Photocatalytic Processes with Polyoxotungstates: Oxidation of Cyclohexylamine

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Photochemical excitation of $(nBu_4N)_4W_{10}O_{32}$ in the presence of cyclohexylamine leads to the monoelectronic reduction of the decatungstate ($\phi = 8 \times 10^{-2}$) with the formation of cyclohexylamine radical species which can be detected by ESR spin–trapping investigations. Using this technique we could also reveal the presence of OH radicals coordinated to the polytungstate "surface". In the presence of oxygen, catalytic cycles are realized with the formation of the following cyclohexylamine oxidation products: $C_6H_{10}{=}NOH$ (44%), $C_6H_{10}{=}O$ (18%), $C_6H_{11}NO_2$ (22%), $C_6H_{10}{=}NC_6H_{11}$ (0.7%), $C_6H_{11}NHOH$ (14%). The overall photooxidation quantum yield is 1.5×10^{-1}. Under prolonged irradiation, we observe only a slow degradation of the photocatalyst with the oxidation of about 10^4 mol of cyclohexylamine/mol of consumed decatungstate. Under aerobic conditions, WO_3 and TiO_2 photoexcited powder suspensions present a very similar behavior, confirming that polyoxometalates can be considered models of transition metal oxides able of mimicking the interactions between the organic substrates and solid surfaces of interest in heterogeneous catalysis.

Introduction

There is a growing interest, in the fields of both fine and industrial chemistry, in new efficient catalytic systems capable of performing oxidations of organic substrates by molecular oxygen under mild conditions.[1]

Several authors recently focused their research interest on the development of new oxidation photocatalysts based on metal porphyrin complexes.[2] These are commonly used in homogeneous phases, but "composite" systems in which the metal complex is bound on the surface of semiconducting oxides have shown an interesting activity.[3] We report here, as a part of our continuing work in this field, an investigation on the use of polyoxotungstates as photocatalysts.

It has often been stated that polyoxometalates (POMs) can be considered soluble models of semiconductor metal oxide surfaces.[4] At the same time, their ability to undergo photoinduced multielectron transfer without changing their structure makes them very attractive catalysts in the oxidation of organic substrates in the presence of oxygen.[5] The proposed photochemical pathway of the polyoxotungstate action involves the absorption of light by the ground state, producing a charge-transfer-excited state. This process leads to the multielectron reduction of the polyoxotungstate with the formation of well-characterized blue complexes. In the presence of O_2, which is able to regenerate the initial form of the POM, catalytic cycles can be realized.

In this study we examine, for the first time, the photochemical and photocatalytic properties of $(nBu_4N)_4W_{10}O_{32}$ in the presence of cyclohexylamine ($CyNH_2$). As part of our interest in the oxidation reactions of amines,[6] $CyNH_2$ has been chosen as the photooxidizable substrate because of the industrial interest in obtaining new catalytic methods for its monooxygenation, under mild conditions. In addition, we also report a comparison between the photocatalytic properties of $W_{10}O_{32}{}^{4-}$ and those of powder WO_3 and TiO_2. Other authors have followed this comparative approach before.[7]

Experimental Section

Materials. $W_{10}O_{32}{}^{4-}$ was prepared according to the Klemperer method.[8] $CyNH_2$ was reagent grade (Carlo Erba) and was used immediately after distillation. 5,5-Dimethylpyrroline *N*-oxide (dmpo) was a commercial product (Aldrich) and was used as received. All the solvents were spectroscopic grade commercial products. TiO_2 (Degussa P-25) and WO_3 (Merck) were commercially available.

Apparatus. UV–vis spectra were recorded on a Kontron spectrophotometer, Model Uvikon 860. X-Band ESR spectra were obtained with a Bruker 220 D spectrometer that was calibrated by using α,α'-diphenylpicrylhydrazyl. ^1H NMR measurements were carried out with a Bruker instrument, Model AC 200/I. The qualitative analyses of the products were performed with a Hewlett Packard 5890 gas chromatograph equipped with a Hewlett Packard mass spectrometer, Model 5971. The quantitative analyses were carried out with a Carlo Erba gas chromatograph, Model HRGC FRACTOVAP 4160, equipped with a flame ionization detector.

Irradiations were carried out with a medium-pressure Hanau Q 400 mercury lamp. The required wavelength ranges were selected using glass cutoff filters. When necessary, monochromatic light was obtained with Corning filters. These filters can selectively isolate the 365–366-nm line of the medium-pressure mercury lamp.

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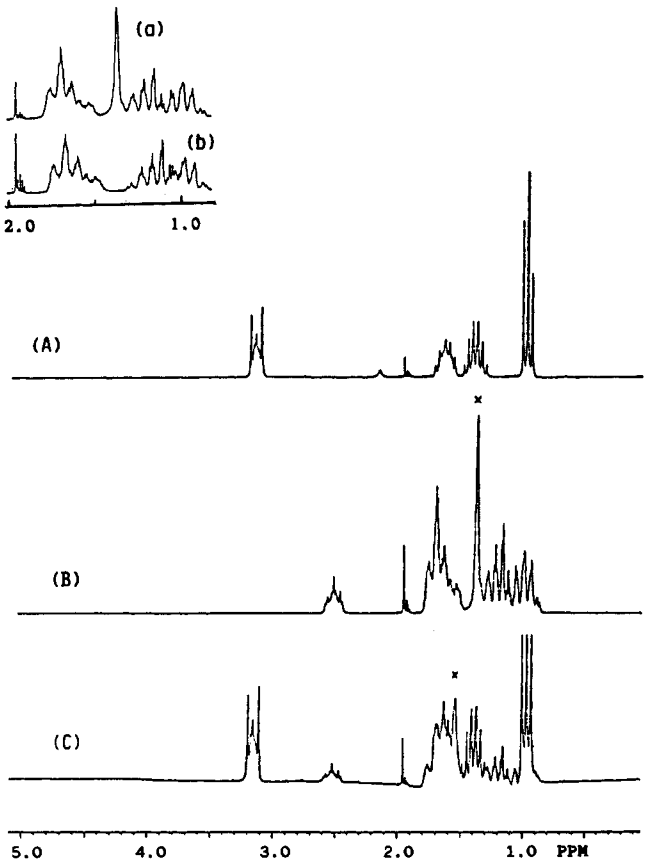

