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Photochemical and catalytic properties of dimeric species of molybdenum(V)

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Abstract

The chemistry and photochemistry of molybdenum coordination compounds in its several oxidation states is of great importance from basic as well as applied points of view. Molybdenum is a relevant element for the synthesis of many homogeneous and heterogeneous catalysts. This element is also essential in several enzymatic systems. One of the characteristics of the molybdenum chemistry is related to the easy conversion between its oxidation states and to the changes of coordination number, observed particularly between Mo^{III}, Mo^{V} and Mo^{VI}. Many aspects of the chemistry of Mo^{V} have been reviewed. However, the thermal and photochemical reactivity of its complexes was not completely well understood until few years ago. Our studies have shown that aqueous solutions of $Mo_2O_4(H_2O)_{6-x}L_x^{n+}$ complexes (where L is a monodentate ligand, such as H_2O, Cl^-, NCS^-, Br^- or bidentate such as cysteine), present dual reactivity; ligand–metal charge transfer (LMCT) and photolabilization of the ligand. The excitation induces photolabilization resulting in the formation of a single bridged μ-oxo-dimer that undergoes dissociative disproportionation into monomeric Mo^{IV} and Mo^{VI} species. Mo^{IV} reacts with coordinated water leading to H_2 and Mo^{VI}. Photoreduction of the complexes to $Mo^{IV}Mo^{V}$ dimers which can be characterized as an LMCT process has also been reported. The main objective of the present review is to present an update of data obtained from studies performed on these systems and the contribution of our laboratory to the understanding of the photochemical and catalytic properties of the di μ-oxo-dimers of molybdenum(V).

Keywords: Oxo-molybdenum(V); Photochemistry; Catalytical properties

1. Introduction

The chemistry and photochemistry of molybdenum coordination compounds have received special attention from basic and applied research. Several aspects of the reactivity and photochemistry of their complexes in different oxidation states have been reported in the literature [1–6]. From the chemical point of view, the use of molybdenum complexes in chiral synthesis is a very important and increasing field of research [3].

Molybdenum, which can be considered as a trace element, presents several oxidation states, and therefore may change easily its co-ordination number and to form mono and binuclear oxo complexes with several ligands. The propensity of oxo-molybdenum species in higher oxidation states to form di, tri and polynuclear complexes is well documented [7–12]. Research results on synthesis, X-ray structure of several complexes, advances in problems associated to oxygen-atom transfer, binuclear complexes of molybdenum in different oxidation states, polymeric species of molybdenum, including their non linear optical properties have been recently reviewed [13].

Charge transfer processes in the coordination complexes of molybdenum are relevant in several reactions, including redox enzymatic systems [14].

A very interesting review about the photochemistry and photophysics of molydenum complexes with d^n ($n = 5$, 4 and 2), metal center has been published previously [15]. Coordination compounds of molybdenum in different oxidation states have also been proposed as photocatalysts [16].

In the present review we will mainly focus our attention on molybdenum(V) species, particularly oxo molybdenum complexes and the contribution of our laboratory to the understanding of the photochemistry and spectroscopic properties of unstable intermediates in aqueous solutions.

2. Oxo monomers of molybdenum(V)

From magnetic circular dichroism studies of tetrapropylammonium salts of $Mo^VOCl_4^-$ compounds assignment of ligand field and charge transfer states have been proposed [17]. Its temperature dependence presents a typical behaviour which is characteristic of a paramagnetic ground state. Although the crystal structure of systems involving the $Mo^VOCl_4^-$ chromophore are well known, its electronic structure is still a matter of controversy. The ligand field energy ordering $d_{xy} < d_{xz}, d_{yz} < d_{x^2-y^2} < d_{z^2}$ has been proposed for $Mo^VOCl_4^-$, which is in agreement with that established for systems with one unpaired electron in the d_{xy} orbital [18] though the orbitals involved in the electronic transitions are not completely identified. Recently, magnetic circular dichroism (MCD) measurements led to the assignment of the to $d_{xy} \rightarrow d_{xz}, d_{yz}$ and $d_{xy} \rightarrow d_{x^2-y^2}$ ligand field transitions to lie at low energy in this chromophore [17]. The $d_{xy} \rightarrow d_{xz}, d_{yz}$ transition corresponding to a $n \rightarrow \pi^*$ excitation has also been observed in the $[WOCl_4(H_2O)]^-$ chromophore. The energy at which this transition is observed is rather insensitive to the metal center [17,18], i.e. 16 000 and 15 300 cm^{-1} for Mo and W, respectively. This transition displays a vibronic structure arising from the coupling with the totally symmetric Mo–O stretching. The energy of the Mo–O vibrational strech in the ground and excited states are 1012 and 900 cm^{-1}, respectively. This difference suggests an increase in the antibonding character of the excited state. The transition $d_{xy} \rightarrow d_{x^2-y^2}$ involves excitation from a nonbonding orbital (n) to an equatorial antibonding orbital (σ^*). In contrast to the $n \rightarrow \pi^*$ excitation, this transition is strongly dependent on the metal center as expected from the spectrochemical series. A third band can be observed in this chromophore, being assigned to charge transfer (CT) transition from a $b_1(Cl)$ to $b_2(d_{xy})$ state.

Resonance Raman studies have been performed on oxo-molybdenum(V) (di-μ-oxo and di-μ-sulphido) complexes for providing electronic features in complexes used as models for molybdenum containing enzymes. Enhanced Raman lines have been reported for $\nu(M{=}O)$ and $\nu(Mo{-}S)$ bands of several molybdenum complexes which are excited by charge transfer (CT) transitions [19].

The d^1 complexes, $MoOX_4^-$ ($X = Cl$, Br) show fluorescence emission in solid state as observed in other d^1 systems. The fluorescence of $[MoOCl_4(CH_3CN)]^-$ and $[MoOBr_4(CH_3CN)]^-$ in CH_3CN solutions have also been reported, whereas $[MoOCl_4(H_2O)]^-$ and $[MoOBr_4(H_2O)]^-$ show fluorescence emission in CH_2Cl_2. Emission assigned to the $^2E \rightarrow {}^2B_2$ transition is detected at 950 nm for $X = Cl$ and

900–905 nm for X = Br [20]. The existence of long lived excited states in several of these complexes make them suitable for bimolecular photoredox reactions.

3. Thermal properties of μ-oxo-dimers of molybdenum(V)

Some studies on the reactivity and catalytical properties on oxygen atom transfer (AOT) reactions of these complexes have been made in the last years. Some attention has been paid to the molybdenum–pterin complexes, which have been proposed as models for understanding the biochemistry of pterin-containing enzymes [21,22].

The disadvantage of polynucleation in those studies has been pointed out. Although polynucleation is particularly important in molybdenum(V) complexes, it can be restrained using bulky ligands [21]. Advances on the knowledge of factors and conditions for controlling the 'nuclearity' of reactions products have been reported from studies of binuclear μ-oxo and μ-oxo-μ-disulfido complexes of molybdenum(V) and molybdenum(VI) employing hydrotis(3,5-dimethylpyrazol-1-yl)borate as tridentate ligand [23].

