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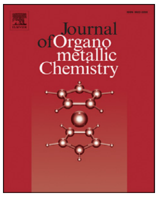

Promotion of phosphoester hydrolysis by MoO_2Cl_2L (L = bipyridine derivatives, H_2O, no ligand), $MoO_2(CH_3)_2L$ (L = bipyridine derivatives) and related inorganic–organic hybrids in aqueous media

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ABSTRACT

The compounds MoO_2Cl_2L (L = 2,2′-bipyridine (bipy) (**1**); 4,4′-di-*tert*-butyl-2,2′-bipyridine (di-^{t}Bu-bipy) (**2**)), $[MoO_2Cl_2(H_2O)_2]\cdot(\text{diglyme})_2$ (**3**), MoO_2Cl_2 (**4**), $MoO_2(CH_3)_2L$ (L = bipy (**5**); di-^{t}Bu-bipy (**6**)), $[MoO_3(\text{bipy})]_n$ (**7**), $\{[MoO_3(\text{bipy})][MoO_3(H_2O)]\}_n$ (**8**), $[Mo_8O_{22}(OH)_4(\text{di-}^t\text{Bu-bipy})_4]$ (**9**) and MoO_3 (**10**) were tested as phosphoester bond hydrolysis promoters in aqueous media. Sodium *para*-nitrophenylphosphate (*p*NPP) was used as a model substrate for the phosphoester bond hydrolysis reaction, which was performed at 55 °C, using D_2O as solvent and 100 or 10 mol% of the chosen promoter. The progression of all the reactions was monitored by ^1H NMR spectroscopy. All studied systems promote phosphoester bond hydrolysis. The best performance was obtained with MoO_2Cl_2L compounds (**1**–**4**) and with the inorganic–organic hybrid $\{[MoO_3(\text{bipy})][MoO_3(H_2O)]\}_n$ (**8**). The studied compounds originate either homogeneous or solid/liquid biphasic systems. For the biphasic systems (**1**, **2**, **5**–**9**), the solid phase was recovered at the end of the reaction and characterized by FT-IR spectroscopy.

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1. Introduction

Organophosphorus pesticides are the most widely used type of pesticide in the world. They constitute a vast category of chemicals specifically designed for the control of pests, weeds or plant diseases. Their application is still the most effective and accepted means for the protection of plants from pests, and has contributed significantly to enhanced agricultural productivity and crop yields [1a]. Unfortunately, organophosphate pesticides are also the most important cause of severe toxicity and death from acute poisoning worldwide, with more than 200,000 deaths each year in developing countries [1a,b]. Moreover, their accumulation in the environment is a recognized ecological threat with harmful effects on human beings or other mammalian species due to possible long-term exposure to sublethal doses. The toxic effect of organophosphorus pesticides has a cumulative nature and entails various degenerative disorders of the nervous system. Additionally, organophosphorus pesticides are strong mutagens, causing multiple chromosomal aberrations and carcinogenesis [1c].

Chemically, organophosphate pesticides are esters of phosphoric acid (phosphoesters). The chemistry of pesticides is entwined with that of nerve agents (chemical weapons, such as sarin) since they possess similar structural features and formulas. Whereas pesticides are less immediately toxic when compared with nerve agents, their heavier use and looser monitoring is perhaps cause for greater concern [1a].

Hydrolysis products of organophosphate pesticides are either non-toxic, or have a substantially lower toxicity than the original substrates [1c]. Thus, hydrolysis is considered to be an interesting strategy to eliminate organophosphate pesticides. In the absence of a catalyst or enzyme, phosphoester hydrolysis may be extremely slow under normal conditions. For this reason, over time, a growing interest in the metal promoted hydrolysis of phosphoesters has arisen. In recent years, a range of metal complexes containing Cu^{2+}, Ln^{3+}, Co^{3+}, Zn^{2+}, Mn^{2+}, Fe^{3+} and Zr^{4+} has proven to exhibit high activity toward phosphoester cleavage [2].

