

Oxidation of bromide by chlorate catalysed by Mo^V

L.S. Villata, D.O. Mártire, A.L. Capparelli *

Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Casilla de Correo 16, Sucursal 4, 1900, La Plata, Argentina

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Abstract

The kinetics of the catalytic effect of Mo₂O₄(H₂O)₆²⁺ on the bromide oxidation by chlorate was studied at different temperatures (22–39°C) in acid aqueous solutions under conditions of excess bromide ion by monitoring the formation of Br₃⁻ at 265 nm. The initial rate of Br₃⁻ formation at 25°C is represented by the following equation:

$$d[\text{Br}_3^-]/dt = \{1.1 \times 10^{-5}[\text{H}^+]^2 + (0.012 + 0.04[\text{H}^+])\}[\text{Br}^-][\text{ClO}_3^-]$$

where the brackets indicate molar concentrations and time is expressed in seconds. A mechanism, which includes the formation of a dimeric molybdenum complex as rate determining step, is proposed to account for the experimental results.

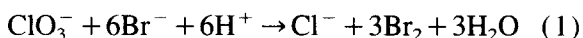
Keywords: Bromide oxidation; Chlorate; Molybdenum; Tribromide

1. Introduction

The oxidation of halides (especially bromide and chloride) may be of considerable practical importance in the commercial production of bromine and chlorine. Therefore, extensive work has been carried out on oxidations of halides in both thermal [1–5] and photochemical [6] systems.

The halate ions are often ultimately reduced to the corresponding halide ions [7]. The potentials for the conversion of halate to halide are more favorable in acid solutions and the reactions are more rapid.

The oxidation of halides by halates in acid solutions share common kinetic features [1–3]. The general rate law for the oxidation of bromide by chlorate (reaction (1))

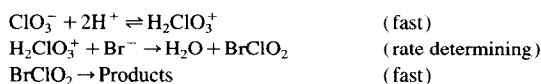


is given by:

$$v = k_o[\text{ClO}_3^-][\text{H}^+]^2[\text{Br}^-] \quad (2)$$

The proposed mechanism for the reaction involves an intermediate of the type BrClO₂ (Scheme 1) [2]. In this mechanism complex BrClO₂ decomposes rapidly after formation.

Hirade [1] found that in sulfuric or phosphoric media, secondary reactions of H₂SO₄ or H₃PO₄ with chloric acid occurred and thus, the rate law in these cases was different from that given by Eq. (2). This was not the case for the reaction in nitric acid and should not be the case for perchloric medium either.



Scheme 1.

* Corresponding author.

Molybdate ion, MoO_4^{2-} , and other catalysts accelerate the iodide oxidation by bromide [4,5]. In the present work we studied the catalytic effect of $\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6^{2+}$ ion on reaction (1).

2. Experimental

NaBr (Mallinckrodt, analytical reagent), KClO_3 (Merck, p.a.), and HClO_4 (Merck, p.a.) were used without further purification.

Aqueous solutions of $\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6^{2+}$ were prepared according to Sykes et al. [8]. Water was distilled and passed through a Millipore system. The ionic strength (3 M) was controlled with $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (Merck, p.a.).

UV–visible absorption spectra were recorded on a CARY 3 computer-controlled spectrophotometer. Spectra at different temperatures, ranging from 22 to 39°C were taken. Most experiments were carried out at room temperature (25 ± 1)°C.

Absorption spectra of several aqueous solutions containing bromide ion (0.1 to 1.5 M), chlorate ion (1×10^{-4} – 1.2×10^{-3} M), $\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6^{2+}$ (1×10^{-5} – 4×10^{-4} M) and various concentrations of HClO_4 (0.25–1.5 M) were measured at different times after mixing the reactants.

In order to study the effect of dissolved gases on the reaction rate, some of the solutions were bubbled with air, He, O_2 , CO_2 , or N_2 .

