Destruction of toxic organophosphorus and organosulfur pollutants by perpropionic acid: the first stable, industrial liquid water-miscible peroxyacid in decontamination

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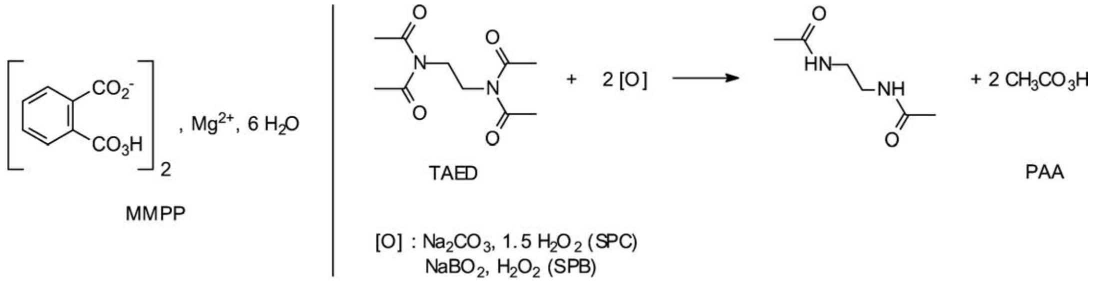
Use of commercial perpropionic acid (PPA), the first stable, industrial and water-miscible peroxyacid, allows the destruction of toxic organophosphorus and organosulfur compounds under micellar conditions. The destruction of paraoxon (*O*,*O*-diethyl *O*-*p*-nitrophenylphosphate), di-*n*-butyl sulfide and 2-chloro-2′-phenyldiethyl sulfide has been studied.

Destruction de polluants organophosphorés et organosoufrés toxiques par l'acide perpropionique: le premier peracide stable, industriel, liquide miscible à l'eau en décontamination. L'utilisation de l'acide perpropionique (APP), produit industriel, stable, liquide, miscible à l'eau, pour détruire les organophosphorés et organosoufrés en milieu micellaire est décrite. Les réactivités de ce peracide vis-à-vis du paraoxon (*O*,*O*-diéthyl *O*-*p*-nitrophénylphosphate), insecticide bien connu, du di-*n*-butyl sulfure et du 2-chloro-2′-phényldiéthyl sulfure, demi-moutarde modèle, représentants des familles de toxiques, sont étudiées.

During the past years, we have described the easy, rapid and total destruction of toxic organophosphorus and organosulfur compounds by peroxyacids in micellar solutions.[1–8] There are two general pathways to achieve the chemical destruction of toxic pollutants: (a) use of synthesized or commercial peroxyacids[1–6] and (b) *in situ* generation of the peroxyacid by reaction of hydrogen peroxide with an initiator.[7,8] Both alternatives have given very good results in the mild, complete and rapid destruction of organophosphorus and organosulfur compounds (insecticides or warfare agents). In the first case, magnesium monoperphthalate (MMPP) has been used[5,6] and, in the second alternative, shown in Scheme 1, the generation of peracetic acid (PAA) by the reaction of sodium percarbonate (SPC) or sodium perborate (SPB) with different initiators like tetracetylethylenediamine (TAED) has proved to be very efficient.[7] The results obtained have been discussed and extended in the literature.[9–13]

In this paper we describe our results using a new stable, industrial, liquid, water-miscible peroxacid, perpropionic acid (PPA),[14] and the destruction of paraoxon and two sulfides (di-*n*-butyl sulfide and 2-chloro-2′-phenyldiethyl sulfide) by this compound.

In the first step of the work, the product has been used in decontamination by destruction of organophosphorus and/or organosulfur pollutants. The industrially available solution is to dilute with its azeotropic solvent,[15] to be used for the destruction of great amounts of toxic compounds.



