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Kinetics and Mechanism of Selenium(IV) Oxidation of Ascorbic Acid in Aqueous Perchlorate Solutions

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The kinetics of oxidation of L-ascorbic acid by selenium(IV) in aqueous solutions of perchloric acid at a constant ionic strength of 1.0 mol dm^{-3} has been investigated spectrophotometrically. A first order reaction in ascorbic acid and a fractional order with respect of selenium(IV) were observed. The rate of reaction was found to be acid catalyzed. The results obtained at various hydrogen ion concentrations indicate that the ascorbate anion plays a role in the reaction kinetics through formation of a complex ion intermediate. The activation parameters have been evaluated and a tentative reaction mechanism was suggested.

INTRODUCTION

Selenium dioxide is a powerful oxidizing agent and has been used extensively in the oxidation of many organic compounds.¹⁻⁶ The kinetics of oxidation of ascorbic acid by this oxidant in perchloric acid has not received much attention, even though Ghorge and co-workers⁷ examined the present reaction gravimetrically in concentrated solutions of HCl ($1.2\sim 6.0 \text{ mol dm}^{-3}$). They reported that the reaction kinetics was simple second-order overall, and the reaction did not depend on the pH in this concentration range. The mechanism proposed by them could not explain some of the experimental facts and this led us to reinvestigate the kinetics of this reaction, at relatively lower concentrations of aqueous HClO_4 ($0.1\sim 1.0 \text{ mol dm}^{-3}$), spectrophotometrically. Our preliminary experiments indicated that the reaction rate was dependant on the pH of the reaction, where increasing the hydrogen ion concentration catalyzed the oxidation process. The main object of this work is to put forward rate laws consistent with the experimental data with a view of obtaining unequivocal information on the reaction mechanism.

EXPERIMENTAL

Materials and Method

Stock solution of (0.01 mol dm⁻³) of selenium dioxide was prepared by dissolving the BDH sample in bidistilled water. The solution was standardized at equal intervals by both iodometric⁸ and permanganometric⁹ methods. All other reagents were of analytical grade and their solutions were prepared by dissolving the appropriate amounts in doubly distilled water.

Kinetic Measurements

The kinetic test of this reaction were carried out in a temperature controlled water-bath (± 0.05 °C). The reaction flask containing ascorbic acid and HClO₄-NaClO₄ solution mixture was kept in the thermostat together with a stock solution of selenium dioxide. When the two flasks attained the thermostat temperature, the required volumes of oxidant and substrate were syringed out and poured into the reaction cell. The course of reaction was followed by recording the decrease in absorbance of ascorbic acid at 242 nm, its absorption maximum, as a function of time. The absorption measurements were followed spectrophotometrically in a thermostated cell compartment at the desired temperature using a Shimadzu UV -200 S double beam spectrophotometer. The cell used was of 1 cm pathlength. It was verified that there is no interference due to other reagents or reaction products at λ_{\max} of the ascorbic acid. The reactions were followed up to not less than two half-lives of reaction completion and the rate constants were estimated at a point before selenium metal began to form.

All kinetic data presented in this work were obtained under pseudo first-order conditions where the selenium(IV) was present in a large excess over the ascorbic acid concentration.

RESULTS

Stoichiometry

The stoichiometry of the overall reaction of Se(IV) with excess ascorbic acid in 1.0 mol dm⁻³ HClO₄ acid, adjusted to constant ionic strength, was determined. A stoichiometric ratio of 2.05 ± 0.05 ($[\text{ascorbic acid}]_{\text{consumed}}/[\text{Se(IV)}]_0$) was obtained for several different initial concentrations of ascorbic acid. Similar values for the stoichiometry were also obtained from experiments at $[\text{H}^+] = 0.13$ and 0.5 mol dm⁻³ and ionic strength of unity. The product analysis indicates formation of selenium metal, and this result conforms to the following stoichiometry



The formation of the product was in good agreement with that observed earlier.^{7,10}

Selenium(IV) Species

Selenious acid has a dissociation constant of 3.0×10^{-3} mol dm⁻³ at 25 °C and the Ramman spectrum shows that it is negligibly dissociated in aqueous solutions.¹² Selenium(IV) is known to dimerize in concentrated solutions¹¹ and the dimerization constant is 5.6 ± 1.0 at 25 °C and ionic strength of 1.0 mol dm⁻³ NaClO₄. In view of this dimerization, the experiments of the present work were performed in a concentration range of $(0.79 \sim 4.75) \times 10^{-3}$ mol dm⁻³ of Se(IV), where the percentage of the monomer was as high as 99~92%. According to these reports, selenium dioxide may be presumed to exist mainly in the form of Se(IV) under all of our experimental conditions.