Steric protection of the metal center appears to contribute to preventing comproportionation and dinucleation reactions (Eq. (1)) leading to Mo(V) species [23].

$$[\mathrm{Mo^{IV}OL_2}]^{2-} + [\mathrm{Mo^{VI}O_2L_2}]^{2-} \rightarrow (\mathrm{Mo_2^{V}O_3L_4})^{4-} \quad (1)$$

The μ-oxo dimolybdenum(V) complexes have *cis*-configuration between terminal oxo and bridged oxo ligands. It has been postulated that the formation of a μ-oxo bridge involves the attack of one of the two oxo ligands of $[\mathrm{Mo^{VI}O_2}]^{2+}$ on the vacant *trans* position in $[\mathrm{Mo^{IV}O}]^{2+}$ [24].

The formation of binuclear $[\mathrm{Mo_2^{V}O_3}]^{4+}$ complexes through this process is characteristic of many synthetic systems. The comproportionation of $\mathrm{Mo^{IV}}$ and $\mathrm{Mo^{VI}}$ species may be a reversible or an irreversible process. It is not always easy to distinguish between the formation of mononuclear $\mathrm{Mo^{IV}}$ or binuclear $\mathrm{Mo^{V}}$ complexes [25].

The three species described in Eq. (1) are in equilibrium in non aqueous solutions [26,27]. The position of the equilibrium depends on the steric properties of the ligands. Bulky bi- or tridentate ligands prevents the comproportionation [28,29]. Consequently, the extent of Reaction (1) appears to be an important factor in biological processes, as observed in the bacteria respiratory chain. The effect of bulky ligands is increased in donor solvents such as acetonitrile, tetrahydrofurane and dimethylformamide, indicating that these solvents prevent the formation of the μ-oxo bridge [24–26,30,27–29].

Studies on AOT processes involving mono oxo-molybdenum(IV) complexes have been employed as models for simulating the reduced state in active site of molybdoenzymes [26,30]. Pterin-containing molybdenum enzymes catalyze oxygen atom transfer (AOT) reactions. In this frame, comproportionation seems to be another way for AOT.

Experiments suggest that the oxygen atom transferred originates in the molybdenum center exclusively [31]. Catalytic AOT reactions involve $[\mathrm{Mo^{IV}OL_2}]^{2-}$ and $[\mathrm{Mo^{VI}O_2L_2}]^{2-}$ $[\mathrm{L} = \mathrm{S_2C_2(CN)_2^{2-}}$, $o\text{-}\mathrm{S_2C_6H_4^{2-}}]$ complexes. However comproportionantion as described by Eq. (1) makes the interpretation of oxo transfer reactions more complicated. Efforts for understanding the effectiveness of molybdenum(IV) oxo-monomers in AOT reactions have been developed during the last years. The synthesis, structural properties and reactivity of $[Mo^{IV}O(L)_2]^{2-}$, where L represents substituted benzenedithiolate groups, have been proposed as models for this kind of studies [24].

3.1. Photochemical studies

The photochemistry of monomers of Mo^{IV} and Mo^{V}, particularly their cyano and thiocyanato complexes has also been studied [see Ref. [15] and the literature therein]. $Mo_2O_4(CNS)_6^{4-}$ has been identified as a product from the photolysis of $Mo^{III}(NCS)_6^{3-}$ [32].

There is little information about the thermal and photochemical reactivity of Mo macrocycles. One of the few studies was performed on Mo(V) tetrasulfophthalocyanine [33], where Mo^{IV} and Mo^{V} ligand–radical species as common intermediates of the electrochemical and photochemical reactions have been identified.

It is well known that molybdenum in higher oxidation states forms oxo-complexes and polynuclear species where the $Mo_xO_y^{n+}$ moiety is present in solution and even in the solid state. One or more terminal oxygen atoms are present in the complexes, i.e. oxygen atoms bound to a Mo center in some compounds or acting as a bridge between at least two Mo atoms in others.

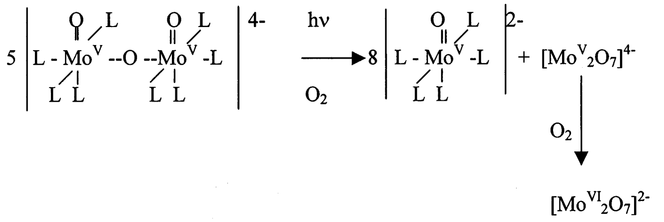
Isopolymolybdates and heteropolymolybdates in the oxidized forms show LMCT bands (O → Mo) in the visible and UV regions. In flash photolysis studies performed on $Mo_7^{VI}O_{24}^{6-}$, no long lived intermediates have been observed, but a mixed valence polmolybdate (Mo^{VI}–O–Mo^{V}) has been postulated [34].

Molybdenum(V) in acid aqueous solutions is able to form dimers, the single-bridged $Mo_2O_3^{4+}$ (*cis* and *trans*) and double-bridged $Mo_2O_4^{2+}$ (*trans*) species being the most representative. The structure of the latter complexes can be described as two distorted octahedral sharing a O–O edge. X-ray studies suggest a partial bonding between two Mo–Mo atoms, but even a bond order of 1 has been proposed. Moreover, the double bridge Mo_2O_2 is not strictly planar.

The linear geometry assigned to the single bridged Mo–O–Mo indicates a strong π interaction, which allows spin pairing. This is characteristic of diamagnetic d^1–d^1 complexes containing the Mo_2O_3 functional group. However, the complex $Mo_2O_3(TPP)_2$ (TPP = tetraphenylporphyrin) departs from the general rule [35].

There are few studies on the photochemistry of the single bridged complexes with the Mo_2O_3 core. As stated before, these complexes undergo thermal disproportionation in non aqueous solutions. Therefore, they can show thermally reversible photochemical disproportionation, similar to that observed for W(V) complexes. This behaviour has been observed in the d^1–d^1 molybdenum dithiocarbamate complex $[(Mo^{V}O\{S_2CN(CH_3Ph)_2\}_2)_2O]$ [36]. The photochemistry of this complex appears to be interesting because its photoproducts $[(Mo^{IV}O\{S_2CN(CH_3Ph)_2\}_2)_2O]$ and $[(Mo^{VI}O\{S_2CN(CH_3Ph)_2\}_2)_2O]$ are known compounds. $[(Mo^{V}O\{S_2CN(CH_3Ph)_2\}_2)_2O]$ presents significant photosensitivity and it has been reported that the optical density of unstirred solutions at 519 nm decreases nearly 11% when left in the spectrophotometer, but after irradiation recombination took place and the optical density fully recovered in stirred solution left in the dark. A molar absorption coefficient at 519 nm (ε_{519}) equal to 1.9×10^4 M^{-1} cm^{-1} has been reported for this complex.

