

The catalytic effect of Mo^V on the oxidation of iodide by chlorate

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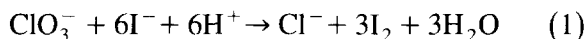
Abstract

The kinetics of the catalytic effect of Mo₂O₄(H₂O)₆²⁺ on the iodide oxidation by chlorate was studied at different temperatures (25–45°C) in Ar-saturated acid aqueous solutions under conditions of excess iodide ion by monitoring the formation of I₃⁻ at 352 nm. The initial reaction rate at 30°C is represented by the following equation: $v = 1/3 \text{ d}[I_3^-]/\text{d}t = k_{\text{Mo}}[H^+]^2[I^-][ClO_3^-]$ with $k_{\text{Mo}} = 9 \times 10^{-5} \text{ s}^{-1} \cdot \text{M}^{-3} + 0.73 \text{ s}^{-1} \cdot \text{M}^{-3} [H^+]^{-1}[\text{Mo}_2\text{O}_4^{2+}]$ 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: Catalysis; Iodide oxidation; Chlorate; Mo^V; Triiodide

1. Introduction

The oxidation of halides has been extensively studied [1–7]. The rate law for the oxidation of iodide by chlorate (Eq. (1)) [1,2].

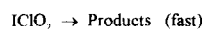
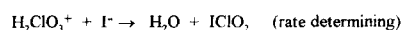
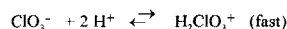


is given by:

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

The proposed mechanism considers the nucleophilic attack of I⁻ ion on the reactive intermediate H₂ClO₃⁺, the hydrated ClO₂⁺ [1,3,4] ion, which yields an intermediate of the type ICLO₂ (Scheme 1) [1]. In this mechanism complex ICLO₂ decomposes rapidly after formation.

We have recently studied the catalytic effect of Mo₂O₄(H₂O)₆²⁺ ions on the oxidation of



Scheme 1.

bromide by chlorate [8]. Molybdate ions, MoO₄²⁻, and other catalysts accelerate the iodide oxidation by bromate [9,10]. In the present work we report on the catalytic effect of Mo₂O₄(H₂O)₆²⁺ ions on Eq. (1).

2. Experimental

NaI (Mallinckrodt, analytical reagent), KClO₃ (Merck, p.a.), and HClO₄ (Merck, p.a.) were used without further purification.

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Aqueous solutions of $\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6^{2+}$ were prepared according to Sykes et al. [11]. Water was distilled and passed through a Millipore system. The ionic strength (3 M) was controlled with $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ free of chlorate ions (Merck, p.a.).

UV-visible absorption spectra were recorded on a CARY 3 computer-controlled spectrophotometer. Spectra at different temperatures, ranging from 25 to 45°C were taken. Most experiments were carried out at $30 \pm 1^\circ\text{C}$. In order to avoid the undesirable oxidation of iodide by oxygen, the solutions were carefully bubbled with Ar.

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 $\epsilon^{295} = 3546 \text{ M}^{-1} \cdot \text{cm}^{-1}$ [11]. These spectra are not modified upon addition of iodide in a perchloric medium. If the solutions additionally contain chlorate ions, the slow appearance of a band with $\lambda^{\text{max}} = 352 \text{ nm}$ is observed. Typical changes in the absorption spectrum are shown in Fig. 1.

The slow raise of the band with a maximum at $\lambda = 352 \text{ nm}$ was also observed (Fig. 1) for perchloric solutions containing chlorate and iodide ions without $\text{Mo}_2\text{O}_4^{2+}$. This observation made us assign this band to the formation of I_3^- ($\lambda^{\text{max}} = 352 \text{ nm}$; $\epsilon^{352}(\text{I}_3^-) = 26400 \text{ M}^{-1} \cdot \text{cm}^{-1}$) [2,12,13] through Eq. (3) ($K = 770 \text{ M}^{-1}$ [2,13] at 25°C).



After mixing chlorate and iodide in an acid medium, the absorbance at $\lambda = 352 \text{ nm}$ increased linearly with time for several minutes, as shown in Fig. 2. In order to study the reaction kinetics, the slope of the linear plots of A^{352} vs. time (k_{obs}) were determined under different experimental conditions.