[Se(IV)] and [Ascorbic acid] Dependences

The reaction order with respect to ascorbic acid in aqueous HClO_4 medium was determined under pseudo first-order conditions where the $[\text{Se(IV)}]$ was presented in a large excess over the ascorbic acid concentration. Plots of $\log(\text{absorbance})$ versus time were linear up to 90% of the reaction completion. This linearity indicates that the reaction is first-order with respect to [ascorbic acid]. The first-order dependency was indicated not only by the linearity of the pseudo first-order plots, but also by the independence of the observed first order rate constants on different initial ascorbic acid values varied from 4×10^{-5} to 9×10^{-5} mol dm^{-3} in a number of steps at constant concentration of all other reagents. However, the first-order dependency was not maintained with respect to the Se(IV) concentration.

The values of pseudo first-order rate constants, k_{obs} , and the second-order rate constants k_2 (derived from dividing k_{obs} by $[\text{Se(IV)}]_0$) were calculated using the method of least-squares and summarized in Table I.

TABLE I

Rate constants for the oxidation of ascorbic acid by Se(IV) ion. [ascorbic acid] = 8.36×10^{-5} mol dm^{-3} , $[\text{H}^+] = 1.0$ mol dm^{-3} , $I = 1.0$ mol dm^{-3} and temp. = 25 °C

$10^4[\text{Se(IV)}]$ mol. dm^{-3}	$10^3 k_{\text{obs}}$ s^{-1}	k_2 $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
7.91	1.24	0.78
15.82	2.27	0.72
23.73	3.30	0.70
31.64	4.28	0.67
34.55	5.22	0.66

Dependence of Reaction Rate on Ionic Strength

In order to investigate the effect of ionic strength on the rate of reaction, kinetic runs were performed at $[\text{H}^+] = 0.5$ mol dm^{-3} with increasing addition of NaClO_4 up to 3.0 mol dm^{-3} . The values of k_{obs} were found to increase with increasing ionic strength. A plot of $\ln k_{\text{obs}}$ against $\sqrt{I}/(1+\sqrt{I})$ of the Brönsted-Bjerrum equation was linear with a positive intercept. Although the ionic strengths employed here lie far outside the Brönsted-Bjerrum region, the ionic strength dependency is qualitatively as expected for the charges involved.¹³

Dependence of the Reaction Rate on Hydrogen Ion Concentration

To clarify the influence of $[\text{H}^+]$ on the oxidation rates and to elucidate the reaction mechanism, kinetic measurements were carried out in HClO_4 - NaClO_4 mixtures of different $[\text{H}^+]$ and constants of ionic strength and temperature. An increase in HClO_4 concentration was found to accelerate the reaction rate. When the second order rate constants were plotted against $[\text{H}^+]$, curved lines passing through the origin were obtained as shown in Figure 1.

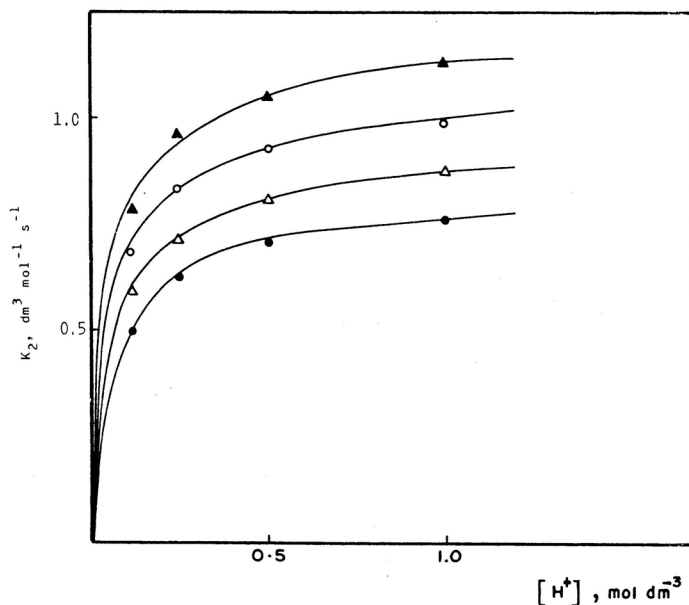


Figure 1. Hydrogen ion dependence of the oxidation of ascorbic acid by Se(IV) ion in HClO_4 medium. $[\text{Se(IV)}] = 9.89 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{ascorbic acid}] = 8.36 \times 10^{-5} \text{ mol dm}^{-3}$, $I = 1.0 \text{ mol dm}^{-3}$ [●]: 25; [Δ]: 30; [○]: 35; [▲]: 40 °C.