3. Results and discussion

UV–visible absorption spectra of $\text{Mo}_2\text{O}_4^{2+}$ in acid solutions show an absorption maximum at 295 nm with an $\epsilon^{295} = 3546 \text{ M}^{-1} \text{ cm}^{-1}$ [8]. These spectra are not modified upon addition of bromide in perchloric medium. If the solutions additionally contain chlorate ion, the slow appearance of a band with $\lambda^{\text{max}} = 265 \text{ nm}$ is observed. Depending on the experimental conditions, the slow increase of absorbance proceeds during a variable period of time, ranging from a few hours up to several days. Typical changes in the absorption spectrum are shown in Fig. 1.

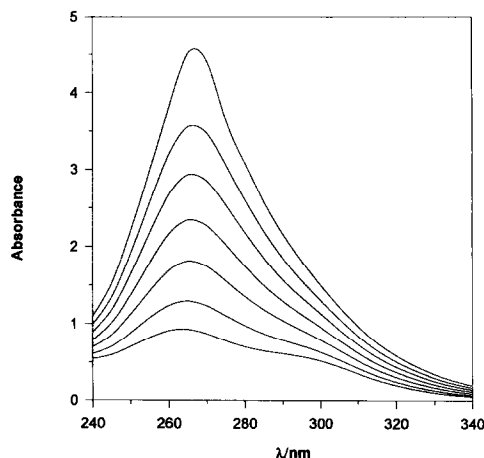


Fig. 1. Room-temperature changes in the absorption spectrum of an aqueous solution containing 0.5 M Br^- , 7.9×10^{-4} M ClO_3^- , 1.6 M H^+ , and 10^{-4} M $\text{Mo}_2\text{O}_4^{2+}$. The lowest trace shows the spectrum taken 2.5 min after mixing the reagents. The other spectra were taken at the following times: 10, 20, 30, 40, 50, and 60 min.

The slow rise of the band with maximum at $\lambda = 265 \text{ nm}$ was also observed (Fig. 1) for perchloric solutions containing chlorate and bromide ions without $\text{Mo}_2\text{O}_4^{2+}$. In this case, the rise was even slower than that observed for solutions containing $\text{Mo}_2\text{O}_4^{2+}$. The appearance of the band with maximum at 265 nm was also detected in mixtures containing bromide and chlorate ion in hydrochloric (instead of perchloric) medium and was also observed when either bromide or chlorate ions were not present. These observations indicate that the band must be assigned to a product which is slowly formed by reaction of bromide and chlorate ions in acid medium.

The behaviour shown in Fig. 1 was not observed when the solutions were bubbled with different gases (He, air, N_2 , O_2 , CO_2) immediately after mixing the reagents, as shown in Fig. 2 for He.

For air-saturated (not bubbled) solutions, the band with maximum at 265 nm disappeared after either bubbling of gases (He, air, N_2 , CO_2 , and even atmospheric air) or extraction with CH_2Cl_2 .

Should the products of reaction (1) be responsible for the absorption band with maximum at 265 nm, then this absorption band should be present in the spectra of mixtures of bromine and chloride in acid medium. However, mixtures of chloride and bromine at concentrations even

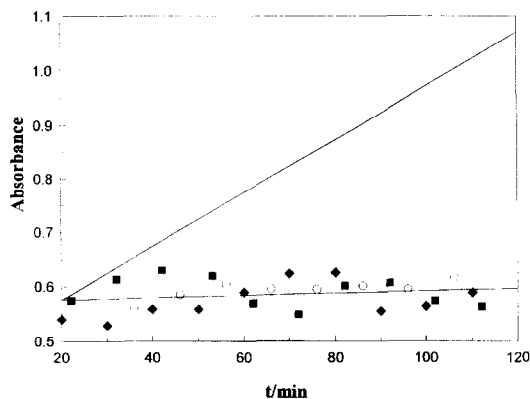


Fig. 2. Effect of bubbling different gases (■: O₂; ○: He; ◆: N₂) on the absorbance at 265 nm for an aqueous solution (0.5 M Br⁻, 1.76 × 10⁻³ M, 0.5 M H⁺, 10⁻⁴ M Mo₂O₄²⁺).

