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Flash-photolysis of di-μ-oxo-bis(oxomolybdate(V)) in the presence of bromide ion

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Abstract

The photolysis of aqueous acid solutions of $Mo_2O_4^{2+}$ containing bromide ion as a ligand was studied by flash-photolysis. The decay of the detected reaction intermediates follows a first order kinetics. The observed rate constant, determined at different temperatures is inversely dependent on hydrogen ion concentration and independent of bromide ion concentration. The results are interpreted in terms of a reaction mechanism which proposes the decay of the reaction intermediate $Mo_2O_3(H_2O)_7Br^{3+}$ leading to the formation of Mo(VI) and H_2, detected as reaction products. © 1997 Elsevier Science S.A.

Keywords: Flash-photolysis; Molybdenum dimers; Bromide ion

1. Introduction

The photolysis of di-μ-oxocomplexes of molybdenum (V) in aqueous solutions shows dual photoreactivity, i.e., ligand photolabilization and ligand photo-oxidation [1–5].

The photolabilization mechanism was studied by flash-photolysis of aqueous solutions of $Mo_2O_2(\mu\text{-}O)_2(H_2O)_6^{2+}$ and $Mo_2O_2(\mu\text{-}O)_2(H_2O)_mL_{6-m}^{n+}$ with $L = Cl^-$, and NCS^- [1,3,4]. The results were interpreted by proposing the decay of the single-bridged reaction intermediate $Mo_2O_2(\mu\text{-}O)(H_2O)_8^{4+}$, which is in rapid equilibrium with its basic form, $Mo_2O_2(\mu\text{-}O)(H_2O)_7(OH)^{3+}$. The molybdenum (V) intermediates disproportionate to give molybdenum (IV) and molybdenum (VI). The final products (Mo(VI) and H_2) indicate that the overall process is the oxidation of Mo(V) by water.

We here report on the effect of bromide ion as ligand on the photolabilization mechanism.

2. Materials and methods

NaBr (Mallinckrodt, analytical reagent) and $HClO_4$ (Merck, p.a.) were used without further purification. Water was distilled and passed through a Millipore system.

The ionic strength was controlled with $NaClO_4 \cdot H_2O$ (Merck, p.a.). The content of chlorate ion of perchlorate samples prepared with $NaClO_4$ purchased from different companies was checked by a colorimetric method [6]. Some of them were not suitable for the experiments since they contained appreciable amounts of $NaClO_3$, which in acid medium is reduced by Br^- through a Mo (V)-catalysed reaction [7].

Aqueous solutions of $Mo_2O_4\ (H_2O)_6^{2+}$ were prepared according to Sasaki and Sykes [8]. The concentration of the solutions was determined by measuring the absorbance at 295 nm ($\epsilon^{295} = 3546\ M^{-1}\ cm^{-1}$) [8].

UV-Vis absorption spectra were recorded on a CARY 3 computer- controlled spectrophotometer.

The flash photolysis apparatus was a Xenon Co model 720C with modified optics and electronics [3,9]. A 20 cm-long quartz cell was employed for the experiments. The analysis lamp was a halogen–tungsten Riluma PN240, 24 V, 240 W. The output of the monochromator (Bausch and Lomb, high intensity) irradiated a RCA 1P28 photomultiplier. The signal was taken by a digital oscilloscope (Leader LBO-

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5825) and stored in a personal computer. The digitized data were stored in a personal computer. The cell was carefully washed and refilled with fresh solutions after every flash. The experiments were carried out in the temperature range 20–35 °C. Most of the solutions were bubbled with N_2.

The reported first-order decay rate constants were averages of at least 10 signals obtained in the wavelength range 380–480 nm.

