A Kinetic Study of the Oxidation of L-Ascorbic Acid by Chromium(VI)

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Abstract

The reaction between chromium(VI) and L-ascorbic acid has been studied by spectrophotometry in the presence of aqueous citrate buffers in the pH range 5.69–7.21. The reaction is slowed down by an increase of the ionic strength. At constant ionic strength, manganese(II) ion does not exert any appreciable inhibition effect on the reaction rate. The rate law found is

$$r = K_p k_r[\text{Cr(VI)}][\text{L-ascorbic acid}][\text{H}^+]/(1 + K_p[\text{H}^+])$$

where K_p is the equilibrium constant for protonation of chromate ion and k_r is the rate constant for the redox reaction between the active forms of the oxidant (hydrogenchromate ion) and the reductant (L-hydrogenascorbate ion). The activation parameters associated with rate constant k_r are $E_a = 20.4 \pm 0.9$ kJ mol^{-1}, $\Delta H^{\neq} = 17.9 \pm 0.9$ kJ mol^{-1}, and $\Delta S^{\neq} = -152 \pm 3$ J K^{-1} mol^{-1}. The reaction thermodynamic magnitudes associated with equilibrium constant K_p are $\Delta H^0 = 16.5 \pm 1.1$ kJ mol^{-1} and $\Delta S^0 = 167 \pm 4$ J K^{-1} mol^{-1}. A mechanism in accordance with the experimental data is proposed for the reaction.

Introduction

The reactions of oxidation of L-ascorbic acid to L-dehydroascorbic acid have received a great deal of attention because of the important role that the redox chemistry of L-ascorbic acid plays in human nutrition [1]. Thus, the kinetics of the reactions of L-ascorbic acid with a high number of oxidizing agents have been studied [2]. In particular, its reaction with chromium(VI) is especially interesting, because it might be involved either in the development [3] or in the prevention [4] of cell malignancy provoked by chromium(VI), which is known to be a powerful carcinogen [5].

Although the chromium(VI) / L-ascorbic acid reaction has been studied in acidic solutions [6], the reaction under neutral conditions has received little attention [7]. We have studied that reaction under near-physiological conditions (pH range 5.69–7.21) in citric acid-sodium citrate buffers, the reaction stoichiometry in those media being:

$$(1) \qquad 2CrO_4^{2-} + 3HA^- + 13H^+ = 2Cr^{3+} + 3A + 8H_2O$$

where HA^- and A stand for L-hydrogenascorbate ion and L-dehydroascorbic acid, respectively. The results found are presented and discussed in this article.

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Experimental

Materials and Methods

The solvent was twice-distilled water. The other reagents (potassium dichromate, L-ascorbic acid, citric acid, sodium citrate, sodium chloride, zinc sulfate, and manganese(II) sulfate) were used without further purification (analytical quality).

The kinetic runs were followed by monitoring the decay of chromium(VI) at 370 nm by means of a Varian Cary 219 UV-Vis spectrophotometer. The pHs were measured with a Metrohm 605 pH-meter provided with a combination electrode.

Determination of Kinetic Data

The reaction was too fast to be followed by conventional spectropotometry under pseudo-first-order conditons. In addition, the integrated second-order rate law based on the reaction stoichiometry, eq. (1), showed in all cases a slight curvature. As a result, initial rates were extrapolated from a fit of the absorbance data to the equation:

$$1/(A - A_\infty)^m = a + bt \tag{2}$$

where A and A_∞ are the absorbances at time t and at the end of the reaction, respectively, whereas a, b, and m are fitting parameters. Excellent fits were thus obtained in all kinetic runs up to 50% of Cr(VI) reduction. The initial rates were then obtained as:

$$r_0 = (b/m\varepsilon l)(A_0 - A_\infty)^{m+1} \tag{3}$$

where A_0 is the initial absorbance, ε the molar absorptivity of chromium(VI) at 370 nm, and l the optical pathlength (1 cm).

All the kinetic data were obtained as the averages of duplicate determinations (average standard deviation ± 1.0%).