The values of k_{obs} were found to be higher in the presence of $\text{Mo}_2\text{O}_4^{2+}$ than in the absence of

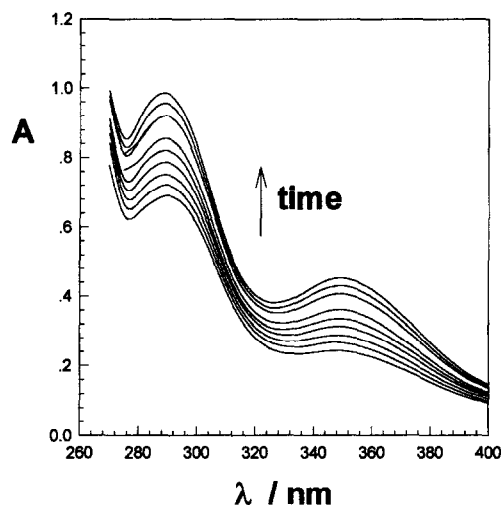


Fig. 1. UV-visible absorption spectra of an Ar-saturated acid ($[\text{H}^+] = 0.5 \text{ M}$) aqueous solution containing $10^{-4} \text{ M ClO}_3^-$, 0.2 M I^- , and $1.19 \times 10^{-4} \text{ M Mo}_2\text{O}_4^{2+}$ at 30°C.

this ion. In order to determine whether $\text{Mo}_2\text{O}_4^{2+}$ is a catalyst or whether it is consumed by the reaction, an extraction with carbon tetrachloride was done in a solution, 24 h after the reaction was started. The absorption spectrum of the solution after the extraction in the range 250–400 nm was coincident with that of the same solution taken immediately after mixing the reactants, as shown in Fig. 3. Since in the absence

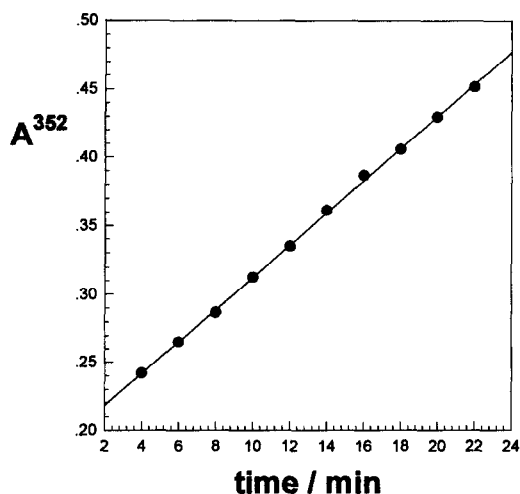


Fig. 2. Linear dependence of A^{352} on time for an acid aqueous acid ($[\text{H}^+] = 0.5 \text{ M}$) solution containing $10^{-4} \text{ M ClO}_3^-$, 0.2 M I^- , and $1.19 \times 10^{-4} \text{ M Mo}_2\text{O}_4^{2+}$ at 30°C.

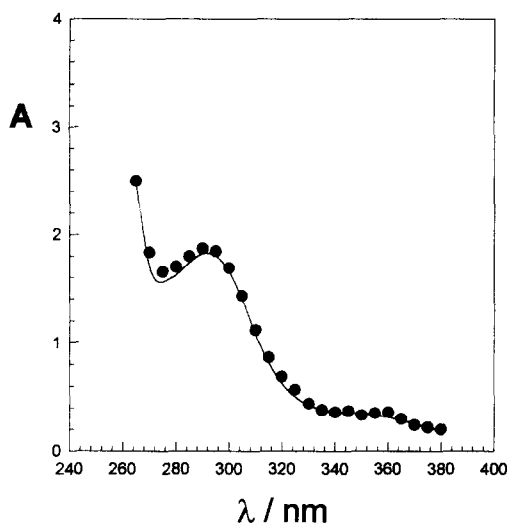


Fig. 3. UV-visible absorption spectra of an acid ($[H^+] = 0.8$ M) aqueous solution containing 1.58×10^{-4} M $Mo_2O_4^{2+}$; 10^{-4} M ClO_3^- and 0.2 M I^- under the following conditions: immediately after mixing the reactants (solid line) and after 24 h of reaction at $30^\circ C$ and iodine extraction with CCl_4 (circles).

of I_3^- the absorption in this wavelength range is mainly due to $Mo_2O_4^{2+}$, this ion is not consumed by Eq. (1) and has a catalytic effect on the oxidation of iodide by chlorate in a perchloric medium.

In order to study the effect of iodide concentration on the reaction kinetics, k_{obs} was determined for a series of Ar-saturated acid ($[H^+] = 0.5$ M) solutions containing 1.19×10^{-4} M $Mo_2O_4^{2+}$, 10^{-4} M ClO_3^- and variable amounts of iodide (in the range from 0.1 to 0.5 M) at $30^\circ C$. The linear dependence of k_{obs} on $[I^-]$ is shown in Fig. 4.