higher than those expected to be formed by reaction (1) under our experimental conditions, do not show the band with maximum at 265 nm. Thus, this band should result from the interaction of a slowly formed reaction product with one of the reactants. This hypothesis was confirmed by the appearance of the band in mixtures of bromine and bromide, either with or without Mo₂O₄²⁺. The intensity of this band did not change with time.

The formation of Br₃⁻ [9] in bromine solutions containing bromide ion (reaction (3))



with an equilibrium constant $K_3 = 17 \text{ M}^{-1}$ [10] at 25°C is well known and a band with maximum at 265 nm is characteristic of Br₃⁻. Thus, the slow growth of absorption at around 265 nm is due to formation of Br₃⁻.

The decrease of the absorption band after bubbling gases through and after extraction with CH₂Cl₂ is due to elimination of Br₂ from the solution, which shifts equilibrium (3) to the left.

In order to determine whether Mo₂O₄²⁺ is a catalyst or whether it is consumed by the reaction, the growth of the band with maximum at 265 nm was followed for an aqueous solution ([ClO₃⁻] = 1 × 10⁻³ M, [Br⁻] = 0.5 M, [Mo₂O₄²⁺] = 1 × 10⁻⁴ M, [H⁺] = 0.5 M) during 24 h. After extracting with CH₂Cl₂, the absorption spectrum of the solution in the range 280–340 nm was coincident with that of the solution taken immediately after mixing the reactants. Since

Mo₂O₄²⁺ is the only reactant that appreciably absorbs in that range, we infer that this ion is not consumed by reaction (1) and has a catalytic effect on the oxidation of bromide by chlorate in perchloric medium. Mo₂O₄²⁺ solutions were obtained by dissolving (NH₄)₂MoOCl₅ in acid medium [8] and thus, the catalytic effect on bromide oxidation could be due to chloride ion. However, no catalytic effect of chloride ion was observed for an aqueous solution ([ClO₃⁻] = 1 × 10⁻³ M, [Br⁻] = 0.5 M, [H⁺] = 0.5 M) containing NaCl at concentrations even higher than those present in a 1 × 10⁻⁴ M solution of Mo₂O₄²⁺.

Perchloric solutions containing chlorate, bromide and Mo₂O₄²⁺ show a linear increase of A²⁶⁵ (and hence, [Br₃⁻]) with time during the first hours (Fig. 2). The slopes of the linear plots of A²⁶⁵ vs. time for the first hour (k_{ob}) were determined under different experimental conditions. The effects of [Br⁻] and [ClO₃⁻] on k_{ob} for [H⁺] = 1.5 M and [Mo₂O₄²⁺] = 10⁻⁴ M are shown in Figs. 3 and 4.

The effects of [H⁺] and [Mo₂O₄²⁺] on k_{ob} were also analysed. To this purpose, k_{ob} was determined for solutions of various concentrations of Mo₂O₄²⁺ at different proton concentrations ([H⁺] = 0.25, 0.5, 0.75, and 1.0 M) for [Br⁻] = 0.5 M and [ClO₃⁻] = 1.76 × 10⁻³ M.

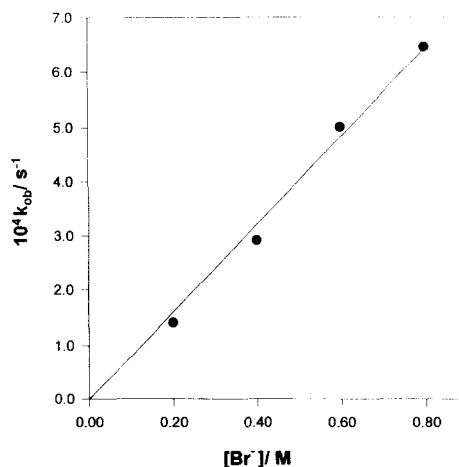


Fig. 3. Effect of bromide ion concentration on k_{ob} for a solution containing 1.5 M H⁺, 10⁻⁴ M Mo₂O₄²⁺, and 10⁻³ M ClO₃⁻.