Scheme 1

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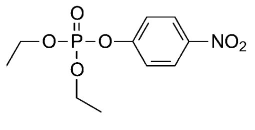
$CH_3CH_2CO_3H$

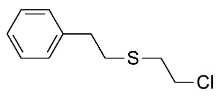
perpropionic acid

$(nC_4H_9)_2S$

di-*n*-butyl sulfide



Paraoxon

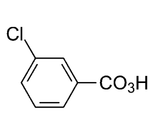


2-chloro-2'-phenyldiethyl sulfide

Results and discussion

Synthesis of perpropionic acid

Addition of hydrogen peroxide to propionic acid in the presence of catalytic amounts of boric acid leads to perpropionic acid in good yields.[15] When the reaction is run in a solvent like ethyl propionate, the aqueous solution can be dried by careful azeotropic distillation giving stable perpropionic acid.[15] The stability of PPA has been compared to that of MMPP or *m*-chloroperoxybenzoic acid (*m*-CPBA)



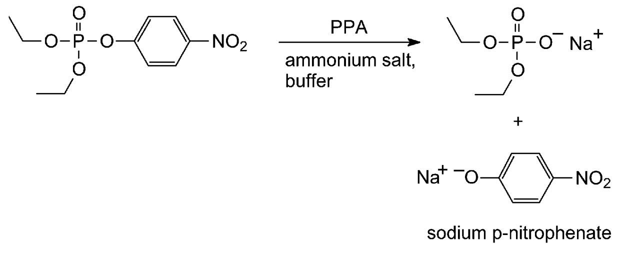
m-CPBA

As seen in Table 1, the commercial anhydrous perpropionic acid in solution is more stable than MMPP and *m*-CPBA when heated between 60 and 80 °C. The solid MMPP and *m*-CPBA contain water, which is known to decrease the stability of the peroxyacids.[16,17]

In aqueous medium at pH = 8 to 10, in the decontamination reaction, the same difference of stability is observed.[14] Besides the good stability, perpropionic acid is a liquid, miscible in all proportions with water.

Dephosphorylation of paraoxon by perpropionic acid

Many insecticides are organophosphates[18–20] very difficult to destroy by hydrolysis. The dephosphorylation of paraoxon (*O*,*O*-diethyl *O*-*p*-nitrophenylphosphate) by perpropionic acid was studied:



sodium p-nitrophenate

The influence of the pH on the rate and the micellar catalysis effect of ammonium salts **1–6** was determined as described in previous work:[1] the reaction is followed by UV-visible spectrometry by measuring the sodium *p*-nitrophenate concentration at 402 nm.[6]

$C_6H_4CH_2\overset{+}{N}(CH_3)_3,\ Br^-$ **1**

$N(CH_2CH_2)_3\overset{+}{N}C_{16}H_{33},\ Br^-$ **2**

$(CH_3)_2\overset{+}{N}(CH_2CH_2OH)C_{16}H_{33},\ Br^-$ **3**

$CH_3\overset{+}{N}(CH_2CH_2OH)_2C_{16}H_{33},\ Br^-$ **4**

$(CH_3)_3\overset{+}{N}C_{16}H_{33},\ Br^-$ **5**

$(CH_3)_3\overset{+}{N}C_{16}H_{33},\ Cl^-$ **6** (CTACl)

Table 1 Thermal stability of commercial peroxyacids

	Half-life of peroxy compounds/h			
Peroxyacid	60 °C	70 °C	80 °C	Solubility(H_2O, 20 °C)/g L^{-1}
PPA (17%)	120	50	20	Miscible
MMPP	18	15	10	220
m-CPBA	12	8	6	1.5

pH Effect. The reaction was studied at pH 6 to 10 in micellar medium (CTACl) at 25 °C. The rate constant, k_{obs}, varies from 0.03×10^{-3} s^{-1} (pH 6) to 6.7×10^{-3} s^{-1} (pH 10), in Table 2. The plot of log k_{obs} *versus* the pH value (Fig. 1) seems to have two different slopes. The explanation may be that from pH 6 to 8.3, the mechanism of the reaction is different from that at pH 8.3 to 10. The higher rate can be explained by a higher concentration of percarboxylate between 8.3 and 10: the pK_A of perpropionic acid is around 8.2 in micellar 3×10^{-3} mol L^{-1} CTACl medium.[21] This work is in accordance with of the literature.[21,22]

Half-life for paraoxon destruction by perpropionic acid. The reaction of perpropionic acid with paraoxon in the presence of various ammonium salts **1–6** was studied at pH = 9 and 10. The values of the half-life (Table 3) are around 150 s. The micellar effect of various ammonium salts above their micellar critical concentration has already been explained in our previous work with other peroxyacids.[1–8] Perpropionic acid has the same reactivity with paraoxon as the other peroxyacids,[1–8] but the increase in the rate by the micellar effect is low due to the presence of azeotropic solvent (ethyl propionate).