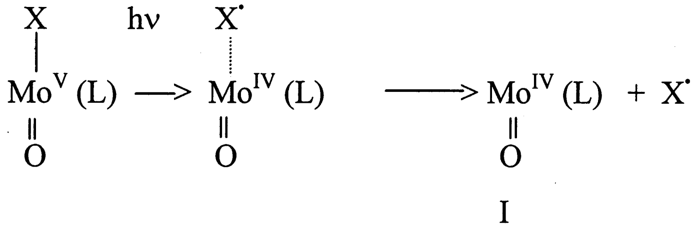
Photolytic ligand redistribution has been reported for $[Mo_2^VO_3(NCS)_8]^{4-}$ complexes leading to the mononuclear and paramagnetic $[Mo^VO(NCS)_5]^{2-}$ species. The synthesis, NMR, paramagnetic and IR spectroscopic properties of single bridged complexes of $[N(CH_3)_4]_4[Mo_2^VO_3(NCS)_8]$, $[N(CH_2CH_3)_4]_4[Mo_2^VO_3(NCS)_8]$, and $[N(CH_3)_4]_4[Mo_2^VO_4(NCS)_6]$, $[N(CH_3)_4]_2[Mo^VO(NCS)_5]$, $[N(CH_3)_4]_4[Mo^VO(NCS)_5]$ have been reported recently [37]. The photolysis of complexes containing the Mo_2O_3 core in non aqueous solutions has also been reported [36,37]. The mononuclear complexes have been obtained as photoproducts of the previous compounds. The presence of O_2 appears to be an important factor for reproducible synthetic scale photolysis of $[N(CH_3)_4]_4[Mo_2^VO_3(NCS)_8]$. The following reaction scheme (Eq. (2)) has been proposed for this system in acetonitrile solutions.



(2)

$[Mo_2^VO_3(NCS)_8]^{4-}$ does not participate in a thermal disproportionation equilibria, but the reported results show that the complex is photosensitive. The observed reaction seems to be associated to the initial photolysis of isothiocyanate ligands and not to the bridging oxo-chromophore.

Charge transfer photochemistry studies on Mo^V complexes have been performed on coordination compounds with porphyrines and phthalocyanines as ligands. In these studies, all the porphyrin complexes analyzed were oxo compounds of Mo^V with a different ligand in axial position. Under these conditions, LMCT processes can be detected. As reported in the literature, when $Mo^VO(tpp)X$ (where $X = Br^-$, Cl^-, NCS^-, etc) is the ligand in axial position, the molecule absorbs visible radiation and a homolytic cleavage is observed, generating the corresponding $X^•$ radical, which is able to oxidize the solvent by hydrogen abstraction. However, if $X^•$ is $I^•$ or $NCS^•$, its dimerization competes with the oxidation reaction path [38]. The quantum yield of most reactions is lower of 10^{-3}.



I

(3)

Photoreaction following excitation of the LMCT state and photo-assisted reduction by dioxygen have been observed in similar complexes with alkoxo axial ligands [39–42]. In all these processes, Mo^{V} is reduced to Mo^{IV}. The whole process may be represented by the following reaction scheme (Eq. (3))

In the presence of dioxygen, intermediate I undergoes a series of reactions leading to μ-oxo molybdenum(V) dimers.

Some aspect of the chemicalreactivity, photochemical and catalytic properties of Mo^{VI} [43–49] and Mo^{V} [50–61] have been studied in our laboratory during the last years. In this review, we present the current state of knowledge about the photochemistry and catalytic properties of di-μ-oxomolybdenum(V) complexes in aqueous and non aqueous solutions.

4. Photochemical studies on $[Mo_2O_4(H_2O)_{6-n}L_n]^{2-n}$ in acidic aqueous solutions

Several studies on the photo-induced charge transfer on ($[Mo_2O_4(H_2O)_{6-n}L_n]^{2-n}$, $L = H_2O$, Cl^-, CNS^-, Br^-, cysteine) in acidic solution were carried out [50–58].

In a similar way as reported for molybdenum(II) complexes, photo-active dimers are observed in the +5 oxidation state of this metal, with the $Mo_2O_4^{2+}$ core, and various ligands [50–59,62]. Flash photolysis studies performed on acidic solutions of these complexes show that excitation in the range from 250 to 340 nm leads to dual photoreactivity: photo-labilization and photo-oxidation of the ligand. This behavior has been attributed to the population of different excited states caused by wide-range light absorption [62]. After irradiation, Mo^{VI} and H_2 are detected as reaction products.

4.1. Flash photolysis results

We have investigated the generation and decay of transients under conventional conditions of flash photolysis. Only first order kinetics have been observed. The experimental first order rate constant k_{1app}, is independent of the dioxygen concentration, but appears to be dependent on the ligand concentration with the exception of bromide.

The observed intermediates absorb in the range from 400 to 500 nm. Their spectra are independent on proton concentration but depends on the nature of the ligand L and its concentration. The lack of absorption band around 700 nm [7,62,63], excludes formation of Mo^{IV}–Mo^{V} dimers in the conventional flash photolysis experiments. The formation of Mo^{V}–Mo^{VI} intermediates can be also discarded based on the fact that the life time of this intermixed valence complexes is lower than 200 μs and Mo–Mo cleavage is pH independent [62,64]. This behaviour contrasts with the experimental results observed in all the systems studied, where the intermediates decayed within the millisecond time range and showed a clear pH dependence. The spectra of these intermediates were not affected by dioxygen, suggesting that the observed decay did not involve Mo^{IV} or Mo^{V} oxo monomers.

It has been proposed that the primary photochemical process leads to a partial bridge opening without change in the metal center's oxidation state [50–58]. MO calculations identify the HOMO in the dimers as Mo–Mo σ_d–σ_d character with traces of oxygen bridge and that transitions involved at 300 nm presents a Mo–Mo anti-bonding character [65]. We have observed that transitions around 300 nm are effective in inducing photochemical transformation in these complexes. Similar behaviour has been observed in dimers of Mo^{II} [66]. Therefore, μ-oxo bis-(oxomolybdenum(V)) complexes have been proposed as intermediates, where the moiety (Mo_2O_3) is present. Moreover, the presence of Mo_2O_3 moiety has been reported as an intermediate in the disproportionation of $Mo_2O_4^{2+}$ complexes in strong alkaline aqueous solutions and in excess of cyanide ion, where the final products are $[MoO_2(CN)_4]^{4-}$ and MoO_4^{2-}. Monomeric Mo^{IV} species are very unstable in aqueous solutions, reducing water molecules of the environment to H_2 [67,68].

