Mechanism and Kinetics of the 2,2′-Bipyridyl Catalysis of the Chromium(VI) Oxidation of Malic Acid

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A spectrophotometric study of the kinetics and mechanism of the oxidation of malic acid (Mal) by chromium(VI) catalyzed by 2,2′-bipyridyl (bpy) in aqueous acidic medium was conducted in a temperature range of ~298 to 313 K. This reaction was found to be pseudo-first order with respect to Cr(VI) and first order with respect to malic acid. Under the conditions of the pseudo-first order ([Mal]$_o$ >> [Cr(VI)]$_o$), the observed rate constant (k_{obs}) increased with the increase in [H$^+$] and [bpy]. There was a weak negative salt effect. Based on the experimental results, a possible reaction mechanism for this oxidation catalyzed by bpy is proposed. The rate equation derived from this mechanism can explain all the experimental phenomena.

Keywords: Chromium(VI), Malic acid, 2,2′-Bipyridyl, Catalytic kinetics and mechanism

INTRODUCTION

Malic acid is widely used in medications, foods, industry and so forth. It is not only a fine acidity agent and acidity seasoning agent, but also of physiological importance. In addition, malic acid can be used as a monomer both in synthesizing plastics with biological degradation and to reduce water pollution caused during algae production, thus ecologically benefiting the environment [1].

The toxic, mutagenic, and carcinogenic properties of Cr(VI) are well established. While there is overwhelming evidence to show that Cr(VI) complexes are mutagenic in bacterial and mammalian cells, most of the Cr(III) complexes have been shown to be nonmutagenic [2-4]. The conversion of Cr(VI) to

Cr(III) can lessen the harmful effect on the environment and biological systems. At present, although there have been some reports regarding this type of reaction system [5,6], thorough research into a plausible reaction mechanism is lacking. Therefore, we herein present further study on the reaction kinetics and mechanism of the oxidation of malic acid (Mal) by chromium(VI) catalyzed by 2,2′-bipyridyl (bpy).

EXPERIMENTAL

Materials and Apparatus

All reagents used, including K$_2$Cr$_2$O$_7$, HClO$_4$, Mal and bpy, were of analytical grade. All solutions were prepared with doubly distilled water. Dioxane was added in order to increase the solubility of bpy in water. The ionic strength was maintained by adding NaClO$_4$. The kinetics were measured

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using a UV-8500 spectrophotometer (Techcomp Scientific Instrument Co., Ltd., China) fitted with a 501 thermostat (±0.1 ºC, Shanghai Laboratory Instrument Works, China).

All kinetics measurements were carried out under pseudo-first order conditions. A solution (2 ml) containing a known concentration of $K_2Cr_2O_7$, $HClO_4$ and a reductant solution (2 ml) of an appropriate concentration were transferred separately to the upper and lower branch tubes of a λ-type two-cell reactor. After thermal equilibration at the desired temperature in a thermobath, the two solutions were thoroughly mixed and immediately transferred into a 1-cm thick rectangular quartz cell maintained at a constant temperature (±0.1 ºC). The reaction process was monitored automatically by recording the disappearance of Cr(VI) at various time intervals at 350 nm.

To analyze the products, solutions of $K_2Cr_2O_7$, $HClO_4$, Mal and bpy were mixed well at room temperature. The reaction mixture was allowed to stand in the dark to ensure completion. The oxidation product was identified by spot test [7]. A solution of chromium trichloride was used as a standard to analyze the product's UV spectrum.

RESULTS AND DISCUSSION

The spot test revealed that the oxidation product was the corresponding ketonic acid. The product's UV spectrum ranged from 539-572 nm with a maximum absorption peak at 550 nm. On the basis of this finding, we concluded that both reaction products were chromium(III) ion [8]. Furthermore, no rate decrease or polymerization was observed upon addition of acrylonitrile to the reaction mixture under the protection of nitrogen, indicating the absence of free radical intermediates during the course of the reaction.

