

Research Letter

Kinetic and Mechanistic Study of the Reduction of Chromium(VI) by Lactic Acid

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The kinetics and mechanism of the reduction of chromium(VI) by lactic acid (Lac) in aqueous acidic medium was studied with spectrophotometry in a temperature range of 298.15 K~313.15 K. Under the conditions of the pseudo-first order ($[\text{Lac}]_0 \gg [\text{Cr(VI)}]_0$), the observed rate constant (k_{obs}) increased with the increase in $[\text{Lac}]$ and $[\text{H}^+]$. There is no salt effect. Based on the experimental results, a probable reaction mechanism of oxidation was proposed. The rate equation derived from the mechanism could explain all the experimental phenomena. Activation parameters along with rate constant of the rate-determining step have been evaluated.

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1. Introduction

Lactic acid is widely used in medications, foods, agriculture, industry, and so forth. It is a fine pH regulator and has an importance physiological function. Lactic acid can be used to prepare degradable plastics and agroplastic film [1], which can reduce soil and water pollution.

Chromium exists usually in both trivalent and hexavalent forms in aqueous systems. However, these two oxidation states are characterized by markedly different physical/chemical behavior and toxicity. Cr(III) is readily precipitated or absorbed on a variety of inorganic and organic surfaces at near neutral pH [2, 3]. Cr(III), as an essential trace metal nutrient, also improves lipid profile and glucose tolerance by increasing the level of high density lipoprotein cholesterol and decreasing total serum cholesterol [4]. In contrast, the hexavalent form is of prime concern because of its high toxicity. Cr(VI) usually occurs as the highly soluble anion. The main sources of chromium pollution are mining, leather tanning, cement industries, electro plating, production of steel and other metal alloys, photographic material, and corrosive paints [5–7]. The hexavalent form of chromium has been demonstrated to be associated with the toxic parameters and classified as human carcinogen and mutagen [8]. Breathing high levels of hexavalent chromium can damage and irritate nose, lungs,

stomach, and intestine [9–11]. At present, there have been some researches regarding this type of reaction system [12, 13], while thorough research is essential for understanding its role in the oxidation of some organic compounds. The objectives of this research were to evaluate the kinetics of chromate reduction by lactic acid and investigate their redox mechanisms.

2. Experimental

2.1. Reagents and Apparatus

All chemicals used were of AR grade, and doubly distilled water was used throughout the work. NaClO_4 and HClO_4 were used to adjust ionic strength and acidity of the reaction, respectively. The study was performed with a TU-1900 UV-Vis spectrophotometer fitted with a 501-thermostat (± 0.1 K, Shanghai).

2.2. Kinetic Measurements and Product Analysis

Under pseudo-first-order condition ($[\text{Lac}]_0 \gg [\text{Cr(VI)}]_0$), the reaction was initiated by mixing the Cr(VI) to lactic acid solution, and the kinetics was followed at 350 nm by