In order to check the effect of dissolved oxygen, the first order decay constant, k_{obs}, was determined for two different 1.9×10^{-4} M $Mo_2O_4^{2+}$ acid solutions ($[H^+]=0.5$ M) of 3 M ionic strength ($NaClO_4$) containing 0.5 M Br^- at room temperature. One of them was bubbled with N_2 and the other one with O_2. The effect of $Mo_2O_4^{2+}$ concentration on the decay kinetics of the intermediate was analysed by comparing k_{obs} for N_2-bubbled acid ($[H^+]=0.5$ M) aqueous solutions of 3M ionic strength containing 0.5 M Br^- and two different amounts of $Mo_2O_4^{2+}$ (4.8×10^{-5} M and 2.4×10^{-4} M).

The nature of the photolysis products was tested immediately after irradiating acid ($[H^+]=0.2$ M) aqueous solutions containing 0.01 M Br^- and 5×10^{-4} M $Mo_2O_4^{2+}$ of 3M ionic strength at room-temperature with a high pressure mercury lamp (Osram HBO, 100 W). Mo(VI) was detected by UV–Vis absorption spectroscopy [10] (Fig. 1). Vacuum sealed samples were employed for the analysis of H_2 by gas chromatography with a Varian Aerograph Series 1700 equipment, provided with a ionization detector and a 5A molecular sieves column at 70 °C. No other gases were detected as reaction products.

3. Results

A transient species is observed in the flash-photolysis experiments of aqueous acid solutions of $Mo_2O_4^{2+}$ in the presence of bromide ion. The decay of this transient follows a first-order rate law. This process, observed at $\lambda^{obs}=380$–480 nm, was detected in a time scale of 50 to 500 ms/division on the oscilloscope screen depending on the experimental conditions.

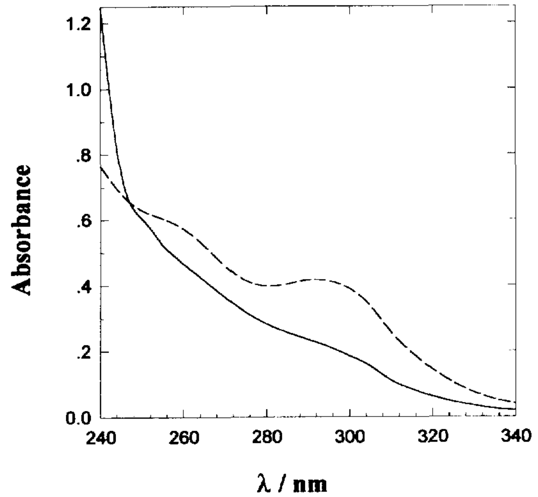


Fig. 1. Absorption spectrum at room temperature before (- - -) and after (———) irradiation of a 1×10^{-4} M $Mo_2O_4^{2+}$ acid solution ($[H^+]=0.5$ M), containing 0.01 M Br^-. The ionic strength is 3 M ($NaClO_4$).

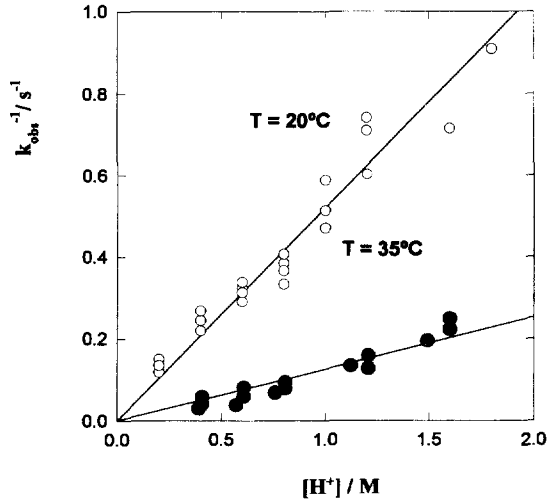


Fig. 2. Experimental dependence of k_{obs}^{-1} on $[H^+]$ for aqueous 10^{-4} M $Mo_2O_4^{2+}$ solutions of various concentrations of bromide ion and 3 M ionic strength at different temperatures, as indicated.