The linear effect of $[ClO_3^-]$ on k_{obs} at $30^\circ C$ is shown in Fig. 5 for acid ($[H^+] = 0.5$ M) solutions containing 1.34×10^{-4} M $Mo_2O_4^{2+}$ and 0.5 M I^- .

The effects of $[H^+]$ and $[Mo_2O_4^{2+}]$ on k_{obs} were also analyzed. To this purpose, k_{obs} was determined for solutions of various concentrations of $Mo_2O_4^{2+}$ (5×10^{-5} – 5×10^{-4} M) at different proton concentrations (0.4–1.2 M) for $[I^-] = 0.5$ M and $[ClO_3^-] = 1.0 \times 10^{-4}$ M. The linear dependence of k_{obs} on $[Mo_2O_4^{2+}]$ for $[H^+] = 0.4, 0.5$ and 1.0 M at $30^\circ C$ is shown in Fig. 6.

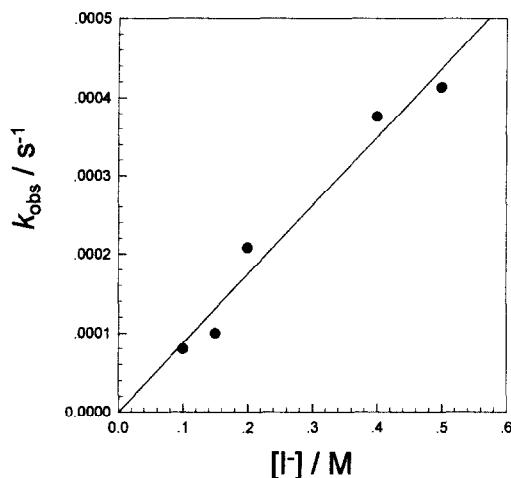


Fig. 4. Iodide ion concentration effect on k_{obs} for an Ar-saturated acid ($[H^+] = 0.5$ M) aqueous solution containing 10^{-4} M ClO_3^- , 1.19×10^{-4} M $Mo_2O_4^{2+}$ and variable amounts of iodide at $30^\circ C$.

All k_{obs} values obtained for $[I^-] = 0.5$ M and $[ClO_3^-] = 1.0 \times 10^{-4}$ M at $30^\circ C$ fit to Eq. (4).

$$k_{obs} = (3.6 \pm 0.5) \times 10^{-4} \text{ s}^{-1} \cdot \text{M}^{-2} [H^+]^2 + (2.9 \pm 0.2) \text{ s}^{-1} \cdot \text{M}^{-2} [H^+] \times [Mo_2O_4^{2+}] \quad (4)$$

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

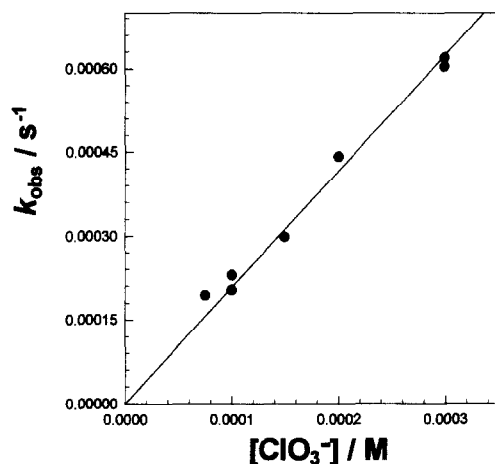


Fig. 5. Chlorate ion concentration effect on k_{obs} for an Ar-saturated acid ($[H^+] = 0.5$ M) aqueous solution containing 1.34×10^{-4} M $Mo_2O_4^{2+}$, 0.5 M I^- , and variable amounts of chlorate ion at $30^\circ C$.

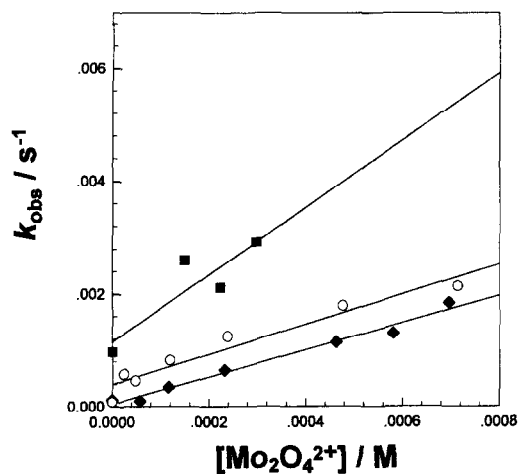


Fig. 6. Effect of $\text{Mo}_2\text{O}_4^{2+}$ on k_{obs} for different acid concentrations: 0.4 M (\blacklozenge); 0.5 M (\circ); and 1.2 M (\blacksquare).