Molybdenum is an essential trace element for plant growth and is commonly used in the form of oxides as fertilizer to avoid molybdenum deficiencies in soils worldwide [3], making molybdenum an attractive candidate for metal promoted hydrolysis of phosphoesters. To the best of our knowledge, the use of molybdenum-containing

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compounds as promoters of phosphoester hydrolysis had until recently been limited to molybdocene derivatives (Cp'_2MoCl_2) [4], molybdates ($MoO_4{}^{2-}$) [5a–c] and polyoxometalates [5d–h], even though molybdenum is known to be a crucial component of both natural and synthetic catalysts [3,5h,6]. For molybdocene derivatives the reactive agents were proposed to be $[Cp'_2Mo(OH)(H_2O)]^+$, which are formed by rapid hydrolysis of the Mo–Cl bonds in Cp'_2MoCl_2. Phosphoester hydrolysis was not catalytic, possibly due to the high stability of Cp'_2Mo-phosphate products [4a,c].

The effect of molybdates on phosphoester hydrolysis was originally studied in the context of organic phosphate estimation by colorimetry [5a–c]. Recently, a growing interest in the phosphoesterase activity of molybdates has arisen, due in part to the promising potential of polyoxomolybdates as therapeutic agents [5d–h,7]. For molybdates, reactive species responsible for phosphoester hydrolysis were proposed to be polyoxomolybdates such as the heptamolybdate anion $[Mo_7O_{24}]^{6-}$ that form upon mild acidification of molybdate solutions. These results showed that negatively charged and saturated complexes could efficiently hydrolyze phosphoester bonds [5f]. Previously, the metal complexes that were found to be active as catalysts for the hydrolysis of phosphoester bonds were generally coordinatively unsaturated and/or positively charged [2a,8], which were assumed to be essential properties for Lewis acid activation via coordination of phosphoryl oxygen(s) to the metal ion.

Very recently, we showed that phosphoester bond hydrolysis of *para*-nitrophenylphosphate (*p*NPP), a commonly used model substrate, could be accelerated by using the complex $MoO_2Cl_2(DMF)_2$ (DMF = dimethylformamide) in water under mild conditions, even when catalytic amounts of complex are used [9]. In that work we found that, at high concentrations of $MoO_2Cl_2(DMF)_2$, hydrolysis of the Mo–Cl bonds in the molecular precursor led to the precipitation of a molybdenum oxide structure formulated as $Mo_2O_6(DMF)$. The latter compound dissolved as the reaction progressed, leading to the formation of hydrolytically active isopolyoxomolybdate and phosphomolybdate species. Encouraged by these results, we decided to explore the phosphoester hydrolysis promoting potential of other complexes of the type $MoO_2X_2L_n$, in the hope of finding more active systems and/or gaining a better understanding of the chemistry of the complexes in aqueous solution and the influence of the ligands X and L. We herein report the performance of the complexes MoO_2Cl_2L (L = 2,2′-bipyridine (bipy), 4,4′-di-*tert*-butyl-2,2′-bipyridine (di-^{t}Bu-bipy), H_2O, no ligand) and $MoO_2(CH_3)_2L$ (L = bipy, di-^{t}Bu-bipy) in the hydrolysis of *p*NPP. The hybrid molybdenum oxide materials $[MoO_3(bipy)]_n$, $\{[MoO_3(bipy)][MoO_3(H_2O)]\}_n$ and $[Mo_8O_{22}(OH)_4(\text{di-}^t\text{Bu-bipy})_4]$ have also been studied since these have been shown in previous work to be products of the hydrolysis of the complexes MoO_2Cl_2L. The family of compounds to be screened was completed by inclusion of the purely inorganic compounds MoO_3 and MoO_2Cl_2.

2. Experimental

2.1. Materials and methods

$Na_2MoO_4 \cdot 2H_2O$ (Fluka, >99%), MoO_2Cl_2 (Sigma–Aldrich), bipy, di-^{t}Bu-bipy (98%, Sigma–Aldrich), diethylene glycol dimethylether (diglyme, 99%, Fluka), hexane (99%, Sigma–Aldrich), acetone (99.5%, Fluka), diethyl ether (99.8%, Sigma–Aldrich), dichloromethane (99.9%, Sigma–Aldrich), acetonitrile (99.5%, Sigma–Aldrich), pentane (99%, Sigma–Aldrich), methylmagnesium chloride solution (CH_3MgCl, 3 M in THF, Fluka), *para*-nitrophenylphosphate disodium salt hexahydrate (*p*NPP, 99%, Alfa Aesar), D_2O (Euroiso-top, 99.96%), and 1,4-dioxane (Fischer Chemical, 99.99%) were obtained from commercial sources and used as received.