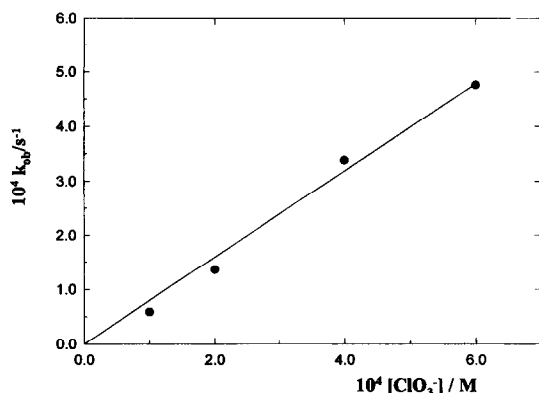


Fig. 4. Effect of chlorate ion concentration on k_{ob} for a solution containing 1.5 M H^+ , $10^{-4} \text{ M Mo}_2\text{O}_4^{2+}$, and 1.5 M Br^- .

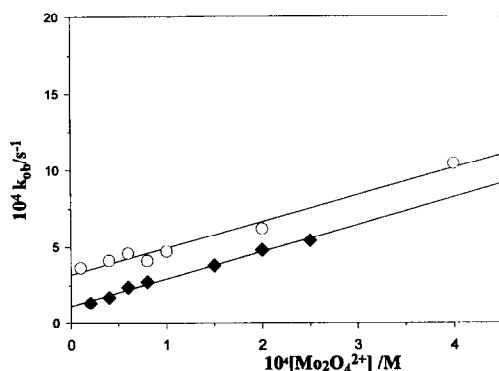


Fig. 5. Effect of $\text{Mo}_2\text{O}_4^{2+}$ concentration on k_{ob} for aqueous solutions containing $10^{-3} \text{ M ClO}_3^-$ and 0.5 M Br^- , at different HClO_4 concentrations: 0.5 M (\blacklozenge) and 1.0 M (\circ).

The linear dependence of k_{ob} on $[\text{Mo}_2\text{O}_4^{2+}]$ for $[\text{H}^+] = 0.5$ and 1.0 M is shown in Fig. 5.

All k_{ob} values obtained for $[\text{Br}^-] = 0.5 \text{ M}$ and $[\text{ClO}_3^-] = 1.76 \times 10^{-3} \text{ M}$ fit Eq. (4).

$$k_{ob} = (3.3 \pm 0.2) \times 10^{-4} [\text{H}^+]^2 + \{(0.4 \pm 0.1) + (1.4 \pm 0.2) [\text{H}^+]\} [\text{Mo}_2\text{O}_4^{2+}] \quad (4)$$

where k_{ob} is given in s^{-1} and the brackets indicate molar concentrations.

The values of k_{ob} along with those calculated with Eq. (4) (k_{ob}^{calc}) are given in Table 1.

From the proportionality of k_{ob} with both $[\text{Br}^-]$ and $[\text{ClO}_3^-]$ (see Figs. 3 and 4), Eq. (5) can be written.

$$k_{ob} = \{0.38 [\text{H}^+]^2 + (4.5 \times 10^2 + 1.6 \times 10^3 [\text{H}^+]) [\text{Mo}_2\text{O}_4^{2+}]\} [\text{Br}^-] [\text{ClO}_3^-] \quad (5)$$