4.2. Nature of the intermediates

In aqueous solutions of $[Mo_2O_4(H_2O)_6]^{2+}$ in the presence of neutral or L^- ligands, coordinated water molecules can be substituted in different degree by L given $[Mo_2O_4(H_2O)_{6-x}L_x]^n$ complexes as seen in the spectral changes observed on the ligand concentration, i.e.:

$$[Mo_2O_4(H_2O)_6]^{2+} + L^- \overset{K_1}{\leftrightarrows} [Mo_2O_4(H_2O)_5L]^n$$
$$+ L^- \overset{K_2}{\leftrightarrows} [Mo_2O_4(H_2O)_4L_2] \overset{K_3}{\leftrightarrows} [Mo_2O_4(L)_6]^{6-}$$

All of these species can be excited after light absorption.

The experimental decay rate constants and the absorption spectra depend on the nature of the intermediates, i.e. $[Mo_2O_3(H_2O)_{8-x}L_x]^n$ and the observed trend can be correlated with the nature of the ligand and its electronic properties. A systematic shift toward the visible can be observed with the degree of substitution and with the donor properties of the ligand.

Photo-labilization induces the formation of μ-oxo single bridged dimers $Mo_2^VO_3(H_2O)_8^{4+}$, $Mo_2^VO_3(NCS)(H_2O)_7^{3+}$, $Mo_2^VO_3(NCS)_2(H_2O)_8^{2+}$, $Mo_2^VO_3(Cl)(H_2O)_7^{3+}$, $Mo_2^VO_3(Br)(H_2O)_7^{3+}$ and their bases $Mo_2^VO_3(H_2O)_7(OH)^{3+}$, $Mo_2^VO_3(CNS)(OH)(H_2O)_7^{2+}$, $Mo_2^VO_3(CNS)_2(OH)(H_2O)_8^{+}$, $Mo_2^VO_3(Cl)(OH)(H_2O)_7^{2+}$, $Mo_2^VO_3(Br)(OH)(H_2O)_7^{2+}$. In all these species, one or at least two water molecules in the coordination sphere are replaced by two or at least one ligands. The observed decay involved both kind of complexes. These intermediates are precursors in the formation of Mo^{VI} and hydrogen as reaction products.

Scheme 1 has been proposed for describing the observed behaviour.

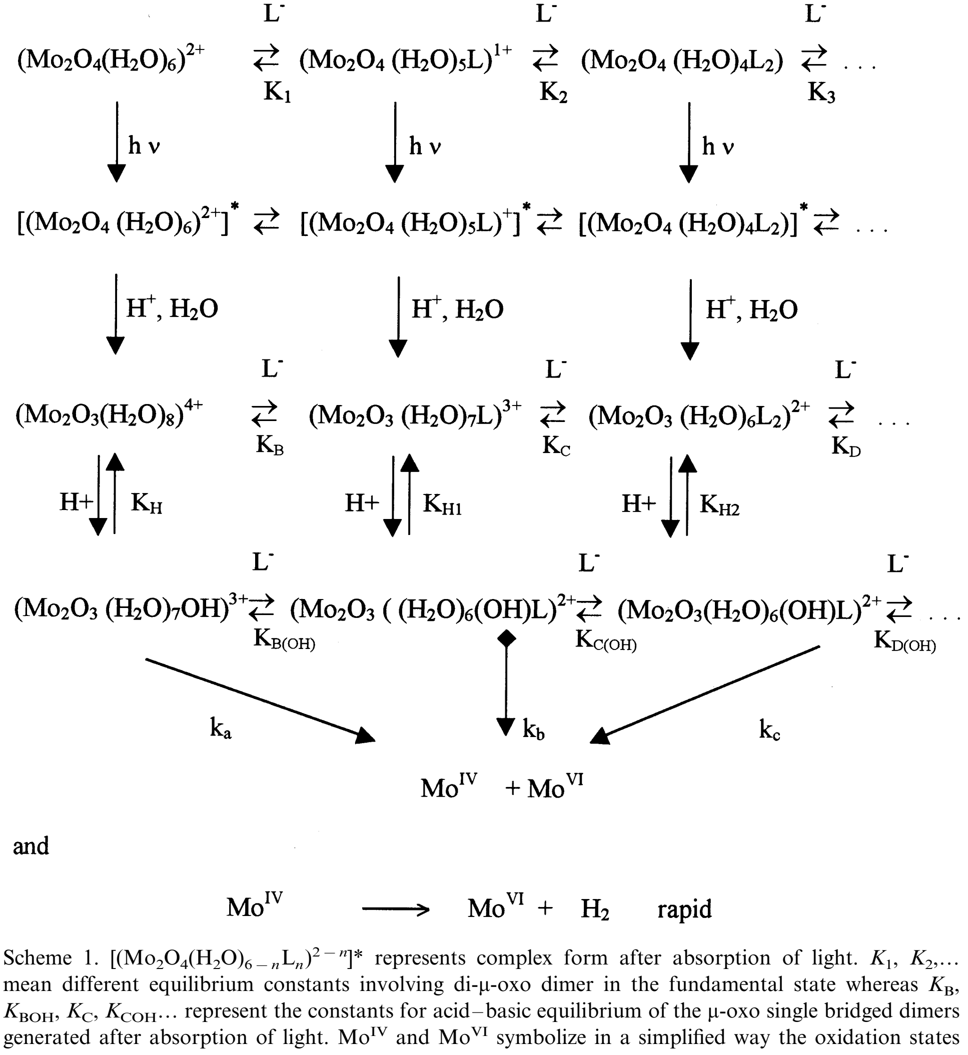
From Scheme 1, the experimental or observed rate constant can be expressed as [50–58]:

$$k_{1app} = \frac{k_a K_H + K_{H1} k_b K_B[L] + \ldots}{[H^+]\{1 + K_H/[H^+] + [L](K_B + (K_H/[H^+])K_{B(OH)} + \ldots)\}} \tag{4}$$

The equilibrium constants involved in this expression have been reported for H_2O, Cl^- and NCS^- (see Table 1). Br^- departs from the observed behavior for the other ligands, i.e. k_{1app}^{-1} is linear on $[H^+]$ but independent of $[Br^-]$. This behavior has been interpreted considering that (a) $K_B > K_C$, which means that only the concentration of the monobromide complexes is relevant in the mechanism depicted in Scheme 1; (b) $[Br^-]$ $(K_B + (K_H/[H^+])K_{B(OH)}) \gg 1 + (K_H/[H^+])$, i.e. the concentration of the monobromide complexes is much higher than those of $Mo_2O_3(H_2O)_8^{4+}$ and $Mo_2O_3(H_2O)_7OH^{3+}$.

The different kinetic parameters and equilibrium constants reported in our studies for these ligands at room temperature are listed in Table 1.

Single bridged species can also exist in an *trans–cis* equilibrium and a rate constant of 2.4×10^4 s^{-1} for the *cis–trans* isomerization has been measured [62].



