

PHOTOOXIDATION OF (\pm)-2-BUTANOL TO 2-BUTANONE USING POLYOXOMOLYBDATE(VI) CATALYSTS: A CLEAN AND HIGH YIELD ROUTE

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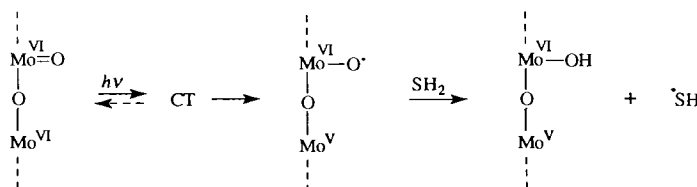
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Abstract—No colour change occurred when a colourless, aqueous solution of the β -octamolybdate(VI) salt $[\text{Et}_3\text{NH}]_4[\text{Mo}_8\text{O}_{26}]$ (**1**) was irradiated with UV light ($\lambda = 254$ nm). Similarly, an irradiated solution of **1** in a water:(\pm)-2-butanol mixture also remained colourless and no gaseous hydrogen evolved. In contrast, aqueous solutions of the alkali and alkaline earth metal containing salts $[\text{Et}_3\text{NH}]_3[\text{NaMo}_8\text{O}_{26}]$ (**2**) and $[\text{Et}_3\text{NH}]_2[\text{Mg}(\text{H}_2\text{O})_6\text{Mo}_8\text{O}_{26}] \cdot 2\text{H}_2\text{O}$ (**3**) both turned blue ($\lambda_{\text{max}} = 725$ nm) when irradiated with UV light. Irradiated solutions of **2** and **3** in a water:(\pm)-2-butanol mixture also turned blue, and 2-butanone along with hydrogen gas were produced in almost quantitative yield over a 24 h reaction period. Likewise, an aqueous solution containing **1** and excess of an alkali or alkaline earth metal chloride salt (e.g. NaCl, KCl, MgCl_2 , CaCl_2 or SrCl_2) also catalysed the photooxidation of (\pm)-2-butanol. Product yields were again $\geq 90\%$.

The excited states of some iso- and hetero-polyoxometalates, accessible with near UV or blue light, are known to oxidize alkanes¹ and conventionally far more reactive organic molecules such as aldehydes, carboxylic acids and alcohols to form C=C and C=O bonds.^{2,3} Formation of one-electron reduced polyoxometalate blue complexes follow zero order kinetics.⁴ Reduction is characterized by a broad intense electronic absorption band around 700 nm, which is generally proportional to the number of added electrons. The reduced polyoxometalate blue species are readily reoxidized, a feature necessary for catalytic applications. Furthermore, the IR, UV-vis and NMR

spectral properties of the polyoxometalates remain the same before and after catalytic photochemical dehydrogenation of the organic substrates, indicating that little if any polyoxometalate decomposition occurs during the redox chemistry.⁵

Using elegant flash photolysis experiments Kraut *et al.*⁶⁻⁹ have shown that in simple iso- and hetero-polyoxomolybdates the primary processes involving the charge-transfer (CT) excited states are completed within a few nanoseconds. The photoactive species was identified as a reduced polyoxomolybdate with an oxygen radical ligand, formed from an upper oxygen-to-metal charge-transfer state (Scheme 1).



Scheme 1.

Molecular orbital calculations⁹ have shown that the highest occupied molecular orbital (HOMO) is delocalized over a limited number of oxide ions

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whose positions depend on the nuclear structure of the polyoxomolybdate. Calculations⁹ on $[\text{Mo}_7\text{O}_{24}]^{6-}$ have shown a localization of electronic charge in accordance with the ESR spectrum of the species.¹⁰ For $[\text{Mo}_8\text{O}_{26}]^{4-}$ and $[\text{Mo}_7\text{O}_{24}]^{6-}$ the lowest lying excited state has been ascribed to $\text{O}^{2-} \rightarrow \text{Mo}^{\text{VI}}$ ligand-to-metal charge-transfer (LMCT). The lowest unoccupied molecular orbital (LUMO) populated in these transitions is believed to be localized in only two or three molybdenum ions and receives insignificant contributions from orbitals centred on the oxide ligands.⁹ Yamase^{11,12} has reported that photoexcitation of $\text{O} \rightarrow \text{Mo}$ LMCT bands of alkylammonium polyoxomolybdate solids leads to a situation where the d^1 electron in the lattice consisting of edge-sharing MoO_6 octahedra is almost localized at a single MoO_6 octahedron where a hydrogen-bonding proton can be transferred from an alkylammonium nitrogen atom to a bridging oxygen atom to produce a $\text{Mo}^{\text{V}}\text{O}_5(\text{OH})$ centre. It was stressed that the photo-reducible site of alkylammonium polyoxomolybdates in aqueous solution is not always the same as in the crystal, due to changes in the hydrogen-bonding network upon dissolution of the solids in water.

