

# New $\omega$ -phthalimidoperoxyalkanoic acids in decontamination. Destruction of some toxic organophosphorus and organosulfur pollutants

Claude Lion,<sup>\*a</sup> Louis Da Conceição,<sup>a</sup> Gérard Delmas<sup>b</sup> and Gilbert Magnaud<sup>b</sup>

<sup>a</sup> Institut de Topologie et de Dynamique des Systèmes de l'Université de Paris 7—Denis Diderot, (CNRS UPRESA 7086) 1 rue Guy de la Brosse, 75005 Paris, France.

E-mail: lion@paris7.jussieu.fr

<sup>b</sup> Centre d'Expertise et d'Essais, Centre d'Etudes du Bouchet (CEB), Ministère de la Défense Nationale, B.P. 3, 91710 Vert Le Petit, France

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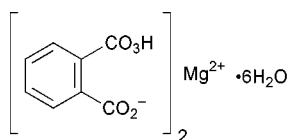
Chemical decontamination of toxic compounds (chemical warfare agents and/or insecticides) is of increasing importance. In this study, we report the use of  $\omega$ -phthalimidoperoxyalkanoic acids **2** in the destruction of paraoxon (*O,O*-diethyl-*O*-*para*-nitrophenylphosphate), a well-known insecticide, and 2-chloro-2'-phenyldiethyl sulfide (a half mustard). We show that while all the peroxyacids used in this series allow the destruction of toxic compounds, the length  $n$  of the alkanic side chain is important to the choice of the optimal industrial compound, which is **2d** ( $n = 5$ ).

**Synthèse et réactivité d'une nouvelle série d' $\omega$ -phthalimidoperoxyacides. Application à la destruction de polluants organophosphorés et organosoufrés.** La décontamination chimique de composés toxiques dans les séries des organophosphorés et organosoufrés est d'une grande importance. Nous décrivons ici nos résultats sur la recherche de réactifs susceptibles de détruire des composés dans ces familles de toxiques; il s'agit d'une série d'acides  $\omega$ -phthalimidoperoxyacides **2**. Nous rationalisons, optimisons et justifions le choix du meilleur candidat en fonction de la longueur de la chaîne alkyle du peroxyacide **2d** ( $n = 5$ ).

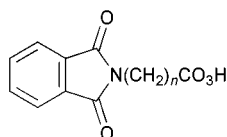
In our previous work, we described the use of peroxyacids for the destruction of toxic organophosphorus (OP) and organosulfur (OS) compounds.<sup>1–6</sup> Industrial magnesium monoperoxyphthalate (MMPP, **1**) is a very efficient product for achieving the complete reaction in a mild aqueous medium at pH close to 9 in a very short time.<sup>5–7</sup>

Other peroxyacids for the decontamination of organophosphorus and organosulfur toxic compounds have been studied; we recently reported that the industrial phthalimidoperoxyhexanoic acid (PAP, Eureco®) **2d** ( $n = 5$ ) is the best peroxy compound for the destruction of pollutants.<sup>8–10</sup>

We describe in this work a series of these peroxyacids and the strategy concerning the choice of **2d** as the best compound (low price, water solubility and high reactivity) in the family **2a–2f**.



MMPP 1



- 2a**  $n = 1$   
**b**  $n = 3$   
**c**  $n = 4$   
**d**  $n = 5$  (PAP-Eureco)  
**e**  $n = 6$   
**f**  $n = 10$

## Results and discussion

$\omega$ -Phthalimidoperoxyalkanoic acids have been widely used as bleaching additives in detergents<sup>11</sup> but nothing was known about the reaction of these compounds with

organophosphorus and organosulfur toxics. We describe here: (i) a general and easy pathway for obtaining the  $\omega$ -phthalimidoperoxyalkanoic acids with different chain lengths and (ii) a comparative study of the activity of the peroxyacids with organophosphorus and organosulfur compounds.