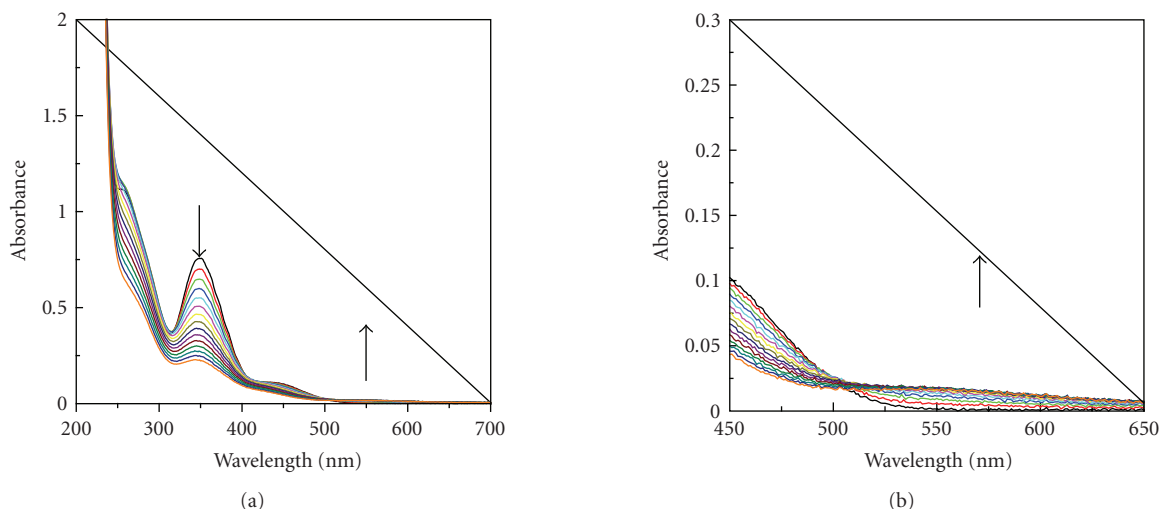


FIGURE 1: Spectra changes during the reduction of Cr(VI) by lactic acid at 298.15 K. $[\text{Cr(VI)}] = 2.5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[\text{Lac}] = 0.10 \text{ mol}\cdot\text{L}^{-1}$, $[\text{HClO}_4] = 0.50 \text{ mol}\cdot\text{L}^{-1}$, $[\text{DMSO}] = 0.20 \text{ mol}\cdot\text{L}^{-1}$, $\Delta t = 150$ seconds.

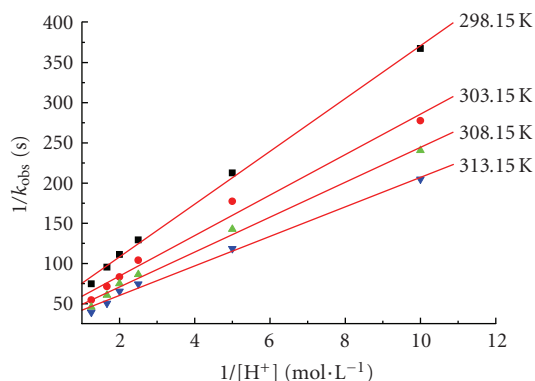


FIGURE 2: Plots of $1/k_{\text{obs}}$ versus $1/[\text{H}^+]$. $[\text{Cr(VI)}] = 2.5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[\text{Lac}] = 0.50 \text{ mol}\cdot\text{L}^{-1}$, $[\text{DMSO}] = 0.20 \text{ mol}\cdot\text{L}^{-1}$, $I = 1.0 \text{ mol}\cdot\text{L}^{-1}$.

monitoring decrease in absorbance due to Cr(VI) (Figure 1). The pseudo-first-order rate constants, k_{obs} , were obtained as in the previous work [14]. The way for product analysis was similar to previous study [15], and the product was identified as the pyruvic acid and Cr(III) [16, 17].

3. Results and Discussions

3.1. Rate Dependence on $[\text{H}^+]$

It was observed that the rate constants increased by increasing $[\text{H}^+]$, and the plots of $1/k_{\text{obs}}$ versus $1/[\text{H}^+]$ are linear with positive intercept (Figure 2).

3.2. Rate Dependence on $[\text{Lac}]$

The influence of lactic acid on the rate of reaction was studied at different temperatures. The plots of k_{obs} versus $[\text{Lac}]$ are straight lines which pass the grid origin (Figure 3).

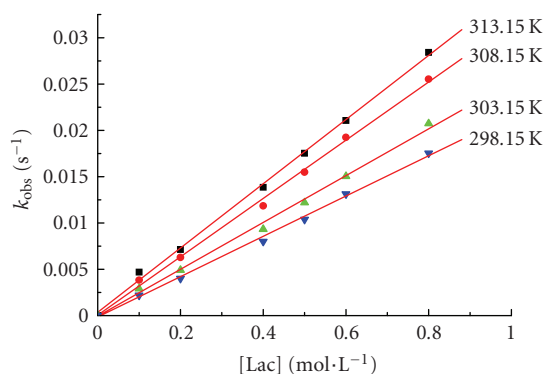


FIGURE 3: Plots of k_{obs} versus $[\text{Lac}]$. $[\text{Cr(VI)}] = 2.5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[\text{HClO}_4] = 0.50 \text{ mol}\cdot\text{L}^{-1}$, $[\text{DMSO}] = 0.20 \text{ mol}\cdot\text{L}^{-1}$, $I = 1.0 \text{ mol}\cdot\text{L}^{-1}$.

3.3. Effect of Solvent and Ionic Strength (I)

The addition of solvent DMSO accelerates the rate of reduction of Cr(VI) by lactic acid. When no catalyst or high concentration of acid exists, the oxidation of DMSO is slow so it can be ignored [18–20]. The increase of ionic strength of the reaction almost has no impact on the rate of reaction, indicating that there is no salt effect (Table 1).