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

$$k_{\text{obs}} = \left\{ 7.2 \text{ s}^{-1} \cdot \text{M}^{-4} [\text{H}^+]^2 + 5.8 \times 10^4 \text{ s}^{-1} \cdot \text{M}^{-4} [\text{H}^+] [\text{Mo}_2\text{O}_4^{2+}] \right\} [\text{I}^-] \times [\text{ClO}_3^-] \quad (5)$$

Table 1

Experimental and calculated values of k_{obs} at 30°C ($[\text{I}^-] = 0.5 \text{ M}$; $[\text{ClO}_3^-] = 10^{-4} \text{ M}$)

$[\text{Mo}_2\text{O}_4^{2+}]$ ($\times 10^5 \text{ M}$)	$[\text{H}^+]$ (M)	k_{exp} ($\times 10^5 \text{ s}^{-1}$)	k_{calc} ($\times 10^5 \text{ s}^{-1}$)
0.00	0.4	5.90	5.83
5.79	0.4	10.8	12.5
11.6	0.4	17.2	19.1
23.2	0.4	32.4	32.4
46.3	0.4	57.4	58.8
58.0	0.4	65.2	72.2
69.6	0.4	92.1	85.5
0.00	0.5	3.96	9.11
2.38	0.5	18.8	12.5
4.76	0.5	22.9	15.9
11.9	0.5	41.3	26.1
23.8	0.5	62.3	43.2
47.6	0.5	89.3	77.2
71.4	0.5	106.8	111.3
0.00	1.2	48.5	52.5
14.9	1.2	130.2	103.6
22.3	1.2	105.7	129.1
29.8	1.2	146.5	154.8

Taking into account that Eq. (3) is fast and that $k_{\text{obs}}/\epsilon^{352} (\text{I}_3^-)$ yields the initial rate of formation of I_2 , i.e., when $[\text{I}^-]$ and $[\text{ClO}_3^-]$ can be considered constant, Eq. (6) is obtained:

$$d[\text{I}_2]/dt = \left\{ 2.7 \times 10^{-4} [\text{H}^+]^2 + 2.2 [\text{H}^+] \times [\text{Mo}_2\text{O}_4^{2+}] \right\} [\text{I}^-] [\text{ClO}_3^-] \quad (6)$$

or

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

with k_{Mo} given by Eq. (8).

$$k_{\text{Mo}} = 9 \times 10^{-5} \text{ s}^{-1} \cdot \text{M}^{-3} + 0.73 \text{ s}^{-1} \cdot \text{M}^{-3} [\text{H}^+]^{-1} [\text{Mo}_2\text{O}_4^{2+}] \quad (8)$$

k_{obs} was determined at different temperatures for Ar-saturated perchloric solutions containing iodide and chlorate ions ($[\text{I}^-] = 0.5 \text{ M}$, $[\text{HClO}_4] = 0.5 \text{ M}$, $[\text{ClO}_3^-] = 10^{-4} \text{ M}$) with the catalyst ($[\text{Mo}_2\text{O}_4^{2+}] = 1.15 \times 10^{-4} \text{ M}$) and without it. Rate constants k_o and k_{Mo} were obtained from Eqs. (2) and (7), respectively. The linear plots of $\ln k_o$ and $\ln k_{\text{Mo}}$ vs. $1/T$ are shown in Fig. 7. The apparent activation energies obtained for

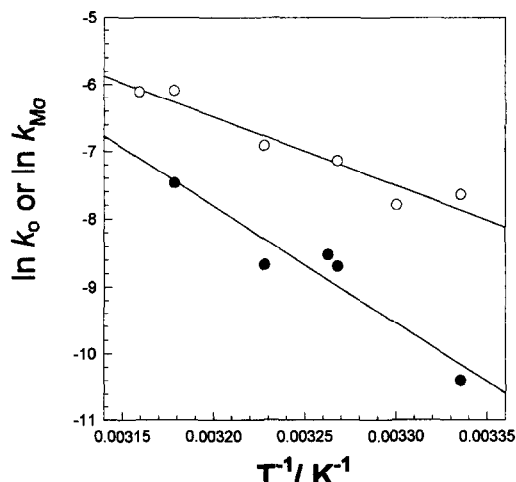
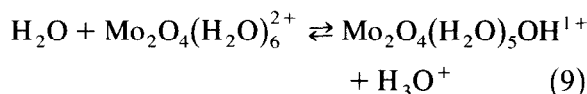


Fig. 7. Arrhenius plots for the catalyzed (\bullet) and the uncatalyzed (\circ) reaction.

the catalyzed and not catalyzed reactions are 84.9 and 144.1 kJ mol⁻¹, respectively.