Taking into account that reaction (3) is fast and that k_{ob}/ϵ^{265} ($\epsilon^{265} = 3.61 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ [11])¹ yields the rate of formation of Br_2 for the first hour, i.e., when $[\text{Br}^-]$ and $[\text{ClO}_3^-]$ can be considered constant, Eq. (6) is obtained:

$$d[\text{Br}_2]/dt = \{1.1 \times 10^{-5} [\text{H}^+]^2 + (0.012 + 0.04 [\text{H}^+]) [\text{Mo}_2\text{O}_4^{2+}]\} [\text{Br}^-] [\text{ClO}_3^-] \quad (6)$$

If the rate law for the catalysed reaction is similar to that for the uncatalysed reaction (Eq. (2)), Eq. (7) can be written.

$$v = \frac{1}{3} d[\text{Br}_2]/dt = k_{\text{Mo}} [\text{H}^+]^2 [\text{Br}^-] [\text{ClO}_3^-] \quad (7)$$

where k_{Mo} is the rate constant in the presence of $\text{Mo}_2\text{O}_4^{2+}$.

¹ A value of $\epsilon^{265} = 3.11 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ was reported for tribromide ion in aqueous solutions containing 20–25% methanol in Ref. (12).

Table 1

Room-temperature experimental and calculated values of k_{ob} for $[\text{Br}^-] = 0.5 \text{ M}$ and $[\text{ClO}_3^-] = 1.76 \times 10^{-3} \text{ M}$

$[\text{Mo}_2\text{O}_4^{2+}] \times 10^4 / \text{M}$	$[\text{H}^+] / \text{M}$	$k_{ob} \times 10^4 / \text{s}^{-1}$	$k_{ob}^{\text{calc}} \times 10^4 / \text{s}^{-1}$
4.0	1.0	10.4	10.2
3.0	1.0	8.32	8.50
2.5	1.0	7.63	7.63
2.0	1.0	7.05	6.78
1.5	1.0	5.53	5.92
1.0	1.0	4.70	5.07
0.6	1.0	4.58	4.37
0.4	1.0	4.10	4.03
0.1	1.0	3.63	3.52
2.5	0.75	4.97	5.33
2.0	0.75	4.73	4.65
1.5	0.75	4.48	3.95
4.0	0.5	5.18	5.02
4.0	0.5	4.63	5.02
3.5	0.5	4.47	4.50
3.0	0.5	4.18	3.97
2.5	0.5	3.18	3.45
2.0	0.5	3.68	2.93
1.5	0.5	2.00	2.40
1.0	0.5	1.98	1.88
0.5	0.5	1.32	1.36
0.2	0.5	1.16	1.04
4.0	0.25	3.73	3.05
3.0	0.25	2.83	2.33

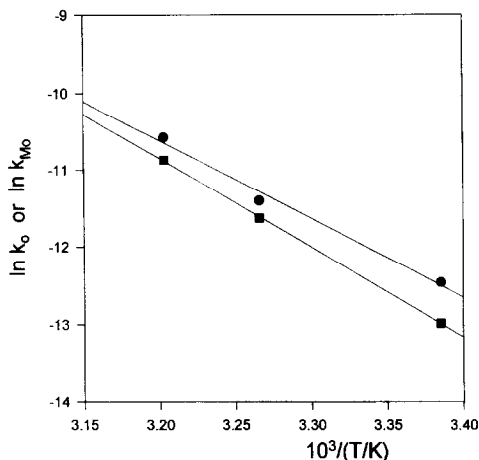


Fig. 6. Arrhenius plots for the catalysed (●) and the uncatalysed (◆) reaction.