3.4. Mechanism

The chromic acid also participates in acid-base equilibrium as follows [21]:

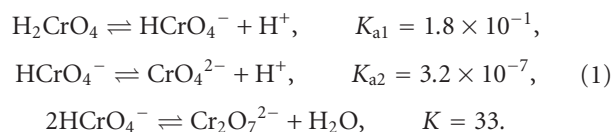
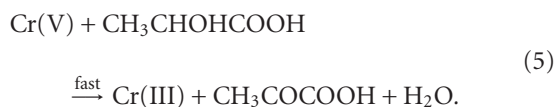
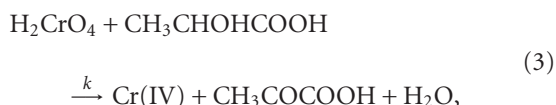


TABLE 1: Effects of [DMSO] and ionic strength on k_{obs} at 298.15 K.

[DMSO]/mol·L ⁻¹	0.050	0.10	0.20	0.30	0.40	0.50
$10^3 k_{\text{obs}}/\text{s}^{-1}$	4.908	5.927	6.466	7.381	7.894	8.328
$I/\text{mol} \cdot \text{L}^{-1}$	0.60	0.80	1.0	1.1	1.2	—
$10^3 k_{\text{obs}}/\text{s}^{-1}$	5.616	5.789	5.790	5.628	6.020	—

[Cr(VI)] = 2.5×10^{-4} mol·L⁻¹, [Lac] = 0.50 mol·L⁻¹, and [HClO₄] = 0.50 mol·L⁻¹.

Hexavalent chromium exists primarily as chromic acid (H₂CrO₄), hydrogen chromate ion (HCrO₄⁻), and chromate ion (CrO₄²⁻), depending on the values of pH. In acidic medium of our experiment, dichromate exists predominantly as monomer (HCrO₄⁻) and chromic acid (H₂CrO₄), and H₂CrO₄ plays a role of active species. Based on the experimental results, we can learn that lactic acid participates in the rate-determined step [22]. From the discussion above, the reaction mechanism was proposed as follows:



Here, reaction (3) is the rate-determined step. Based on the mechanism above, the rate law is derived as follow:

$$-\frac{d[\text{Cr(VI)}]_{\text{T}}}{dt} = k[\text{H}_2\text{CrO}_4][\text{Lac}], \quad (6)$$

$$\frac{d[\text{Cr(VI)}]_{\text{T}}}{dt} = \frac{kK_b[\text{H}^+]}{1+K_b[\text{H}^+]}[\text{Lac}][\text{Cr(VI)}]_{\text{T}}, \quad (7)$$

$$k_{\text{obs}} = \frac{kK_b[\text{H}^+]}{1+K_b[\text{H}^+]}[\text{Lac}], \quad (8)$$

$$K_b = 1/K_{a1}, \text{ so } k_{\text{obs}} = \frac{k[\text{H}^+]}{K_{a1} + [\text{H}^+]}[\text{Lac}], \quad (9)$$

$$\frac{1}{k_{\text{obs}}} = \frac{K_{a1}}{k[\text{Lac}]} \cdot \frac{1}{[\text{H}^+]} + \frac{1}{k[\text{Lac}]}. \quad (10)$$

Reaction (3) shows a redox decomposition with a two-electron transfer (C–H cleavage), and the redox product is pyruvic acid, which is consistent with the experimental phenomena. From (8) and (10), the plots of k_{obs} versus [Lac] are straight lines through the grid origin, and the plots of $1/k_{\text{obs}}$ versus $1/[\text{H}^+]$ are linear with positive intercept. The rate constants of the rate determining step and activation parameters were obtained and presented in Table 2. The effect of solvent on reaction rate is an extremely complicated

TABLE 2: The rate constants and activation parameters for the reduction of Cr(VI) by lactic acid.

T/K	$10^2 k/\text{mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$	Thermodynamic activation parameters (298.15 K)
298.15	4.74	$E_a = 30.98 \text{ kJ} \cdot \text{mol}^{-1}$
303.15	5.93	$\Delta S^\ddagger = -174.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
308.15	7.35	$\Delta H^\ddagger = 28.50 \text{ kJ} \cdot \text{mol}^{-1}$
313.15	8.58	

issue. We hold that the formation of H₂CrO₄ makes its electron density drop. So, the reaction rate increases with the decreasing of the solvent's polarity [23]. This is consistent with the experimental phenomena.

4. Conclusion

The kinetics of the reduction of chromium(VI) by lactic acid in the presence of DMSO has been studied. The active species of Cr(VI) is understood to be H₂CrO₄. Rate constant of the slow step and activation parameters were computed, respectively. The product of Cr(VI) oxidation of lactic acid is pyruvic acid, which suggested that the cleavage of C–H of lactic acid. Mechanism proposed for the reaction is in conformity with the product, mechanistic, and kinetic studies.

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