The promoters $MoO_2Cl_2(bipy)$ (**1**) [10a], $MoO_2Cl_2(\text{di-}^t\text{Bu-bipy})$ (**2**) [10b], $[MoO_2Cl_2(H_2O)_2]\cdot(diglyme)_2$ (**3**) [10c], MoO_2Cl_2 (Sigma–Aldrich) (**4**), $MoO_2(CH_3)_2(bipy)$ (**5**) [10d,e], $MoO_2(CH_3)_2(\text{di-}^t\text{Bu-bipy})$ (**6**) [10f], $[MoO_3(bipy)]_n$ (**7**) [10g], $\{[MoO_3(bipy)][MoO_3(H_2O)]\}_n$ (**8**) [10h], $[Mo_8O_{22}(OH)_4(\text{di-}^t\text{Bu-bipy})_4]$ (**9**) [10i] and MoO_3 (Sigma–Aldrich, >99.5%) (**10**) were synthesized according to the published procedures or obtained from commercial sources and used as received.

FT-IR spectra were recorded as KBr pellets using a Unicam-Mattson 7000 spectrophotometer equipped with a DTGS CsI detector. Solution NMR spectra were recorded on a Bruker Avance II+ 300 MHz (UltraShieldTM Magnet) spectrometer at ambient temperature. Chemical shifts are given in ppm relative to TMS (^{1}H).

2.2. Molybdenum-promoted hydrolysis assays

Sodium *para*-nitrophenylphosphate (3.0 mg, 8×10^{-3} mmol) and dioxane (internal standard, 0.8 mg, 9×10^{-3} mmol) were dissolved in deuterated water in a 5 mm NMR tube bearing a magnetic stirring bar, and heated at 55 °C. The molybdenum compound (10 or 100 mol% relative to *p*NPP) was added, and the progression of the reaction monitored over time by ^{1}H NMR. *Attention*: The magnetic stirring bar was removed immediately before the NMR measurement, and then reintroduced immediately after the measurement. The relative amounts of *p*NPP and *para*-nitrophenol (*p*NPh) in the reaction medium were followed by quantification of the respective areas in comparison to the area of the internal standard. The pH of the solution was measured at the described times and reaction temperature. The pD value of the solution was obtained by adding 0.4 to the pH reading. Before addition of the catalyst the reaction medium had a pD of 7.4. Addition of the metal complexes studied causes significant differences in the pD of the reaction medium. Reactions were not buffered to understand the real impact of each compound *per se* in the hydrolysis reaction.

2.3. Promoter recovery

At the end of the reaction monitoring, biphasic solid–liquid systems were centrifuged (Table 1). The obtained solid was washed with water, methanol and diethyl ether and air-dried. Identification of the solids was performed by FT-IR spectroscopy. Recovered solids were numbered with an asterisk. For example, the solid recovered from a reaction with **1** was identified as **1***. Additional scaled-up (5×) reactions were performed with **1** and **5**, which allowed enough solid to be recovered for use in a second run.

3. Results and discussion

Compounds **1**–**10** were synthesized according to literature procedures (**1**–**3** and **5**–**9**) or obtained commercially (**4** and **10**) as described in the Experimental section [10]. Their structures are illustrated in Chart 1. Reaction of MoO_2Cl_2 with THF afforded $MoO_2Cl_2(THF)_2$, and further addition of one equivalent of bidentate nitrogen donor ligand L (L = bipy or di-^{t}Bu-bipy) resulted in the formation of the complex MoO_2Cl_2L (**1** and **2**) [10a,b]. Treatment of the latter compounds with Grignard reagent at low temperature gave the dimethyl derivatives $MoO_2(CH_3)_2L$ (**5** and **6**) (L = bipy or di-^{t}Bu-bipy) [10d–f]. $[MoO_2Cl_2(H_2O)_2]\cdot(diglyme)_2$ (**3**) was prepared by reflux of an aqueous solution of HCl with MoO_3 and addition of diglyme [10c]. The one dimensional organic–inorganic hybrid material $[MoO_3(bipy)]_n$ (**7**) was prepared by oxidative decarbonylation of $Mo(CO)_4(bipy)$ [10g]. The molybdenum oxide/bipyridine hybrid material $\{[MoO_3(bipy)][MoO_3(H_2O)]\}_n$ (**8**) [10h]

Table 1
Characterization of the hydrolysis reaction system regarding phases and possible identification of the solid phase at the end of the reaction.[a]