Scheme 1. $[(Mo_2O_4(H_2O)_{6-n}L_n)^{2-n}]^*$ represents complex form after absorption of light. K_1, K_2,... mean different equilibrium constants involving di-μ-oxo dimer in the fundamental state whereas K_B, K_{BOH}, K_C, K_{COH}... represent the constants for acid–basic equilibrium of the μ-oxo single bridged dimers generated after absorption of light. Mo^{IV} and Mo^{VI} symbolize in a simplified way the oxidation states of the monomeric molybdenum species arising from the basic forms of the monobridged complexes.

Table 1
The equilibrium constants for H_2O, Cl^- and NCS^-

Ligand	K_Hk_a/s^{-1}	K_B	K_C	ΔH_H+E_a/kJ mol^{-1}	ΔH_B/kJ mol^{-1}
H_2O	5.5	–	–	61.3	–
Cl^-	5.5	11	17	90	42
NCS^-	6.7	1.1×10^4	6.8	[a]	−11.3
Br^-	3.2	–	–	68	–

[a] $K_H.k_a$ in this system show a small temperature dependence [51].

4.3. Spectral characteristics of reaction intermediates

Intermediates absorb in the wavelength range from 400 to 500 nm. Spectral changes have been assigned to transitions involving the Mo_2O_3 core in the single bridged intermediate complexes. In Figs. 1 and 2 the spectra recorded for these intermediates at different ligand concentrations are shown. Transitions in the same wavelength region have been reported in $[Mo_2O_3Cl_8]^{4-}$ complexes in strong acid media [69]. In a similar way, the absorption spectrum for acetonitrile solutions of $Mo_2O_3(CNS)_8(PyrH)_4$ presents a maximun at 517 nm (see Ref. [51] and the literature cited therein).

In this wavelength region (400–500 nm), no other dimeric molybdenum species absorbs. This fact supports the presence of single bridged μ-oxo molybdenum(V) species. Therefore, the photochemical primary processes are associated with the rupture of one of the oxo-bridges in the Mo_2O_4 unit without change in the

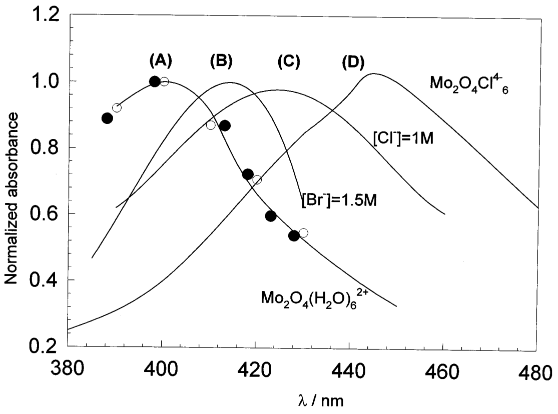


Fig. 1. Absorption spectra of intermediates produced after the flash and normalized to their maximun absorption: (A) The line corresponds to the species obtained in acidic aqueous solutions of $[Mo_2O_4(H_2O)_6]^{2+}$; i.e. $[Mo_2O_3(H_2O)_8]^{2+}$. The same intermediate is generated after flashing solutions of this complex in the presence of chloride ion (○ $[Cl^-]=0.01$ M), bromide (● $[Br^-]=0.1$ M) and NCS^- (not shown) (B) spectrum of the intermediate $[Mo_2O_3(H_2O)_7Cl]^+$ observed in 1 M sodium chloride solutions (C) spectrum of the intermediate $[Mo_2O_3(H_2O)_7Br]^+$ detected in solutions of $[Br^-]=1.5$ M (D) spectrum of $[Mo_2O_3(Cl)_6]^{4-}$. For more details, see text.

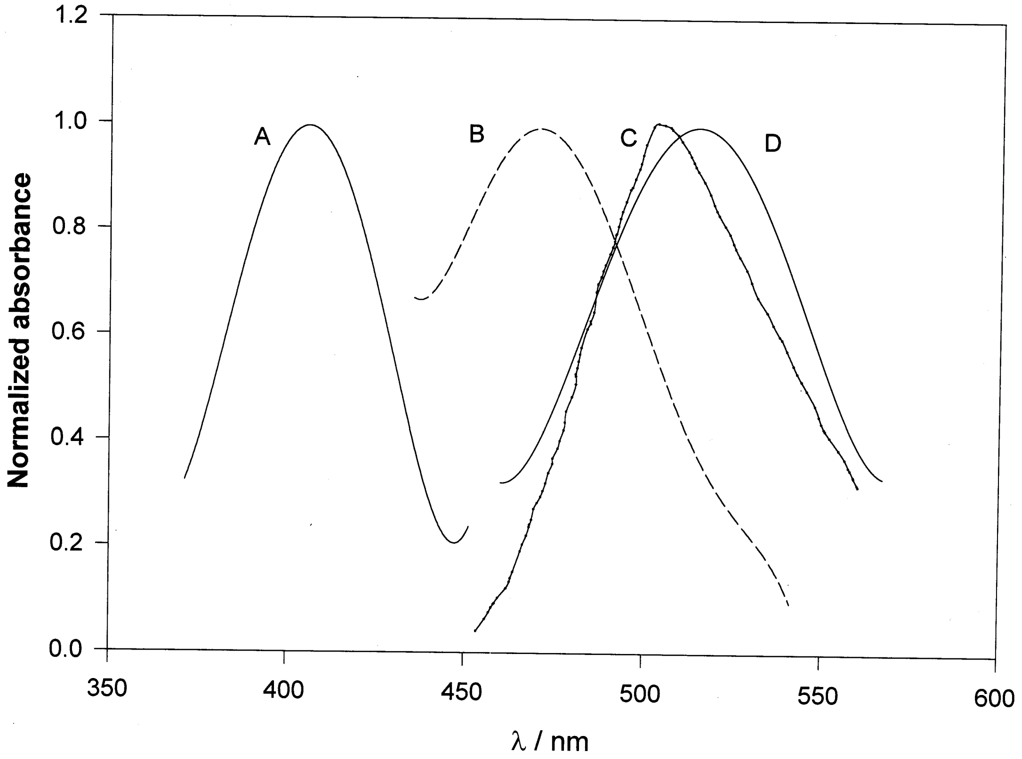


Fig. 2. Absorption spectra of intermediates generated in 10^{-4} M $Mo_2O_4(H_2O)_6^{2+}$ and different NCS^- concentrations at 35°C normalized to their maximum absorption: These spectra were obtained from the time resolved analysis of the absorption spectra of the transients generated after flashing fresh solutions as a function of pH and NCS^-. (A) $[Mo_2O_3(H_2O)_8]^{4+}$, see also Fig. 1; (B) $[Mo_2O_3(H_2O)_7\ (NCS)]^{3+}$; (C) $[Mo_2O_3(H_2O)_6(NCS)_2]^{2+}$; (D) $[Mo_2O_3(NCS)_8](PyrH)_4$, See Ref. [51] for more details.

oxidation state of the metal center. The proton dependence in $k_{1\mathrm{app}}$ has been interpreted by considering that the generated intermediates are in acid–base equilibrium.

