The Reduction of Tris(Benzene-1,2-Dithiolate) Molybdenum(VI) by Water. A Functional Mo-Hydroxylase Analogue System

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Supporting Information

Kinetic Measurements

The preparation of $Mo^{VI}(S_2C_6H_4)_3$ complex has been previously reported.[1] Only recrystallized samples of complex were used for kinetic measurements. Tetrahydrofurane was dried at reflux over CaH_2, and water of low conductivity was bi-distilled prior to use. Stock reactive solutions were prepared under Ar. All kinetic runs were performed in 0.025 M $n-bu_4NClO_4$ to held the ionic strength constant. To purge buffers and $n-bu_4NClO_4$ solutions of O_2(g) which could oxidize reduced complexes, these solutions were degassed (by vacuumm for 30 min), and then saturated with Ar(g) (by bubbling for 30 min).

Absorbance data were collected by using a SF-300 stopped-flow (from Biokine) equipped with a millisecond diode array detector, and working under strictly anaerobic conditions. Reaction mixtures of appropriate concentration were prepared *in situ* by using the mixer facilities given by the SF-300 apparatus, preventing the reaction mixtures to be contaminated by oxygen.

Analysis of Dioxygen: Apparatus and Procedures

A Hewlett Packard 6890 gas chromatograph equipped with a thermal conductivity detector (TCD) and two columns in series (a 183 cm × 0.32 cm stainless steel Prue-column Arawak, 80-100, mesh conditioned and a 15 m × 0.53 mm column packed with molecular sieve 5 Å HP 19095P-MS5) was used to separate permanent gases (H_2, O_2, N_2, CO_2, CO) and light hydrocarbons. High-purity argon (99.9995%) was used as carrier gas flowing at 7.0 mL/min. The temperature of the detector block (TCD), front inlet, and fournace were mantained to 250°C, 120°C, and 30°C respectively during analyses. A calibration of the peak area *vs.* volume of O_2 injected was prepared by injecting known volumes of air into the chromatograph.

Chlorobenzene (2mL), methanol (18 mL), and $Mo^{VI}(S_2C_6H_4)_3$ complex (5-15 mg) were introduced into a 50 mL Schlenk tube containing a magnetic stirring bar and sealed with a rubber septum. This mixture was degassed via 5 freeze/pump/thaw cycles and infused with Argon. Five mL of an aqueous solution of phosphate (pH =6.0) were injected into the reaction tube via a syringe while the above complex solution complex was still frozen, and 2 additional freeze/pump/thaw cycles were performed. At this time, the reaction tube was submerged in a water bath preheated to 40°C. After approximately two hours, the reaction mixture became olive-green. The solution was then stirred at 60°C for an additional hour to ensure complete O_2 evolution.

Calculation of concentration time curves and the reaction rates

Absorbance data for the systems $Mo^{VI}(S_2C_6H_4)_3$ /H_2O and $Mo^{VI}(S_2C_6H_4)_3$ /H_2O/PPh_3 were analyzed by finding the time concentration curves of complexes $Mo^{VI}(S_2C_6H_4)_3$ and $Mo^{V}(S_2C_6H_4)_3^-$. These curves were obtained using GSSKIN[a] algorithm which is based on the widely accepted principles of Global[3] and Factor analysis.[4] Absorbance surfaces $\mathbf{A}(\lambda, t)$, of the type shown in Figure (1) in the manuscript were decomposed into their components: the optical density matrix $\epsilon(\lambda, n)$, and the concentration matrix $\mathbf{C}(n, t)$, which are related by the Lambert-Beer law, see equation (1).[b] The decomposition was carried

[a]GSSKIN is a free C++ Linux based software distributed under GNU license under request. It is based in algorithms similar to those employed by some popular commercial programs as SPECFIT [2]

[b]THe symbol ˜ denotes the transpose matrix. $n = 2$ is the number of absorbing species.