DISCUSSION

The first-order and fractional-order dependences on the substrate and the oxidant concentrations in aqueous HClO_4 media have led us to formulate the following rate expression:

$$-\frac{1}{2} \frac{d[\text{substrate}]}{dt} = -\frac{d[\text{oxidant}]}{dt} = k_2[\text{substrate}][\text{oxidant}]^{0.9} \quad (2)$$

The slight deviation of the reaction order from linearity with respect to $[\text{Se(IV)}]$ may be explained by formation of an intermediate complex between the substrate and oxidant or the formation of a dimer species, $[\text{Se(IV)}]_2$. Under the experimental conditions, the main reactive species are the monomers, while the dimer species are less reactive and hence may be neglected. At a slightly high $[\text{Se(IV)}]$, it is suggested that more than one oxidant molecule complex with the substrate can exist. At least one of the formed complexes appears to resist the oxidation process since increasing the $[\text{Se(IV)}]$ tends to decrease the reaction rate. If all complexes undergo oxidation, increasing Se(IV) concentration should increase the reaction rate. The dependence of k_{obs} values on selenium(IV) concentration was found to follow Michaelis-Menten kinetics.¹⁴ A typical reciprocal plot is shown in Figure 2. The good linearity observed in addition to the positive intercept on $1/k_{\text{obs}}$ axis indicates the formation of an intermediate complex prior to the rate-determining step. The change in color of the solutions as the reaction proceeded may also confirm the formation of such an intermediate.

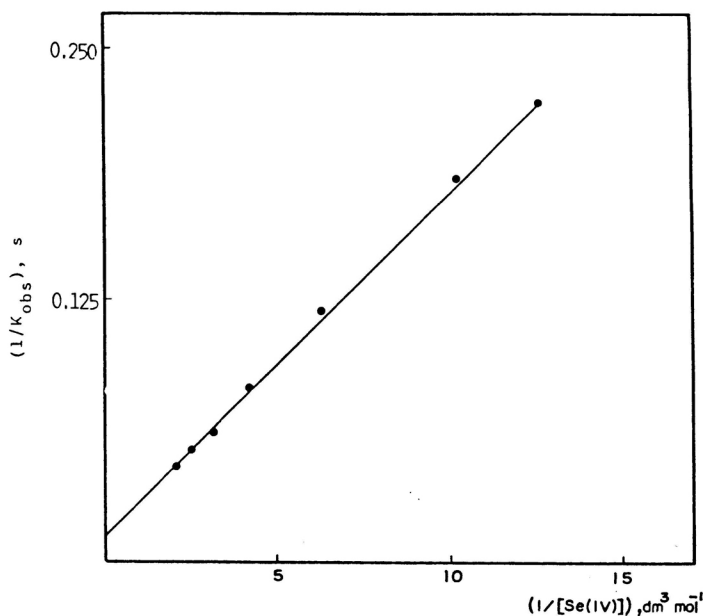


Figure 2. Plot of $1/k_{\text{obs}}$ vs. $1/[\text{Se(IV)}]$ in the oxidation of ascorbic acid by Se(IV) ion in HClO_4 medium. $[\text{ascorbic acid}] = 8.36 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$, $I = 1.0 \text{ mol dm}^{-3}$, and temp. = 25°C .

TABLE II

Hydrogen ion dependence. $[\text{ascorbic acid}] = 8.36 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{Se(IV)}] = 9.89 \times 10^{-4} \text{ mol dm}^{-3}$, $I = 1.0 \text{ mol dm}^{-3}$ and temp. = 25°C

$[\text{H}^+] / \text{mol dm}^{-3}$	0.13	0.25	0.50	1.00
$10^3 k_{\text{obs}} / \text{s}^{-1}$	1.00	1.25	1.40	1.52