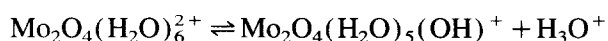
The comparison of Eqs. (6) and (7) yields Eq. (8).

$$k_{\text{Mo}} = \frac{1}{3} \{ 1.1 \times 10^{-5} + (0.012 [\text{H}^+]^{-2} + 0.04 [\text{H}^+]^{-1}) [\text{Mo}_2\text{O}_4^{2+}] \} \quad (8)$$

k_{ob} was determined at different temperatures for perchloric solutions containing bromide and chlorate ions ($[\text{Br}^-] = 1.5 \text{ M}$, $[\text{HClO}_4] = 1.5 \text{ M}$, $[\text{ClO}_3^-] = 10^{-3} \text{ M}$) with the catalyst ($[\text{Mo}_2\text{O}_4^{2+}] = 10^{-4} \text{ M}$) and without it. Rate constants k_0 and k_{Mo} were obtained from Eqs. (2) and (7), respectively. The linear plots of $\ln k_0$ and $\ln k_{\text{Mo}}$ vs. $1/T$ are shown in Fig. 6. The apparent activation energies obtained for the catalysed and uncatalysed reactions are 20.2 and 23.0 kcal/mol, respectively.

The value of k_0 obtained by us at 39°C is $1.9 \times 10^{-5} \text{ s}^{-1} \text{ M}^{-3}$ ($I = 3 \text{ M}$) which is comparable to the only available result reported by Hirade [1] ($6.4 \times 10^{-4} \text{ min}^{-1} = 1.1 \times 10^{-5} \text{ s}^{-1} \text{ M}^{-3}$ at 40°C, $I \approx 1.7 \text{ M}$). Although a decrease of k_0 with increasing ionic strength is expected [13], the magnitude of the error involved in the indirect method employed by Hirade [1] probably accounts for the opposite observed behaviour.

Di- μ -oxo-bis-(oxomolybdate(V)) presents an acid–base equilibrium (reaction (9)) in acid solutions [14,15].



The substitution of bromide ligands for molecules of coordination water at $\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6^{2+}$ occurs [12,16] in Mo^{V} acid solutions containing excess bromide. Thus, the catalyst must be a di- μ -oxo-bis-(oxomolybdate(V)) species with bromide coordinated as ligand.

We propose the mechanism shown in Scheme 2 for the bromide oxidation by chlorate in the presence of $\text{Mo}_2\text{O}_4^{2+}$.

This mechanism contains that proposed for the uncatalysed reaction (Scheme 1) [2]. Two additional rate-determining steps ((III) and (IV)) are included. Reaction intermediate X^+ is a complex with possesses a BrClO_2 moiety similar to the intermediate proposed for the uncatalysed reaction, i.e., complex BrClO_2 (Scheme 1). Additionally, the bromine atom in intermediate X^+ is bound to the double bridged molybdenum (V) structure. Complex X^+ rapidly decomposes into products and $\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_5(\text{OH})^+$. The equilibrium of $\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_5(\text{OH})^+$ with the other partners (equilibria (II) in Scheme 2) is also rapidly achieved.

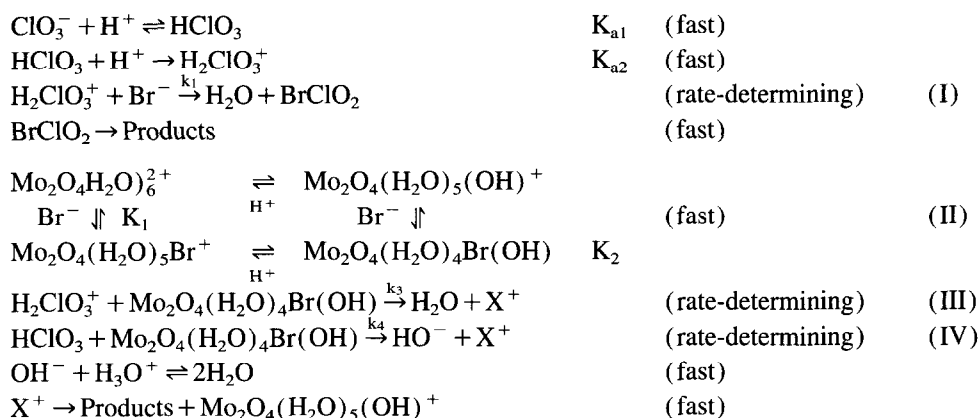
The reactivity of $\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_4\text{Br}(\text{OH})$ is proposed in Scheme 2. Several mechanisms for Mo^{V} oxidation by different agents [15,17,18] postulate the basic form of Mo^{V} dimers as reactive species. The first excited state of $\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_5(\text{OH})^+$ was postulated [19] as the precursor of the single-bridged intermediate of the photolysis of $\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_m\text{L}_{6-m}^{n+}$ [20] for $\text{L} = \text{H}_2\text{O}$, Cl^- , NSC^- .