Organosulfide oxidation

The destruction reaction of organosulfides was studied with two different compounds: easy to handle di-*n*-butyl sulfide and 2-chloro-2′-phenyldiethyl sulfide, a well known mustard.

Di-*n*-butyl sulfide. The oxidation of di-*n*-butyl sulfide by 2 equiv. of perpropionic acid is complete in less than 5 min. The selectivity of the oxidation to sulfoxide or sulfone [eqn. (2)] was studied at different pH, the ratio of these products being determined after 30 min in micellar medium.

$$(nC_4H_9)_2S \xrightarrow[\text{buffer}]{\text{PPA}} (nC_4H_9)_2S(O) + (nC_4H_9)_2S(O)_2$$

The selectivity (Table 4) decreases when the basicity of the solution increases, in accordance with published results on the oxidation of sulfides:[23] under stoichiometric conditions at pH 7 the only product is the sulfoxide, and above pH 9 the sulfone is the only product isolated when excess perpropionic acid is used.

Table 2 Rate constants for degradation (k_{obs}) and half-life ($t_{1/2}$) for paraoxon destruction by perpropionic acid (PPA) with CTACl (**6**) at 25 °C

pH[a]	k_{obs} (10^3)/s^{-1}	$t_{1/2}$/s
6[b]	0.03	~23×10^3
7[c]	0.5	~1300
8[d]	1.2	550
9[d]	5.2	130
10[d]	6.7	105

[a] Reactant concentrations depend on pH. [b] [PPA] = 3.78×10^{-3} mol L^{-1}, [paraoxon] = 3.78×10^{-4} mol L^{-1}. [c] [PPA] = 1.89×10^{-3} mol L^{-1}, [paraoxon] = 1.89×10^{-4} mol L^{-1}. [d] [PPA] = 3.78×10^{-4} mol L^{-1}, [paraoxon] = 3.78×10^{-5} mol L^{-1}; [CTACl] = 3×10^{-3} mol L^{-1}.

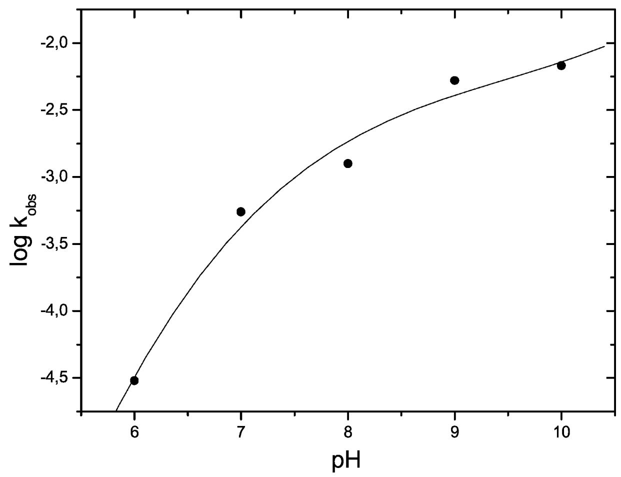


Fig. 1 Variation of log k_{obs} *vs.* pH for the reaction of paraoxon by PPA in the presence of **6** (see Table 2 for conditions).

Under neutral and basic conditions, perpropionic acid exists partly as a percarboxylate anion, which has a specific oxidation reactivity.[23,24] Under neutral conditions, we have a very good method for preparing the sulfoxide when the peracid is used in stoichiometric amounts, and in basic medium the oxidation allows the synthesis of the sulfone.