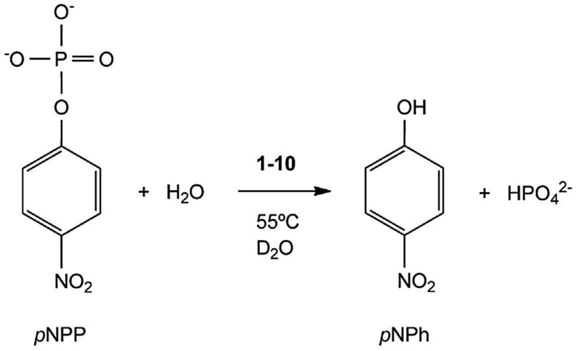
ID[b]	Promoter	System type	Solid identification[d]
1	MoO_2Cl_2(bipy)	Biphasic (S/L)[c]	$[MoO_3(bipy)]_n$ (**1***)
2	MoO_2Cl_2(di-^{t}Bu-bipy)	Biphasic (S/L)[c]	MoO_2Cl_2(di-^{t}Bu-bipy) (**2***)
3	$[MoO_2Cl_2(H_2O)_2]\cdot(diglyme)_2$	Monophasic	–
4	MoO_2Cl_2	Monophasic	–
5	$MoO_2(CH_3)_2$(bipy)	Biphasic (S/L)[c]	$MoO_2(CH_3)_2$(bipy) (**5***)
6	$MoO_2(CH_3)_2$(di-^{t}Bu-bipy)	Biphasic (S/L)[c]	$MoO_2(CH_3)_2$ (di-^{t}Bu-bipy) (**6***)
7	$[MoO_3(bipy)]_n$	Biphasic (S/L)[c]	$[MoO_3(bipy)]_n$ (**7***)
8	$\{[MoO_3(bipy)][MoO_3(H_2O)]\}_n$	Biphasic (S/L)[c]	$[MoO_3(bipy)]_n$ (**8***)
9	$[Mo_8O_{22}(OH)_4$(di-^{t}Bu-bipy)$_4]$	Biphasic (S/L)[c]	$[Mo_8O_{22}(OH)_4$ (di-^{t}Bu-bipy)$_4]$ (**9***)
10	$MoO_3\cdot H_2O$	Monophasic	–

[a] Reaction conditions: 100 mol% of promoter relative to *p*NPP, 55 °C, D_2O, dioxane as internal standard.

[b] Promoter identification number.

[c] Solid/liquid biphasic system.

[d] By FT-IR spectroscopy. Please see the Experimental section for a description of the recovery procedure.



Scheme 1. Mo-promoted hydrolysis reaction studied in this work.

and the octanuclear complex $[Mo_8O_{22}(OH)_4$(di-^{t}Bu-bipy)$_4]$ (**9**) [10i] were obtained by reaction of **1** and **2** with H_2O, respectively.

Compounds **1**–**10** were tested as phosphoester bond hydrolysis promoters. Sodium *para*-nitrophenylphosphate (*p*NPP) was used as a model substrate for the phosphoester bond hydrolysis reaction, which was performed at 55 °C, using D_2O as solvent and 100 mol% of the chosen promoter (Scheme 1). The progression of all the reactions was monitored by ^1H NMR spectroscopy (see Experimental section for details and Fig. 1). Over time, the ^1H NMR spectra of the reaction solutions show that the amount of *p*NPP (doublets at δ 8.21 and 7.31) decreases with the concomitant increase of the hydrolysis product *para*-nitrophenol (*p*NPh) (doublets at δ 8.15 and 6.89).

The results regarding MoO_2X_2L compounds **1**–**6** are depicted in Fig. 2. For comparison purposes this figure also includes results of the reaction performed in the absence of promoter (blank) and previously reported data for $MoO_2Cl_2(DMF)_2$ (DMF = dimethylformamide) and Na_2MoO_4 [9]. The dichloro complexes **1**–**4** and $MoO_2Cl_2(DMF)_2$ present similar hydrolysis promotion profiles, indicating that the neutral ligands L (bipy, di-^{t}Bu-bipy, H_2O, no ligand, DMF) in the compounds MoO_2Cl_2L have no significant impact on the promoter capacity of the systems. However, after the half reaction time all the systems perform significantly better than Na_2MoO_4. Interestingly, the dimethyl derivatives **5** and **6** are also hydrolysis promoters, although they perform significantly slower than their dichloro counterparts. Thus, although the presence of Cl ligands, which could be prone to hydrolysis and substitution by oxygen ligands, is not mandatory for the activity of monomeric systems, it seems to be important for the system performance. Furthermore, for the $MoO_2(CH_3)_2L$ compounds studied, the use of the ligand di-^{t}Bu-bipy has a clear positive effect when compared with the use of the ligand bipy.