out by minimizing the least-squares function ϕ eq.(2), from which the ϵ linear variables were removed previously according to Global Analysis principles.

$$\mathbf{A} = \epsilon\mathbf{C} \rightarrow \epsilon = \mathbf{A}\tilde{\mathbf{C}}(\mathbf{C}\tilde{\mathbf{C}})^{-1} = \mathbf{A}\mathbf{C}^{+} \tag{1}$$

$$\phi = \sum_{\lambda}\sum_{t} r^2_{\lambda,t}, \quad r_{ij} \in \mathbf{R} = \mathbf{A} - \mathbf{A}\mathbf{C}^{+} \tag{2}$$

The optical density spectra are shown in Figure (1), and Figure (2) displays the corresponding time concentration curves. The satisfactory conformance between the observed and calculated time dependence of absorbance is illustrated in Figure (3).

The reaction rate was calculated applaying the differentiation method of Ridders[5] to the concentration time curves in Figure (2) smoothed by natural cubic splines[6]. Figure (4) illustrates the rate *vs.* time curve calculated from the $[\mathrm{Mo^{VI}(S_2C_6H_4)_3}]$ *vs.* time curve from Figure (2).

Derivation of the rate law for the raction of $\mathrm{Mo^{VI}(S_2C_6H_4)_3}$ with water

The Scheme (2) shown in the manuscript can be conveniently represented as:

$$\mathrm{M^{VI}L_3 + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M^{VI}L_3(OH_2)}$$
$$\mathrm{M^{VI}L_3(OH_2) + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} M^{VI}L_3OH^- + H_3O^+}$$
$$\mathrm{M^{VI}L_3OH^- + 2H_2O \xrightarrow{k_3} M^{IV}L_3O_2H_2^{2-} + H_3O^+}$$
$$\mathrm{M^{IV}L_3O_2H_2^{2-} + M^{VI}L_3 \xrightarrow{k_4} M^{V}L_3O_2H_2^{-} + M^{V}L_3^{-}}$$
$$\mathrm{M^{V}L_3O_2H_2^{-} + M^{VI}L_3 + 2H_2O \xrightarrow{k_5} M^{IV}L_3^{2-} + M^{V}L_3^{-} + O_2 + 2H_3O^+}$$
$$\mathrm{M^{IV}L_3^{2-} + M^{VI}L_3 \xrightarrow{k_6} 2M^{V}L_3^{-}}$$

Scheme A.

where M=Mo and L=$\mathrm{S_2C_6H_4^{2-}}$. Since the above spectral analysis indicates that no absorbing intermediates are formed in appreciable quantities, we have applied the steady-state hypotheses to all intermediate species appearing in Scheme (A), see equations (3-7),

$$\frac{d[\mathrm{M^{VI}L_3(OH_2)}]}{dt} = k_1[\mathrm{M^{VI}L_3}][\mathrm{H_2O}] - (k_{-1} + k_2[\mathrm{H_2O}])[\mathrm{M^{VI}L_3(OH_2)}] + k_{-2}[\mathrm{H_3O^+}][\mathrm{M^{VI}L_3OH^-}] \approx 0 \tag{3}$$

$$\frac{d[\mathrm{M^{VI}L_3OH^-}]}{dt} = k_2[\mathrm{H_2O}][\mathrm{M^{VI}L_3(OH_2)}] - (k_{-2}[\mathrm{H_3O^+}] + k_3[\mathrm{H_2O}])[\mathrm{M^{VI}L_3OH^-}] \approx 0 \tag{4}$$

$$\frac{d[\mathrm{M^{IV}L_3O_2H_2^{2-}}]}{dt} = k_3[\mathrm{M^{VI}L_3OH^-}][\mathrm{H_2O}] - k_4[\mathrm{M^{IV}L_3O_2H_2^{2-}}][\mathrm{M^{VI}L_3}] \approx 0 \tag{5}$$