The photosensitivity of the polyoxomolybdate renders the excited state a better oxidizing reagent than the ground state, and it is thus the blue mixed-valence intermediary that is thought to be responsible for the photoinduced oxidation of the organic substrates present in the solution. The main process is hydrogen abstraction from the organic substrate SH_2 which contains a labile hydrogen atom, e.g. primary and secondary alcohols (Scheme 1).

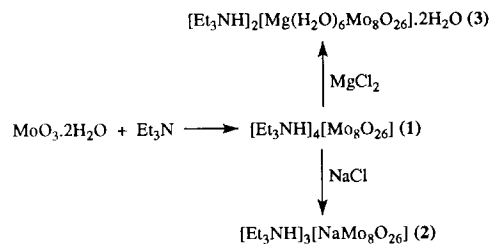
The photooxidation of alcohols to ketones using polyoxometalate(VI) catalysts has received considerable attention. For example, deaerated, acidified aqueous solutions containing the ions $[\text{W}_7\text{O}_{24}]^{6-}$, $[\text{Mo}_7\text{O}_{24}]^{6-}$ and $\beta\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$ have each been used to oxidize methanol, ethanol and 2-propanol upon UV irradiation.⁶ Under similar experimental conditions methanol and 2-propanol have been oxidized using heteropolyoxomolybdate(VI) anions of the general formula $[\text{M}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{n-}$ ($\text{M} = \text{Cr}^{\text{III}}$, Al^{III} , Ni^{II} , Rh^{III} and Fe^{III}).⁸ Hill *et al.*¹ carried out the photocatalytic conversion of (\pm) -2-butanol to 2-butanone in acetonitrile solution using the iso- and heteropolyoxotungstate(VI) ions $[\text{W}_{10}\text{O}_{32}]^{4-}$ and $\alpha\text{-}[(\text{PO}_4)\text{W}_{12}\text{O}_{36}]^{3-}$. Fox *et al.*¹³ found that methanol, 2-propanol, (\pm) -2-butanol, cyclobutanol and benzhydrol were oxidized to the corresponding carbonyls upon photoexcitation of $\text{Na}_3[(\text{PO}_4)\text{W}_{12}\text{O}_{36}]$ in water (pH = 1) and $(\text{Pr}_4\text{N})_3[(\text{PO}_4)\text{W}_{12}\text{O}_{36}]$ in acetonitrile.

In this paper we present a clean and almost quan-

titative method for the catalytic photooxidation of (\pm) -2-butanol to 2-butanone using polyoxomolybdate(VI) salts containing (or in the presence of) an alkali or alkaline earth metal cation.

RESULTS AND DISCUSSION

The water-soluble β -octamolybdate(VI) salts $[\text{Et}_3\text{NH}]_4[\text{Mo}_8\text{O}_{26}]$ (**1**),¹⁴ $[\text{Et}_3\text{NH}]_3[\text{NaMo}_8\text{O}_{26}]$ (**2**)¹⁴ and $[\text{Et}_3\text{NH}]_2[\text{Mg}(\text{H}_2\text{O})_6\text{Mo}_8\text{O}_{26}] \cdot 2\text{H}_2\text{O}$ (**3**)¹⁵ were prepared as outlined in Scheme 2. When a deaer-



Scheme 2.

ated, colourless, aqueous solution of the Mo_8 salt (**1**) was irradiated with UV light ($\lambda = 254$ nm) for up to 12 h no colour change was observed. Similarly, an irradiated solution of **1** in a water : (\pm) -2-butanol mixture also remained colourless and no gaseous hydrogen was evolved. In contrast, an aqueous solution of the Na/ Mo_8 salt (**2**) became visibly dark blue in colour after being irradiated for *ca* 3 h. No hydrogen gas was given off during this reaction. A similar 3 h irradiation period was required before a solution of **2** in a water : (\pm) -2-butanol mixture turned visibly blue in colour, and hydrogen gas was evolved during the reaction. The reactivity of the Mg/ Mo_8 salt (**3**) was found to be essentially identical to that of **2**, with the irradiated water and water : (\pm) -2-butanol solutions containing **3** again turning visibly blue after *ca* 3 h. In the case of the Na/ Mo_8 salt (**2**) formation of the one-electron reduced polyoxomolybdate blue complex was characterized by the broad absorption band at $\lambda_{\text{max}} = 725$ nm in its electronic spectrum, and there was a gradual build up in the concentration of this blue species in solution during the time of irradiation (Fig. 1). The blue colour was rapidly bleached (in *ca* 40 s) when the solution was exposed to air. However, when the blue solution was stored under N_2 it retained its colour over a long period of time. In these photooxidation experiments the polyoxomolybdate : (\pm) -2-butanol ratio was *ca* 1 : 800, and an overall catalytic cycle for the conversion of (\pm) -2-butanol to 2-butanone is illustrated in Scheme 3.

