# Oxidation of Alkynes Catalyzed by Mo(VI) and W(VI) Polyoxometalates

Francesco Paolo Ballistreri, Salvatore Failla, Emanuela Spina, and Gaetano Andrea Tomaselli*

*Dipartimento Scienze Chimiche, University of Catania, Viale A. Doria 6, 95125 Catania, Italy*

*Received July 29, 1988*

Oxidation of alkynes, both terminal and internal, is performed by hydrogen peroxide in the presence of catalytic amounts of (cetylpyridinium)$_3$PM$_{12}$O$_{40}$ (M = Mo(VI), W(VI)). A comparison with the analogous oxidation reactions catalyzed by Na$_2$MO$_4$ reveals that PM$_{12}$O$_{40}$$^{3-}$ anions are more efficient catalysts than MO$_4$$^{2-}$ in the oxidation of terminal alkynes to carboxylic acids. The higher catalytic activity of peroxometalates allows the oxidation of internal alkynes by hydrogen peroxide, which does not occur with MO$_4$$^{2-}$ salts.

Owing to the rapid developments of phase-transfer procedures, the catalyzed oxidations by hydrogen peroxide find increasing synthetic applications.[1-6] Basically, the procedures involve the formation of a peroxometal complex in the aqueous phase via addition of hydrogen peroxide to the metal derivatives and the transfer, by a suitable phase-transfer agent, of the peroxidic species into an organic phase containing the substrate.

In most of the reported studies the metal precursor is a salt of general formula Na$_2$MO$_4$ (M = Mo(VI) or W(VI)) dissolved in fairly acidic aqueous solutions. It is well known that, under these conditions, upon addition of hydrogen peroxide an oxodiperoxomolybdenum or -tungsten complex is formed of general formula MO(O$_2$)$_2$, which represents the real oxidant species.[5] Recently, however, the attention has been focused on heteropolyacids such as H$_3$PM$_{12}$O$_{40}$,[7-9] which also add hydrogen peroxide to form peroxometal species, whose structure is not yet well characterized.

Although quantitative data are lacking in the literature, there is some evidence that peroxo complexes formed from heteropolyacids may be more effective than those formed from simple anions in the oxidation of alkenes and alcohols.[7-9] Recently we turned our attention to the oxidation of acetylenic compounds observing that such substrates, usually rather reluctant to undergo oxidative reactions, are easily oxidized by peroxomolybdenum or peroxotungsten complexes.[5,6,10] However, the presence of a mercuric salt as cocatalyst is a necessary requisite. Therefore, it was of some interest to ascertain whether, also in alkyne oxidations, peroxometal complexes derived from heteropolyacids could behave as effective oxidants as compared with simple peroxometal species. Moreover, the need of the presence of the mercuric salt, which may have some interactions with heteropolyacids, makes it difficult to predict the behavior of the oxidations.

## Results and Discussion

The results, collected in Table I, provide some useful information on the general features of the alkynes oxidation by peroxo species formed from heteropolyacids. The data reported have been obtained by using as precursor tris(cetylpyridinium) 12-molybdophosphate or 12-tungstophosphate (CMP or CWP) and Hg(CF$_3$CO$_2$)$_2$ as cocatalyst. Details on the reaction conditions are provided in Table I. As model substrates, we have used four alkynes where the triple bonds, either internal or terminal, carry both alkyl or aryl substituents. For comparison purposes, Table I collects also the data referring to the oxidation of the same or similar substrates when H$_2$MO$_4$ (obtained from Na$_2$MO$_4$·2H$_2$O and H$_2$SO$_4$) is the precursor of the peroxo species. In this case, the phase-transfer agent is a quaternary ammonium salt (Aliquat)[5,6] or a neutral ligand (hexaethylphosphoric triamide, HEPT).

Inspection of the data of Table I immediately reveals that indeed the peroxo complexes derived from CMP or CWP are remarkably more reactive than usual peroxomolybdenum or peroxotungsten complexes, MO(O$_2$)$_2$, as

(1) Bortolini, O.; Di Furia, F.; Modena, G. Italian Patent Application 25720A, 1981, Italian Patent N. 114265.

(2) Bortolini, O.; Di Furia, F.; Modena, G. Italian Patent Application 25721A, 1981, Italian Patent N. 1142616.

(3) Bortolini, O.; Di Furia, F.; Modena, G.; Seraglia, R. *J. Org. Chem.* **1985**, *50*, 2688.

(4) Bortolini, O.; Bragante, L.; Di Furia, F.; Modena, G. *Can. J. Chem.* **1986**, *64*, 1189.