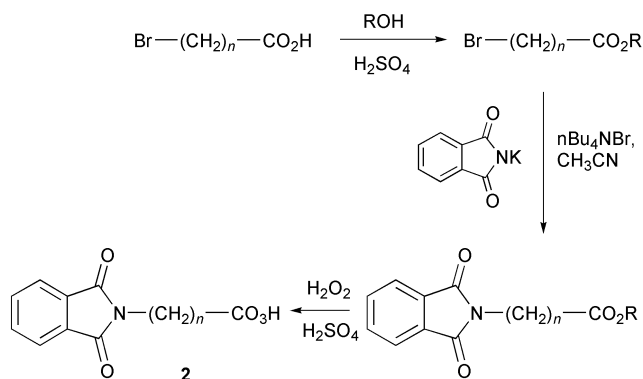
### General pathway for the synthesis of $\omega$ -phthalimidoperoxyacids **2a–f**

The industrial preparation of compounds **2c** ( $n = 4$ ) and **2d** ( $n = 5$ ) uses the condensation of  $\gamma$ -pyrrolidone and  $\epsilon$ -caprolactam with phthalic anhydride in the presence of water at high temperature under pressure.<sup>11</sup> This method gives quantitative yields of the corresponding phthalimidoacids but does not allow the synthesis of other compounds with different chain lengths.

We have developed an easy and general synthesis (Scheme 1) of the peroxyacids **2** with an overall yield of 60–90%. They are prepared by a three-step reaction: (i)  $\omega$ -bromoalkanoic acid esterification, (ii) substitution of the  $\omega$ -bromoalkanoic ester by potassium phthalimide and (iii) perhydrolysis of the  $\omega$ -phthalimidoperoxyalkanoic ester.

### Destruction of *O,O*-diethyl-*O*-*para*-nitrophenylphosphate (paraoxon)

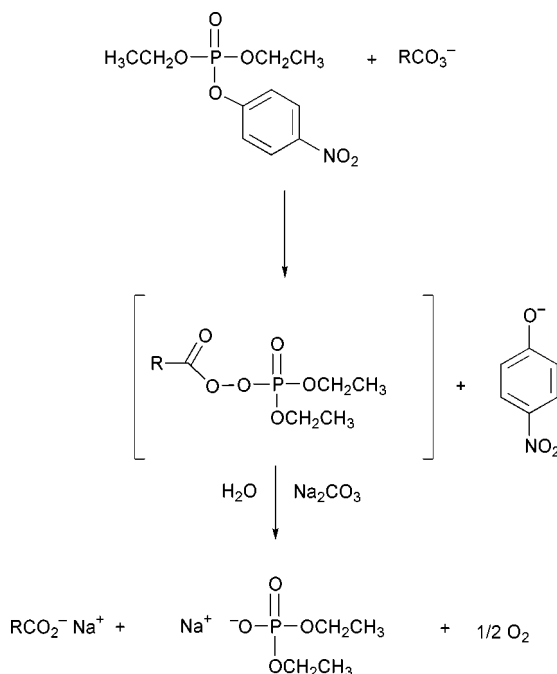
The reaction of peroxyacids **2** with an organophosphorus toxic insecticide, paraoxon, was followed at 25 °C by determining the rate of *para*-nitrophenate formation by UV-visible spectroscopy<sup>1–4</sup> (Scheme 2). Table 1 gives the rate of hydrolysis with or without micellar catalysis by cetyltrimethylammonium bromide (CTABr). In the same way, Fig. 1 presents the reactivity ratio  $k_{\text{mic}}/k_{\text{H}_2\text{O}}$  of peroxyacids **2a–2f** in a basic aqueous medium with and without CTABr. The destruc-



**Scheme 1** General pathway for the synthesis of  $\omega$ -phthalimido-peroxyalkanoic acids.

tion of paraoxon appears to be very fast in a micellar medium for all the peroxyacids, with an enhanced rate for the medium chain length ( $n = 3-6$ ) and an increasing micellar effect up to 300–500 for these compounds.

Table 1 shows that the rates of destruction of paraoxon are the highest for compounds **2b–2d**. Compound **2d** is already a product of great interest for use in detergents and bactericides, it is also one of the best compounds for the destruction of toxic organophosphorus pollutants. The decontamination products (sodium diethylphosphate and sodium *p*-nitrophenate) are non-toxic compounds.