In the photooxidation of (\pm) -2-butanol using **2** and **3** over a total irradiation period of 24 h the

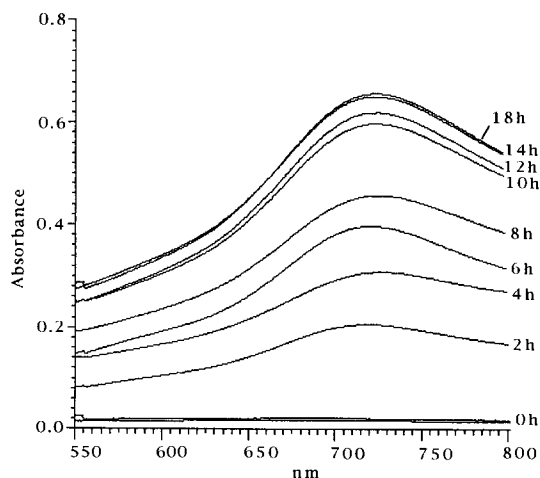
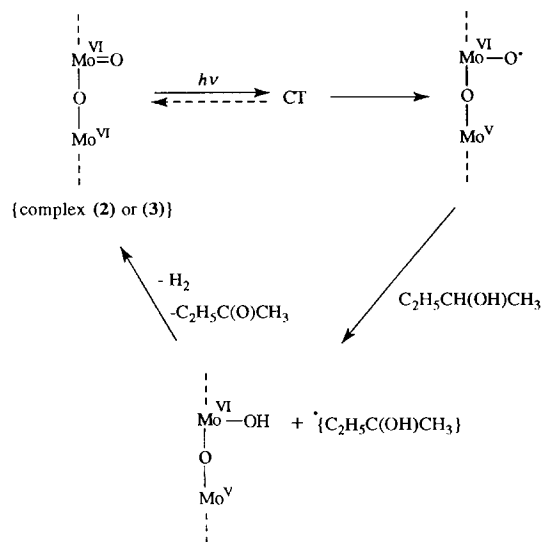


Fig. 1. Electronic spectral study of the build up in the concentration of the photoreduced polyoxomolybdate blue species ($\lambda_{\max} = 725$ nm) as a function of irradiation time (h). Conditions: $[\text{Et}_3\text{NH}]_3[\text{NaMo}_8\text{O}_{26}]$ (**2**) (0.5 g) dissolved in water (200 cm^3), and with (\pm)-2-butanol (20 g) added. Samples (as mixtures of the organic and aqueous phases) were periodically drained from the stirred photoreactor directly into the cuvette (1 cm) and sealed under N_2 to prevent aerial oxidation.



Scheme 3.

yield of 2-butanone in each case was $>90\%$ (Table 1). The rate of hydrogen and 2-butanone production for the photooxidation of (\pm)-2-butanol using the Na/Mo₈ salt **2** is illustrated in Fig. 2. The graph shows that only a small amount of the products (hydrogen and 2-butanone) are formed during the first 3 h of the reaction. Following this *ca* 3 h induction period the reaction accelerates markedly, and after 24 h it is essentially complete.

Under the prevailing experimental conditions for the quantitative measurements the oxidation equivalents represented in the ketone product (2-butanone) correlates well with the quantity of the reduction product (hydrogen gas) that was evolved. Furthermore, recovery of the ketone was simplified by the fact that it formed an immiscible layer above the aqueous layer, and could thus be easily isolated at the end of the reaction. When the 2-butanone produced in the first reaction was separated off the reaction vessel could be recharged with a further batch of (\pm)-2-butanol (20 g) and the catalysis repeated using the same sample of catalyst solution. Five separate batches of (\pm)-2-butanol have been oxidized to 2-butanone using the same solution of catalyst and without any appreciable loss in catalyst activity.