The first order rate constant (k_{obs}) is a function of $[H^+]$ at constant $[Br^-]$ and temperature. Linear dependence of k_{obs}^{-1} with $[H^+]$ are observed at constant temperature, as shown in Fig. 2 for 20 °C and 35 °C. The intercepts are, within the experimental error, equal to zero. Table 1 shows the slopes of these plots at different temperatures.

The slopes shown in Table 1 do not depend on the bromide ion concentration at constant temperature. The average values obtained at every temperature are also listed in Table 1. This behaviour means that k_{obs} is given by Eq. (1).

$$k_{obs}=k_{app}/[H^+] \tag{1}$$

where k_{app} is the reciprocal of the average slopes listed in Table 1.

The linear plot of ln k_{app} vs. T^{-1} is shown in Fig. 3.

From Fig. 3 an apparent activation energy $E_a=55.2\pm3.3$ kJ mol^{-1} is calculated.

The dissolution of oxygen and the concentration of $Mo_2O_4^{2+}$ (results not shown) had no effect on k_{obs}.

Table 1
Slopes of the straight lines obtained from the plots of k_{obs}^{-1} vs. $[H^+]$ at different temperatures and constant concentration of $Mo_2O_4^{2+}$ (10^{-4} M) and ionic strength (3 M)

$[Br^-]$/M	Slopes/ s M^{-1}			
	20 °C	25 °C	30 °C	35 °C
0.1	0.51	0.25	0.22	0.12
0.5	0.52	0.34	0.20	0.12
1.0	0.52	0.31	0.24	0.13
1.5	0.49	0.36	0.30	–
Average slope	0.51 ± 0.01	0.31 ± 0.06	0.24 ± 0.05	0.12 ± 0.01

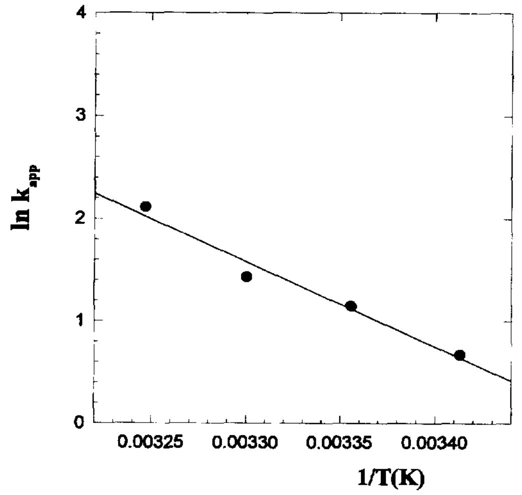


Fig. 3. Arrhenius plot for k_{app}. The plotted values are the reciprocal of the average slopes given in Table 1.

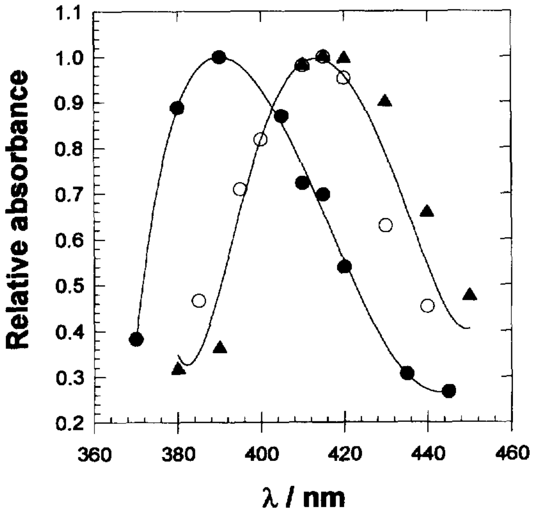


Fig. 4. Normalized absorption spectra taken immediately after the lamp pulse obtained from flash-photolysis experiments of 10^{-4} M $Mo_2O_4^{2+}$ solutions of 3 M ionic strength containing: 0.1 M Br^- and 1.5 M H^+ (●); 1.5 M Br^- and 1.5 M H^+ (○); and 1.5 M Br^- and 0.1 M H^+ (△).