Performing the reaction with catalytic amounts of **1** and **2** (10 mol% of complex relative to *p*NPP; homogeneous reaction conditions, i.e., one monophasic liquid phase) also enables an accelerated *p*NPP hydrolysis, but at a slower rate (Fig. 2). A similar behavior was reported for the complex $MoO_2Cl_2(DMF)_2$ [9].

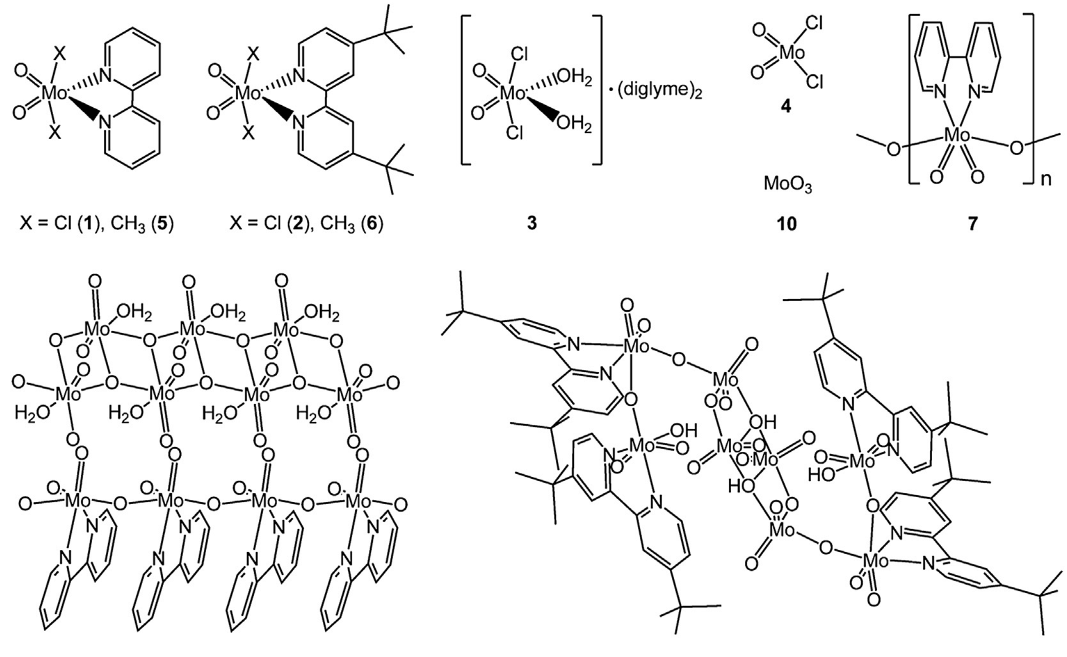


Chart 1. Molybdenum-containing compounds used in this work.