Kinetic Evaluation

Under the conditions of $[Mal]_o \gg [Cr(VI)]_o$, the plots of $\ln(A_t - A_\infty)$ *vs.* time t are linear, where A_t and A_∞ stand for the absorbance at time t and infinity, respectively. When the concentration of the oxidant is changed within the
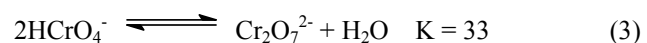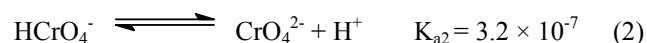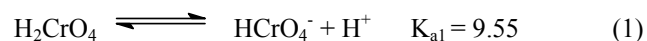
experimental range, there is no change in the slope of the line (Table 1), which indicates that the order with respect to Cr(VI) is unity. The pseudo-first order rate constants k_{obs} were evaluated using the least-squares method. To calculate k_{obs}, generally more than 11 A_t values within three times the half-life were used. The rate constants reported here are the averages of at least three independent runs. Deviations in duplicate determinations are generally less than ±5% [9].

At fixed [Cr(VI)], [$HClO_4$], [bpy], [dioxane], the ionic strength μ and temperature T, the k_{obs} increases with the increase of [Mal] and the plots of k_{obs} *vs.* [Mal] at different temperatures are straight lines passing through the origin (relative coefficient r $\geqslant$ 0.996), indicating that the reaction is first order with respect to Mal（Table 2）. Where other factors are fixed, the k_{obs} increased with the increase in [H^+]（Table 3）. The plot of k_{obs} *vs.* [H^+] results in a straight line.

The spectrum remained almost unchanged during the oxidation of bpy by Cr(VI) for over an hour. This indicates that the reaction rate was very slow, so the oxidation of bpy by Cr(VI) can be ignored in this reaction system. The k_{obs} increased with increasing [bpy], and has a fractional order with respect to bpy（Table 4）. The k_{obs} increased with increasing [dioxane]（Table 5）. The k_{obs} decreased slightly with an increase in μ（Table 6）, indicating the presence of a negative salt effect, which is consistent with the common regulation of the kinetics [10].

Reaction Mechanism

Chromic acid also participates in the acid-base equilibrium as follows [11]:

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+ \qquad K_{a1} = 9.55 \qquad (1)$$

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+ \qquad K_{a2} = 3.2 \times 10^{-7} \quad (2)$$

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O \quad K = 33 \qquad (3)$$

Dissociation of chromic acid depends on the pH of the reaction medium. In solutions at pH > 6.0, CrO_4^{2-} exists as a

Table 1. Variation of k_{obs} Varying with Different Concentrations of Cr(VI) at T = 303.15 K[a]

$10^4 C$ (M)	2.00	3.00	4.00	4.50
$10^4 k_{obs}$ (s^{-1})	8.754	8.747	8.756	8.746

[a][Mal] = 0.07 M; [HClO$_4$] = 0.116 M; [bpy] = 4.00 × 10^{-3} M; [dioxane] = 1.403 × 10^{-4} M; μ = 0.118 M.

Table 2. Variation of $10^4 k_{obs}$ (s^{-1}) with Different Concentrations of Malic acid at Different Temperatures[a]

C (M) / T (K)	0.02	0.04	0.06	0.08	0.10	n	r
303.15	2.195	4.527	6.562	8.523	9.677	0.94	0.996
308.15	2.601	5.250	7.684	9.838	11.08	0.92	0.997
313.15	3.073	6.272	8.958	11.89	13.98	0.95	0.999

[a][Cr(VI)] = 5.00 × 10^{-4} M; [HClO$_4$] = 0.112 M; [bpy] = 4.00 × 10^{-3} M; [dioxane] = 1.403 × 10^{-4} M; μ = 0.114 M; n_{ap} and r stand for slope and relative coefficient, respectively, of the plot of lnk_{obs} vs. ln[Mal].