The observed photoinactivity of $[\text{Et}_3\text{NH}]_4[\text{Mo}_8\text{O}_{26}]$ (**1**) in water at neutral pH is not totally surprising in view of the fact that it is known that β -octamolybdates only retain their solid state structure in acidified aqueous solution (pH 2–3) and in acetonitrile or similar organic solvent.² Indeed, the ammonium and tetrabutylammonium salts $[\text{NH}_4]_4[\text{Mo}_8\text{O}_{26}]$ and $[\text{tBu}_4\text{N}]_4[\text{Mo}_8\text{O}_{26}]$, respectively, do photolyse in acetonitrile, whilst the potassium salt $\text{K}_4[\text{Mo}_8\text{O}_{26}]$ is photoactive in aqueous solution at pH 3–4.⁹ Thus, in the case of **1** it would appear that upon dissolution of the salt in water (pH 7) the β - $[\text{Mo}_8\text{O}_{26}]^{4-}$ ion breaks down to give other molybdate species which are themselves not photochemically active.

In contrast to the photoinactivity exhibited by **1** the Na/Mo₈ and Mg/Mo₈ salts $[\text{Et}_3\text{NH}]_3[\text{NaMo}_8\text{O}_{26}]$ (**2**) and $[\text{Et}_3\text{NH}]_2[\text{Mg}(\text{H}_2\text{O})_6\text{Mo}_8\text{O}_{26}] \cdot 2\text{H}_2\text{O}$ (**3**), respectively, were both highly photoreactive, suggesting that their activity is linked to the presence of the Na^+ and Mg^{2+} ions. The solid state structure of **2**¹⁴ shows the Na^+ ion sandwiched between two β - $[\text{Mo}_8\text{O}_{26}]^{4-}$ ions, being coordinated to four oxygen atoms on one face of each β - $[\text{Mo}_8\text{O}_{26}]^{4-}$ ion. Similarly, in the salt **3** the octahedral $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ ion is also sandwiched between two β - $[\text{Mo}_8\text{O}_{26}]^{4-}$ ions, being hydrogen bonded to three oxygen atoms on one face of each β - $[\text{Mo}_8\text{O}_{26}]^{4-}$ ion.¹⁵ Conductivity measurements carried out on dilute aqueous solutions of **2**¹⁴ and **3**¹⁵ have shown that the two salts behave as strong electrolytes ($\Lambda_{\text{M}} = 885$ and 421 $\text{S cm}^2 \text{ mol}^{-1}$, respectively), indicating that their sandwich structures collapse in solution to give essentially free hydrated $[\text{Et}_3\text{NH}]^+$, Na^+ (or Mg^{2+}) and molybdate anions. The results of the present photochemical experiments involving **2** and **3** indicate that these free molybdate ions are either β - $[\text{Mo}_8\text{O}_{26}]^{4-}$ ions or some other photoreactive polyoxomolybdate

Table 1. Yield of 2-butanone for each catalyst system^a

Catalyst (weight used)	% Yield of 2-butanone
[Et ₃ NH] ₄ [Mo ₈ O ₂₆] (1) (0.5 g)	0
[Et ₃ NH] ₃ [NaMo ₈ O ₂₆] (2) (0.5 g)	94
[Et ₃ NH] ₂ [Mg(H ₂ O) ₆ Mo ₈ O ₂₆] · 2H ₂ O (3) (0.5 g)	92
1 (0.4 g) + NaCl (0.4 g)	94
1 (0.4 g) + KCl (0.4 g)	93
1 (0.4 g) + MgCl ₂ (0.4 g)	90
1 (0.4 g) + CaCl ₂ (0.4 g)	93
1 (0.4 g) + SrCl ₂ (0.4 g)	91

^a 24 h irradiation time; 20 g (±)-2-butanol; room temperature.

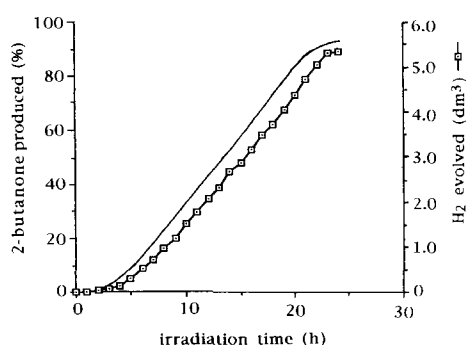


Fig. 2. Hydrogen and 2-butanone production for the photooxidation of (±)-2-butanol using [Et₃NH]₃[NaMo₈O₂₆] (**2**). Conditions: **2** (0.5 g) dissolved in water (200 cm³), and with (±)-2-butanol (20 g) added. Evolved H₂ was measured volumetrically at 20°C and at atmospheric pressure. Samples (as mixtures of the organic and aqueous phases) were periodically taken from the stirred photoreactor directly into the gas chromatograph and the peak areas for 2-butanone and unreacted (±)-2-butanol were calculated.