**Scheme 2** General pathway for the destruction of paraoxon by peroxyacids.

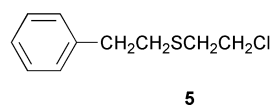
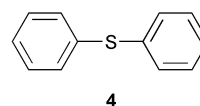
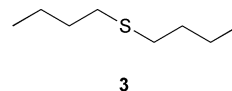
**Table 1** Kinetics of the dephosphorylation of paraoxon by peroxyacids **2**<sup>a</sup>

Peroxyacid ( <i>n</i> )	$10^5 k_{\text{H}_2\text{O}}/\text{s}^{-1}{}^b$	$10^3 k_{\text{mic}}/\text{s}^{-1}{}^c$	$k_{\text{mic}}/k_{\text{H}_2\text{O}}$
<b>2a</b> (1)	3.4	8.1	240
<b>2b</b> (3)	4.0	11.5	288
<b>2c</b> (4)	3.4	11.5	333
<b>2d</b> (5)	2.7	11.0	407
<b>2e</b> (6)	1.8	9.9	542
<b>2f</b> (10)	3.4	6.9	200

<sup>a</sup> All reactions were carried out at 25 °C, pH = 10, [paraoxon] =  $3.78 \times 10^{-5}$  mol L<sup>-1</sup>, [peroxyacid] = [CTABr] =  $2 \times 10^{-3}$  mol L<sup>-1</sup>. <sup>b</sup>  $k_{\text{H}_2\text{O}}$ : without CTABr. <sup>c</sup>  $k_{\text{mic}}$ : with CTABr.

## Oxidation of organosulfur compounds

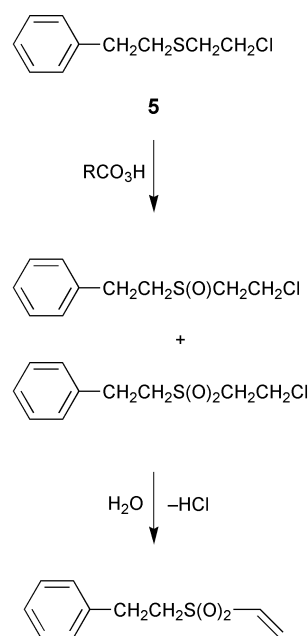
The reaction was tested with di-*n*-butyl sulfide (**3**), diphenyl sulfide (**4**) and 2-chloro-2'-phenyldiethyl sulfide, the half mustard **5**. The oxidation was followed by gas chromatography.<sup>7</sup> With an excess of the peroxyacid **2** (3 mol of peroxyacid per mol of sulfide), after 5 min no sulfide was left. Table 2 gives the ratio of sulfoxide : sulfone obtained after this period and after 30 min, only the sulfone is isolated quantitatively. For compound **5**, the chlorosulfone gives subsequently



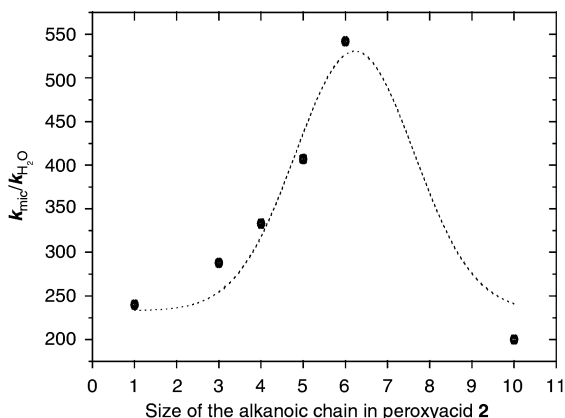
**Table 2** Oxidation of organosulfur substrates **3–5** in micellar medium by peroxyacids **2**<sup>a</sup>

Peroxyacid ( <i>n</i> )	Sulfoxide : sulfone selectivity <sup>b</sup>					
	pH = 7			pH = 10		
	<b>3</b>	<b>4</b>	<b>5</b>	<b>3</b>	<b>4</b>	<b>5</b>
<b>2a</b> (1)	0 : 100	0 : 100	40 : 60	22 : 78	0 : 100	0 : 100
<b>2b</b> (3)	0 : 100	0 : 100	10 : 90	16 : 84	0 : 100	0 : 100
<b>2c</b> (4)	0 : 100	0 : 100	10 : 90	0 : 100	0 : 100	0 : 100
<b>2e</b> (6)	0 : 100	0 : 100	10 : 90	0 : 100	0 : 100	0 : 100
<b>2f</b> (10)	0 : 100	0 : 100	10 : 90	0 : 100	0 : 100	0 : 100

<sup>a</sup> All reactions were carried out at 25 °C in micellar medium for 5 min. The peroxyacid/sulfide molar ratio is constant and equal to 3. Yields are quantitative (98–100%). <sup>b</sup> The sulfoxide : sulfone selectivity, determined by GC using the internal standard method, is given with  $\pm 2\%$  precision.