Absorption at 400 nm has been attributed to the $Mo_2O_3(H_2O)_8^{4+}$ complex. When the H_2O molecules are substituted by other ligands a red shift in the spectrum is observed. $[Mo_2O_3(H_2O)_7CNS]^{3+}$ and $[Mo_2O_3(H_2O)_6(CNS)_2]^{2+}$ complexes absorb at 475 and 505 nm respectively in agreement with the more efficient electron donor properties of SCN^-. A similar pattern is observed for the $[Mo_2O_3(H_2O)_7Cl[^{3+}$ ($\lambda_{max} = 425$ nm) complex.

4.4. Theoretical interpretation

The first order rate constant observed in the millisecond time scale for $L = H_2O$, Cl^- and NCS^- as ligands has been ascribed to the decay of only one species, i.e. $Mo_2^VO_3(H_2O)_7(OH)^{3+}$ (See Scheme 1).

This interpretation has been supported by MO calculations in the frame of the extended Hückel method (HMO). The stability of all the previously mentioned complexes has been estimated [56]. The HMO calculations showed that the bond order in the basic forms $Mo_2O_4(H_2O)_4L(OH)^{m+}$ ($L = H_2O$, NCS^-, Cl^- and Br^-) in the excited state is much lower than that calculated for the acid form. These results support the experimental evidence that the basic species is a precursor for the single-bridged intermediates proposed in Scheme 1.

4.5. Other species or intermediates

There are other possible ways for these species to decay. We have previously described one reaction channel: the dimer can disproportionate into Mo^{IV} and Mo^{VI}. However, there is a second reaction channel which can be considered. The presence of Mo^V–O–Mo^{IV} dimer has been detected by pulse radiolysis and laser flash photolysis experiments [62]. Such transient mixed-valence species suggest that the photoreduction of the complex induces a simultaneous oxidation of coordinated ligand.

In this regard, studies performed in chloride solutions rebeal a process with a lifetime shorter than 2 ms which can be detected at wavelengths lower than 380 nm. The experimental pseudo-first order rate constant associated with this process depends on the $Mo_2O_4(H_2O)_6^{2+}$ concentration. The spectrum of the intermediate is quite similar to that reported for the ion radical $Cl_2^{-\bullet}$ ($\lambda_{max} = 340$ nm, $\varepsilon_{340} = 8800 \pm 500$ M cm^{-1} [70]) which can be generated from the oxidation of the coordinated Cl^- with the consequent photoreduction of the dimer $Mo_2O_4(H_2O)_5Cl^+$ as described in the following reaction.

$$Mo_2O_4(H_2O)_5Cl^+ \xrightarrow{h\nu} Mo^{IV}O(H_2O)_3O_2Mo^VO(H_2O)_3^+ + Cl^\bullet \tag{5}$$

The subsequent reaction with chloride ions leads to the ion radical $Cl_2^{-\bullet}$, which disappears by reacting with $Mo_2O_4(H_2O)_5Cl^+$ or through the diffusion controlled step

$$Cl_2^{-\bullet} + Cl_2^{-\bullet} \rightarrow 2Cl^- + Cl_2 \qquad (6)$$

The decay of $Cl_2^{-\bullet}$ has been detected in pulse radiolysis studies in an acidic solution of $[Mo_2O_4(H_2O)_6]^{2+}$ in the presence of excess of chloride[62]. In those experiments, the formation of mixed valence V–IV complexes has been detected at wavelengths higher than 600 nm, these complexes being characterized by low molar absorption coefficient [7,62,63]. In a similar way, ligand photooxidation of coordinated NCS^- in $[Mo_2O_3(H_2O)_7NCS]^{3+}$ and $[Mo_2O_3(H_2O)_6(NCS)_2]^{2+}$ complexes can not be discarded [51]. This photoxidation may form $(NCS)_2^{-\bullet}$ radical which absorbs at ca. 480 nm with a molar absorption coefficient of 8×10^3 M^{-1} cm^{-1} and a lifetime of the order of 0.1 ms [71].

4.6. Effect of the ionic strength

The ionic strength influences the reaction rate. This effect has been observed in our studies, particularly in bromide solutions [57,58].

Rate constants involving ionic reactions are proportional to the activity factor $\gamma_{\pm}$. In media of high ionic strength ($I > 1$ M), the following equation has been proposed for $\gamma_{\pm}$ (see Ref. [58] and literature cited therein).

$$\log \gamma_{\pm} = -0.1916\,|z_+z_-|\,(Ia^{-1})^{1/3}(0.75 + 0.25c_s m_s^{-1}) \qquad (7)$$

with a the average ionic diameter, c_s the molar concentration of the solution, m_s the molal concentration of the solution. A very good correlation with the theoretical expression (Eq. (7)) (compared with the standard Debye–Huckel·s limit law) and the experimental results could be found. The negative slope observed in the linear plot of $\log k_{obs}$ vs. $[(I)^{1/3}(0.75 + 0.25c_s/m_s]$ supports that the decaying intermediate proposed in Scheme 1 is positively charged.

4.7. Studies in non-aqueous solutions

Few studies on the photochemistry of di-μ-oxo molybdenum(V) complexes in organic solvents have been performed. For instance. the photochemistry of the following complexes have been studied in extremely dried solvents: $[(MoO\text{-}\{S_2CN(CH_3Ph)_2\}_2)_2O]$, $[N(CH_3)_4]_4[Mo_2^VO_3(NCS)_8]$, $[N(CH_2CH_3)_4]_4[Mo_2^VO_3(NCS)_8]$ and $[N(CH_3)_4]_4[Mo_2^VO_4(NCS)_6]$ and $[N(CH_3)_4]_2[Mo^VO(NCS)_5]$ [36,37].

We have studied the flash photolysis of pyridinium di-μ-oxo-bis (oxo tris (isothiocyanate) molybdate(V), $[(PyrH)_4Mo_2^VO_4(NCS)_6]$, in ethyl acetate [53]. Irradiation with light in the range from 280 to 340 nm induces the formation of an intermediate with an absorption maximum at ca. 520 nm. This intermediate decays following first order kinetics and an activation enthalpy of 58 kJ mol^{-1} and activation entropy of -30 J K^{-1} mol^{-1} at 25°C. Oxygen does not affect the observed decay. This intermediate was identified as a single bridged dimeric molybdenum(V). The bridge rupture process should increase the polar character of the activated complex, electrostriction and the introduction of solvent molecules in the coordination sphere may be responsible for the observed negative activation entropy. Traces of water is the source of hydrogen as reaction product.