The absorption spectra of the transient species, obtained immediately after the lamp pulse, under different experimental conditions are shown in Fig. 4.

The position of the absorption maximum is dependent on bromide concentration and independent of proton concentration (Fig. 4). The shift of the absorption maximum to longer wavelengths with increasing ligand concentration was observed for other ligands [3,4].

The dependence of k_{obs} on the solution ionic strength, I, (see Fig. 5) was verified for N_2-saturated 1.9×10^{-4} M $Mo_2O_4^{2+}$ acid ($[H^+]=0.5$ M) solutions containing 0.5 M Br^- at room temperature.

4. Discussion

Under our experimental conditions only one first order decay was observed for every solution, which suggests that all the transient species decay through the same reaction pathway. Our observations seem to indicate that the species $Mo_2O_3(H_2O)_6OHBr^{2+}$ is responsible for the decay, as shown in the proposed reaction mechanism which is depicted in Scheme 1.

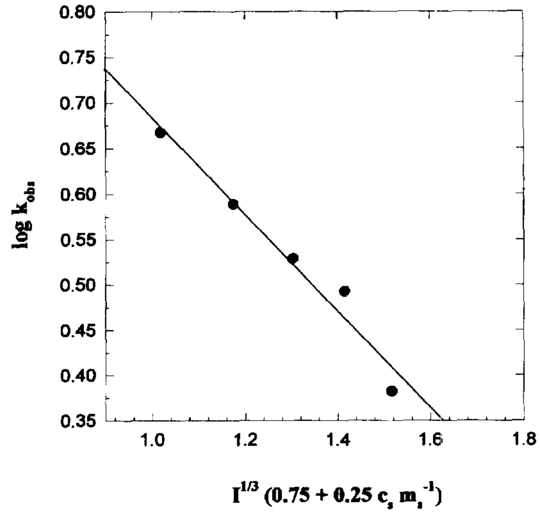
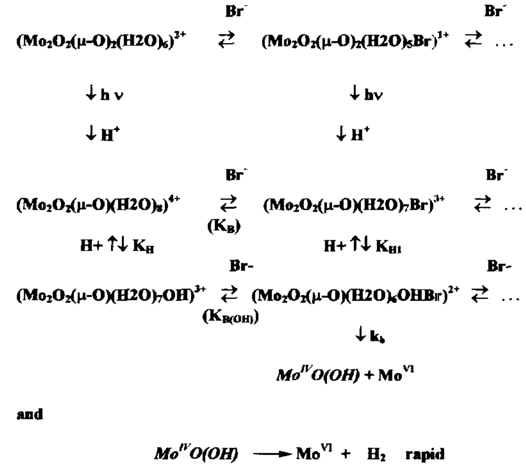


Fig. 5. Ionic strength dependence of log k_{obs} for N_2-saturated 1.9×10^{-4} M $Mo_2O_4^{2+}$ acid ($[H^+]=0.5$ M) solutions containing 0.5 M Br^- at room temperature. Molal concentrations were calculated from density data taken from Ref. [17].



Scheme 1.

If in the flash photolysis experiments, in the wavelength range from 380 to 480 nm the decay of the total concentration of reaction intermediates (represented as I) is monitored, the rate law predicted by the mechanism shown in Scheme 1 is given by Eq. (2),

$$-\mathrm{d}[I]/\mathrm{d}t = k\,[I] = k_b[Mo_2O_3(H_2O)_6OHBr^{2+}] \qquad (2)$$

where $[I] = [Mo_2O_3(H_2O)_8^{4+}] + [Mo_2O_3(H_2O)_7Br^{3+}] + [Mo_2O_3(H_2O)_7OH^{3+}] + [Mo_2O_3(H_2O)_6OHBr^{2+} + \cdots$. Although, this sum covers all species with different degree of substitution, i.e., $Mo_2O_3(H_2O)_{8-x}Br_x^{4-x}$ with $x=0$, 1, 2,

…, and their basic forms, only those shown in Scheme 1 are relevant for our analysis.