Figure 1. Changes in the proton NMR spectrum of $CyNH_2$ upon addition of $W_{10}O_{32}^{4-}$: (A) $W_{10}O_{32}^{4-}$ (2×10^{-3} mol dm^{-3}) in CD_3CN; (B) $CyNH_2$ (1.5×10^{-1} mol dm^{-3}) in CD_3CN; (C) like (B), saturated with $W_{10}O_{32}^{4-}$. Insert: (a) NMR spectrum of $CyNH_2$ in CD_3CN; (b) like (a) in the presence of D_2O.

Procedures. Acetonitrile solutions of $W_{10}O_{32}^{4-}$ (about 1×10^{-3} mol dm^{-3}) containing $CyNH_2$ (0.5 mol dm^{-3}) were irradiated in a 1-cm spectrophotometric cell or a quartz ESR flat cell at 22 ± 1 °C. The powder photocatalysts (10 mg/mL) were suspended in acetonitrile (3 mL), and the suspensions were irradiated in the presence of $CyNH_2$ (0.5 mol dm^{-3}). The solutions containing the heterogeneous catalyst powders were continuously stirred during irradiation.

When deaeration was required, reaction vessels were connected to a vacuum line and solutions degassed to less than 10^{-5} Torr by means of at least five vacuum-line freeze–thaw–pump cycles. When necessary, the samples were kept under O_2 atmosphere (about 760 Torr). The light intensity was measured by the ferrioxalate actinometric method.[9]

The quantum yield of $CyNH_2$ oxidation ($\lambda = 365$ nm) in semiconductor suspensions is given as the ratio of the number of moles of oxidized reagent to the number of moles of incident photons. The amount of semiconductor powder used was such that most of the light was absorbed by the particles near the optical window. The quantum yield calculated in this way is a lower limit, in that the amount of true absorbed light is lower than that of the incident light because of scattering phenomena.

ESR spin-trapping investigations have been carried out as described by us previously[10] and by Yamase[11] in a system similar to the one investigated here. Blank experiments were run with solutions containing dmpo and $W_{10}O_{32}^{4-}$ in the absence of $CyNH_2$. In every case, no signal of significant intensity was observed.

Results and Discussion

Formation of the $CyNH_2/W_{10}O_{32}^{4-}$ Complex. ^1H NMR data indicate the formation of a complex between $CyNH_2$ and $W_{10}O_{32}^{4-}$ in CH_3CN. Figure 1 shows the changes in the proton NMR spectrum of $CyNH_2$ upon addition of the decatungstate. The more significant effect is a shift (downfield from TMS) of the resonance at 1.37 ppm to lower fields (0.20 ppm). Since this signal is reduced in intensity by addition of D_2O (see insert in Figure 1), it can be ascribed to the NH_2 group of the amine.

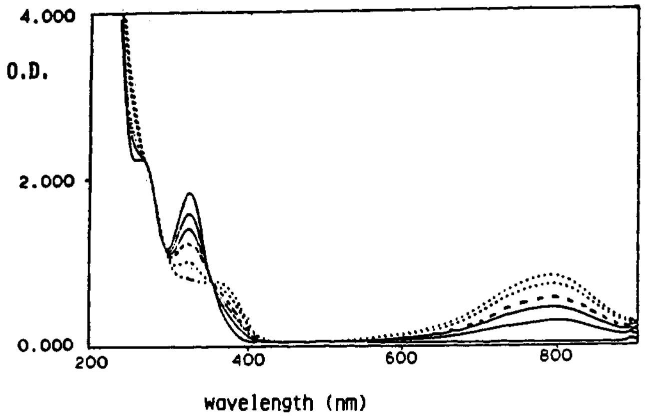

Figure 2. Spectral changes upon 365-nm irradiation of a deaerated CH_3CN solution containing $W_{10}O_{32}^{4-}$ (1.5×10^{-4} mol dm^{-3}) and $CyNH_2$ (5×10^{-1} mol dm^{-3}).

We infer that the shift of the NH_2 protons of $CyNH_2$ in the presence of $W_{10}O_{32}^{4-}$ is due to strong interactions between the amine and the decatungstate, such as hydrogen bonds, leading to the formation of a complex between $CyNH_2$ and $W_{10}O_{32}^{4-}$ (equilibrium 1). An analogous conclusion has been drawn by

$$W_{10}O_{32}^{4-} + CyNH_2 \rightleftarrows [W_{10}O_{32}^{4-},CyNH_2] \qquad (1)$$

Fox et al. in a study on the photocatalytic oxidation of alcohols by heteropolytungstates.[7b] In that work, the authors have demonstrated that precomplexation of alcohols with heteropolytungstates is possible and must precede the photoredox process. In particular, the triplet of the hydroxyl and the quartet of the methylene group of 1-propanol, upon addition of $PW_{12}O_{40}^{3-}$, simplify to a singlet and a triplet, respectively.