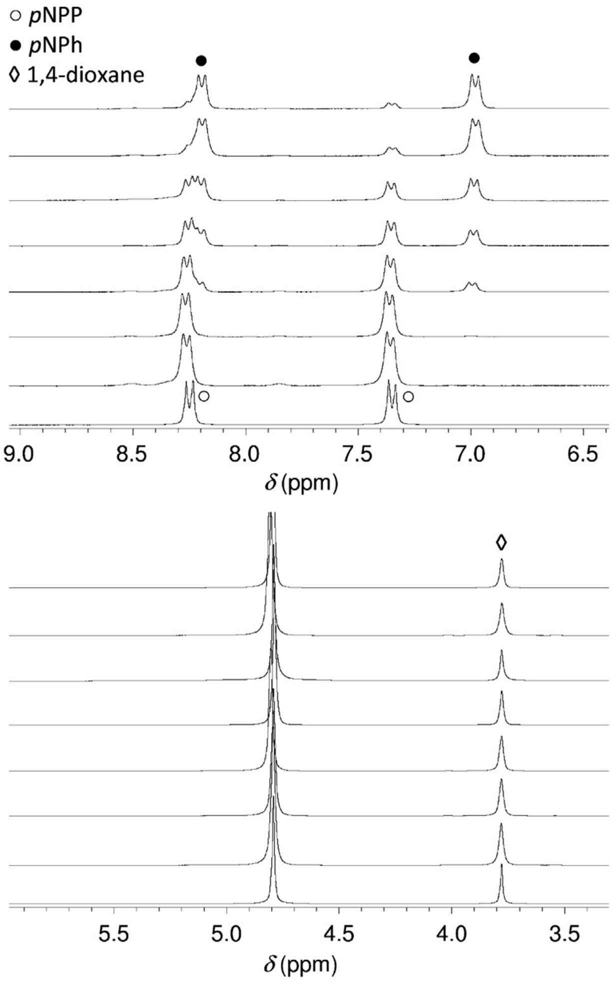


Fig. 1. Representative ^{1}H NMR spectra (300 MHz, detail 6.5–9.0 ppm and 3.5–6.0 ppm) of the *p*NPP hydrolysis reaction. Reaction conditions: 100 mol% of **8** relative to *p*NPP, 55 °C, D_2O, 1,4-dioxane as internal standard.

Among the studied polynuclear systems (**7**–**9**), the best system is the hybrid $\{[MoO_3(bipy)][MoO_3(H_2O)]\}_n$ (**8**), which equals the performance of the mononuclear systems bearing chloro ligands (**1** and **2**) and surpasses the commercial molybdenum oxide **10** (Fig. 3).

When the amount of promoter used is 100 mol% relative to pNPP, compounds **1**–**10** originate either homogeneous (**3**, **4** and **10**) or solid/liquid biphasic (**1**, **2**, **5**–**9**) systems (Table 1). For the biphasic systems, the solid phase (denoted **N***) was recovered at the end of the reaction (please see the Experimental section for details) and characterized by FT-IR spectroscopy. Our previous studies on the reaction of the complexes MoO_2Cl_2L (L = bipy, di-^{t}Bu-bipy) with water (which resulted in the isolation of the hybrid materials **8** and **9**) [10h,i], together with the synthesis and characterization of $[MoO_3(bipy)]_n$ (**7**) by oxidative decarbonylation of $Mo(CO)_4(bipy)$ [10g], helped in the identification of the recovered solids. The FT-IR spectra of **1***, **7*** and **8*** were all identical to that for the as-prepared material **7** (Fig. S1 in the Supplementary data). For the dichloro complex **2**, the spectrum of the recovered solid **2*** showed some differences from that for **2** (Fig. S2), although there was still a good match between the two spectra concerning the characteristic Mo–O vibrations between 850 and 950 cm^{-1} and the organic ligand modes between 1000 and 1700 cm^{-1}. Three possible products of the reaction of **2** with water are the oxo-bridged dinuclear species $[\{MoO_2Cl(di\text{-}^tBu\text{-}bipy)\}_2(\mu_2\text{-}O)]$ [11] and $[\{MoO_2(\mu_2\text{-}O)(di\text{-}^tBu\text{-}bipy)\}_2]$ [10h,12], and the octanuclear compound **9** [10h]. However, the changes noted in the spectrum of **2*** are not consistent with any of these structures. For the remaining biphasic systems, the FT-IR spectra of the recovered solids (**5***, **6*** and **9***) were identical to those exhibited by the promoters initially used (Fig. S2). The dichloro compounds **1**, **3**, **4** and $MoO_2Cl_2(DMF)_2$ all resulted in acidic pD values of 1.4, which indicates that hydrolysis of the Mo–Cl bonds had occurred to give HCl and an acidic solution. By contrast, a pD value of 6.4 was obtained after addition of $MoO_2Cl_2(di\text{-}^tBu\text{-}bipy)$ (**2**). This is consistent with the FT-IR result and indicates that the presence of the di-^{t}Bu-bipy ligands renders the complex less soluble and/or more stable towards hydrolysis of the Mo–Cl bonds. Despite this contrasting behavior of **2** (vs. **1**, **3**, **4** and $MoO_2Cl_2(DMF)_2$), it presents a similar hydrolysis promotion profile to the other four dichloro compounds, as noted above (Fig. 2).