The mechanism proposed in Scheme 2 predicts the rate law given in Eq. (10).

$$v = \frac{1}{3} \frac{d[\text{Br}_2]}{dt} = \{ k'_1 + (k'_3 [\text{H}^+]^{-1} + k'_4 [\text{H}^+]^{-2}) [\text{Mo}_2\text{O}_4^{2+}] \} [\text{Br}^-] [\text{ClO}_3^-] [\text{H}^+]^2 \quad (10)$$

where $k'_1 = k_1 \cdot K_{a1} \cdot K_{a2}$; $k'_3 = k_3 \cdot K_{a1} \cdot K_{a2} \cdot K_1 \cdot K_2$; $k'_4 = k_4 \cdot K_{a1} \cdot K_1 \cdot K_2$

The comparison of Eqs. (6) and (10) yields $k'_1 = 3.7 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$, $k'_3 = 1.3 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$, and $k'_4 = 4.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at 25°C.



Scheme 2.

The higher atomic charge on a bromine atom of a solvated bromide ion than on a bromine covalently bound to molybdenum in $\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_4\text{Br}(\text{OH})$ [19] predicts that steps (III) and (IV) are thermodynamically more favorable than step (I) (Scheme 2). This is probably the reason for the lower activation energy for the catalysed reaction ($20.2 \text{ kcal mol}^{-1}$) than for the uncatalysed reaction ($23.0 \text{ kcal mol}^{-1}$).

Linn et al. [21] studied the oxidation kinetics of $\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6^{2+}$ by chlorate ion in acid medium. It should be clear that the effect reported in the present work is not due to the reaction of Mo^V with chlorate [21] because the rate of Br_3^- (which is proportional to the oxidation rate of Br^-) was measured in all the kinetic experiments. Furthermore, should the kinetic parameters reported by Linn et al. [21] be valid under our experimental conditions, a $\text{Mo}_2\text{O}_4^{2+}$ consumption of more than 5% per hour should be observed. However, no $\text{Mo}_2\text{O}_4^{2+}$ consumption was detected by us during a much longer period of time (vide supra).

The different behaviour observed under our experimental conditions must undoubtedly be related to the presence of bromide ion. Linn et al. [21] proposed the formation of an intermediate ($\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_5\text{ClO}_3^+$) in which chlorate is coordinated to Mo, as rate-determining step of the oxidation of Mo^V by chlorate. This intermediate yields Mo^{VI} and Cl^- . A similar intermediate X^+

is proposed in Scheme 2. However, once X^+ is formed, it rapidly decomposes into products and $\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_5(\text{OH})^+$, i.e., a bromide ligand is oxidised instead of the metal, as occurs in the absence of the reductant bromide ligands [21].

4. Conclusions

The oxidation of bromide by chlorate in acid medium is catalysed by Mo^V . The rate law for the catalysed reaction is dependent on medium acidity and catalyst concentration. The results are well-fitted by a mechanism which includes the formation of a Mo^V dimeric complex as rate determining step.

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References

- [1] J. Hirade, J. Chem. Soc. Jpn., 10 (1935) 97.