(5) Ballistreri, F. P.; Failla, S.; Tomaselli, G. A. *J. Org. Chem.* **1988**, *53*, 830.

(6) Ballistreri, F. P.; Failla, S.; Tomaselli, G. A. *The Role of Oxygen in Chemistry and Biochemistry*; Ando, W., Morooka, Y., Eds.; Elsevier: Amsterdam, 1988; p 33, 341.

(7) Matoba, Y.; Inone, H.; Akagi, J.; Okabayashi, T.; Ishii, Y.; Ogawa, M. *Synth. Commun.* **1984**, *14*, 865 and references therein.

(8) Yamawaki, K.; Yoshida, T.; Nishihara, H.; Ishii, Y.; Ogawa, M. *Synth. Commun.* **1986**, *16*, 537.

(9) Ishii, Y.; Yamawaki, K.; Yoshida, T.; Ura, T.; Ogawa, M. *J. Org. Chem.* **1987**, *52*, 1868.

(10) Ballistreri, F. P.; Failla, S.; Tomaselli, G. A.; Curci, A. *Tetrahedron Lett.* **1986**, *27*, 5139.

Table I. Oxidation of Alkynes with Tris(cetylpyridinium) 12-Molybdophosphate or 12-Tungstophosphate and Hydrogen Peroxide at 40 °C in Dichloroethane/Water.[a] Comparison between the Catalytic Activities of $PMo_{12}O_{40}^{3-}$ and $MO_4^{2-}$ Salts

| run no. | alkyne (mmol) $R_aC{\equiv}CR_b$ $R_a$ | $R_b$ | convsn (%) | time | products (yields, %) | catalyst |
|---|---|---|---|---|---|---|
| 1 | $C_6H_5$ | $C_6H_5$ (2.8) | 88 | 22 h | $C_6H_5COOH$ (196); $C_6H_5COCOC_6H_5$ (6) | $PMo_{12}O_{40}^{3-}$ |
| 1a | $C_6H_5$ | $C_6H_5$ (3.4)[b] | 0 | 36 h | | $MoO_4^{2-}$ |
| 2 | $C_6H_5$ | H (3.0) | 100 | 10 min | $C_6H_5COOH$ (60); HCOOH (60); $C_6H_5COCH_3$ (18) | $PMo_{12}O_{40}^{3-}$ |
| 2a | $C_6H_5$ | H (6.2)[c] | 40 | 60 min | $C_6H_5COCHO$ (100); n.d. | $MoO_4^{2-}$ |
| 2b | $C_6H_5$ | H (6.2)[c,d] | 84 | 30 min | $C_6H_5COOH$ (71); $C_6H_5COCHO$ (13); n.d. | $MoO_4^{2-}$ |
| 3 | $n$-$C_3H_7$ | $n$-$C_3H_7$ (2.6) | 100 | 13 h | $CH_3(CH_2)_2COOH$ (106); $CH_3(CH_2)_2COCO(CH_2)_2CH_3$ (1); $CH_3(CH_2)_2CO(CH_2)_3CH_3$ (22); $CH_3CH_2CH{=}CHCO(CH_2)_2CH_3$ (7) | $PMo_{12}O_{40}^{3-}$ |
| 3a | $n$-$C_7H_{15}$ | $n$-$C_7H_{15}$ (3.0)[b] | 7 | 15 h | $CH_3(CH_2)_6COCO(CH_2)_6CH_3$ (100) | $MoO_4^{2-}$ |
| 4 | $n$-$C_4H_9$ | H (2.2) | 100 | 20 min | $CH_3(CH_2)_3COOH$ (69); HCOOH (72); $CH_3(CH_2)_3COCH_3$ (11) | $PMo_{12}O_{40}^{3-}$ |
| 4a | $n$-$C_4H_9$ | H (4.8)[c] | 29 | 30 min | $CH_3(CH_2)_3COCHO$ (100) | $MoO_4^{2-}$ |
| 4b | $n$-$C_4H_9$ | H (4.9)[c,d] | 88 | 40 min | $CH_3(CH_2)_3COOH$ (59); $CH_3(CH_2)_3COCHO$ (29); n.d. | $MoO_4^{2-}$ |
| 5 | $C_6H_5$ | $C_6H_5$ (3.1) | 93 | 20 h | $C_6H_5COOH$ (175); $C_6H_5COCOC_6H_5$ (7) | $PW_{12}O_{40}^{3-}$ |
| 5a | $C_6H_5$ | $n$-$C_3H_7$ (4.7)[b] | 2 | 17 h | $C_6H_5COCO(CH_2)_2CH_3$ (100) | $WO_4^{2-}$ |
| 6 | $C_6H_5$ | H (3.1) | 100 | 10 min | $C_6H_5COOH$ (90); HCOOH (91); $C_6H_5COCH_3$ (3); n.d. | $PW_{12}O_{40}^{3-}$ |
| 6a | $C_6H_5$ | H (6.1)[c] | 100 | 2 h | $C_6H_5COOH$ (93); $C_6H_5COCHO$ (8); n.d. | $WO_4^{2-}$ |
| 7 | $n$-$C_3H_7$ | $n$-$C_3H_7$ (3.2) | 96 | 19 h | $CH_3(CH_2)_2COOH$ (94); $CH_3(CH_2)_2CO(CH_2)_3CH_3$ (15); $CH_3(CH_2)_2COCO(CH_2)_2CH_3$ (3); $CH_3CH_2CH{=}CHCO(CH_2)_2CH_3$ (15) | $PW_{12}O_{40}^{3-}$ |
| 7a | $n$-$C_7H_{15}$ | $n$-$C_7H_{15}$ (3.0)[b] | 3 | 15 h | $CH_3(CH_2)_6COCO(CH_2)_6CH_3$ (100) | $WO_4^{2-}$ |
| 8 | $n$-$C_4H_9$ | H (2.2) | 100 | 20 min | $CH_3(CH_2)_3COOH$ (79); HCOOH (62); $CH_3(CH_2)_3COCH_3$ (21) | $PW_{12}O_{40}^{3-}$ |
| 8a | $n$-$C_4H_9$ | H (5.3)[c] | 60 | 2 h | $CH_3(CH_2)_3COCHO$ (21); n.d. | $WO_4^{2-}$ |
| 8b | $n$-$C_4H_9$ | H (5.3)[c,d] | 100 | 2 h | $CH_3(CH_2)_3COCHO$ (10); n.d. | $WO_4^{2-}$ |