It was also found that the rate constant increased with increasing the hydrogen ion concentration and showed a tendency to approach the infinity limiting value when the $[\text{H}^+]$ was increased beyond 1.0 mol dm^{-3} .^{*} The values of the rate constants, k_2 , are listed in Table II. The pronounced deviation from linearity (Figure 1) indicates that the observed rate constants obey the general rate law

$$k_{\text{obs}} = a + b [\text{H}^+] / (1 + c [\text{H}^+]) \quad (3)$$

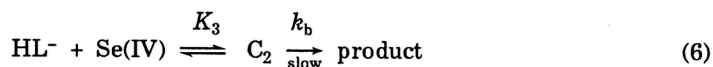
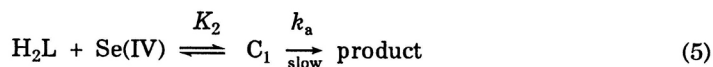
where one or two of the parameters a , b and c may be too small to detect experimentally in any particular case.

^{*} This indicates that the rate of reaction is pH-independent beyond $\text{pH} \leq 0$, as observed earlier.⁷

Hence, the catalytic behaviour of $[H^+]$ and the reciprocal plot of $1/k_{\text{obs}}$ versus $1/[\text{Se(IV)}]$ suggest that the reaction mechanism can be visualized by a fast dissociation of the substrate



where H_2L represents the undissociated ascorbic acid and HL^- is the ascorbate anion. The two most likely reaction mechanisms which may be suggested involve the following two competitive reactions



Intermediates C_1 and C_2 are formed and subsequently undergo further dissociation to give the products. Considering that the dissociation of such intermediates are the rate-determining steps, the change in the observed rate constant with the change in the hydrogen ion concentration may be expressed by equation (7)

$$\text{Rate} = \frac{(k_a K_2 + k_b K_1 K_3 [H^+]) [\text{H}_2\text{L}]_T [\text{Se(IV)}]}{1 + K_1 [H^+] + [\text{Se(IV)}] (K_2 + K_1 K_3 [H^+])} \quad (7)$$

where $[\text{H}_2\text{L}]_T$ is the analytical total concentration of L-ascorbic acid

$$[\text{H}_2\text{L}]_T = [\text{H}_2\text{L}] + [\text{HL}^-] + [\text{C}_1] + [\text{C}_2] \quad (8)$$

The experimental results described here are not in agreement with the rate equation (7) since the plots of the rate constant against $[H^+]$ gave sigmoidal curves passing through the origin (Figure 1). This means that the first term corresponding to the undissociated species of equation (5) is relatively small and, hence, reaction (5) can be neglected. Then, the rate law in terms of the form $b[H^+]/(1 + c[H^+])$ may reasonably be taken to reflect an operation of a mechanism in which ascorbate affects the reaction rate.¹⁵⁻¹⁷ Reaction (6) may, therefore, be considered as the sole mechanism and the rate law is

$$\text{Rate} = \frac{k_b K_1 K_3 [H^+] [\text{H}_2\text{L}]_T [\text{Se(IV)}]}{1 + K_1 [H^+] + [\text{Se(IV)}] (K_2 + K_1 K_3 [H^+])} \quad (9)$$

Under the condition of $[\text{Se(IV)}] \gg [\text{ascorbic acid}]$, the rate law can be expressed by

$$\text{Rate} = k_{\text{obs}} [\text{H}_2\text{L}]_T \quad (10)$$

Comparing equation (9) and equation (10) and considering that $K_1 K_3 [H^+] [\text{Se(IV)}] \ll (1 + K_1 [H^+])$ under our experimental conditions, the following relationship is obtained

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1}{k_b K_1 K_3 [\text{H}^+]} + \frac{1}{k_b K_3} \right) \frac{1}{[\text{Se(IV)}]} + K' \quad (11)$$

According to equation (11), at constant $[\text{H}^+]$ a plot of k_{obs}^{-1} versus $[\text{Se(IV)}]^{-1}$ should be a straight line with a positive intercept on k_{obs}^{-1} axis, as observed experimentally. Again, a plot of k_{obs}^{-1} against $[\text{H}^+]^{-1}$ gave a good straight line with a negligible intercept on k_{obs}^{-1} axis. Hence, equation (11) can be simplified to (12) which is considered as the appropriate rate equation for the oxidation of ascorbic acid by Se(IV) ion,

$$\frac{1}{k_2} = \frac{[\text{H}^+]^{-1}}{k'_b} + \frac{1}{k''_b} \quad (12)$$

where k_2 represents the second order constant, $k'_b = k_b K_1 K_3$ and $k''_b = k_b K_3$, respectively. Equation (12) indicates that a plot of $1/k_2$ versus $1/[\text{H}^+]$ should be linear. The available data satisfied this requirement as shown in Figure 3. From the slopes and intercepts, the value of K_1 can be evaluated. It was found that K_1 in the range 10^{-3} mol dm^{-3} at 25 °C is in good agreement with that reported elsewhere.¹¹ The values of k'_b and k''_b were calculated by the least-squares method.