anion. This assumption prompted the idea of adding a simple alkali or alkaline earth metal salt to an aqueous solution of **1** and examining the catalytic activity of the resulting blend. Thus, when a solution mixture comprising (±)-2-butanol, water, **1** and excess of a metal chloride (NaCl, KCl, MgCl₂, CaCl₂ or SrCl₂) was irradiated with UV light the solution turned blue, and hydrogen gas along with 2-butanone were produced. The time taken for these reaction mixtures to turn visibly blue was approximately the same as that required in the reactions where **2** and **3** were used (*ca* 3 h). In addition, the product yields in these reactions were very similar to those obtained when **2** and **3** were used as the catalysts (Table I).

The exact role that the alkali and alkaline earth metal ions play in the above photocatalysis experiments is not clearly understood at the present time.

However, it would appear that the inclusion of such a metal cation in a reaction solution containing a dissolved β-octamolybdate salt is imperative for the formation of the photoexcited blue species, and hence for the catalytic oxidation reaction to occur.

EXPERIMENTAL

Starting materials were obtained from commercial sources and used without further purification. [Et₃NH]₄[Mo₈O₂₆] (**1**),¹⁴ [Et₃NH]₃[NaMo₈O₂₆] (**2**)¹⁴ and [Et₃NH]₂[Mg(H₂O)₆Mo₈O₂₆] · 2H₂O (**3**)¹⁵ were prepared according to the literature procedures. A Normag Photoreactor equipped with a 15-W mercury low-pressure immersion lamp (λ = 254 nm) was used for the photochemical reactions. Electronic spectra of aqueous solutions of the complexes were run on a Milton Roy Spectronic 3000 Array. (±)-2-Butanol and 2-butanone were detected and quantified using a Pye Unicam Series 204 gas chromatograph equipped with a carbowax 20 M column, a flame ionization detector and linked to an Omniscribe Series D5000 integrator. Verification of the assignment of 2-butanone was made by ¹H NMR spectroscopy using a Bruker AC 80 spectrometer, and also by gas chromatography-mass spectrometry (GCMS) using a Shimadzu GC-14A chromatograph coupled to a Kratos Profile HV-4 mass spectrometer. Hydrogen gas evolution was measured volumetrically at room temperature.

Photochemical reactions

(i) *Photooxidation of (±)-2-butanol using the polyoxomolybdate salts 1, 2 and 3.* The polyoxomolybdate salt (0.5 g) was dissolved in water (200 cm³) and (±)-2-butanol (20 g) was then added. The resulting colourless solution was stirred for 15 min to ensure thorough mixing. The solution was then

poured into the Normag Photoreactor and deaerated using a flow of N_2 . The flow of N_2 was stopped and the stirred solution was then irradiated for a period of 24 h. After the first *ca* 3 h of irradiation the solution became visibly blue in colour, and the intensity of the colour deepened as irradiation time increased. During the reaction two immiscible layers formed. The top colourless organic layer comprised 2-butanone containing some dissolved (\pm)-2-butanol, whilst the bottom blue aqueous layer contained the blue polyoxomolybdate species along with some unreacted (\pm)-2-butanol. Samples of the reaction mixture were taken periodically and analysed by gas chromatography (to measure relative concentrations of (\pm)-2-butanol and 2-butanone), and by UV-vis spectrophotometry (to monitor the build up in the concentration of the polyoxomolybdate blue species). The volume of evolved H_2 gas was also measured periodically. At the end of 24 h the two-phase mixture was removed from the reactor and poured into a separating funnel. The aqueous layer rapidly changed from blue to colourless. The 2-butanone top layer was separated off, and the aqueous layer was put back into the reactor for reuse for the photooxidation of a further batch of (\pm)-2-butanol (20 g).

(ii) *Photooxidation of (\pm)-2-butanol using 1 plus added alkali or alkaline earth metal chlorides.* In these reactions **1** (0.4 g) and the alkali or alkaline earth metal chloride (0.4 g) were dissolved in water (200 cm^3) and (\pm)-2-butanol (20 g) was then

added. The reaction was then continued in the same manner as outlined in (i) above.

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