[a] All the experiments were run in the presence of $Hg(OCOCF_3)_2$ (0.8 mmol) under nitrogen atmosphere, using 1 mL of 70% $H_2O_2$ (20.5 mmol) or 2 mL of 35% $H_2O_2$. [b] From ref 6, at $T$ = 20 °C. [c] From ref 5, at $T$ = 20 °C. [d] In the presence of the neutral phase-transfer HEPT.

far as the oxidation of internal alkynes is concerned. In fact when $MO(O_2)_2$ is the oxidant, even for very long reaction times (36 h), no conversion of diphenylacetylene (run 1a) is observed. By contrast, the oxidation by the peroxocomplexes derived from CMP or CWP (runs 1 and 5) provides quantitative yields of oxidized products in 20 h. In this case 2 mol of benzoic acid per mole of diphenylacetylene are obtained due to the oxidative cleavage of the triple carbon–carbon bond. Even larger rate accelerations are observed in the case of dialkylalkynes, as 4-octyne (runs 3 and 7) in comparison with 8-hexadecyne (runs 3a and 7a). The oxidation of 4-octyne gives, as in the case of diphenylacetylene, 2 mol of acid per mole of alkyne, as the main product, together with the $\alpha,\beta$-unsaturated derivative and small amounts of the 1,2-dicarbonyl compound. In addition, also present is the ketone (propyl butyl ketone) derived from the hydration of the triple bond.

In the case of terminal alkynes the main oxidation products with CMP or CWP are represented by acids (runs 2, 4, 6, and 8), resulting from the cleavage of the triple bond, as the formation of benzoic and formic acids both in nearly equal amount seems to support. Likewise, oxidations of terminal alkynes by $Na_2MoO_4$ + $H_2O_2$ in the presence of a neutral ligand as HEPT (runs 2b and 4b) or by $Na_2WO_4$ + $H_2O_2$ in the presence of both a cationic phase-transfer agent and of HEPT (runs 8a and 8b) yield mainly carboxylic acids. A comparison between the two oxidizing systems (polyoxometalates + $H_2O_2$ and $Na_2MO_4$ + $H_2O_2$), under these conditions, would indicate a better activity for the system employing the polyoxometalates. However, the two oxidizing systems are not any more comparable in the case of $Na_2MoO_4$ + $H_2O_2$ in the presence of a cationic phase-transfer agent since different reaction products are formed (ketoaldehydes and carboxylic acids), unless the products are formed in faster steps which follow the rate-determining step. It appears that the presence of the mercuric salt does not cause major inconvenience. In fact, a careful analysis of the products of oxidation indicates that when CMP or CWP is the precursor of the peroxocomplex, minute amounts of products derived from the Hg-catalyzed hydration of the triple bond, i.e., propyl butyl ketone or acetophenone from 1-hexyne or phenylacetylene, respectively, are formed. No such products are observed when $Na_2MO_4$ is the metal catalyst. This seems to suggest that some interaction between CMP or CWP and terminal alkynes in the presence of the mercuric cocatalyst does occur. It is, however, difficult, at this stage, to provide a rationale of this behavior. This has to wait for further mechanistic studies. At any rate the data presented and discussed here clearly indicate that, also in alkynes oxidation, heteropolyacids are more effective than simple anions in catalyzing the oxidations to carboxylic acids by hydrogen peroxide. Experiments aimed at elucidating the nature of this increased ability are currently in progress in this laboratory.