Considering that the equilibria involving species $Mo_2O_3(H_2O)_8^{4+}$, $Mo_2O_3(H_2O)_7Br^{3+}$, $Mo_2O_3(H_2O)_7OH^{3+}$, and $Mo_2O_3(H_2O)_6OHBr^{2+}$ are fast, Eq. (3) can be written.

$$-\mathrm{d}[I]/\mathrm{d}t=\frac{[Mo_2O_3(H_2O)_8^{4+}]K_{H1}}{[H^+]}k_bK_B[Br^-] \qquad (3)$$

The total concentration of reaction intermediates [I] is given by Eq. (4).

$$[I]=[Mo_2O_3(H_2O)_8^{4+}]\{1+K_H/[H^+]+[Br^-](K_B+(K_H/[H^+])K_{B(OH)}+\cdots)\} \qquad (4)$$

If Eq. (3) is multiplied and divided by [I], Eq. (5) results.

$$-\frac{\mathrm{d}[I]}{\mathrm{d}t}=[I]\frac{K_{H1}k_bK_B[Br^-]}{[H^+]\{1+K_H/[H^+]+[Br^-](K_B+(K_H/[H^+])K_{B(OH)}+\cdots)\}} \qquad (5)$$

The linear dependence of k_{obs}^{-1} on $[H^+]$ (Fig. 2) and the independence of k_{obs} on $[Br^-]$ is predicted by Eq. (5) under the following conditions:

(a) $K_B > K_C$, …, which means that only the concentration of the monobromo complexes is relevant.

(b) $[Br^-]\ (K_B+(K_H/[H^+])\ K_{B(OH)}) \gg 1+(K_H/[H^+])$, i.e., the concentration of the monobromocomplexes are much higher than those of $Mo_2O_3(H_2O)_8^{4+}$ and $Mo_2O_3(H_2O)_7OH^{3+}$.

Under these conditions, the mechanism proposed in Scheme 1 predicts Eq. (6) for k_{obs}^{-1}.

$$k_{obs}^{-1}=\frac{[H^+]}{K_{H1}k_b}+\frac{K_{B(OH)}}{k_bK_B} \qquad (6)$$

The comparison of Eqs. (1) and (6) leads us to assume that $K_{B(OH)}/k_b\,K_B < [H^+]/K_{H1}\,k_b$, which can be explained as follows:

The plot of k_{obs}^{-1} vs. $[H^+]$ (Fig. 2) had a slope of 0.30 s M^{-1} at 25 °C and a zero intercept within the experimental error. The expected value for K_{H1} can be assumed of the same order of magnitude as K_H, i.e. approx. 10^{-2} [13,14]. From this value k_b should be close to 3×10^2 s^{-1}. If we assume that, at every temperature $K_B \cong K_{B(OH)}$, then the intercepts in Fig. 2 are expected to be of the order of 10^{-3} s. This value is equal to zero within our experimental error.

The zero intercepts for the plots of k_{obs}^{-1} vs. $[H^+]$ mean that k_{obs} is proportional to K_{H1} k_b. A decrease of K_{H1} with increasing ionic strength [14] is expected which is in line with our observations for k_{obs}.

Rate constants involving ionic reactions are proportional to the activity factor $\gamma_\pm$ [15]. In media of high ionic strength ($I>1$ M), Eq. (7) was proposed for $\gamma_\pm$ [16,17].