- [2] J.O. Edwards, *Chem. Rev.*, 50 (1952) 455.
- [3] A.J. Downs and C.J. Adams, in A.F. Trotman-Dickenson (Ed.), *Comprehensive Inorganic Chemistry*, Vol. 2, Pergamon Press, Oxford, 1975, p. 1433.
- [4] I.M. Kolthoff and R. Belcher, *Volumetric Analysis*, Vol. III, Interscience, New York, 1957, p. 269.
- [5] A.F.M. Barton and G.A. Wright, *J. Chem. Soc. (A)*, (1968) 1747.
- [6] (a) A. Slama-Scwok, S. Gershuni, J. Rabani, H. Cohen and D. Meyerstein, *J. Phys. Chem.*, 89 (1985) 2460; (b) J. Metcalfe, *J. Chem. Soc., Faraday Trans. I*, 79 (1983) 1721; (c) H.D. Scharf and R. Weitz, *Tetrahedron*, 35 (1979) 2255.
- [7] R.C. Thompson, in A.G. Sykes (Ed.), *Advances in Inorganic and Bioinorganic Mechanisms*, Vol. 4, Academic Press, Harcourt Brace Jovanovich, London, 1986.
- [8] Y. Sasaki and A.G. Sykes, *J. Chem. Soc., Dalton Trans.*, (1974) 1468.
- [9] (a) M.S. Matheson and L.I. Grossweiner, *J. Phys. Chem.*, 61 (1957) 1089; (b) M.S. Matheson, W.A. Mulac, J.L. Weeks and J. Rabani, *J. Phys. Chem.*, 70 (1966) 2092; (c) D. Zehavi and J. Rabani, *J. Phys. Chem.*, 76 (1972) 312.
- [10] (a) M. Eigen and K. Kustin, *J. Am. Chem. Soc.*, 84 (1962) 1355; (b) R.O. Griffith, A. Mc Keown and A.G. Winn, *Trans. Faraday Soc.*, 28 (1932) 101.
- [11] P.R. Carter and N. Davidson, *J. Phys. Chem.*, 56 (1952) 877.
- [12] G.E. Meister and A. Butler, *Inorg. Chem.*, 33 (1994) 3269.
- [13] F. Basolo and R.G. Pearson, *Mechanisms of Inorganic Reactions. A Study of Metal Complexes in Solution*, John Wiley and Sons, Inc., New York, 1967.
- [14] Y. Sasaki, *Bull. Chem. Soc. Jpn.*, 50 (1974) 1939.
- [15] G.R. Cayley, R.S. Raylor, R.K. Wharton and A.G. Sykes, *Inorg. Chem.*, 16 (1977) 1377.
- [16] B. Jezowska-Trzebiatowska, M.F. Rudolf, L. Natkaniec and H. Sabat, *Inorg. Chem.*, 13 (1974) 617.
- [17] D.O. Mártire, M.R. Féliz and A.L. Capparelli, *Polyhedron*, 10 (1991) 359.
- [18] H. Diebler and C. Millan, *Polyhedron*, 5 (1986) 5539.
- [19] D.O. Mártire, L.S. Villata and A.L. Capparelli, *Polyhedron*, 13 (1994) 1411.
- [20] M.C. González, M.R. Féliz, E.A. San Román and A.L. Capparelli, *J. Photochem. Photobiol. A: Chem.*, 48 (1989) 69; (b) D.O. Mártire, M.C. González, M.R. Féliz, L. Cafferata and A.L. Capparelli, *Int. J. Chem. Kin.*, 23 (1991) 457; (c) M.R. Féliz and G. Ferraudi, *Inorg. Chem.*, 28 (1989) 4422; (d) L.S. Villata, M.C. González, M.R. Féliz, A.L. Capparelli and S. Signorella, *J. Photochem. Photobiol. A: Chem.*, 69 (1993) 277.
- [21] D.E. Linn, Jr., S.K. Ghosh and E.S. Gould, *Inorg. Chem.*, 28 (1989) 3225.