Photoreduction of $W_{10}O_{32}^{4-}$. Details of the photoredox chemistry of $W_{10}O_{32}^{4-}$ have been published in a series of Yamase's studies.[12] Irradiation ($\lambda = 365$ nm) of oxygen-free CH_3CN solutions of $W_{10}O_{32}^{4-}$ in the presence of $CyNH_2$ results in the formation of blue species. The UV–vis spectral variations displayed in Figure 2 show that the 325-nm band is progressively lost while the growth of two bands at 375 and 780 nm is observed. Complete restoration of the initial spectrum occurs upon exposure of the solution to air. On the basis of literature data,[5,13] the observed spectral behavior indicates that photochemical excitation leads to the reduction of $W_{10}O_{32}^{4-}$.

It is well-known that the reduction of polyoxotungstates can be easily followed by ESR spectroscopy.[14] Indeed, this process is known to be accompanied by the appearance, in the ESR spectrum at low temperature, of a signal consisting of a single isotropic line with a g value of about 1.8.[14d] Those authors report that the signal intensity increases until ca. 1.5 electrons are added; then it decreases on further reduction because the 2-electron species is diamagnetic as a result of pairing when the second electron is added to the decatungstate. In our case, irradiation of the $W_{10}O_{32}^{4-}/CyNH_2$ system leads to the formation of the typical ESR singlet at $g = 1.84$, indicating the reduction of $W_{10}O_{32}^{4-}$ to $W_{10}O_{32}^{5-}$. On the other hand, since the signal intensity

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Table 1. Quantum Yield Values for the Different Systems Investigated[a]

system	10ϕ
$W_{10}O_{32}^{4-} \xrightarrow[CyNH_2]{h\nu} W_{10}O_{32}^{5-}$	$0.8 + 0.1^b$
$W_{10}O_{32}^{4-} \xrightarrow[ethanol]{h\nu} W_{10}O_{32}^{5-}, W_{10}O_{32}^{6-}$	$4.0 + 0.4^b$
$CyNH_2 \xrightarrow[W_{10}O_{32}^{4-}]{h\nu, O_2}$ products	$1.5 + 0.2^c$
$CyNH_2 \xrightarrow[TiO_2]{h\nu, O_2}$ products	$1.4 + 0.2^d$
$CyNH_2 \xrightarrow[WO_3]{h\nu, O_2}$ products	$\leq 0.01^d$

[a] Irradiations were carried out at 25 °C; excitation light 365 nm. [b] Ratio of moles of photoreduced $W_{10}O_{32}^{4-}$ (initial concentration of the oxidized POM 1.5×10^{-4} mol dm^{-3}) to moles of photons absorbed by a deaerated CH_3CN solution containing $CyNH_2$ (5×10^{-1} mol dm^{-3}). [c] Ratio of moles of oxidized $CyNH_2$ (initial concentration 5×10^{-1} mol dm^{-3}) to moles of photons absorbed by a deaerated CH_3CN solution containing $W_{10}O_{32}^{4-}$ (1×10^{-2} mol dm^{-3}), in the presence of 760 Torr of oxygen. [d] Ratio of moles of oxidized $CyNH_2$ (initial concentration 5×10^{-1} mol dm^{-3}) to moles of incident photons on a powder suspension of the semiconductor in CH_3CN, in the presence of 760 Torr of oxygen.

increases continuously upon irradiation, we infer that $W_{10}O_{32}^{4-}$ undergoes only 1-electron photoreduction.

When changes in absorbance at 780 nm in the UV–vis spectrum, reported in Figure 2, were monitored as a function of irradiation time, a linear plot was obtained, indicating that the photoreaction follows zero-order kinetics, allowing us to calculate a photoreduction quantum yield of 8×10^{-2} (Table 1).

On the basis of the above results, we propose that the photoexcitation of the complex between $CyNH_2$ and $W_{10}O_{32}^{4-}$ yields an excited state in which an electron transfer from the amine to the decatungstate leads to the reduction of W(VI) to W(V), in accord with the mechanism reported by Fox for the photoreduction of heteropolytungstates by alcohols:[7b]

$$[W_{10}O_{32}^{4-}, CyNH_2] \xrightarrow{h\nu} [W_{10}O_{32}^{5-}, CyNH_2^{\bullet +}] \qquad (2)$$

It seemed interesting to study, for comparison purposes, the behavior in ethanol of the POM investigated. In Figure 3A we report the UV–vis spectral variations obtained when deaerated solutions of $W_{10}O_{32}^{4-}$ were irradiated in the presence of ethanol. Under these conditions, the formation of the blue species with λ_{max} = 780 nm is accompanied by the formation of another blue species with λ_{max} = 630 nm, which is missing when $CyNH_2$ is used as photoreducing agent.