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

with a: average ionic diameter, c_s: molal concentration of the solution, m_s: molar concentration of the solution. The negative slope of the linear plot of log k_{obs} vs. $[(I)^{1/3}(0.75+0.25\,c_s\,m_s^{-1})]$ shown in Fig. 5 further supports the proposed mechanism.

The activation energy (E_a) predicted by the mechanism shown in Scheme 1, is given by $E_a=\Delta H_1+E_{ab}$, with ΔH_1: enthalpy change for deprotonation of reaction intermediate, which can be assumed to be of the same order of magnitude as the enthalpy change for the similar reaction involving $Mo_2O_3(H_2O)_8^{4+}$ and E_{ab}: activation energy for the decay of reaction intermediate $Mo_2O_3(H_2O)_7Br^{3+}$. The experimental value for E_a (55.2 kJ mol^{-1}) is similar to that determined in the literature for the photolysis of $Mo_2O_4(H_2O)_6^{2+}$ in the presence and absence of other ligands [1,3,4]. However, in these cases the apparent activation energy was given by $\Delta H+E_a'$ (E_a': the activation energy for the decay of the aquo complex $Mo_2O_3(H_2O)_8^{4+}$), which means that $E_a' \cong E_{ab}$.

The mechanism shown in Scheme 1, which includes more than one intermediate, accounts for the observed change of the transient absorption spectra with bromide ion concentration (Fig. 4).

The observed transient spectra and the independence of k_{obs} on the presence of dissolved oxygen, suggest that the monitored intermediates are molybdenum dimers. Should the intermediates be Mo(V) or Mo(VI) oxo-monomers, oxygen would affect the reaction rate [10]. Due to their relatively long lifetimes, the observed pH-dependence of k_{obs}, and the lack of absorption bands around 700 nm [2,10,11], the intermediates could not be Mo^V-Mo^{VI} dimers. For these reasons, the reaction intermediates included in Scheme 1 should be μ-oxo bis-(oxomolybdenum(V)) (Mo_2O_3) complexes.

Similar reaction intermediates were proposed for the photolysis of $Mo_2O_4\,(H_2O)_6^{2+}$ in the absence of any other ligand [1] and in the presence of Cl^- [3] and NSC^- [4]. However, in all these cases the experimental rate-law supported the dissociation of the same intermediate, i.e., $Mo_2O_3(H_2O)_8^{4+}$.

In a previous study [5], we were able to correlate differences in electronic energy for reaction (8), ΔE_8, estimated from extended Hückel calculations, with the corresponding values for its equilibrium constant, K_8, determined from flash-photolysis experiments for $L=H_2O$ [1], NCS^- [3], and Cl^- [4].

$$L^-+Mo_2O_3(H_2O)_8^{4+} \rightleftarrows Mo_2O_3(H_2O)_7L^{3+}+H_2O \qquad (8)$$

Should that correlation be valid for $L=Br^-$, then the expected value for K_8 would be the order of 10^{15}, which supports the high stability of the monosubstituted single-bridged complex. This is in line with the postulation of the decay of $Mo_2O_3(H_2O)_7Br^{3+}$ Scheme 1, instead that of $Mo_2O_3(H_2O)_8^{4+}$, as for $L=Cl^-$ and NCS^-.

The disproportionation of single-bridged intermediates to Mo(IV) and Mo(VI) followed by rapid oxidation of the very reactive Mo(IV) monomers [12], which are not detectable within our experimental time-response, is proposed in Scheme 1.

5. Conclusions

The photolysis of aqueous acid solutions of $Mo_2O_4^{2+}$ containing bromide ion as a ligand leads to the formation of single-bridged intermediates yielding Mo(VI) and H_2 as reaction products. The rate constant for the first order decay of the intermediate, k_{obs}, is not dependent on the concentration of bromide ligand. This behaviour, which differs from that observed for Cl^- and NCS^- as ligands, is interpreted in terms of the higher stability of the monosubstituted single-bridged complexes in the case of Br^- as ligand.

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