2-Chloro-2′-phenyldiethyl sulfide. The β-chlorosulfides are generally toxic compounds[25] and their chemistry has been studied.[26,27] Our previous work[1–8] has shown that 2-chloro-2′-phenyldiethyl sulfide is destroyed by some peroxyacids. With perpropionic acid, the reaction is complete in less than 1 min in micellar medium: the reaction gives 2-chloro-2′-phenyldiethyl sulfoxide, 2-chloro-2′-phenyldiethyl sulfone and phenethyl(vinyl)sulfone (Scheme 2). The relative proportions of these three products at different sulfide/perpropionic acid ratios at pH values from 7 to 10 were determined. The sulfide is oxidised in less than 1 min; the product ratios are given in Table 5. In micellar solution, all the sulfide is oxidised to sulfone, and compared to the oxidation of di-*n*-butylsulfide under the same conditions, 2-chloro-2′-phenyldiethyl sulfide goes more readily to 2-chloro-2′-phenyldiethyl sulfone, which by loss of HCl yields phenethyl(vinyl)sulfone. The greater reactivity of 2-chloro-2′-phenyldiethyl sulfide can be explained by activation *via* the well known cyclic ethylenesulfonium intermediate.[28]

Conclusion

Anhydrous perpropionic acid is able to destroy easily, quickly and under mild conditions some pollutants: organophosphorus compounds (paraoxon) and organosulfides (*i.e.*, 2-chloro-2′-phenyldiethyl sulfide). The interest of perpropionic acid compared to other peroxyacids such as magnesium monoperphthalate or peracetic acid is that this product is an industrial, stable, water-miscible liquid.

Table 3 Half-life ($t_{1/2}$) for paraoxon destruction by perpropionic acid[a]

	$t_{1/2}$/s	
Ammonium salt	pH 9	pH 10
None	417	280
1	325	265
2	270	145
3	156	145
4	160	114
5	170	135
6	114	125

[a] [PPA] = 3.78×10^{-4} mol L^{-1}, [paraoxon] = 3.78×10^{-5} mol L^{-1}, [ammonium salt] = 10^{-3} mol L^{-1}, all reactions at 25 °C.

Table 4 Selectivity of di-*n*-butyl sulfide oxidation by perpropionic acid (PPA)[a]

	PPA concentration (10^2)/mol L^{-1} (sulfide/PPA ratio)[b]				
pH	5 (1/1)	10 (1/2)	15 (1/3)	20 (1/4)	25 (1/5)
7	100/0	54/46	20/80	20/80	12/88
8	91/9	51/49	17/83	11/89	5/95
9	84/16	43/57	11/89	6/94	0/100
10	79/21	38/62	9/91	0/100	0/100

[a] [di-*n*-butylsulfide] = 5×10^{-2} mol L^{-1}, [CTACl] = 10^{-2} mol L^{-1}, all reactions at 25 °C for 30 min. [b] Selectivity (di-*n*-butyl sulfoxide/di-*n*-butyl sulfone ratio) determined by GC after calibration using an internal standard. Results are reproducible to ±2%.

Experimental

Chemicals

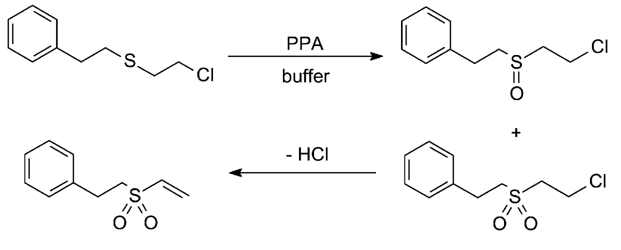
Perpropionic acid (17% by weight) was provided by Atofina. MPPM, *m*-CPBA, paraoxon, di-*n*-butyl sulfide, benzyltrimethylammonium bromide (**1**) cetyltrimethylammonium bromide (**5**) and CTACl (**6**) were purchased from Aldrich. 2-Chloro-2′-phenyldiethyl sulfide[29] and ammonium salts **2**, **3** and **4**[30] were synthesised as described previously. Commercial buffer solutions (Titrisol®, Merck) were used and specific conditions for each reaction are described in the tables.