Unfortunately, the value of k_b could not be evaluated because of the unavailability of the dissociation constant K_1 and the formation constant K_3 at various temperatures. Therefore, the apparent rate constants k'_b and k''_b are considered to be the products of the rate constants, the dissociation constants and the formation constants.

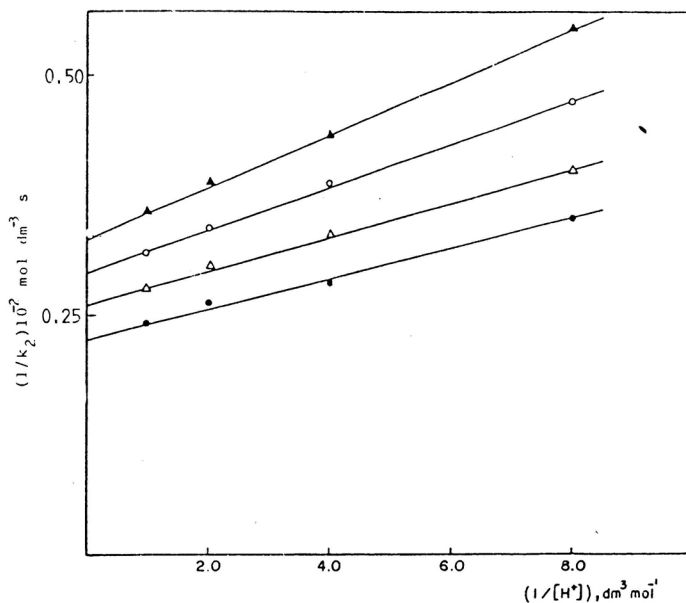


Figure 3. Hydrogen ion dependence of the oxidation of ascorbic acid by Se(IV) ion in HClO_4 medium. $[\text{Se(IV)}] = 9.89 \times 10^{-4}$ mol dm^{-3} , $[\text{ascorbic acid}] = 8.36 \times 10^{-5}$ mol dm^{-3} , $I = 1.0$ mol dm^{-3} , [●]: 25; [Δ]: 30; [○]: 35; [▲]: 40 °C.

A question of basic interest in connection with Se(IV) as a multiequivalent oxidant is whether electron-transfer proceeds through successive one-electron changes $\text{Se(IV)} \rightarrow \text{Se(III)} \rightarrow \text{Se(II)}$ or by a simultaneous two-electron transfer in a single step $\text{Se(IV)} \rightarrow \text{Se(II)}$.

Assuming the steady-state approximation of Se(III) in the former mechanism, a rate equation similar to that defined by eq. (2) is obtained. This fact may suggest that the present redox reaction follows the successive one-electron change mechanism. It appears that while the two equivalent pathway is more favourable on the energetic grounds,^{18,19} it is not prominent kinetically. Unfortunately, not enough kinetic data are available on the oxidation of organic compounds by Se(IV) ion to make a reliable comparison. However, we prefer to think in terms of the successive one-electron transfer mechanism through the formation of an intermediate complex ion of inner-sphere type for the oxidation of L-ascorbic acid by selenium dioxide.

Furthermore, this oxidation process has been carried out in HCl media of a wide range of the $[\text{H}^+]$ ($0.05 \sim 1.0 \text{ mol dm}^{-3}$). The kinetic results obtained were found to be quite different from those observed in HClO_4 solutions. Therefore, further work is in progress along with the oxidation of other substrates by this oxidant in order to gain more information on the reaction mechanism.

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SAŽETAK

Kinetika i mehanizam oksidacije askorbinske kiseline sa Se(IV) u kiselinu vodenim otopinama perklorata

R. M. Hassan

Navedena reakcija je istraživana spektrofotometrijskim postupkom pri 1.0 M ionskoj jakosti. Reakcija je katalizirana protonom a askorbatni anion stvara složeni međuprodukt. Određeni su aktivacijski parametri reakcije te predložen njen mehanizam.