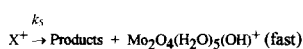
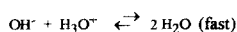
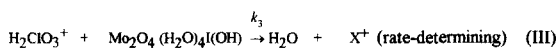
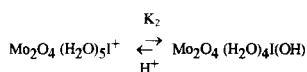
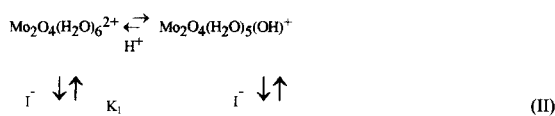
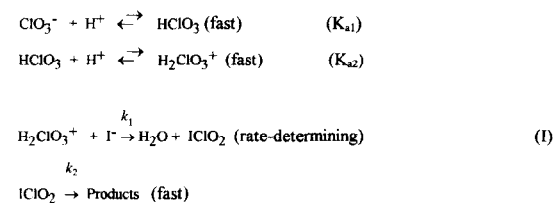
The reaction mechanism for the catalyzed reaction should consider that di- μ -oxo-bis-(oxomolybdate (V)) presents an acid–base equilibrium (Eq. (9)) in acid solutions [14,15].



We propose the mechanism shown in Scheme 2 for the iodide oxidation by chlorate in the presence of Mo₂O₄²⁺.

This mechanism contains all the reaction steps proposed for the not catalyzed reaction (Scheme 1) [1]. An additional rate-determining step is included. Reaction intermediate X⁺ is a complex which rapidly decomposes into products and Mo₂O₄(H₂O)₅(OH)⁺. The equilibrium of Mo₂O₄(H₂O)₅(OH)⁺ with the other partners (equilibria (II) in Scheme 2) is also rapidly achieved.

The reactivity of Mo₂O₄(H₂O)₄I(OH) is proposed in Scheme 2. Several mechanisms for



Scheme 2.

Mo^V oxidation by different agents [15–17] postulate the basic form of Mo^V dimers as reactive species. The first excited state of Mo₂O₄(H₂O)₅(OH)⁺ was postulated [18] as the precursor of the single-bridged intermediates of the photolysis of Mo₂O₄(H₂O)_mL_{6-m}ⁿ⁺ [19–22] for L = H₂O, Cl⁻, NSC⁻.

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

$$\begin{aligned} v &= 1/3d[\text{I}_2]/dt \\ &= \left\{ k_1 K + k_3 K K_1 K_2 [\text{H}^+]^{-1} [\text{Mo}_2\text{O}_4^{2+}] \right\} \\ &\quad \times [\text{H}^+]^2 [\text{I}^-] [\text{ClO}_3^-] \quad (10) \end{aligned}$$

with $K = K_{a1} K_{a2}$.

The comparison of Eqs. (6) and (10) yields $k_1 K = 9.0 \times 10^{-5} \text{ M}^{-3} \cdot \text{s}^{-1}$ and $k_3 K K_1 K_2 = 0.73 \text{ M}^{-3} \cdot \text{s}^{-1}$.

A similar mechanism was proposed to account for the Mo₂O₄²⁺ catalysis of the oxidation of bromide with chlorate under similar experimental conditions [8]. In that case, an additional rate determining step was included in the mechanism. However, $k_1 K$ and $k_3 K K_1 K_2$ were obtained from the kinetic analysis and the reported values were lower than those reported here for the oxidation of iodide.

Linn et al. [23] studied the oxidation kinetics of Mo₂O₄(H₂O)₆²⁺ by chlorate ions in an acid medium. Should the kinetic parameters reported by Linn et al. [23] be valid under our conditions, a Mo₂O₄(H₂O)₆²⁺ consumption of more than 5% per hour would be observed. However, no Mo₂O₄(H₂O)₆²⁺ consumption was detected by us during a much longer period of time. The different behavior observed under the present conditions was also reported in the presence of excess bromide ion [8]. Linn et al. [23] proposed the formation of the intermediate (Mo₂O₄(H₂O)₅ClO₃⁺) as rate determining step. This intermediate yields Mo^{VI} and Cl⁻. A similar intermediate (X⁺) is proposed in Scheme 2 and in the Mo^V catalysis of bromide oxidation by chlorate. However, in these systems 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., the halide ligand is oxidized instead of the metal, as occurs in the absence of halides.

4. Conclusions

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

Acknowledgements

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