$$\frac{d[\mathrm{M^{V}L_3O_2H_2^{-}}]}{dt} = k_4[\mathrm{M^{IV}L_3O_2H_2^{2-}}][\mathrm{M^{VI}L_3}] - k_5[\mathrm{M^{V}L_3O_2H_2^{-}}][\mathrm{M^{VI}L_3}] \approx 0 \tag{6}$$

$$\frac{d[\mathrm{M^{IV}L_3^{2-}}]}{dt} = k_5[\mathrm{M^{V}L_3O_2H_2^{-}}][\mathrm{M^{VI}L_3}] - k_6[\mathrm{M^{VI}L_3}][\mathrm{M^{IV}L_3^{2-}}] \approx 0 \tag{7}$$

The reaction rate is then given by the following expression,

$$r = \frac{1}{4}\frac{d[\mathrm{M^{V}L_3^{-}}]}{dt} = k_3[\mathrm{M^{VI}L_3OH^-}][\mathrm{H_2O}] = \frac{k_1k_2k_3[\mathrm{H_2O}]^3[\mathrm{M^{VI}L_3}]}{k_{-1}k_{-2}[\mathrm{H_3O^+}] + k_3(k_{-1} + k_2[\mathrm{H_2O}])[\mathrm{H_2O}]} \tag{8}$$

The pH dependent component in the denominator of equation (8) is related to the protonation and water decooordination of the $M^{VI}L_3OH^-$ intermediate, whereas the pH independent component represent the attack by a water molecule. The magnitude of the former quantity is dominant because experimental data in Figure (5) indicate that reaction rate is proportional to the $[Mo^{VI}(S_2C_6H_4)_3]/[Mo^{V}(S_2C_6H_4)_3^-]$ quotient, which is equal to $[Mo^{VI}(S_2C_6H_4)_3]/[H_3O^+]$ since $[Mo^{V}(S_2C_6H_4)_3^-] = [H_3O^+]$ according to the charge balance. Therefore, the equation (8) reduces to equation (9).

$$r \approx k_3 K_1 K_2 [H_2O]^3 \frac{[M^{VI}L_3]}{[H_3O^+]},\ K_1 = \frac{k_1}{k_{-1}},\ K_2 = \frac{k_2}{k_{-2}} \tag{9}$$

Derivation of the rate law for the reaction of $Mo^{VI}(S_2C_6H_4)_3$ with PPh_3 and water in buffered media

Scheme (1) in the manuscript is modified to Scheme (B) when phosphine and buffer (HB, B^-) are present in the reaction media,

$$M^{VI}L_3 + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M^{VI}L_3(OH_2)$$

$$M^{VI}L_3(OH_2) + B^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} M^{VI}L_3OH^- + HB$$

$$M^{VI}L_3OH^- + PPh_3 + H_2O \xrightarrow{k_3'} M^{IV}L_3^{2-} + OPPh_3 + H_3O^+$$

$$M^{IV}L_3^{2-} + M^{VI}L_3 \xrightarrow{k_4} 2M^{V}L_3^-$$

Scheme B.

The steady-state expressions coming out from Scheme (2) are,

$$\frac{d[M^{VI}L_3(OH_2)]}{dt} = k_1[M^{VI}L_3][H_2O] - (k_{-1} + k_2[B^-])[M^{VI}L_3(OH_2)] + k_{-2}[HB][M^{VI}L_3OH^-] \approx 0 \tag{10}$$

$$\frac{d[M^{VI}L_3OH^-]}{dt} = k_2[B^-][M^{VI}L_3(OH_2)] - (k_{-2}[HB] + k_3'[PPh_3])[M^{VI}L_3OH^-] \approx 0 \tag{11}$$

$$\frac{d[M^{IV}L_3^{2-}]}{dt} = k_3'[PPh_3][M^{VI}L_3OH^-] - k_4[M^{VI}L_3][M^{IV}L_3^{2-}] \approx 0 \tag{12}$$