Other authors observed that the photochemical excitation of $W_{10}O_{32}^{4-}$ in the presence of alcohols results in the reduction of the decatungstate.[14d] It has been demonstrated that the absorption at 630 nm denotes the formation of a 2-electron-reduced and diprotonated species. In agreement with that work, we propose that photoreduction of $W_{10}O_{32}^{4-}$ by ethanol occurs according to eqs 3–5. The photoreduction quantum yield value is reported in Table 1.

$$W_{10}O_{32}^{4-} + CH_3CH_2OH \xrightarrow{h\nu} W_{10}O_{32}^{5-} + CH_3CH^{\bullet}OH + H^+ \qquad (3)$$

$$W_{10}O_{32}^{5-} + H^+ \rightarrow HW_{10}O_{32}^{4-} \qquad (4)$$

$$2HW_{10}O_{32}^{4-} \rightarrow H_2W_{10}O_{32}^{4-} + W_{10}O_{32}^{4-} \qquad (5)$$

On the basis of the reported redox potentials for $W_{10}O_{32}^{4-}$ [14d] and for the oxidation of ethoxy radicals,[15] a reduction of $W_{10}O_{32}^{4-}$ to $W_{10}O_{32}^{5-}$ is possible. From the same literature data, one concludes that further reduction of $W_{10}O_{32}^{5-}$ by the reducing

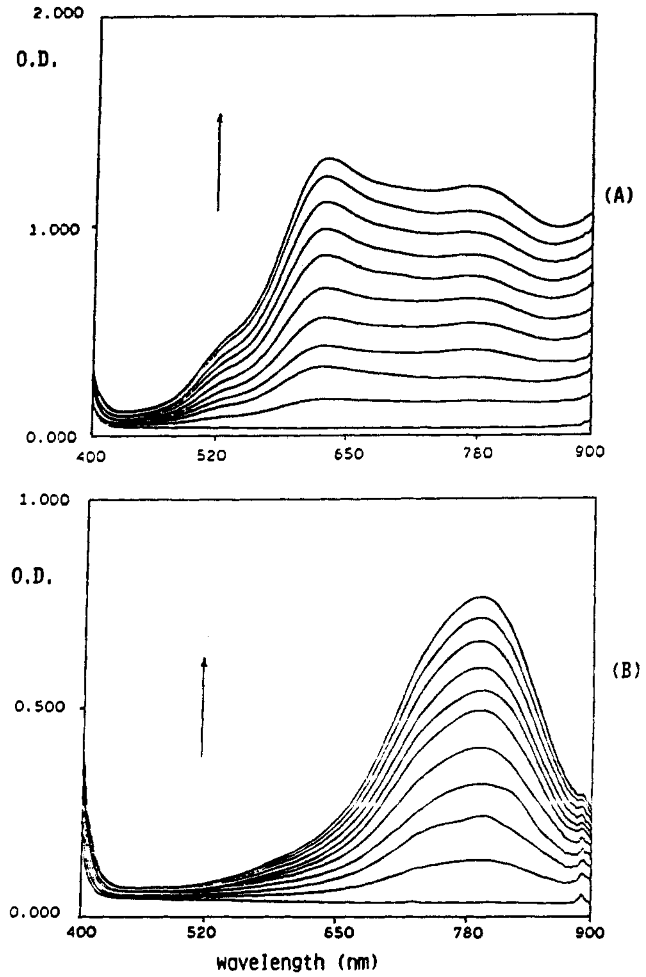
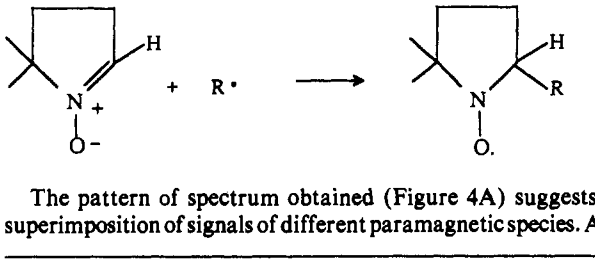


Figure 3. (A) Spectral changes upon 365-nm irradiation of a deaerated CH_3CN solution containing $W_{10}O_{32}^{4-}$ (1.5×10^{-4} mol dm^{-3}) and ethanol (5×10^{-1} mol dm^{-3}). (B) Spectral changes upon 365-nm irradiation of a deaerated CH_3CN solution containing $W_{10}O_{32}^{4-}$ (1.5×10^{-4} mol dm^{-3}) and $CyNH_2$ (5×10^{-1} mol dm^{-3}).

alcohol radicals is possible if the reduction potential of this species is lowered, for example by protonation.

A disproportionation reaction (eq 5) is not likely when $W_{10}O_{32}^{4-}$ is irradiated in the presence of $CyNH_2$, since the protonation of the amine occurs in competition with the protonation of $W_{10}O_{32}^{5-}$ (reaction 4). This is a possible explanation of the lack of the band at 630 nm in spectrum 3B. One should also note, in addition, that, in the presence of $CyNH_2$, the radicals formed are less reducing than those of alcohols.

ESR Spin-Trapping Investigation. In order to confirm the formation of an amino radical during irradiation, solutions containing $W_{10}O_{32}^{4-}$ and $CyNH_2$ were irradiated inside the ESR cavity in the presence of 5,5-dimethylpyrroline *N*-oxide (dmpo). This species in known to trap radicals to give more stable nitroxides according to eq 6.[16] In some instances, the nature of the trapped radical (R) can be identified by the parameters obtainable from the ESR spectrum.