Results

The initial rate was directly proportional to the initial concentration of chromium(VI) (Table 1). Thus, the first-order rate constants were calculated as $k_1 = r_0/[Cr(VI)]_0$. A double-logarithmic plot of the first-order rate constant against the initial concentration of L-ascorbic acid was linear with a slope near unity (0.93 ± 0.02, Fig. 1). Thus, the second-order rate constants were calculated as $k_2 = r_0/[Cr(VI)]_0[\text{L-ascorbic acid}]_0$. The logarithm of the second-order rate constant decreased linearly with $I^{1/2}/(1 + I^{1/2})$ in the range of ionic strength 0.163-0.291 mol dm^{-3} (NaCl), the slope being −1.08 ± 0.09 (Fig. 2).

Since the reactions of chromium(VI) with many reductants are known to be inhibited by manganese(II) ion [8,9], the effect of manganese(II) sulfate on the reaction rate was investigated at constant ionic strength ($[MnSO_4] + [ZnSO_4]$ = constant). In the concentration range studied ($[MnSO_4]$ = 0 − 7.63 × 10^{-3} mol dm^{-3}), no appreciable inhibition effect was found.

TABLE I. Initial rates and first-order rate constants at various initial concentrations of chromium(VI) for its reduction by L-ascorbic acid (2.75×10^{-3} mol dm^{-3}) in the presence of aqueous citrate buffers (pH 6.84, ionic strength 0.82 mol dm^{-3}) at 25.0°C.

$[Cr(VI)]_0 \times 10^4$ (mol dm^{-3})	$r_0 \times 10^6$ (mol dm^{-3} s^{-1})	$k_1 \times 10^2$ (s^{-1})[a]
0.81	0.82 ± 0.01	1.01 ± 0.01
1.63	1.69 ± 0.02	1.04 ± 0.01
3.00	3.15 ± 0.01	1.05 ± 0.01
5.15	5.24 ± 0.04	1.02 ± 0.01
6.17	6.22 ± 0.04	1.01 ± 0.01

[a] Calculated as: $k_1 = r_0/[Cr(VI)]_0$. Average value: $k_1 = (1.03 \pm 0.02) \times 10^{-2}$ s^{-1}.

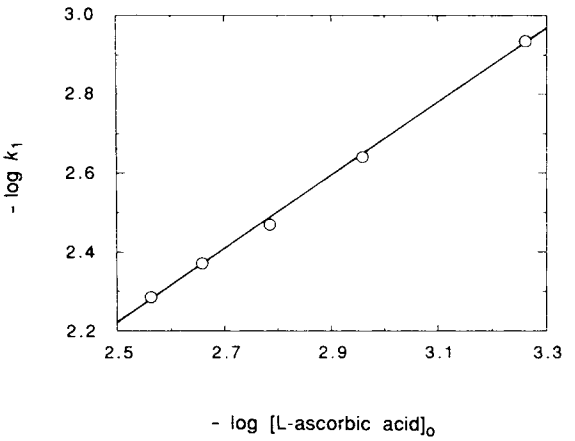

Figure 1. Double-logarithmic plot of the first-order rate constant against the initial L-ascorbic acid concentration for its oxidation by chromium(VI) (1.63×10^{-4} mol dm^{-3}) in the presence of aqueous citrate buffers (pH 7.19, ionic strength 0.82 mol dm^{-3}) at 25.0°C. Slope 0.93 ± 0.02.

The reaction was accelerated by an increase of the acidity of the medium; a double-reciprocal plot of the second-order rate constant against the hydrogen ion concentration was linear (Fig. 3). The second-order rate constant fulfilled the Arrhenius equation in the temperature range 14.7–35.1°C at all the pHs studied. The resulting apparent activation energy was considerably affected by the pH (Table II).

Hence, the experimental rate law found in this work for the title reaction was:

$$r = a[Cr(VI)][\text{L-ascorbic acid}][H^+]/(1 + b[H^+]) \quad (4)$$

where a and b are empiric parameters determined from the intercept and slope of the $1/k_2$ vs. $1/[H^+]$ linear plots.