The rate law (13) was obtained by solving the equation system (10-12) considering that $[HB]/[B^-] = [H_3O^+]/K_{HB}$, the K_{HB} representing the equilibrium dissociation constant of HB.

$$r = \frac{k_1 k_2 k_3' [H_2O][B^-][M^{VI}L_3][PPh_3]}{k_{-1}k_{-2}[HB] + k_3'(k_{-1} + k_2[B^-])[PPh_3]} = \frac{k_1 k_2 k_3' K_{HB}[H_2O][M^{VI}L_3][PPh_3]}{k_{-1}k_{-2}[H_3O^+] + k_3' K_{HB}(k_{-1}/[B^-] + k_2)[PPh_3]} \tag{13}$$

The apparent rate constant deduced was given by equation (14),

$$k_{obs} = \frac{k_1 k_2 k_3' K_{HB}[H_2O][PPh_3]}{k_{-1}k_{-2}[H_3O^+] + k_3' K_{HB}(k_{-1}/[B^-] + k_2)[PPh_3]} \tag{14}$$

Reaction of $Mo^{V}(S_2C_6H_4)_3^-$ with dioxygen

The $Mo^{V}(S_2C_6H_4)_3^-$ complex can be oxidized slowly by air ($k_{obs} < 10^{-4}s^{-1}$, neutral media, room temperature, air satured solution) to regenerate $Mo^{VI}(S_2C_6H_4)_3$ without appreciable decomposition. Figure (6) illustrates the spectrophotometric course of this reaction under more forcing conditions (pH =1.4 in air satured THF:water medium (11.1 M) at 34°C).

Figures

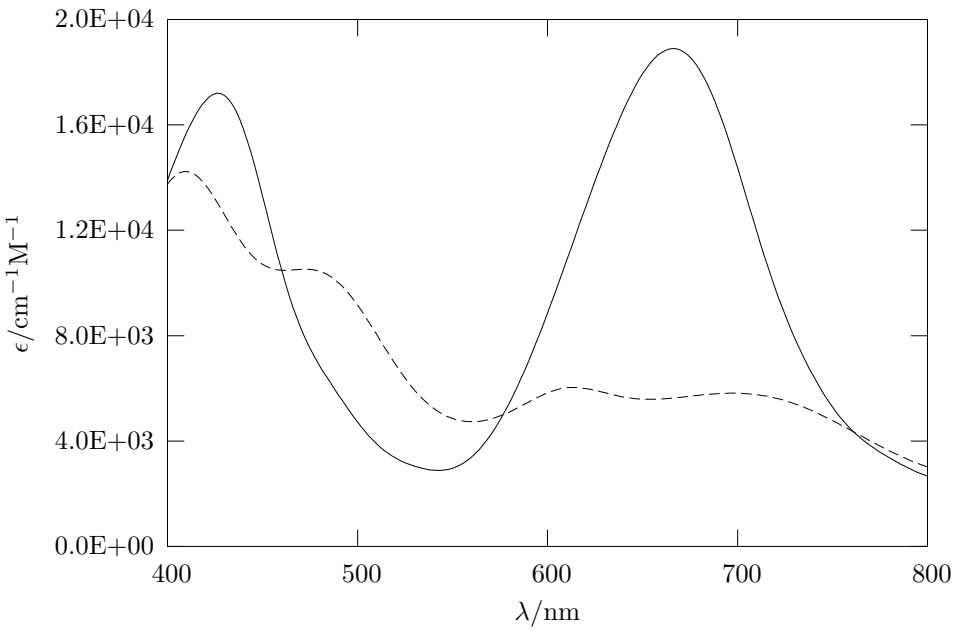

Figure 1: Optical density spectra for $Mo^{VI}(S_2C_6H_4)_3$ (solid line) and $Mo^{V}(S_2C_6H_4)_3^-$ (dashed line) obtained from the analysis of the absorbance data shown in Figure (4).

