTAC	*t*-BuOH
1	4	54	18	24
2	3	55	18	24
3	2	55	18	25
4	1	56	18	25
5	4	58	19	19
6	3	58	19	19
7	2	59	19	19
8	1	59	20	20
9	4	60	20	16
10	3	61	20	16
11	2	61	20	16
12	1	62	21	17
13	2	66	18	14
14	1	67	18	14
15	1	71	15	12
16	3	64	17	17
17	2	64	17	17
18	1	65	17	17
19	1	69	15	15

[a] ME = microemulsion; C16 = *n*-hexadecane; CTAC = cetyltrimethylammonium chloride (cetyl = hexadecyl). Weight percentages may add up to 99% or 101% owing to round-off. All C_{16} percentages are integers.

Let us pause a moment and recapitulate the eight-component microemulsion as originally envisioned: (1) water; (2) hydrocarbon (hexadecane); (3) surfactant (CTAC); (4) cosurfactant (*tert*-butanol); (5) decontaminant (hypochlorite); (6) mustard simulant (DBS); (7) GB simulant (NPDPP); (8) VX simulant (EDP). Those engaged in "single molecule" organic chemistry may reel in dismay over this seemingly hopeless mixture, but *organization* - that key word - comes to the rescue.

Nineteen microemulsions, listed in Table I, were investigated. Actually, many more than these were screened, but the ones cited include our most effective, and they suffice to illustrate the important points. All microemulsions in Table I fall into the oil-in-water category as depicted in Figure 1. Water is the continuous phase and major component, consistent with our wish to keep costs down and the microemulsions non-flammable. Little difference exists among the microemulsions except that the percentage of hexadecane within each series varies by a factor of four.

Hydrolysis of NPDPP was so fast that the kinetics had to be followed by stopped-flow spectrophotometry according to the following procedure: A syringe was filled with 1.0 ml of 1×10^{-4}M NPDPP dissolved in one of the microemulsions. A second syringe was filled with 1.0 ml 5.25% hypochlorite (0.7 M). The syringes were emptied simultaneously into a mixing cell where the ensuing reaction was monitored at 400 nm for the production of 4-nitrophenolate. The component solutions were equilibrated at 25.0°C prior to mixing, but neither of them were buffered per se. The observed rate constants and corresponding half-lives are recorded in Table II.

Owing to the manner in which the kinetics were obtained, the microemulsion compositions under actual reaction conditions were not those given in Table I. Thus, the microemulsions contained more water than indicated as a result of the 1:1 dilution with aqueous hypochlorite during the stopped-flow experiments. For example, the diluted ME-11 can be calculated to consist of 0.5% hexadecane, 81% water, 10% CTAC, and 8.3% *tert*-butanol. Dilution with hypochlorite never affected the clarity of the microemulsions.

It is obvious from Table II that the hypochlorite-catalyzed hydrolysis of NPDPP in the microemulsion systems is extremely fast, the half-life averaging about one second. The following two comparisons testify to the speed of the NPDPP hydrolysis: (*a*) The half-life of NPDPP in a pH 8.0 buffer at 25°C is about 2 days. (*b*) The metallo-micelle, one of the more potent catalysts known[12] to hydrolyze NPDPP, never achieved a half-life greater than about 12 seconds. Note that GB, being a more reactive substrate than NPDPP, should be destroyed even faster than the 0.5–1.5 second half-lives reported in Table II.

If 6-year old bleach was used in the kinetics, then the rate constants diminished by a factor of two. Moreover, the rates decreased three-fold when hypochlorite was mixed with the microemulsion and allowed to stand 24 hours before addition of NPDPP. Presumably, hypochlorite was consumed by slow oxidation of surfactant and/or cosurfactant, suggesting that hypochlorite should be added to the microemulsion just prior to use. This is not a problem for most laboratory work, but for applications outside the laboratory, an inability to store microemulsion/hypochlorite mixtures on the shelf, ready to use, must be regarded as a limitation to the method.

Once it was established that the microemulsions were a potent means for destroying NPDPP, we attempted to "deactivate" mixtures of all three simulants (NPDPP, EDP, and DBS) simultaneously. Thus, 0.1M NPDPP (2 μl in CH_3CN), EDP (0.1 g), and DBS (0.2 g) were added to 20 g ME-12. This was mixed with an equal volume of 5.25% sodium hypochlorite. In stopped-flow experiments with the mixture, the NPDPP was shown to hydrolyze at a rate equivalent to that in the absence of the other two simulants. In other words, there is no evidence that EDP and DBS interfere with hydrolysis of NPDPP. The disappearance of EDP and DBS was followed by TLC (4:2:1 hexane/ethyl acetate/ethanol on silica). TDP was totally hydrolyzed (or possibly oxidized) within 5 minutes, whereas all the DBS was gone within 30 seconds (consistent with previous results). Rapid concurrent destruction of GB, VX, and mustard simulants had been achieved!

It is now necessary to confront an issue mentioned in the introduction: reaction capacity. If a compound does not dissolve in a reaction medium, then the reaction of the compound, when exposed to that medium, may be extremely slow no matter how large the "homogeneous" rate constant. This is exactly the case with the hydrolysis of mustard in water. Although mustard hydrolysis is fairly rapid, a mustard layer can lie unaltered for months on a water surface. The amount of mustard entering the water and hydrolyzing is simply too miniscule to contribute substantially to the total destruction of the mustard layer. To drive the point home, consider a compound whose solubility is 10^{-7} M in an aqueous reaction medium. Although reaction of the compound at 10^{-8} M may be fast, the same system using compound in excess of its solubility (*e.g.* the equivalent of 1 M) could be worthless. Reaction capacity is an important but often ignored parameter.