4.8. Cysteine complexes of molybdenum(V)

The structure of the binuclear complex di-μ-oxo-bis (L-cysteinato)-oxomolybdate(V) ($Na_2Mo_2O_4(cys)_2$) has been extensively investigated during the last thirty years [3,7,11,14]. Alkaline solutions of this complex disproportionate to Mo^{VI} and Mo^{IV}. The Mo^{IV} complexes generated by this way act as two-electron reductants with respect to acetylene and nitrogen [68].

We have performed a flash photolysis study of this complex in the pH range from 0.5 to 6.0 [55]. Mo^{VI} and H_2 are the reaction products. The flash photolysis results can be analyzed in very acidic solutions, being rather complex the intermediate decays at pH higher than 3. The complex is rather unstable in aqueous solutions. The absorption band in the wavelength region 275–350 shifted from 325 nm at pH 6.5 to 295 nm at pH 1.3, the latter being characteristic of the $Mo_2O_4(H_2O)_6^{2+}$ complex. [55]. Therefore, cysteine molecules in acid solutions can be displaced from the coordination sphere by water molecules. The extent of this process is pH dependent.

At $pH < 2$ the decay of two intermediates is observed, one absorbing at 400 nm and the second one at 415 nm. Both intermediates decay through a first order kinetics and can be observed in two well separated time windows. This behavior suggests the existence of different substituted complex species in aqueous solutions. The transient spectrum of the intermediate absorbing at 400 nm is coincident with ($Mo_2O_3(H_2O)_7(OH)^{3+}$) being the same experimental rate constant as that obtained from the aqueous $Mo_2O_4(H_2O)_6^{2+}$ complex. The second intermediate presents a longer lifetime and its spectrum is pH dependent. This second intermediate has been identify as the cysteine single bridged μ–oxo-molybdenum (V) dimer complex $[Mo_2O_3(H_2O)_6cys]^{2+}$. Both complexes disproportionate as suggested in Scheme 1.

In the pH range 4–6, analysis of the flash photolysis results becomes rather complex [72]. The complexity of this system can be attributed to the low stability of the di-μ-oxo-bis (L-cysteine)-oxomolybdenum(V) in acidic media (pH 3–6) in the presence of dioxygen. A study performed recently in our laboratory under such conditions shows that this complex decays to molybdenum(VI). The decomposition of this complex depends on pH and $[O_2]$ [59]. The pH effect on the reaction rate indicates that acid/base equilibria are involved. The mechanism shown in the following Scheme 2 considers the dependence of k_{obs} on both the pH and $[O_2]$:

From the analysis of reaction involved in Scheme 2, the following parameters have been reported: $k_1 = 6 \times 10^{-3}$ M^{-2} s^{-1}; $k_2 = 0.19$ M^{-1} s^{-1} and $K = 1.1 \times 10^{-5}$ (pK 5.0 ± 0.2). This pK value does not correspond to the deprotonation of the molybdenum (V) moiety (pK 2) [73,74] and thus, it should be related to ligand deprotonation. The pK value kinetically determined in this work is lower than that corresponding to the sulfhydryl group of free cysteine (pK 8.33). Although the pK values of $Mo_2O_4(cyst)_2^{-2}$ are not known, the pK of the sulfhydryl group of cysteine

$$\begin{array}{l} Mo_2O_4\,(cyst)_2^{-2} \xrightarrow{O_2} \longrightarrow Mo\,(VI) \quad k_1 \\ H^+ \uparrow\downarrow \; K \\ A^{\cdot} \qquad\qquad \xrightarrow{O_2} \longrightarrow Mo\,(VI) \quad k_2 \\ O_2 + 4\,H^+ \longrightarrow 2\,H_2O \end{array}$$

Scheme 2.

coordinated to divalent transition metals is of the order of 6.30 (see Ref. [59] and the literature cited therein). The decrease of the sulfhydryl pK when cysteine is complexed allows us to assume that the equilibrium shown in Scheme 3 involves the deprotonation of the sulfhydryl group in the $Mo_2O_4(cyst)_2^{-2}$ complex as a requisite to the two- electron oxidation of $Mo_2O_4(cyst)_2^{-2}$ by molecular oxygen.

4.9. Catalytic properties of $Mo_2O_4^{2+}$

Molybdenum-based compounds are effective catalysts in many redox processes and have the capacity to induce multi-electron reduction processes.

Recently we reported the catalytic effect of the $Mo_2O_4^{2+}$ complexes in the oxidation of halides by chlorate in acid media [60,61].

$$ClO_3^- + H^+ \rightleftarrows HClO_3 \qquad \text{(fast)} \qquad \text{(I)}$$

$$HClO_3 + H^+ \rightleftarrows H_2ClO_3^+ \qquad \text{(fast)} \qquad \text{(II)}$$

$$H_2ClO_3^+ + X^- \xrightarrow{k_1} H_2O + XClO_2 \qquad \text{(rate determining)} \qquad \text{(III)}$$

$$XClO_2 \rightarrow \text{Products} \qquad \text{(fast)}$$

$$\begin{array}{ccc} Mo_2O_4(H_2O)_6^{2+} & \underset{H^+}{\rightleftarrows} & Mo_2O_4(H_2O)_5(OH)^+ \\ X^- \downarrow\uparrow & & X^- \downarrow\uparrow \\ Mo_2O_4(H_2O)_5\,X^+ & \underset{H^+}{\rightleftarrows} & Mo_2O_4(H_2O)_4X(OH) \end{array} \qquad \text{(fast)} \qquad \text{(IV)}$$

$$H_2ClO_3^+ + Mo_2O_4(H_2O)_4X(OH) \xrightarrow{k_3} H_2O + Y^+ \qquad \text{(rate determining)} \qquad \text{(V)}$$

$$OH^- + H_3O^+ \rightleftarrows 2\,H_2O \qquad \text{(fast)} \qquad \text{(VI)}$$

$$Y^+ \rightarrow \text{Products} + Mo_2O_4(H_2O)_5(OH)^+ \qquad \text{(fast)} \qquad \text{(VII)}$$

Scheme 3.

Table 2
Parameters of the rate constant for bromide and iodide oxidation by chlorate catalysed reaction by $[Mo_2O_4]^{2+}$ complexes

	Br^- ($t = 20°C$)	I^- ($t = 30°C$)
$a/M^{-3}\ s^{-1}$	3.3×10^{-4}	9.0×10^{-5}
$b/M^{-3}\ s^{-1}$	1.4	0.73

Halides are slowly oxidised by chlorate in acidic media. Extensive work has been carried out on the thermal [75–78] and photochemical [78] reactions. A mechanism was proposed a long time ago [75]. The molybdate ion, MoO_4^{2-}, as well as other catalysts, accelerate the iodide oxidation by chlorate [77,78]. We have shown that the bromide and iodide oxidation by chlorate is also accelerated in the presence of $Mo_2O_4(H_2O)_6^{2+}$ complexes. This effect was studied at different temperatures in acidic aqueous solutions by monitoring the formation of Br_3^- and I_3^- at 265 nm and 352 nm, respectively, in the temperature range from 20 to 45°C and a $pH < 2$ [60,61].