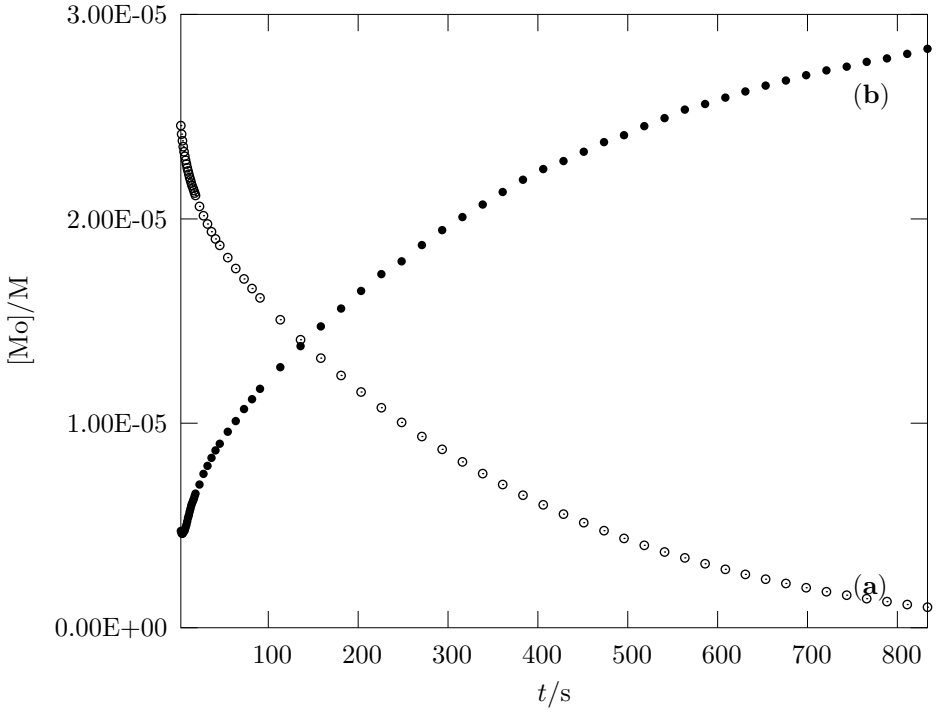

Figure 2: Variation with time of $[Mo^{VI}(S_2C_6H_4)_3]$ (**a**) and $[Mo^{V}(S_2C_6H_4)_3^-]$ (**b**) obtained from the analysis of the absorbance data shown in Figure (3).