Thermal stability of peracids

Several samples of commercial peracids (10 × 20 mmol) were heated in a drying oven or in an oil bath at the desired temperature. Every hour (10 points per day), a portion of the sample (2 mmol) was taken and dissolved in 20 mL of distilled water. To this solution was quickly added 15–20 mL of a solution of acetic acid in water (0.1 mol L^{-1}) to reach pH 4–5, a few drops of a starch solution and 2 mL of an aqueous solution of potassium iodide (KI 15% by weight). Iodine formation was determined by titration with an aqueous solution of sodium thiosulfate (0.1 mol L^{-1}) until the brown-blue colour had disappeared.[31]

Kinetic measurement of paraoxon destruction by perpropionic acid

The dephosphorylation of paraoxon was determined by visible absorption spectroscopy at 402 nm. Pseudo-first order rate constants, k_{obs}, were calculated according to the equation $(A_f–A_t) = (A_f–A_i)\ \exp(-k_{obs} \times t)$, where A_i and A_f are the initial and final absorbances, and A_t that at time t.[32] Reactant



Scheme 2

Table 5 Selectivity of 2-chloro-2′-phenyldiethyl sulfide oxidation by perpropionic acid (PPA)[a]

	PPA concentration (10^2)/mol L^{-1} (sulfide/PPA ratio)[b]		
pH	15 (1/3)	20 (1/4)	25 (1/5)
7	0/79/21	0/92/8	0/92/8
8	0/77/23	0/92/8	0/91/9
9	0/73/27	0/90/10	0/89/11
10	0/72/28	0/86/14	0/86/14

[a] [2-Chloro-2′-phenyldiethyl sulfide] = 5×10^{-2} mol L^{-1}, [CTACl] = 10^{-2} mol L^{-1}, all reactions at 25 °C for 30 min. [b] Selectivity (2-chloro-2′-phenyldiethyl sulfoxide/2-chloro-2′-phenyldiethyl sulfone/phenethyl(vinyl)sulfone ratio) determined by GC and mass spectrometry after calibration using an internal standard. Results are reproducible to ±2%.

concentrations and experimental conditions are given in the tables.

General procedure for sulfide oxidation by perpropionic acid

Micellar buffer solutions of sulfides (CTACl, 10^{-2} mol L^{-1}) were mixed with a buffered aqueous solution of perpropionic acid (1–5 equiv.), and the pH was brought to its initial value with 0.1 mol L^{-1} KOH solution. The reaction was stopped after 30 min with saturated $Na_2S_2O_3$ solution. The aqueous solution was extracted with ethyl acetate, dried over $MgSO_4$ and filtered. A weighed sample of hexadecane or dodecanol (standard) was added to the organic solution and the oxidation products identified by gas chromatography and mass spectrometry.[12b,29]

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References

1 C. Lion, M. Hedayatullah, C. Charvy, G. Delmas, G. Magnaud and H. Sentenac-Roumanou, *Bull. Soc. Chim. Belg.*, 1997, **106**, 221.

2 G. Delmas, M. Desgranges, C. Lion, G. Magnaud and H. Sentenac-Roumanou, *Fr. Pat.*, 96 03 204, 1996.

3 M. Hedayatullah, C. Lion, A. Tourki, G. Delmas and G. Magnaud, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1994, **89**, 1.

4 C. Lion, L. Da Conceição and H. Sayag, *C. R. Acad. Sci., Sér. IIc*, 1999, **2**, 57.

5 G. Delmas, M. Desgranges, C. Lion, M. Magnaud and H. Sentenac-Roumanou, *Fr. Pat.*, 2 676 368, 1991.

6 C. Lion, J. P. Boukou-Poba and M. Hedayatullah, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1991, **56**, 213.

7 C. Lion, M. Hedayatullah, C. Charvy, S. Briand, S. Vincent and L. Fosset, *Bull. Soc. Chim. Belg.*, 1995, **104**, 515.

8 C. Lion, L. Da Conceição and M. Hedayatullah, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2000, **161**, 97.

9 C. A. Bunton, M. M. Mhala and J. R. Moffatt, *J. Phys. Org. Chem.*, 1990, **5**, 390.

10 D. M. Davies and M. E. Deary, *J. Chem. Soc., Perkin Trans. 2*, 1992, 559.

11 Y-C. Yang, *Acc. Chem. Res.*, 1999, **32**, 109.

12 (*a*) F. Gonzaga, E. Perez, I. Rico-Lattes and A. Lattes, *Langmuir*, 1999, **15**, 8328; (*b*) F. Gonzaga, E. Perez, I. Rico-Lattes and A. Lattes, *New J. Chem.*, 2001, **25**, 151.

