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A Stopped-Flow Study of the Oxidation Raction of Ascorbic Acid with Chromic Acid

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Ascorbic acid (AH_2) in the presence of mild oxidizing agents becomes readily oxidized to dehydroascorbic acid (A). The oxidation process of ascorbic acid with molecular oxygen, strongly catalyzed by the metal ions [1, 2], as well as oxidation with various oxidizing agents, have been thoroughly studied. An extensive review of mechanistic studies made on the oxidation process of ascorbic acid with hydrogen peroxide, nitrous acid, Fe(III), Cu(II), Pd(II), Ag(I), V(V), Hg(II), hexacyanoferrate(III), peroxydisulphate, light platinum metals and of the aerobic oxidation was provided by Mushran and Agrawal [3].

In the present paper the kinetics and mechanism of the reaction between ascorbic acid and chromium(VI) in acid media is examined by the stopped-flow method.

Experimental

Stock solution of chromium(VI) was prepared from $Na_2CrO_4 \cdot 2H_2O$ and was standardized iodometrically. Solutions of known ascorbic acid concentrations were made by accurate weighing of the amount required and dissolving it quickly in bidistilled water. Perchloric acid solutions were prepared from 70% perchloric acid. The ionic strength was adjusted by introducing suitable quantities of 1 *M* $NaClO_4$ solution into the solution to be investigated.

The stoichiometric formula was established in the following manner. Solutions of reactants containing known amounts of Na_2CrO_4 in $HClO_4$ and slight excess ascorbic acid were mixed at 25 °C and the amount of ascorbic acid left was determined by titrating against standard iodine solution with a starch indicator. The quantity of dehydroascorbic acid formed in the reaction was determined by the Roe procedure [4] modified by Khan and Martell [5]. Three moles of ascorbic acid were found to react with two moles of Cr(VI) yielding three moles of dehydroascorbic acid.

All kinetic experiments in a stopped-flow apparatus described in a previous paper [6]. A decrease in the transmission of chromium(VI) at 350–500 nm was followed during the course of reaction. Excess of ascorbic acid and perchloric acid was used for all kinetic experiments. Pseudo-

TABLE 1. Kinetic Data for the Oxidation Reaction of Ascorbic Acid with Chromium(VI) at 25 °C.

10^4 [Cr(VI)] (*M*)	10^2 [AH_2] (*M*)	10^2 [$HClO_4$] (*M*)	10^2 [$NaClO_4$] (*M*)	k_{exp} (sec^{-1})
0.500	1.00	1.00	4.00	1.16
1.00	1.00	1.00	4.00	1.17
2.00	1.00	1.00	4.00	1.14
4.00	1.00	1.00	4.00	1.15
2.00	0.125	1.00	4.00	0.144
2.00	0.250	1.00	4.00	0.299
2.00	0.500	1.00	4.00	0.568
2.00	2.00	1.00	4.00	2.32
2.00	4.00	1.00	4.00	4.61
2.00	0.500	2.00	3.00	1.14
2.00	0.500	4.00	1.00	2.24
2.00	1.00	1.00	0.00	1.47
2.00	1.00	1.00	2.50	1.23
2.00	1.00	1.00	5.00	1.08
2.00	1.00	2.00	48.0	1.19
2.00	1.00	5.00	45.0	3.05
2.00	1.00	10.0	40.0	5.73
2.00	1.00	20.0	30.0	11.2
2.00	1.00	40.0	10.0	19.6
2.00	1.00	50.0	0.00	25.4

first-order rate constants were determined from the slopes of logarithm of absorbance *vs.* time plots.

Results and Discussion

The results of reaction rate measurements under various conditions are summarized in Table I. The reaction is precisely of the first order with respect to Cr(VI) and ascorbic acid. The first order with respect to hydrogen ions at low perchloric acid concentrations is decreased slightly at high acidities.