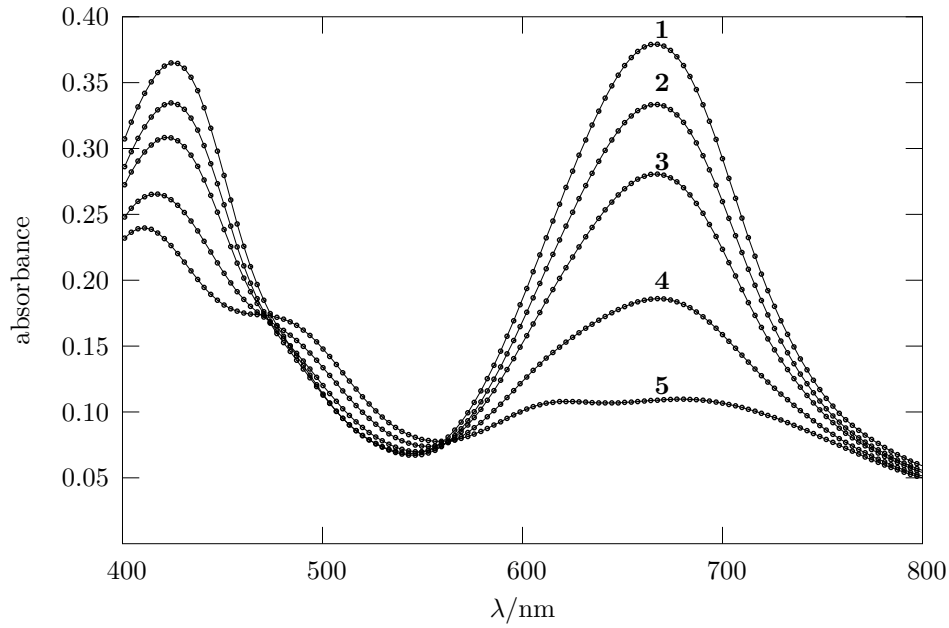

Figure 3: Measured absorbance (symbols), and calculated absorbance (solid line) obtained from the spectral analysis procedure: **1** $t = 2.7$s, **2** $t = 18.9$s, **3** $t = 81.2$s, **4** $t = 293$s, and **5** 743s. $[\mathrm{Mo^{VI}(S_2C_6H_4)_3}\ ] = 2.82 \times 10^{-5}$ M. $[\mathrm{H_2O}] = 7.9$ M. $[n - \mathrm{bu_4NClO_4}] = 0.04$ M. $T = 22.3^{\circ}$C.

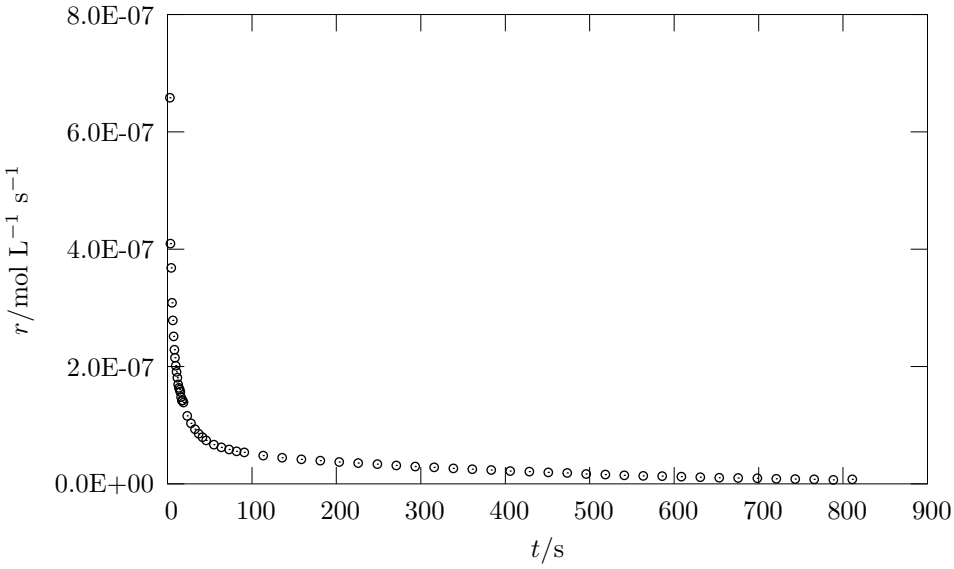

Figure 4: Variation with time of the reaction rate ($r = -d[\mathrm{Mo^{VI}(S_2C_6H_4)_3}\ ]/dt$) obtained differentiating the $[\mathrm{Mo^{VI}(S_2C_6H_4)_3}\ ]$ data in Figure (2).