The oxidation of halides (X^-) by halates in acid solutions share common kinetic features, i.e., in the case of ClO_3^-, $v(M^{-1}\ s^{-1}) = k_o[ClO_3^-][H^+]^2[X^-]$. In the presence of Mo^V species, the initial rate maintains the general form $v(M^{-1}\ s^{-1}) = (1/3)d[X_3^-]/dt = k_{Mo}[ClO_3^-][H^+]^2[X^-]$, but now $k_{Mo} = \{a + b[Mo_2O_4^{2+}]/[H^+]\}$. Molybdenum(V) acts as a catalyst and is completely recovered after the halide oxidation by chlorate. The values for the constants a and b for Br^- and I^- are given in Table 2.

Scheme 3 describes the catalytic effect of Mo^V.

In this scheme the non catalyzed reactions are included (Reactions I–III). Two additional rate determining steps ((IV) and (V)) are now introduced. Reaction intermediate Y^+ is a complex containing $XClO_2$. Additionally, the halide atom in the intermediate Y^+ is bound to the doubly bridged molybdenum (V) structure. Complex Y^+ rapidly decomposes into products and $Mo_2O_4(H_2O)_5(OH)^+$. The equilibrium of $Mo_2O_4(H_2O)_5(OH)^+$ with the other partners (equilibrium II in Scheme 3) is also rapidly achieved.

Recently, the photoreduction of acetylene on TiO_2 using Mo_2O_4(diethyldithiocarbamate)$_2$ as a catalyst has been reported [16]. Although, earlier studies have shown that ionic compounds of Mo^{VI} (i.e. MoS_4^{2-}) are much better photoreduction catalysts than oxo ions [79], it appears that the $Mo_2O_4^{2+}$ core plays a more important role in the observed catalytic activity.

5. Other complexes of interest in the chemistry of molybdenum

Molybdenum complexes containing sulphur ligands and disulphide species as ligands have been extensively reviewed in the literature [7]. Such studies on these complexes is a relevant research field because their potential participation in biological processes and their use as industrial catalysts for hydrodesulfurization [79]. Thus, new molybdenum(II) complexes with thioetherthiolate ligands containing XS_4 donor atoms ($X = S$, O, NH) have been synthesised and their reactivity toward small molecules (CO, NO, NO^+, N_3^- and N_2) have been studied [12].

Molybenum(II) forms di- and polynuclear complexes. $Mo_2(H_2O)_n^{4+}$, $Mo_2Cl_8^{4-}$, $Mo_2Cl_8H^{3-}$ and $Mo_2Br_8^{4-}$ complexes exhibiting photoredox processes through a LMCT excited state, produce hydrogen and the oxidized complex when their acidic aqueous solutions are irradiated at 254 nm. The quantum yield is in most cases very small (i.e. values lower than 0.1 or even less have been reported) [80]. Complexes such as Mo_2^{II} $(O_2P(OC_6H_5)_2)_4$ undergo photochemical transformations when they are irradiated with visible light ($\lambda > 530$ nm) in non aqueous solutions. Formation of mixed valence Mo(II)–Mo(III)) has been reported [66].

The flash photolysis of di-μ-thio-bis(oxo-molybdenum(V)) complexes in acidic aqueous solutions were studied in our laboratory [81]. A first order kinetics was observed for the intermediate decay at the pH and temperature range studied (pH 0.1–2; $t = 25$–45°C). H_2S, H_2 and Mo^{VI} are the final products observed on the flashed solutions. Three intermediates can be observed in the millisecond time window. Two of them present a similar behaviour than that reported for other complexes described in this paper, i.e. they decay to yield Mo^{VI} and H_2 through a dimeric single bridged Mo^{V} species. The third one shows an absorption band around 510 nm. Dioxygen accelerates the reaction kinetics. Both facts strongly suggest the formation of Mo^{IV} species in this system. An estimated molar absorption coefficient $\varepsilon_{510} \approx 2400$ M^{-1} cm^{-1} is reported. This value is similar to that observed in $Mo(S_2)$ containing complexes [82]. Because sulfur-containing ligands seem to be very versatile and can be readily oxidized or reduced, it has been admitted that sulfur ligands in the bridging positions are oxidized to yield the S_2^- moiety. $Mo_2^{IV}O_2(S_2)$ complexes are produced after the flash, being these complexes precursors of the formation of Mo^{VI} and H_2. Monomeric Mo^{IV} or Mo^{V} which react very fast in acidic solutions, have not been considered as intermediates in these experiments. Such internal redox reactions are observed in several Mo–S complexes [83]. The closeness of the energy levels available to Mo^{IV}, Mo^{V} or Mo^{VI} by S or the significant bonding interaction between the two bridging sulphur atoms and the terminal oxygen atom and the charge distribution throughout the $Mo^{V}(\mu\text{-}S)_2Mo^{V}$ centre may be the possible explanation for this redox capacity observed in these compounds [83,84].

In these systems, Mo^{VI} can be present in equilibrium as molybdate, thiomolybdate and dithiomolydate. In acidic medium, $MoO_2S_2^{-2}$ suffers hydrolysis through a series of complex reactions. The sequence of reactions can be observed from some milliseconds, as can be seen in stopped flow experiments, to more than 1 h [85]. Moreover, when acidic solutions of MoO_2S_2 are stored in the dark in a closed vessel formation of $Mo^{V}(\mu\text{-}S_2)Mo^{V}$ complex can be seen after several hours. This kind of complexes can be obtained after heating alkaline solutions of thiomolydate solutions. The previous observation suggests that this process can be also induced by hydrogen ions.

Photochemical studies on $(Cp)_2Mo^{V}S_4$–$(Cp)_2Mo^{IV}S_2(S_2)$ (Cp is cyclopentadienyl) performed by irradiating with visible light showed that ligand labilization and ligand oxidation are intimately related by protonation equilibria where an internal redox process is also involved [86].

Photo-induced ligand redistribution has also been reported on quadruply bound cis-$[Mo_2Cl_2(6\text{-mhp})_2(PR_3)_2]$ (mhp = 2-hydroxy-6-methylpyridine; PR_3, phosphine derivatives, PEt_3, PMe_2Ph, $PMePh_2$) complexes.[87]. The synthesis of these electron rich d^4–d^4 core complexes has been reported. These compounds are photoactive and significant changes in the absorption spectra are detected at $\lambda > 400$ nm when irradiated at $\lambda_{exc} > 435$ nm in deoxygenated solution in DMF, benzene and THF. Photoproducts, $[Mo_2Cl_3(6\text{-mhp})(PR_3)_3]$ and $[Mo_2Cl_3(6\text{-mhp})_3(PR_3)]$, show different stabilities which depend on the solvent. Moreover, back reactions to give the starting complex have been observed in some experimental conditions.

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