Table 3. Variation of k_{obs} with Different Concentrations of H$^+$ at T = 308.15 K[a]

C (M)	0.0388	0.0776	0.116	0.155	0.194
$10^4 k_{obs}$ (s^{-1})	2.397	4.964	7.656	10.49	13.04

[a][Cr(VI)] = 5.00 × 10^{-4} M; [Mal] = 0.07 M; [bpy] = 4.00 × 10^{-3} M; [dioxane] = 1.403 × 10^{-4} M; μ = 0.302 M.

Table 4. Variation of $10^4 k_{obs}$ (s^{-1}) with Different Concentrations of bpy at Different Temperatures[a]

C (M) / T (K)	0.0010	0.0012	0.0016	0.0025	0.0050	n	r
298.15	2.842	3.259	3.708	4.590	6.575	0.52	0.999
303.15	3.614	4.090	4.676	5.699	8.220	0.50	0.999
308.15	4.559	5.077	5.880	7.114	9.842	0.50	0.999
313.15	5.467	6.193	7.320	8.584	11.37	0.43	0.997

[a][Cr(VI)] = 5.00 × 10^{-4} M; [Mal] = 0.07 M; [HClO$_4$] = 0.116 M; [dioxane] = 1.403 × 10^{-4} M; μ = 0.118 M.

Table 5. Variation of k_{obs} (s^{-1}) with Different Concentrations of Dioxane at T = 308.15 K[a]

$10^4 C$ (M)	2.806	4.208	5.611	7.014	8.417
$10^3 k_{obs}$ (s^{-1})	0.9768	1.005	1.046	1.098	1.124

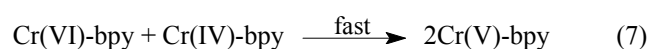[a][Cr(VI)] = 5.00 × 10^{-4} M; [Mal] = 0.07 M; [HClO$_4$] = 0.116 M; [bpy] = 4.00 × 10^{-3} M; μ = 0.118 M.

Table 6. Variation of k_{obs} at Different Ionic Strengths (μ) at 308.15 K[a]

μ (M)	0.168	0.218	0.268	0.318	0.368
$10^4 k_{obs}$ (s^{-1})	8.447	8.191	7.811	7.640	7.455

[a][Cr(VI)] = 5.00 × 10^{-4} M; [Mal] = 0.07 M; [HClO$_4$] = 0.116 M; [dioxane] = 1.403 × 10^{-4} M; [bpy] = 4.00 × 10^{-3} M.

major species; in acidic medium (pH = 1.3-2.2) $Cr_2O_7^{2-}$ and $HCrO_4^-$ are the reactive species; in a strong acid medium (pH < 1), H_2CrO_4 is the major existing species [12]. By calculation, we show that $HCrO_4^-$ is the main species over our experimental range of [H$^+$]. Cr(VI) and Cr(V) behave similarly in a C-H bond rupture, whereas Cr(IV) is responsible for the C-C bond cleavage products [6]. The oxidation product of malic acid is the corresponding ketonic acid, which is the product of the C-H bond rupture. Therefore, both Cr(V) and Cr(VI) react with malic acid. From the experimental results, the reaction is first order with respect to H$^+$ and malic acid, indicating that malic acid and H$^+$ take part in the rate-limiting step. Here, k_{obs} increases with increasing [bpy] and the order with respect to bpy is found to be fractional, so bpy participates in an equilibrium before the rate-determining step [10].

In view of the above results and discussions, the following plausible reaction mechanism is proposed:

$$\text{Complex} + R + H^+ \xrightarrow{k} \text{Cr(IV)-bpy} + \text{Products} \quad (6)$$

$$\text{Cr(VI)-bpy} + \text{Cr(IV)-bpy} \xrightarrow{\text{fast}} 2\text{Cr(V)-bpy} \quad (7)$$