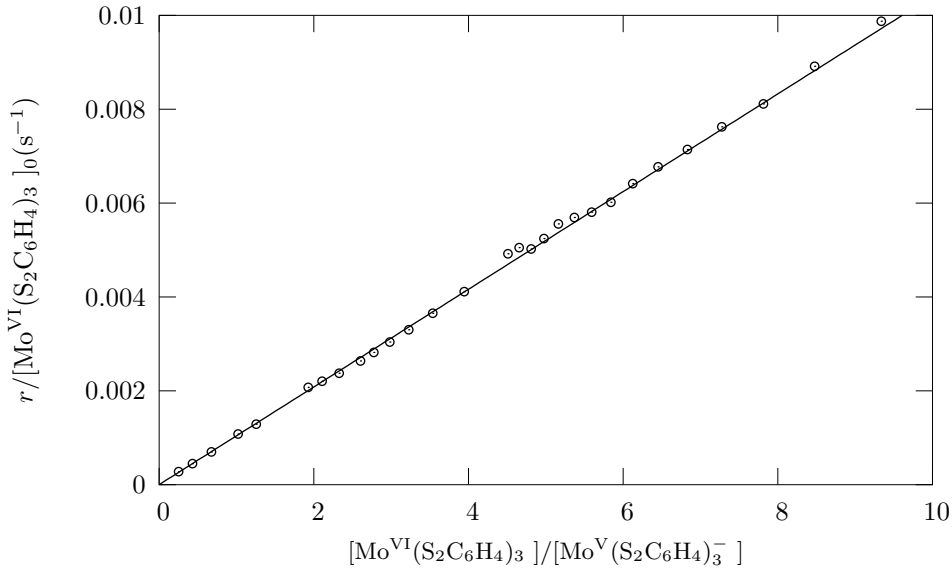

Figure 5: Variation of $r/[Mo^{VI}(S_2C_6H_4)_3\ ]_{t=0}$ with the quotient $[Mo^{VI}(S_2C_6H_4)_3\ ]/[Mo^{V}(S_2C_6H_4)_3^-\ ]$ for the rate values given in Figure (**??**), and the concentration values shown in Figure (2)

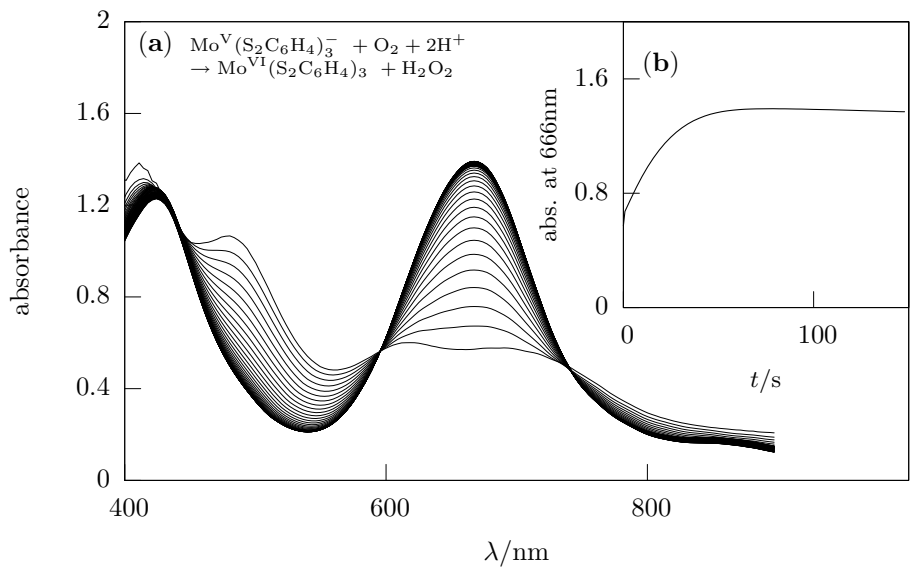

Figure 6: (**a**) Changes of spectra for the reaction between $Mo^{V}(S_2C_6H_4)_3^-$ and O_2 in THF : water (11.1 M) media at pH =1.4. $[Mo^{V}(S_2C_6H_4)_3^-\ ] = 6.6 \times 10^{-5}$ M; $T = 21.3^{o}$C. (**b**) Change of absorbance with time at 666 nm.

References

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