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The pattern of spectrum obtained (Figure 4A) suggests the superimposition of signals of different paramagnetic species. After

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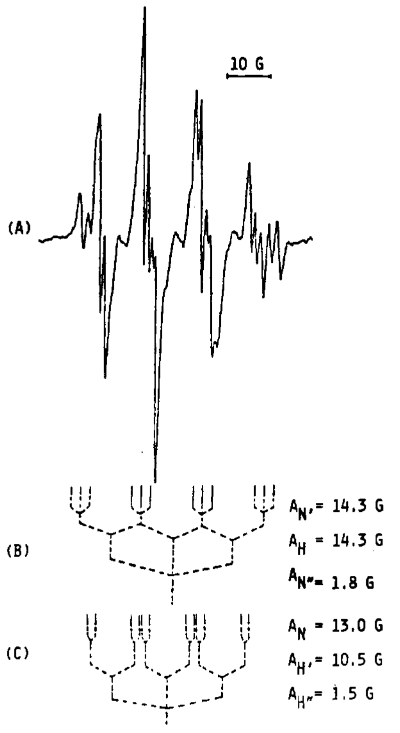


Figure 4. (A) ESR spectrum obtained during irradiation (λ > 310 nm) of deaerated solutions of $W_{10}O_{32}^{4-}$ (3.5×10^{-3} mol dm^{-3}) and $CyNH_2$ (5×10^{-1} mol dm^{-3}), in the presence of dmpo (4×10^{-2} mol dm^{-3}). (B) Diagram reconstruction of the ESR spectrum (A) reported in Figure 5. (C) Diagram reconstruction of the ESR spectrum obtained as a difference between spectrum 4A and spectrum 5A.

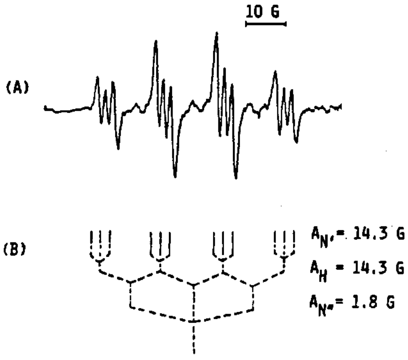
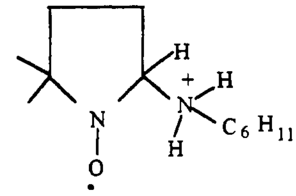


Figure 5. ESR spectrum, with the diagram reconstruction presented, in the dark, by deaerated solutions of $W_{10}O_{32}^{4-}$ (3.5×10^{-3} mol dm^{-3}) and $CyNH_2$ (5×10^{-1} mol dm^{-3}), in the presence of dmpo (4×10^{-2} mol dm^{-3}) previously irradiated at λ > 310 nm.

light is switched off, some signals disappear, leaving only the spectrum shown in Figure 5A. This consists of a 1:2:2:1 quartet of 1:1:1 triplets which can be attributed to an adduct between dmpo and a nitrogen-centered radical. The values of the hyperfine splitting constants have been found to be A_{N1} = 14.3 G, A_H = 14.3 G, and A_{N2} = 1.8 G, where A_{N1}, A_H, and A_{N2} are the couplings to the nitrogen and β-proton of the dmpo and the coupling to the nitrogen of the trapped aminyl radical.

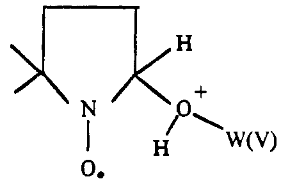
Dmpo has been previously employed to trap radicals formed from amines. In particular, Chen[17] reports that, when hexylamine is photochemically or electrochemically oxidized, the amine radical cation can be trapped by dmpo. The resulting ESR spectrum presents hyperfine splitting constants very close to those obtained in this work. On these bases, the spectrum reported in Figure 5 can be assigned to adduct I formed upon trapping of the $RNH_2^{\bullet+}$ radical cation by dmpo.



adduct I

The diagram reconstruction reported in Figure 4C shows that substraction of the spectrum attributed to adduct I from that obtained under irradiation reveals the presence of 12 lines. These signals are the result of the interaction of the unpaired electron with the nitrogen and the β-proton of dmpo and with another hydrogen atom, indicating the possible formation of an adduct between dmpo and the OH$^\bullet$ radical. There are several data in the literature concerning the trapping of OH$^\bullet$ radicals by dmpo.[18] The dmpo–OH adduct is known to give a 1:2:2:1 pattern of four lines which can be interpreted as equivalent hyperfine splitting from both the β-hydrogen and the nitroxide nitrogen ($A_N = A_H$ = 14.8 G). On the other hand, a recent work[19] has shown that a trapped OH$^\bullet$ radical coordinated to a ruthenium complex can give a somewhat different ESR spectrum which consists of nine lines ascribed to the interaction of the unpaired electron with one nitrogen atom and two nearly equivalent hydrogen atoms. In that work, the presence of a number of lines higher than that normally obtained for the dmpo–OH adduct has been ascribed to the high acidity of the proton of the OH group as promoted by the ruthenium atom.

On the basis of the above observations, it seems reasonable to ascribe the spectrum reported in Figure 4C to the formation of the adduct **II** between dmpo and the OH$^\bullet$ radical coordinated to the metal center. The formation of this species will be discussed in the section regarding the mechanism of $CyNH_2$ oxidation.



adduct II

Spin adducts of the hydroxyl radicals with dmpo were observed by Yamase upon irradiation of polymolybdate[11b] and polytungstate systems.[11a] However, in those cases the OH$^\bullet$ radicals originated from the oxidation of water, and the well-known 1:2:2:1 quartet characteristic of the dmpo–OH adduct was observed.