Discussion

In the pH range of our work (5.69–7.21), most of the chromium(VI) was present either as chromate ion or as hydrogenchromate ion [10], and the predominant form of the reductant was L-hydrogenascorbate ion [11]. The

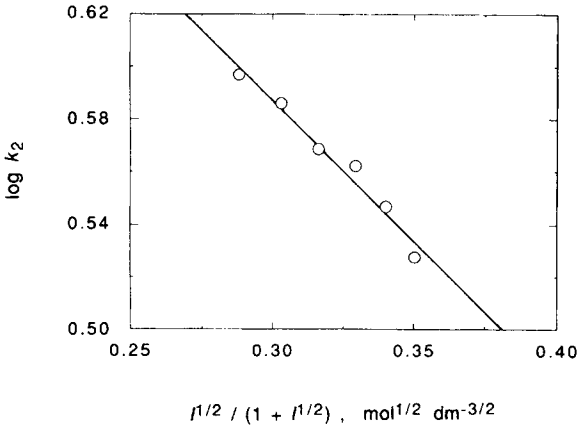

Figure 2. Dependence of the second-order rate constant on the ionic strength for the oxidation of L-ascorbic acid (1.10×10^{-3} mol dm^{-3}) by chromium(VI) (1.63×10^{-4} mol dm^{-3}) in the presence of aqueous citrate buffers (pH 7.01, ionic strength 0.163 mol dm^{-3}) at 25.0°C. The ionic strength was varied in the range 0.163 – 0.291 mol dm^{-3} by addition of NaCl (0 – 0.128 mol dm^{-3}). Slope -1.08 ± 0.09.

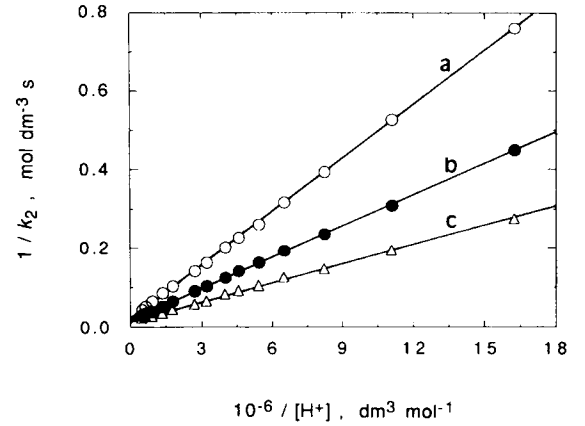

Figure 3. Dependence of the second-order rate constant on the hydrogen ion concentration for the oxidation of L-ascorbic acid (5.49×10^{-4} mol dm^{-3}) by chromium(VI) (1.63×10^{-4} mol dm^{-3}) in the presence of aqueous citrate buffers (pH 5.69 – 7.21, ionic strength 0.82 mol dm^{-3}) at 14.7 (a), 25.0 (b), and 35.1 (c) °C.

experimental rate law, eq. (4), is consistent with the rate-determining step being the $HCrO_4^- - HA^-$ reaction. Although chromium(VI) has a notable tendency to experiment condensation reactions with both organic [12, 13] and inorganic [14] compounds containing hydroxyl groups, the strongly reducing properties of L-hydrogenascorbate ion make unlikely that the formation of a Cr(VI)-ascorbate ester be required for the redox reaction to take place.

Since a feature common to many two-equivalent reductions of chromium(VI) is to be inhibited by manganese(II) ion [9], the finding that the title reaction is not inhibited by that ion seems to suggest that it occurs via a one-equivalent reduction process. This conclusion is supported by the

TABLE II. Apparent activation energies at different pH values for the reduction of chromium(VI) (1.63×10^{-4} mol dm^{-3}) by L-ascorbic acid (5.49×10^{-4} mol dm^{-3}) in the presence of aqueous citrate buffers (ionic strength 0.82 mol dm^{-3}) within the temperature range 14.7–35.1°C.

pH	E_a(kJ mol^{-1})
5.69	27.5 ± 0.4
5.81	26.9 ± 1.7
5.95	28.2 ± 0.8
6.14	31.5 ± 0.9
6.26	31.7 ± 0.5
6.43	32.9 ± 0.9
6.51	33.5 ± 1.0
6.60	33.6 ± 0.6
6.66	33.9 ± 0.7
6.74	33.9 ± 0.8
6.82	34.0 ± 1.3
6.92	35.8 ± 0.5
7.05	36.5 ± 0.4
7.21	36.7 ± 0.7

fact that both chromium(V) and an L-ascorbate radical have been detected by EPR spectroscopy as intermediates in the reduction of chromium(VI) by L-ascorbic acid in aqueous neutral solution [15]. It is also coherent with the fact that the L-ascorbate radical is relatively stable due to the spread of its odd electron over a highly conjugated system [16]. Thus, the rate-determining step occurs by transfer of either one electron or a hydrogen atom from HA^- to $HCrO_4^-$. Electron transfer seems to be supported by quantum-chemical studies [17].