## Experimental Section

**Materials.** Phenylacetylene, 1-hexyne, 4-octyne, and diphenylacetylene are commercially available products (Aldrich), which were purified by distillation or crystallization. 1,2-Dichloroethane was purified by standard procedures from highly pure commercial samples. Tris(cetylpyridinium) 12-Molybdophosphate or 12-tungstophosphate was prepared by following the original procedure reported by Ishii et al.[9] by adding an aqueous solution of $H_3PMo_{12}O_{40}{\cdot}nH_2O$ or $H_3PW_{12}O_{40}{\cdot}nH_2O$ (5.1 g in 10 mL) to an aqueous solution of cetylpyridinium chloride (3.0 g in 70 mL). After stirring for 2 h, the resulting precipitate was filtered off, washed several times with distilled water, and dried in vacuo. Satisfactory elemental analyses were obtained. The IR (KBr)

spectrum is in accord with the reported literature data.

**General Procedure for Oxidation of Alkynes.** In a typical run, 2 mL of a solution of the desired alkyne (3 mmol) in DCE was added to a dichloroethane/water solution (13 mL) containing tris(cetylpyridinium) 12-molybdophosphate or 12-tungstophosphate (150 mg, ≈0.13 mmol), Hg(OCOCF$_3$)$_2$ (0.8 mmol), and hydrogen peroxide (20.5 mmol) under vigorous stirring in a glass reactor maintained at 40 °C. The alkyne is added as the last reagent, following the hydrogen peroxide addition, to minimize the formation of products arising from the hydration of the triple bond. At the end of the reaction, the two phases were separated and the organic phase was analyzed by GC-MS.

As an example of the preparative procedure, the isolation of the reaction products, included the carboxylic acids, from the reaction mixture is reported. In this case at the end of the reaction, the two phases were separated in a separatory funnel. The aqueous layer was acidified by H$_2$SO$_4$ at pH ≈ 1 and extracted with ethyl ether. The ethereal extract was joined to the organic phase and the resulting solution was dried on Na$_2$SO$_4$ and reduced to a small volume by solvent evaporation. The products in the organic phase were isolated by column chromatography (silica gel, cyclohexane–ethyl acetate, 9:1, or petroleum ether–diethyl ether, 8:2) and identified by comparison with authentic samples and by their $^1$H NMR, IR, and mass spectra.

The yields of products were determined by quantitative GLC analysis (internal standard) using a 3% OV-17 on 80/100 Supelcoport column, with a Shimadzu Chromatopac C-E1B integrator and only for 1-hexyne an 80/100 Carbopack C/0.1% SP-1000 column with a Hewlett-Packard 5890A instrument equipped with a Perkin-Elmer LCI-100 integrator. The organic acids were determined as their ethyl esters, by treating the organic phase with ethyl alcohol and a few drops of 96% H$_2$SO$_4$, until complete transformation into the ester at room temperature (≈15 h) and analyzing it by GLC in the same conditions adopted for 1-hexyne.

**Registry No.** C$_6$H$_5$C≡CC$_6$H$_5$, 501-65-5; C$_6$H$_5$C≡CH, 536-74-3; CH$_3$(CH$_2$)$_2$C≡C(CH$_2$)$_2$CH$_3$, 1942-45-6; CH$_3$(CH$_2$)$_3$C≡CH, 693-02-7; C$_6$H$_5$COCOC$_6$H$_5$, 134-81-6; C$_6$H$_5$COOH, 65-85-0; C$_6$H$_5$CO-CH$_3$, 98-86-2; CH$_3$(CH$_2$)$_2$COCO(CH$_2$)$_2$CH$_3$, 5455-24-3; CH$_3$(CH$_2$)$_2$COOH, 107-92-6; CH$_3$(CH$_2$)$_2$CO(CH$_2$)$_3$CH$_3$, 589-63-9; CH$_3$CH$_2$CH=CHCO(CH$_2$)$_2$CH$_3$, 762-06-1; CH$_3$(CH$_2$)$_3$COCH$_3$, 591-78-6; HCOOH, 64-18-6; (cetylpyridinium)$_3$PMo(VI)$_{12}$O$_{40}$, 88418-08-0; (cetylpyridinium)$_3$PW(VI)$_{12}$O$_{40}$, 115031-77-1.