Photocatalytic Properties of the $CyNH_2/W_{10}O_{32}^{4-}$ System. It is clear that, for efficient catalysis to be observed, one must easily restore the POM in its orginal oxidized state. The choice of O_2 as an electron acceptor to reoxidize the POM is straightforward since, on the one hand, it is largely available and, on the other hand, the nature of its reduction products is well-known and their reactivity toward organic compounds has been extensively investigated. The kinetics of reoxidation of POMs by O_2 has been studied in recent years.[5b,20] It has been well established that the reoxidation of $W_{10}O_{32}^{5-}$ by O_2 occurs through eq 7 or 8.

$$2W_{10}O_{32}^{5-} + {}^{1}/{}_{2}O_2 + 2H^+ \rightarrow 2W_{10}O_{32}^{4-} + H_2O \quad (7)$$

$$W_{10}O_{32}^{5-} + O_2 \rightarrow W_{10}O_{32}^{4-} + O_2^{-} \quad (8)$$

In line with this, when $CyNH_2/W_{10}O_{32}^{4-}$ solutions were irradiated under O_2 at a pressure of 760 Torr, no spectral variation was observed, indicating that $W_{10}O_{32}^{5-}$ is not accumulated in detectable amounts. On the other hand, some oxidation of $CyNH_2$ is likely to take place also in the absence of O_2. However, in this

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Table 2. Product Distribution[a] When 30% of CEA was Photooxidized[b]

product	yield, % $W_{10}O_{32}^{4-}$ [c]	yield, % TiO_2 [d]
$C_6H_{10}=NOH$	44	23
$C_6H_{10}=O$	18	30
$C_6H_{11}NO_2$	22	17
$C_6H_{10}=NC_6H_{11}$	0.7	30
$C_6H_{11}NHOH$	14	

[a] Yields are calculated on the converted amine. [b] Irradiations were carried out at $\lambda \geq 310$ nm for about 50 h, at 25 °C, in the presence of 760 Torr of oxygen. [c] Homogeneous solutions of $W_{10}O_{32}^{4-}$ (1×10^{-2} mol dm^{-3}) in CH_3CN containing $CyNH_2$ (5×10^{-1} mol dm^{-3}). [d] Heterogeneous system constituted by powder suspensions of TiO_2 in CH_3CN containing $CyNH_2$ (5×10^{-1} mol dm^{-3}).

case, since there is no catalyst regeneration, the concentration of the products formed is near or below the detection limit of the analytical technique employed here.

We have tested the ability of photoexcited $W_{10}O_{32}^{4-}$ to operate as a catalyst in the oxidation of $CyNH_2$ by irradiating solutions of the POM under an O_2 pressure of 760 Torr. The products were detected by mass spectroscopy and gas chromatography. No attempt has been made to isolate pure products since this is beyond the scope of the present work which, at this stage, mainly focuses on the mechanism of product formation.

After 50 h of irradiation, 30% of $CyNH_2$ was oxidized, the product distribution is reported in Table 2. The overall quantum yield for the photooxidation of $CyNH_2$ by $W_{10}O_{32}^{4-}$ is reported in Table 1. Since its value is higher than that for the photoreduction of the decatungstate, it is likely that the photochemical process is accompanied by a thermal radical chain oxidation of $CyNH_2$.

The stability of $W_{10}O_{32}^{4-}$ during the photocatalytic process can be defined by following the variations of the UV–vis spectrum. Under prolonged irradiation, we observe only a slight decrease of absorbance in the whole range of wavelengths. This behavior suggests that the decatungstate undergoes a slow degradation process. On the basis of the absorbance decrease, we have evaluated a ratio between the moles of photooxidized $CyNH_2$ and the moles of degradated $W_{10}O_{32}^{4-}$ of about 10^4.

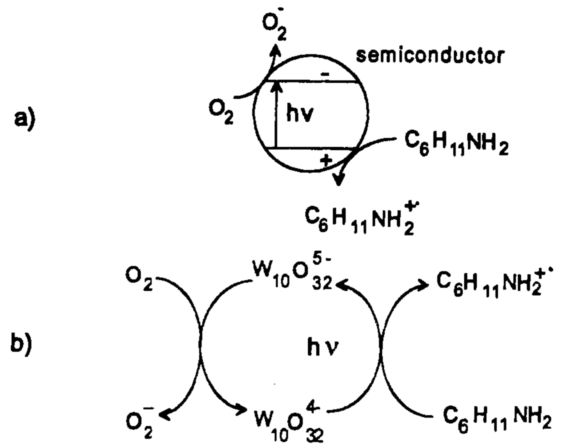
Oxidation of $CyNH_2$ with Photoexcited Powder Semiconductors. The intriguing analogy between the POMs and photosensitive oxides[7] prompted us to extend our investigations of the photocatalytic properties of $W_{10}O_{32}^{4-}$ to those of the semiconducting oxides WO_3 and TiO_2.

Irradiation of a semiconductor with light of suitable wavelength causes electrons to absorb enough energy to be promoted to a quasi-free state in the conduction band, leaving positive holes in the valence band. The separated charges are bound to recombine unless efficient electron-transfer reactions involving electron acceptors and donors in the solution will occur.

On each particle, a reduction reaction and an oxidation reaction proceed in parallel. In this respect, a suspension of semiconductor particles behaves as an ensemble of microelectrodes in an open circuit where, at steady state, the reduction and oxidation processes proceed at equal rates. The possible interaction among the reduction and oxidation products must be taken into account when the catalytic system is used for practical purposes.