**Scheme 3** Oxidation of compound **5**.



**Fig. 1** Micellar catalysis of the dephosphorylation of paraoxon ( $k_{mic}/k_{H_2O}$  vs. length of the side chain in **2**).

the corresponding harmless vinylsulfone by HCl elimination (Scheme 3). The length of the side chain here has very little influence on the rate of the oxidation reaction.

In another study on the oxidation of toxic organosulfur analogues (**3**, **4** and **5**) in real conditions at the CEB, we used a fivefold excess of peroxyacid **2d** over the sulfide compound. This system allowed the quantitative oxidation of the sulfide with more than 99% sulfone production.

Our work has shown that  $\omega$ -phthalimidoperoxyalkanoic acids **2a–f** are very good decontaminants of organophosphorus and organosulfur pollutants. The length of the side chain has a great influence on the rate and efficiency of the decontamination of organophosphorus compounds in micellar medium. The optimal length of the chain is between perbutanoic **2b** ( $n = 3$ ) and perheptanoic **2e** ( $n = 6$ ) acids. In the oxidation of organosulfides, the length of the chain has no importance; the sulfone is obtained quantitatively in a very short period of time. Among the products, the industrial  $\omega$ -phthalimidoperoxyhexanoic acid (PAP, Eureco®) **2d** ( $n = 5$ ), which is also a very good detergent and bactericide, is also the best chemical decontaminant in the series.

## Experimental

### Materials and methods

Ethyl 4-bromobutyrate, ethyl 7-bromoheptanoate, 2-phthalimidoacetic acid, phthalimide potassium salt, 5-bromopentanoic acid, 11-bromoundecanoic acid, di-n-butyl sulfide, diphenyl sulfide, the corresponding sulfoxide and sulfone and paraoxon were purchased from Aldrich. 2-Chloro-2'-phenyldiethyl sulfide, the corresponding sulfoxide, the sulfone and the vinylsulfone have been previously described.<sup>12</sup> The other products are prepared as indicated below. All physical spectra (NMR, IR, mass, UV) are in accordance with the structures. The reaction kinetics of peroxyacids with paraoxon has already been described.<sup>1–4</sup> The oxidation of sulfide was followed by gas chromatography.<sup>7,12</sup>

### Synthesis of the esters

**Methyl 5-bromopentanoate.** Heating 5-bromoheptanoic acid (18.1 g, 0.1 mol) in 200 mL of dry refluxing methanol with a few drops of sulfuric acid, gives the corresponding ester (16.0 g, 82%). Bp 101–103 °C/15 mm; lit.<sup>13</sup> 91 °C/12 mm.

**Methyl 11-bromoundecanoate.** Using the same procedure, 23.4 g (88 mmol) of 11-bromoundecanoic acid yields 93% (22.8 g, 82 mmol) of the ester. Bp 120–122 °C/0.5 mm; lit.<sup>14</sup> 126–128 °C/0.65 mm.

### Ethyl and methyl $\omega$ -phthalimidoalkylcarboxylates

These compounds were obtained following the literature procedure<sup>15</sup> by refluxing the potassium phthalimide salt

with the bromoester in acetonitrile for 4 h. Ethyl 4-phthalimidobutyrate: 98% yield. Mp 68–70 °C. Methyl 5-phthalimidopentanoate, ethyl 7-phthalimidoheptanoate and methyl 11-phthalimidoundecanoate (yields 98, 77 and 99%) are yellow, quite pure oils, (determined by TLC), which were used without further purification.

### General procedure for preparation of the peroxyacids

The general method for the peroxidation of acids or esters has been described in the literature.<sup>16</sup> addition of hydrogen peroxide (30%, 110 volumes) to the acid or the ester in concentrated sulfuric acid at a temperature below 10 °C.