Therefore, the opening steps of the mechanism that can be proposed for the title reaction are:

$$CrO_4^{2-} + H^+ \rightleftharpoons HCrO_4^- \tag{5}$$

$$HCrO_4^- + HA^- \xrightarrow{\text{slow}} HCrO_4^{2-} + HA\cdot \tag{6}$$

where HA· is the L-hydrogenascorbate free radical.

The rate law that can be deduced from the proposed mechanism is:

$$r = K_p k_r[\text{Cr(VI)}][\text{L-ascorbic acid}][H^+]/(1 + K_p[H^+]) \tag{7}$$

where K_p and k_r stand for the equilibrium constant corresponding to the protonation of chromate ion, eq. (5), and the rate constant corresponding to the redox rate-determining step, eq. (6), respectively, whereas [Cr(VI)] is the total oxidant concentration ($[CrO_4^{2-}] + [HCrO_4^-]$). Equation (7) is in perfect agrement with the experimental rate law, eq. (4), and also with the effect of ionic strength on the observed second-order rate constant (Fig. 2) [18(a)].

The determination of the empiric parameters a and b of eq. (4) at five different temperatures in the range 14.7–35.1°C has allowed to obtain the corresponding values of K_p and k_r. In that temperature range, rate constant k_r fulfils the Arrhenius equation (Fig. 4(a)), whereas equilibrium constant K_p fulfils the van't Hoff equation (Fig. 4(b)). The activation parameters (E_a, $\Delta H^{\neq}$, and $\Delta S^{\neq}$) associated with rate constant k_r and the reaction

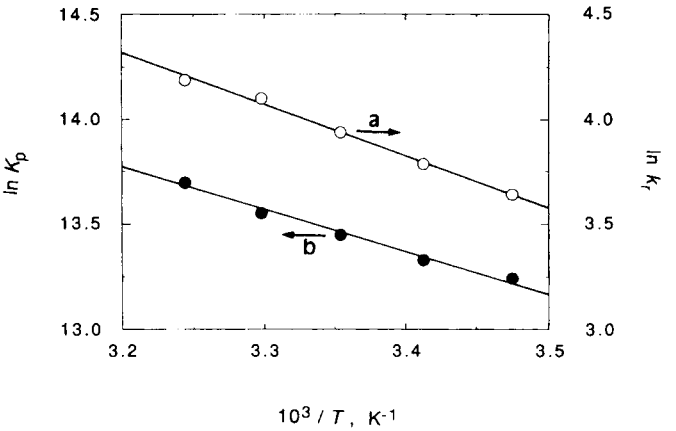

Figure 4. Influence of temperature on both rate constant k_r (Arrhenius plot, a) and equilibrium constant K_p (van't Hoff plot, b) for the reduction of chromium(VI) (1.63×10^{-4} mol dm^{-3}) by L-ascorbic acid (5.49×10^{-4} mol dm^{-3}) in the presence of aqueous citrate buffers (pH 5.69–7.21, ionic strength 0.82 mol dm^{-3}).

TABLE III. Activation parameters (E_a,$\Delta H^{\neq}$, and $\Delta S^{\neq}$) associated with rate constant k_r, and reaction thermodynamic magnitudes (ΔH^0 and ΔS^0) associated with equilibrium constant K_p for the reduction of chromium(VI) (1.63×10^{-4} mol dm^{-3}) by L-ascorbic acid (5.49×10^{-4} mol dm^{-3}) in the presence of aqueous citrate buffers (pH 5.69–7.21, ionic strength 0.82 mol dm^{-3}) within the temperature range 14.7–35.1°C.