Considering the values of protolytic and hydrolytic equilibrium constants in aqueous chromate solutions [7, 8] and ascorbic acid solutions [5] as well as the concentrations used in the present study, one should assume that the main chromium(VI) ions are the $HCrO_4^-$ ions since the quantity of the dimeric form is less than 1% of monomer. According to the suggestions set forth by Haight *et al.* [9] chromium compounds at oxidation states V, IV and III in acid aqueous solutions are: H_3CrO_4, $Cr(H_2O)_6^{4+}$ and $Cr(H_2O)_6^{3+}$. Ascorbic acid occurs in the form of AH_2 and AH^-. Under the conditions studied, the AH^- ion concentration is very low and decreases with the increasing acidity of solution. An increase in the reaction rate with the increasing hydrogen ion concentration suggests that in the rate determining reaction undissociated ascorbic acid molecules and not the AH^- ions are involved [10, 11].

The effect of the hydrogen ion concentration on the reaction rate acceleration may be described by the following equation:

$$HCrO_4^- + H^+ \overset{K_a}{\rightleftharpoons} H_2CrO_4$$

This reaction is postulated as a reasonable way for one hydrogen ion to participate in the formation of the activated complex [12].

The above mentioned facts lead to the assumption that the H_2CrO_4 and AH_2 molecules are kinetic active species and the rate determining step in aqueous acid media is a binuclear process:

$$AH_2 + H_2CrO_4 \xrightarrow[(H^+,\ H_2O)]{k_o} A + Cr(H_2O)_6^{4+}$$

The rate of this process may be described by the kinetic equation:

$$V = \frac{k_oK_a[Cr(VI)]\,[AH_2]\,[H^+]}{1 + K_a[H^+]}$$

where [Cr(VI)] is the total concentration of Cr(VI).

A comparison of this relationship with the expression $V = k_{exp}[Cr(VI)]$ leads to the equation:

$$k_{exp} = \frac{k_oK_a[AH_2]\,[H^+]}{1 + K_a[H^+]}$$

or

$$\frac{[AH_2]}{k_{exp}} = \frac{1}{k_o} + \frac{1}{k_oK_a}\ \frac{1}{[H^+]}$$

Since H_2CrO_4 starts to appear at a moderate acid concentration [13–16] it should be expected that at high acidities the reaction course would deviate from the third-order rate law and the plot of $[AH_2]/k_{exp}$ *versus* $1/[H^+]$ should be linear. The data obtained at the high acid concentration support the suggested mechanism. The values of the rate constant k_o and the equilibrium constant K_a, at 25 °C and I = 0.5 *M* ($NaClO_4$, $HClO_4$), calculated from linear least-square fit of the experimental data to the equation presented above are as follows: $k_o = (1.5 \pm 0.4) \times 10^4$ M^{-1} sec^{-1}, $K_a = 0.4 \pm 0.1$ M^{-1}.

The latter value is in satisfactory agreement with $K_a = 0.35$ at 4 °C, I = 6 *M* ($NaClO_4$, $HClO_4$), obtained by kinetic investigations of the reaction between Cr(VI) and hydrogen peroxide [17], and with $K_a = 0.25$ at 25 °C, I = 1.0 *M* $NaClO_4$ and $K_a = 0.63$ at 25 °C, I = 0, obtained directly by spectrophotometry [16, 18].

The negative salt effect found experimentally is a secondary salt effect and results from shifting the protonization reaction equilibrium of the $HCrO_4^-$ ions. An increase in the ionic strength results in a decrease in concentration of the kinetically active chromium(VI) species and, hence, in a decrease of the reaction rate.

The temperature dependence was studied at four temperatures and yield the activation parameters: $\Delta H^{\ddagger} = 28.5 \pm 1.8$ kJ mol^{-1}, $\Delta S^{\ddagger} = -69.5 \pm 6$ JK^{-1} mol^{-1}. The low entropy of activation confirms the result of stoichiometric analysis that the process under investigation is the oxidation of ascorbic acid to dehydroascorbic acid and not to the cleavage products.

Rapid reduction process of Cr(IV) to Cr(III) may proceed by two ways: *via* Cr(IV)–Cr(VI) interaction:

$$Cr(IV) + Cr(VI) \rightarrow 2\ Cr(V)$$

or, *via* intermediate radicals:

$$Cr(IV) + AH_2 \rightarrow Cr(III) + {\cdot}AH + H^+$$

$${\cdot}AH + Cr(VI) \rightarrow A + H^+ + Cr(V)$$

Chromium(V) being formed in both cases would react with ascorbic acid in the one-step two-electron exchange process.