$$\text{Cr(V)-bpy} + R \xrightarrow{\text{fast}} \text{Cr(III)-bpy} + \text{Products} \quad (8)$$
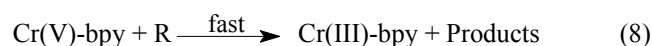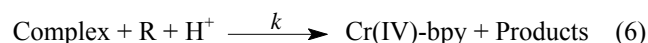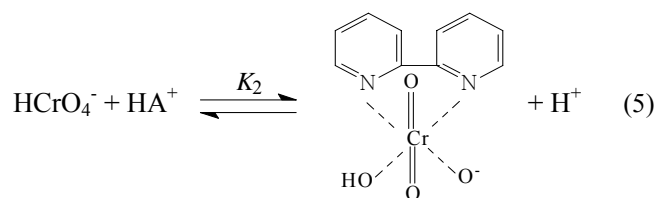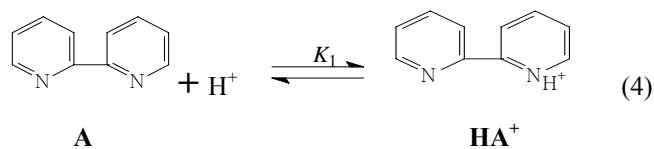
Here, reaction (**6**) is the rate-determining step.

$$[HCrO_4^-]_T = [\text{Complex}]_e + [HCrO_4^-]_e$$

$$= [\text{Complex}]_e \times \frac{1 + K_1 K_2 [A]}{K_1 K_2 [A]}$$

$$[\text{Complex}]_e = \frac{K_1 K_2 [A]}{1 + K_1 K_2 [A]} [HCrO_4^-]_T$$

The subscripts T and e stand for total concentration and equilibrium concentration, respectively. A and R stand for bpy and malic acid, respectively. As the rate of the disappearance of [Cr(VI)]$_T$ was monitored, the rate of the reaction can be derived as:

$$-\frac{d[Cr(VI)]_T}{dt} = k[\text{Complex}]_e [R][H^+]$$

$$= \frac{k K_1 K_2 [A][H^+][R]}{1 + K_1 K_2 [A]} [HCrO_4^-]_T$$

$$= k_{obs} [HCrO_4^-]_T \quad (9)$$

$$k_{obs} = \frac{k K_1 K_2 [A]}{1 + K_1 K_2 [A]} [H^+][R] \quad (10)$$

Table 7. Rate Constants of the Rate-Determining Step and Activation Parameters of Malic acid

T (K)	298.15	303.15	308.15	313.15	Activation parameters (298.15 K)
k (mol^{-2}l^2 s^{-1})	0.1095	0.1333	0.1582	0.1854	E_a = 27.123 kJ mol^{-1} $\Delta H^{\ddagger}$ = 24.644 kJ mol^{-1} $\Delta S^{\ddagger}$ = -180.47 J K^{-1}mol^{-1}

$$[A]_T = [A] + [HA^+]$$

$$\frac{1}{k_{obs}} = \frac{1}{k[R][H^+]} + \frac{1+K_1[H^+]}{kK_1K_2[H^+][R]}\frac{1}{[A]_T} \quad (11)$$

Equation (9) suggests that the reaction should be first order with respect to HCrO$_4^-$. Equation (10) shows that the plots of k_{obs} vs. [R] and [H$^+$] should also be straight lines, which confirms the observations. Equation (11) suggests that the order with respect to bpy is fractional. The plot of 1/k_{obs} vs. 1/[bpy] derived from Eq. (11) at constant [H$^+$] and [R] is linear and the rate constants of the rate-determining step (k) at different temperatures are obtained from the intercepts of the straight lines. The plot of ln$k$ vs. 1/T is also linear. From the slope and the intercept of the line, the activation energy and thermodynamic parameters (t = 25 ºC) were evaluated by a previously published method (Table 7) [13].

The effect of solvent on the reaction rate is an extremely complicated issue. We hold that the increase in volume of the transition complex makes its electron density drop. The reaction rate increases with the decrease in the polarity of the solvent, which favors the formation of the transition complex [14] and is consistent with the experimental phenomena.

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