Constant	E_a (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS^a (J K^{-1} mol^{-1})
k_r	20.4 ± 0.9	17.9 ± 0.9	−152 ± 3
K_p	–	16.5 ± 1.1	167 ± 4

[a] The entropies are referred to the 1 mol dm^{-3} standard state.

thermodynamic magnitudes (ΔH^0 and ΔS^0) associated with equilibrium constant K_p have also been obtained and are given in Table III.

The value determined in this work for K_p at ionic strength 0.82 mol dm^{-3} (citrate buffers) and 25.0°C is 6.95×10^5 dm^3 mol^{-1}. This is in good agreement with the value reported in the literature for that equilibrium constant at ionic strength 3 mol dm^{-3} ($NaClO_4$) and the same temperature, $K_p = 8.13 \times 10^5$ dm^3 mol^{-1} [19]. Moreover, K_p is known to increase with increasing temperature [20], in agreement with the positive value found in this work for the standard reaction enthalpy associated with that equilibrium constant (see Table III).

On the other hand, the negative value of the activation entropy found in Table III for the rate-determining step, eq. (6), is in agreement with a reaction between two like-charged ions [18b].

We can, thus, conclude that the effects of pH, ionic strength, and temperature on the rate of the title reaction confirm that the active forms of the oxidant and reductant for the experimental conditions of this work are, respectively, hydrogenchromate and L-hydrogenascorbate ions.

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Bibliography

[1] G.M. Jaffe, in *Encyclopedia of Chemical Technology,* M. Grayson, Ed., Wiley, New York, 1984, vol. 24, pp. 8–40.
[2] M.B. Davies, *Polyhedron,* **11,** 285 (1992).
[3] P.H. Connett and K.E. Wetterhahn, *J. Am. Chem. Soc.,* **107,** 4282 (1985).
[4] M. Liao, Z. Wang, and T. Yu, *Weisheng Dulixue Zazhi,* **2,** 158 (1988); *Chem. Abstr.,* **112,** 202 (1990).
[5] A. Wedrychowski, W.S. Ward, W.N. Schmidt, and L.S. Hnilica, *J. Biol. Chem.,* **260,** 7150 (1985).
[6] G.V. Rao and P.K. Saiprakash, *Oxid. Commun.,* **11,** 33 (1988).
[7] I. Baldea and L. Munteanu, *Stud. Univ. Babes-Bolyai, Ser. Chem.,* **25,** 24 (1980).
[8] G.P. Haight, T.J. Huang, and B.Z. Shakhashiri, *J. Inorg. Nucl. Chem.,* **33,** 2169 (1971).
[9] J.F. Perez-Benito, C. Arias, and D. Lamrhari, *J. Chem. Soc., Chem. Commun.,* 472 (1992).
[10] R.K. Tandon, P.T. Crisp, J. Ellis, and R.S. Baker, *Talanta,* **31,** 227 (1984).
[11] R.C. Weast, *CRC Handbook of Chemistry and Physics,* CRC Press, Cleveland, 1977, p. D-150.
[12] K.B. Wiberg and H. Schäfer, *J. Am. Chem. Soc.,* **91,** 927 (1969).
[13] N.K. Saran, R.C. Acharya, and S.R. Rao, *J. Indian Chem. Soc.,* **62,** 747 (1985).
[14] D.G. Lee and R. Stewart, *J. Am. Chem. Soc.,* **86,** 3051 (1964).
[15] D.M.L. Goodgame and A.M. Joy, *Inorg. Chim. Acta,* **135,** 115 (1987).
[16] G.P. Laroff, R.W. Fessenden, and R.H. Schuler, *J. Am. Chem. Soc.,* **94,** 9062 (1972).
[17] Y. Abe, H. Horii, S. Taniguchi, S. Yamabe, and T. Minato, *Can. J. Chem.,* **64,** 360 (1986).
[18] R.E. Weston and H.A. Schwarz, *Chemical Kinetics,* Prentice-Hall, Englewood Cliffs, 1972, (a) p. 169, (b) p. 179.
[19] Y. Sasaki, *Acta Chem. Scand.,* **16,** 719 (1962).
[20] D.V.S. Jain and C.M. Jain, *J. Chem. Soc. (A),* 1541 (1967).

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