We have investigated the photocatalytic properties of TiO_2 and WO_3 in the $CyNH_2$ oxidation by irradiation ($\lambda > 350$ nm) of CH_3CN powder suspensions of the semiconductor in the presence of the amine and oxygen. The product distribution when 30% of $CyNH_2$ is oxidized by TiO_2 is reported in Table 2. The ratio between the moles of photooxidized amine and the moles of photons incident on the powder suspension reported in Table 1 indicates that the efficiency of the semiconductor is very close to that of the POM. When the same experiment was carried out by using WO_3 as photoexcited semiconductor, cyclohexanone, cyclohexanone oxime, nitrocyclohexane, and the Schiff base $C_6H_{10}=NC_6H_{11}$ were detected as main products. On the other hand, in this case the photooxidation quantum yield (Table 1) is too low to allow a quantitative analysis of the products.

Scheme 1. Photocatalytic Behavior of $W_{10}O_{32}^{4-}$ and Dispersed Semiconductors in the Presence of $CyNH_2$ and O_2



The redox reactions occurring at the semiconductor–liquid interface are shown in Scheme 1a. Oxygen is widely used as an electron acceptor in photocatalytic systems with dispersed semiconductors. Its reduction generates superoxide and other activated oxygen species. Simultaneously, in agreement with previous analogous works,[21,22] $CyNH_2$ is expected to be oxidized by holes in the valence band, giving a radical cation.

There are formal, if not conceptual, analogies in the photocatalytic behaviors of POMs and semiconductor systems under aerobic conditions. These are illustrated in Scheme 1 for the case of the oxidation of $CyNH_2$.

Probably a still closer relationship can be drawn between the homogeneous photocatalytic behavior of the POMs and that of iron porphyrins.[2b,23] In this latter case, the oxidizable substrate is coordinated to the Fe(III) center. Light induces an intramolecular electron transfer, which leads to the oxidation of the ligand and the formation of Fe(II). This can, in turn, coordinate O_2 with regeneration of the Fe(III) center and reduction of O_2 to O_2^-.

A comparative study of the catalytic behaviors of POMs and semiconductors, in the oxidation of thioethers, was recently published by Chambers and Hill.[7a] A salient feature cited by the authors is the possibility for the POMs, compared to semiconductors, to undergo multielectron reduction and to be able then to operate under anaerobic conditions. In this case, the semiconductor is found to be inactive since electrons accumulate in the conduction band, thus increasing the electron–hole recombination rate. The possibility for the polyoxometalate to undergo multielectron reduction is, however, not general. In fact, the data obtained for the system studied in this work show that the reduction of $W_{10}O_{32}^{4-}$ does not proceed beyond the first reduction.

Mechanism of $CyNH_2$ Oxidation. This work focuses to the formation of cyclohexanone oxime by $CyNH_2$ because of the interest in this intermediate in the production of caprolactam and Nylon 6.

Scheme 2 reports two possible reaction pathways involving the radical cation $C_6H_{11}NH_2^{\cdot+}$ obtained by using both $W_{10}O_{32}^{4-}$ and dispersed semiconductors as photocatalysts. The radical cation can rapidly deprotonate to form an α-aminoalkyl radical (pathway a) or an aminyl radical (pathway f).[24] Reaction of the second

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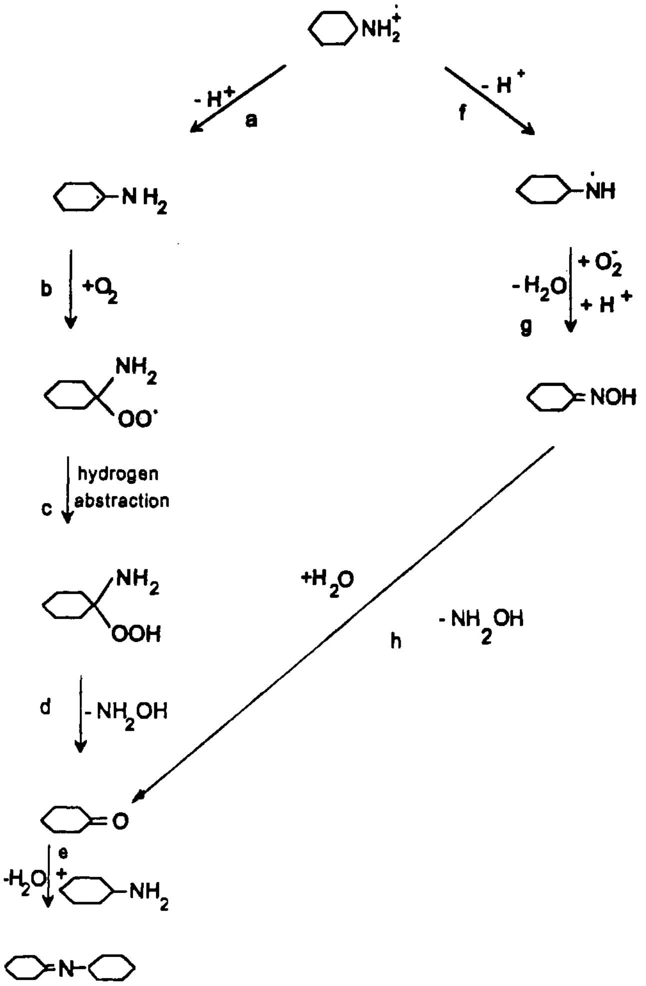
(22) Fox, M. A.; Linding, B. A.; Chen, C. C. *J. Am. Chem. Soc.* **1982**, *104*, 5828.

(23) Maldotti, A.; Bartocci, C.; Chiorboli, C.; Ferri, A.; Carassiti, V. *J. Chem. Soc., Chem. Commun.* **1985**, 881.