For the reactions involving cleavage of the reactant molecule the mechanism considering the Cr(IV)–Cr(VI) interaction was suggested much more frequently [19, 20]. Roček and Radkovsky [21] as well as Nave and Trahanovsky [22] proved the possibility of the formation of intermediate chromium(IV) compounds as active oxidizers and favoured the mechanism involving free radicals.

It is difficult to say which of the two suggested mechanism of Cr(IV) reduction is more probable.

Most of the authors dealing with the oxidation kinetics of ascorbic acid assume the radical reaction mechanism. The presence of free radicals in the oxidation processes of ascorbic acid with various oxidizers was confirmed by the ESR method by Lagercrautz [23], Kirino [24] and Yamazaki and coworkers [25].

References

1 M. M. T. Khan and A. E. Martell, *J. Am. Chem. Soc., 89,* 7104 (1967); *ibid., 90,* 6011 (1968); *ibid., 91,* 4668 (1969).

2 E. Y. Shtamm, A. P. Purmal and Yu. J. Skurlatov, *Int. J. Chem. Kinet., 11,* 461 (1979).

3 S. P. Mushran, M. C. Agrawal, *J. Sci. Ind. Res., 36,* 274 (1977).

4 J. H. Roe, 'Methods of Biochemical Analysis', Vol. 1, pp. 115, 139, Interscience Publishers Inc., New York, (1954).

5 M. M. T. Khan and A. E. Martell, *J. Am. Chem. Soc., 89,* 4176 (1967).

6 T. Banaś, B. Banaś and M. Wolny, *Eur. J. Biochem., 68,* 313 (1976).

7 J. Y. Tong and E. L. King, *J. Am. Chem. Soc., 75,* 6180 (1953).

8 W. G. Davies and J. E. Prue, *Trans. Faraday Soc., 51,* 1045 (1955).

9 G. P. Haight, T. J. Huang and B. Z. Shakhashiri, *J. Inorg. Nucl. Chem., 33,* 2169 (1971).

10 U. S. Mehrotra, M. C. Agrawal and S. P. Mushran, *J. Phys. Chem., 73,* 1996 (1969).

11 U. S. Mehrotra, M. C. Agrawal and S. P. Mushran, *J. Inorg. Nucl. Chem., 32,* 2325 (1970).

12 B. Banaś, *Polish J. Chem., 53,* 1943 (1979).

13 G. P. Haight, Jr., D. C. Richardson and N. H. Coburn, *Inorg. Chem., 3,* 1777 (1964).

14 N. Bailey, A. Carrington, K. A. K. Lott and M. C. R. Symonsons, *J. Chem. Soc.,* 290 (1960).

15 D. G. Lee and R. Stewart, *J. Am. Chem. Soc., 86,* 3051 (1964).

16 J. Y. Tong, *Inorg. Chem., 3,* 1804 (1964).

17 M. Orhanović and R. G. Wilkins, *J. Am. Chem. Soc., 89,* 278 (1967).

18 R. M. Smith and A. E. Martell, 'Critical Stability Constants', Vol. IV, p. 17, Plenum Press, New York, London (1976).

19 J. Hampton, A. Leo and F. H. Westheimer, *J. Am. Chem. Soc., 78,* 306 (1956).

20 J. J. Cawley and T. H. Westheimer, *J. Am. Chem. Soc., 85,* 1771 (1963).

21 J. Roček and A. E. Radkovsky, *J. Am. Chem. Soc., 90,* 2986 (1968).

22 P. M. Nave and W. S. Trahanovsky, *J. Am. Chem. Soc., 92,* 1120 (1970).

23 C. Lagercrautz, *Acta Chem. Scand., 18,* 562 (1964).

24 Y. Kirino, *Chem. Lett.,* 153 (1974).

25 J. Yamazaki, H. S. Mason and L. H. Piette, *J. Biol. Chem., 235,* 2444 (1960).