Additional scaled-up (5×) reactions were performed with **1** and **5**, which allowed enough solid to be recovered for use in a second run. As noted above, **1*** was identified as **7**, while **5*** was identified as **5**. The isolated yields (in mol%, calculated assuming that **1*** = **7** and **5*** = **5**) after the scaled-up runs were 51% for **1*** and 58% for **5***. The hydrolytic performances of the two recovered solids (100 mol% relative to *p*NPP) were similar to their "fresh" counterparts (i.e., **7** and **5**, respectively) (Fig. 4).

The stability of $MoO_2(CH_3)_2(di\text{-}^tBu\text{-}bipy)$ (**6**), $[MoO_3(bipy)]_n$ (**7**) and $[Mo_8O_{22}(OH)_4(di\text{-}^tBu\text{-}bipy)_4]$ (**9**) has been described in previous work in which the compounds were used as catalysts for the liquid-phase epoxidation of olefins at 55 °C with *tert*-butylhydroperoxide as oxidant under non-aqueous conditions [10f,g,i]. Specifically, Mo–CH_3 and Mo–N bonds in the soluble homogeneous catalyst **6** were found to be chemically stable under the reactions conditions used, even in the present of peroxides and alcohols [10f]. In the present study we have found that this stability seems to extend to aqueous media. In parallel with the present work, the catalytic olefin epoxidation systems with **7** and **9** were always biphasic and the IR spectra of the recovered solids were identical to those of the as-synthesized compounds [10g,i].

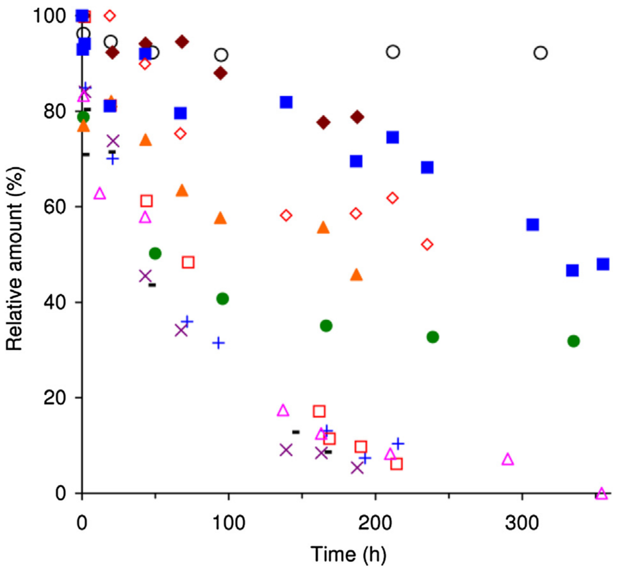


Fig. 2. Hydrolysis profile of *p*NPP either in the absence of promoter (○), or with $MoO_2X_2(bipy)$ (X = Cl (**1**, + (100 mol%) or ■ (10 mol%)), CH_3 (**5**, ♦)), $MoO_2X_2(di\text{-}^tBu\text{-}bipy)$ (X = Cl (**2**, □ (100 mol%) or ◊ (10 mol%)), CH_3 (**6**, ▲)), $[MoO_2Cl_2(H_2O)_2]\cdot(diglyme)_2$ (**3**, ×), MoO_2Cl_2 (**4**, -), $MoO_2Cl_2(DMF)_2$ (△) or Na_2MoO_4 (●). Reaction conditions: 100 mol% promoter relative to *p*NPP (unless otherwise indicated), 55 °C, D_2O, dioxane as internal standard. Reaction pD after promoter addition in parenthesis: **1** (1.4), **2** (6.4), **3** (1.4), **4** (1.4), **5** (7.4), **6** (7.4), $MoO_2Cl_2(DMF)_2$ (1.4), Na_2MoO_4 (7.4).