---

# A New Hydrogen Source. 3. Chemoselective Reduction with Et$_3$NH$^+$H$_2$PO$_2^-$ • $n$ H$_2$O/Raney Nickel and RuCl$_2$(PPh$_3$)$_3$ Reagents

Bui The Khai* and Antonio Arcelli

*Dipartimento di Chimica "G. Ciamician", Università degli Studi, Via Selmi 2, 40126 Bologna, Italy*

Triethylammonium hypophosphite hydrate acts as a NaH$_2$PO$_2$·H$_2$O modified reagent. Some advantages are noted, including higher product selectivity. Pure aromatic and aliphatic aldehydes are obtained from nitriles by the Et$_3$NH$^+$H$_2$PO$_2^-$/Raney nickel system. The homogeneous catalyst can be used with this reagent. The Et$_3$NH$^+$H$_2$PO$_2^-$·$n$H$_2$O/RuCl$_2$(PPh$_3$)$_3$ system selectively reduces aromatic and aliphatic ketones to the corresponding alcohols with excellent yields at room temperature.

In the hydrogenation of organic compounds with gaseous hydrogen, a few problems require attention, for example, the danger of explosion and the fact that special apparatus which works under pressure is required.[1] Hydrogen in the gaseous phase also presents some problems of storage and transportation;[2-5] therefore, some hydrogen carriers such as metal alloy,[3] magnesium anthracene,[4] and cyclohexane[5] have been proposed.

We have recently investigated some new organic compounds which liberate hydrogen at room temperature and pressure with the assistance of a transition-metal catalyst.[6,7] We have found that they can be successfully used as reducing agents and have some advantages such as operating ease and safety during hydrogenation. A high

selectivity in the reduction was observed. For instance, the HCO$_2$H/Et$_3$N reagent rapidly liberates hydrogen gas at 20 °C in the presence of RuCl$_2$(PPh$_3$)$_3$ and selectively reduces the aldehyde group;[6] in the presence of Pd on carbon, it selectively reduces the nitro group.[7]

Now we have also found that the Et$_3$NH$^+$H$_2$PO$_2^-$·$n$H$_2$O reagent rapidly liberates hydrogen in the presence of Raney nickel or RuCl$_2$(PPh$_3$)$_3$ at room temperature and selectively reduces nitrile and ketone groups.

## Results and Discussion

The Et$_3$NH$^+$H$_2$PO$_2^-$·$n$H$_2$O reagent was prepared from equimolar amounts of Et$_3$N and H$_3$PO$_2$ (50%). It is liquid and stable in ambient conditions and soluble in some dry solvents such as THF, dioxane, methanol, ethanol, and DMF. Its activity and selectivity have shown some differences from those of NaH$_2$PO$_2$·H$_2$O. For example,
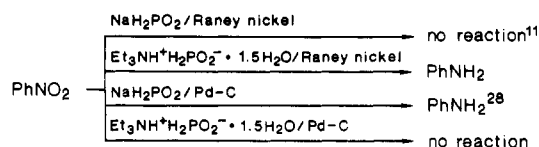


Higher product selectivity has also been found (Table I, experiment no. 4, 5). A great advantage is that a homo-

(1) (a) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; pp 1–8. (b) Brown, C. A.; Brown, H. C. *J. Org. Chem.* **1966**, *31*, 3989.

(2) Kekley, J. H.; Hagler, R. *Int. J. Hydrogen Energy* **1980**, 35.

(3) Imamoto, T.; Mita, T.; Yokoyama, M. *J. Chem. Soc., Chem. Commun.* **1984**, 163.

(4) Bogdanovic, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 262.

(5) Cacciola, G.; Giodano, N.; Restuccia, G. *Int. J. Hydrogen Energy* **1984**, 411.

(6) Khai, B. Th.; Arcelli, A. *Tetrahedron Lett.* **1985**, *26*, 3365, Part I.

(7) Khai, B. Th.; Arcelli, A. *J. Organomet. Chem.* **1986**, *309*, C63, Part II.