(24) (a) Lewis, F. D.; Ho, T. I.; Simpson, J. T. *J. Am. Chem. Soc.* **1982**, *104*, 1924. (b) Lewis, F. D.; Correa, P. E. *J. Org. Chem.* **1981**, *46*, 1077.

Scheme 2. Proposed Mechanism for the Photocatalytic Oxidation of $CyNH_2$



radical with O_2^- could give cyclohexanone oxime (pathway g), which, in turn, hydrolyzes to yield cyclohexanone (pathway h). The Schiff base can be obtained by reaction between cyclohexanone and $CyNH_2$ (pathway e). Cyclohexanone and the Schiff base can also be generated via reaction between the α-aminoalkyl radical and O_2[21] (pathways b–e).

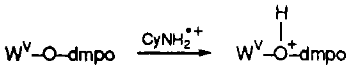
In a previous section we described the results obtained using ESR spin-trapping techniques to demonstrate the formation of radical species. Besides the $C_6H_{11}NH_2^{\bullet+}$ radical, dmpo forms an adduct with an $OH^\bullet$ radical coordinated to a tungsten atom. It is plausible that this species is obtained as a consequence of a direct transfer of a proton from the $C_6H_{11}NH_2^{\bullet+}$ radical cation to the photoreduced POM. This process is illustrated by eq 9 or 10, where the bond between tungsten and oxygen is put into evidence by indicating $W_{10}O_{32}^{5-}$ as $W^V{=}O$.

$$[W^V{=}O,C_6H_{11}NH_2^{\bullet+}] \rightarrow [W^V{-}OH,C_6H_{11}N^{\bullet}H] \quad (9)$$

$$[W^V{=}O,C_6H_{11}NH_2^{\bullet+}] \rightarrow [(W^V)^+{-}OH,(C_6H_{10})^{\bullet}NH_2] \quad (10)$$

Alternatively, dmpo-protonated WV–O• radical adduct may be derived from the protonation of the spin adduct of the WV–O• radical according to eqs 11 and 12.[25]

$$W^V{-}O^\bullet \xrightarrow{dmpo} W^V{-}O{-}dmpo \quad (11)$$



$$W^V{-}O{-}dmpo \xrightarrow{CyNH_2^{\bullet+}} W^V{-}\overset{H}{\overset{|}{O^+}}{-}dmpo \quad (12)$$

The oxidation by photoexcited semiconductors of primary amines bound to a secondary carbon has been already investigated by Fox and Younathan.[21] The major products, in their work, were the corresponding Schiff bases with, in addition, smaller amounts of carbonyl products. They proposed a mechanism which took into account dielectronic oxidations of amines, besides a reaction pathway analogous to that reported in Scheme 2 of this work (pathways a–e). It is likely that the $CyNH_2$ itself can undergo dielectronic oxidation by holes of photoexcited TiO_2. In this case another reaction pathway leading to the observed formation of the Schiff base of $CyNH_2$ is reported in Scheme 3.

Scheme 3. Dielectronic Oxidation of $CyNH_2$

$$(C_6H_{10})^{\bullet}NH_2 \xrightleftharpoons{-e^-} C_6H_{10}{=}NH_2^+ \xrightleftharpoons[\;]{-NH_3,\ +CyNH_2} C_6H_{10}{=}NH^+C_6H_{11} \xrightleftharpoons{-H^+} C_6H_{10}{=}NC_6H_{11}$$

The higher oxidizing power of TiO_2 compared to POM can possibly explain the striking difference in yield of Schiff base observed for the two systems (Table 2). In a previous work[3b] we draw attention to the fact that TiO_2 is not suitable for photosynthetic purposes since complete photodegradation is always a major reaction pathway; surface modification makes the system more versatile by making it less aggressive.

Different experimental conditions (for example, light intensity or the degree of water content in the organic solvent) may favor the further oxidation of $CyNH_2$ to carbonylic products and, thus, explain the fact that Fox et al.[21] do not mention the oxime as one of the final products.

Conclusion

For the first time the photochemical behavior of $W_{10}O_{32}^{4-}$ has been investigated in the presence of $CyNH_2$. The photochemical excitation in the near-ultraviolet region induces an electron-transfer process from the amine to the polytungstate. This process causes the the monoelectronic reduction of $W_{10}O_{32}^{4-}$ with the simultaneous oxidation of $CyNH_2$. The photoreduction of W^{VI} to W^V occurs after the formation of a complex between $W_{10}O_{32}^{4-}$ and $CyNH_2$. Using the ESR spin-trapping technique, we have been able to reveal the presence of $OH^\bullet$ radicals coordinated to the polytungstate "surface".

In the presence of oxygen, catalytic cycles are realized with the formation of several oxidation products of $CyNH_2$ and with high values of the ratios between the moles of oxidized amine and the moles of degradated photocatalyst.

Under aerobic conditions, WO_3 and TiO_2 present a very similar behavior, confirming that POMs can be considered models of transition metal oxides able of mimicking the interactions between organic substrates and solid surfaces of interest in heterogeneous catalysis.

The nature of the products obtained suggests that the photocatalysts investigated are able to catalyze the oxidation of $CyNH_2$ to cyclohexanone oxime with molecular oxygen. This result is of interest for obtaining new catalytic methods for the monooxygenation of $CyNH_2$ under mild conditions.

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[25] We thank one of the reviewers for suggesting this alternative mechanistic pathway.