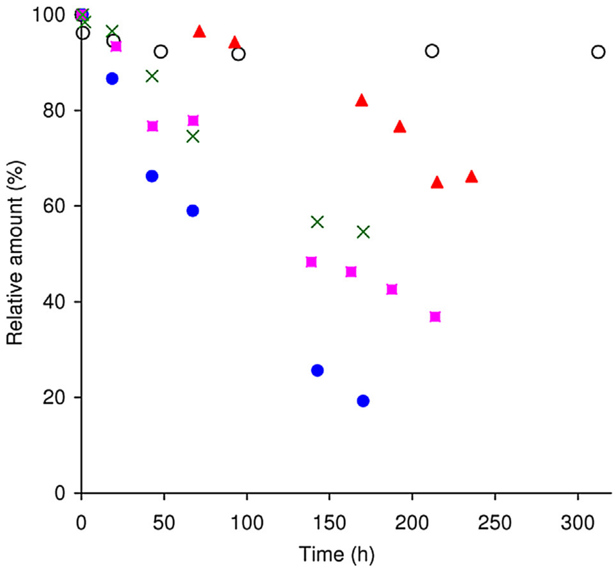


Fig. 3. Hydrolysis profile of *p*NPP either in the absence of promoter (○), or with $[MoO_3(bipy)]_n$ (**7**, ▲), $\{[MoO_3(bipy)][MoO_3(H_2O)]\}_n$ (**8**, ●), $[Mo_8O_{22}(OH)_4(di\text{-}^tBu\text{-}bipy)_4]$ (**9**, ■), or MoO_3 (**10**, ×). Reaction conditions: 100 mol% promoter relative to *p*NPP, 55 °C, D_2O, dioxane as internal standard. The reaction pD after promoter addition was 7.4 in all cases.

4. Conclusions

Insecticidal organophosphates and related nerve agents can be detoxified by hydrolysis of their phosphoester bonds. In the present work we have shown that various types of oxomolybdenum compounds, ranging from simple mononuclear complexes of the type MoO_2X_2L to polynuclear compounds, can promote the hydrolysis of the benchmark substrate sodium *para*-nitrophenylphosphate (*p*NPP). The performance of the dichloro derivatives MoO_2Cl_2L (**1**,**2**; L = bipyridine ligand) matches that of MoO_2Cl_2, and is superior to that of Na_2MoO_4. A disadvantage of MoO_2Cl_2 vs. the bipyridine adducts is that it is less stable and more difficult to handle. The best polynuclear compound studied, $\{[MoO_3(bipy)][MoO_3(H_2O)]\}_n$ (**8**), performs much better than molybdic acid ($MoO_3 \cdot H_2O$) and as good as the mononuclear dichloro derivatives. While MoO_2Cl_2 and $MoO_3 \cdot H_2O$ both give rise to monophasic (homogeneous) systems, the complexes MoO_2X_2L (**1**,**2**,**5**,**6**; X = Cl, CH_3) and compound **8** give rise to biphasic systems (when 100 mol% of promoter is used relative to *p*NPP), and it was possible to recover and identify the solid phases. Whereas both $MoO_2Cl_2(bipy)$ (**1**) and **8** are transformed into the one-dimensional organic–inorganic hybrid material $[MoO_3(bipy)]_n$, which in a separate experiment only performed moderately as a promoter of *p*NPP hydrolysis, complexes **5**, **6** and, to a lesser extent, **2** were recovered unchanged. Future work may focus on complex **2**, investigating the possibility of promoter recycling and reuse.

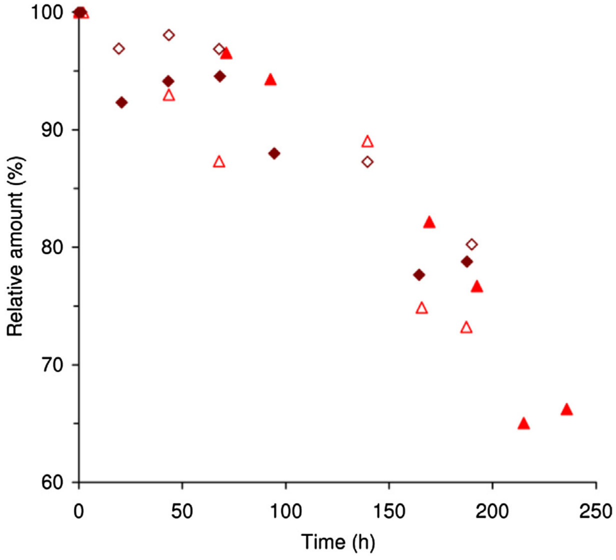


Fig. 4. Hydrolysis profile of *p*NPP with **1*** (△), $[MoO_3(bipy)]_n$ (**7**, ▲), **5*** (◊) and $MoO_2(CH_3)_2(bipy)$ (**5**, ♦). Reaction conditions: 100 mol% promoter relative to *p*NPP, 55 °C, D_2O, dioxane as internal standard. The reaction pD after promoter addition was 7.4 in all cases.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.12.029.

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