Table II Observed rate constants and half-lives for the hydrolysis of NPDPP at 25°C in 1:1 mixtures of a microemulsion and 5.25% sodium hypochlorite [a].

ME	k_{obsd} (sec^{-1})	$t_{1/2}$ (sec)
1	0.49	1.4
2	0.49	1.4
3	0.47	1.5
4	0.47	1.5
5	0.80	0.9
6	0.77	0.9
7	0.75	0.9
8	0.74	0.9
9	1.1	0.6
10	1.0	0.7
11	1.0	0.7
12	0.99	0.7
13	1.2	0.6
14	1.2	0.6
15	1.4	0.5
16	0.97	0.7
17	0.92	0.8
18	0.89	0.8
19	1.3	0.5

[a] The microemulsions are those listed in Table I prior to 1:1 dilution. Rate constants are reproducible to ±10%.

Table III Solubilization of dibutyl sulfide (DBS) in various microemulsions [a].

ME	Capacity (wt-%)
1	5
2	10
3	14
4	17
5	4
6	8
7	12
8	14
9	3
10	8
11	11
12	13
13	5
14	8
15	5
16	3
17	7
18	9
19	6

[a] Measurements accurate to ±10%.

The above considerations prompted us to measure the solubility of dibutyl sulfide (DBS) in the nineteen microemulsions (Table III). DBS was selected for its extreme insolubility in pure water. It is seen that most of the microemulsions can dissolve 5–17% DBS. For example, 100 g ME-7 solubilizes over 10 g DBS, a value that would seem to suffice for most needs. Of course, in order to deactivate such large amounts of agent, one would require a hypochlorite stock containing greater than 5.25% oxidant, thereby avoiding the addition of too much water to the microemulsion.

An early experiment with NPDPP confirmed our system's high reaction capacity. Thus, a microemulsion was prepared with the following composition: hexadecane (4 g); water (60 g); CTAC (18 g); and 1-butanol (18 g). A portion of this microemulsion (10 ml) was mixed with 5.25% hypochlorite (2.0 ml) to oxidize two concentrations of NPDPP ($6.7 \cdot 10^{-5}$ M and $8.3 \cdot 10^{-3}$ M). The rate constants for oxidation differed by less than a factor of two. Elevating the NPDPP concentration to a level of 30 mg/10 ml does not, therefore, impede its hydrolysis.

The rates of NPDPP hydrolysis in a large number of additional microemulsions, too numerous to specify here, were investigated in the course of this research. Only the general conclusions from this work will be mentioned: (*a*) it made little difference whether the oil phase was hexadecane, dodecane, cyclohexane, or 1-(*tert*-butyl)-4-methylbenzene. (*b*) The observed rate constants increased proportionally with the hypochlorite concentration over a 4-fold range. (*c*) Buffering the water at pH 10.0 caused a 2-fold rate decrease. (*d*) As a rule, rates increased and capacity decreased when the water content of the microemulsions was increased.

In summary, the microemulsion systems fill many of the requirements, set forth in the introduction, for a good decontamination system: Reactions are rapid under mild conditions. Components are cheap. Reaction capacity is high. Three simulants can be destroyed simultaneously. And no specialized equipment is needed. The only drawback is that hypochlorite cannot be premixed with the microemulsions and stored prior to use.

Conclusions

Each of the eight microemulsion components has its own particular location and function that enables the system, as a totality, to do something chemically useful: (1) Water comprises the continuous phase in which all other components are dissolved or embedded. (2) Hexadecane, suspended as microdroplets in the water, serves as a repository for the water-insoluble organic reactants. (3) CTAC adsorbs to the hexadecane/water interface and stabilizes the droplets. (4) *Tert*-Butanol also adsorbs to the interface and creates a thermodynamically stable emulsion in concert with CTAC. (5) Hypochlorite dissolves in the aqueous phase and is responsible for hydrolyzing and oxidizing the organic reactants. (6) NPDPP is a GB simulant that resides in the hexadecane droplets. (7) EDP is a VX simulant that also resides in the droplets. (8) DBS is a mustard simulant that joins the other simulants in the hexadecane.

Owing to the huge interface between the hexadecane and the water, the reaction between the water-soluble hypochlorite and the organic-soluble simulants proceeds at an extremely fast rate. Self-assembly is critical to success. It remains only to quote from a recent issue of *Chemistry and Industry*[13]: "Manipulation of the location of reagents and reactive substrate functionality by partitioning in microemulsions is an important strategy for fine-tuning chemical reactivity and selectivity. Perhaps one day all reactions will be routinely performed this way, and the present use of simple monocomponent phases will seem a primitive approach.". This prediction takes on added poignancy with the current environmentally-motivated tendency for industry to convert from organic to aqueous solvents.

Experimental

Materials

NPDPP was prepared and purified by a known method.[14] EDP was synthesized by adding diphenyl chlorophosphonate (4 ml, 21 mmol) to ethanethiol (1.7 ml, 23 mmol) dissolved in 12 ml pyridine. The reaction mixture was then boiled under reflux for 8 h during which a thick precipitate formed. The workup consisted of cooling, acidification with 10% HCl, and extraction with methylene chloride. Removal of the methylene chloride from the extract gave crude product that was crystallized from acetone, mp 74–75°C (lit mp 74.5–75°C).

Kinetics

Reaction rates were determined with the aid of a home-made stopped-flow spectrophotometer according to a procedure given in the text. In order to ensure the reliability of our instrument, we studied a reaction that could be followed by both stopped-flow and conventional spectrophotometry. Rate constants agreed well (*i.e.* $3.2 \cdot 10^{-2}$ sec^{-1} *vs.* $3.3 \cdot 10^{-2}$ sec^{-1}, respectively). Rate constants were determined in duplicate and were reproducible to ±5%.

Acknowledgment

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