**2-Phthalimidoperacetic acid, 2a.** From 2-phthalimidoacetic acid (82%). Mp 116–118 °C; IR (KBr) 1775 ( $\nu_{C=O}$ ), 1730 ( $\nu_{C=O}$ ), 1090 ( $\nu_{C-O-O-H}$ )  $cm^{-1}$ ; active oxygen calc. 20.00, found 19.08%.

**4-Phthalimidoperbutanoic acid, 2b.** From ethyl 4-phthalimidobutyrate (94%). Mp 100–102 °C; IR (KBr) 1770 ( $\nu_{C=O}$ ), 1720 ( $\nu_{C=O}$ ), 1110 ( $\nu_{C-O-O-H}$ )  $cm^{-1}$ ; active oxygen calc. 17.75, found 17.02%.

**5-Phthalimidoperpentanoic acid, 2c.** From methyl 5-phthalimidopentanoate (82%). Mp 80–84 °C; IR (KBr) 1770 ( $\nu_{C=O}$ ), 1715 ( $\nu_{C=O}$ ), 1105 ( $\nu_{C-O-O-H}$ )  $cm^{-1}$ ; active oxygen calc. 16.81, found 16.27%.

**7-Phthalimidoperheptanoic acid, 2e.** From ethyl 7-phthalimidoheptanoate (93%). Mp 90–94 °C; IR (KBr) 1775 ( $\nu_{C=O}$ ), 1710 ( $\nu_{C=O}$ ), 1100 ( $\nu_{C-O-O-H}$ )  $cm^{-1}$ ; active oxygen calc. 15.19, found 14.38%.

**11-Phthalimidoperundecanoic acid, 2f.** From methyl 11-phthalimidoundecanoate (66%). Mp 100–104 °C; IR (KBr) 1770 ( $\nu_{C=O}$ ), 1710 ( $\nu_{C=O}$ ), 1095 ( $\nu_{C-O-O-H}$ )  $cm^{-1}$ ; active oxygen calc. 12.74, found 12.00%.

## References and notes

- 1 C. Lion, C. Charvy and G. Delmas, *Fr. Pat.*, 89.11133, 1989.
- 2 C. Lion, C. Charvy, M. Hedayatullah, P. Bauer, H. Sentenac-Roumanou, B. Despagne and G. Delmas, *Bull. Soc. Chim. Belg.*, 1990, **99**, 127.
- 3 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.
- 4 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.
- 5 (a) MMPP is a Solvay-Interox industrial product; (b) C. Lion, J. P. Boukou-Poba and M. Hedayatullah, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1991, **56**, 213.
- 6 G. Delmas, M. Despagne, C. Lion, G. Magnaud and H. Sentenac-Roumanou, *Fr. Pat.*, 2.276.368, 1991.
- 7 F. Gonzaga, E. Perez, I. Rico-Lattes and A. Lattes, *New J. Chem.*, 2001, **25**, 151.
- 8 (a) PAP (Eureco) is a Montedison-Ausimont industrial product; (b) C. Lion, G. Magnaud, G. Delmas and C. Charvy, *Fr. Pat.*, 96.03204, 1996 and *US Pat.*, 6.143.088, 2000.
- 9 C. Lion, M. Hedayatullah, C. Charvy, G. Delmas, G. Magnaud and H. Sentenac-Roumanou, *Bull. Soc. Chim. Belg.*, 1997, **106**, 221.
- 10 C. Lion, L. Da Conceição and H. Sayag, *C. R. Acad. Sci., Sér. IIC*, 1999, **2**, 57.
- 11 H. Gethöffer, *US Pat.*, 5.061.807, 1991 and *Ger. Pat.*, 4.003.309, 1991.
- 12 A. Leblanc, L. Fosset, G. Magnaud, M. Desgranges, H. Sentenac-Roumanou, C. Lion, C. Charvy and A. Mohri, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1993, **79**, 141 and *Fr. Pat.*, 9203627, 1992.
- 13 S. Hauptmann and K. Hirschberg, *J. Prakt. Chem.*, 1966, **34**, 262.
- 14 H. C. Brown and C. F. Lane, *J. Am. Chem. Soc.*, 1970, **92**, 6660.
- 15 S. Julia, A. Ginebeda and J. Guixer, *J. Chem. Soc., Chem. Commun.*, 1978, 742.
- 16 M. Feldhues and H. J. Schäfer, *Tetrahedron*, 1985, **41**, 4195.