13 T. Cassagne, H-J. Cristau, G. Delmas, M. Desgranges, C. Lion, G. Magnaud, E. Torreilles and D. Virieux, *C. R. Acad. Sci., Ser. IIc*, 2001, **4**, 309.

14 For preliminary work, see: C. Pralus, J.-P. Schirmann, C. Lion and L. Da Conceição, *Fr. Pat.*, 99 13 571, 1999, extended worldwide in 2000. See also L. Da Conceicão, PhD Thesis, University Paris 7, 2001.

15 J.-P. Schirmann, *U.S. Pat.*, 4, 338, 260, 1980.

16 R. E. Ball, J. O. Edwards, M. L. Haggett and P. Jones, *J. Am. Chem. Soc.*, 1967, **89**, 2331.

17 E. Koubek, M. L. Haggett, C. J. Battaglia, K. M. Ibne-Rasa, H. Y. Pyun and J. O. Edwards, *J. Am. Chem. Soc.*, 1963, **85**, 2263.

18 H. Coates, *Ann. Appl. Biol.*, 1949, **36**, 156.

19 L. Ginjaar and S. Vel, *Recl. Trav. Chim. Pays-Bas*, 1958, **77**, 956.

20 F. H. Westheimer, *Science*, 1987, **235**, 1173.

21 S. Bhattacharya and K. Snehalatha, *J. Org. Chem.*, 1997, **62**, 2198.

22 D. F. Evans and M. W. Upton, *J. Chem. Soc., Dalton Trans.*, 1985, 1151.

23 R. Curci, F. DiFuria and J. Modena, *J. Chem. Soc., Perkin Trans. 2*, 1978, 603.

24 S. Oae and T. Takata, *Tetrahedron Lett.*, 1980, **21**, 3213.

25 W. P. Anslow, Jr., D. A. Karnofsky, B. V. Jager and H. W. Smith, *J. Pharmacol. Exp. Ther.*, 1948, **93**, 1.

26 F. M. Menger and A. R. Elrington, *J. Am. Chem. Soc.*, 1990, **112**, 8201.

27 O. Kikuchi, N. Tomisawa, O. Takahashi and K. Morihashi, *Heteroatom Chem.*, 1998, **9**, 503.

28 (*a*) S. P. McManus, N. Neamati-Mazraeh, B. A. Hovanes, M. S. Paley and J. M. Harris, *J. Am. Chem. Soc.*, 1985, **107**, 3393; (*b*) S. P. McManus, N. Neamati-Mazraeh, R. M. Karaman and J. M. Harris, *J. Org. Chem.*, 1986, **51**, 4876; (*c*) M. R. Sedaghat-Herati, S. P. McManus and J. M. Harris, *J. Org. Chem.*, 1988, **53**, 2539.

29 A. Leblanc, L. Fosset, G. Magnaud, M. Desgranges, H. Sentenac-Roumanou, C. Lion, C. Charvy and A. Morhi, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1993, **79**, 141.

30 C. Lion, C. Charvy, M. Hedayatullah, P. Bauer, H. Sentenac-Roumanou, B. Despagne and G. Delmas, *Bull. Soc. Chim. Belg.*, 1990, **99**, 127.

31 B. D. Sully and P. L. Williams, *Analyst*, 1962, 653.

32 (*a*) C. Lion, C. Charvy and G. Delmas, *Fr. Pat.*, 89.11133, 1989; (*b*) C. Lion, M. Hedayatullah, P. Bauer, J. P. Boukou-Poba, C. Charvy, G. Delmas, G. Magnaud, L. Fosset and B. Despagne, *Bull. Soc. Chim. Belg.*, 1991, **100**, 555; (*c*) C. Lion, M. Hedayatullah, P. Bauer, J. P. Boukou-Poba, C. Charvy, G. Delmas, G. Magnaud, L. Fosset and B. Despagne, *Bull. Soc. Chim. Belg.*, 1992, **101**, 249.