

Simultaneous Purification and Desalination of Water using Biodegradable Natural Polymers: A Kinetic Study of Reduction of Toxic Soluble Carcinogen Chromium (VI) to Removable Insoluble Chromium (III) Complexes with formation of Coordination Biopolymer Precursors for Removal of Undesired Poisonous Heavy Metal Ions From WastewaterRefat Hassan^{1,*}, Samia Ibrahim², Ishaq Zaafarany³Department of Chemistry, Faculty of Science, Assiut University, Assiut 71516 Egypt¹Department of Chemistry, Faculty of Science, Assiut University, New Valley Branch, El-Kharja 72511, New Valley, Egypt²Department of Chemistry, Faculty of Applied Sciences, Umm Al-Qura University, Makkah Al-Mukarramah 13401, Saudi Arabia³

ABSTRACT: The high toxicity of chromate anion and the suspected carcinogen and mutagen symptoms makes the chemistry of chromium (VI) in biological systems very important for biochemists and chemists. It is well established that reduction of chromium from toxic soluble Cr(VI) to insoluble Cr(III) complexes can be treated by a multiplicity of reaction techniques depending on the nature of the reducing agent and the reaction conditions. Unfortunately, techniques which are available in the markets still remained expensive and of low efficiency. Therefore pectin as biodegradable, safety, non-expensive natural polymer can be used as a strong reducing agent of toxic Cr(VI) for simultaneous removal of poisonous heavy metal ions and cleaning up the soluble toxic chromium (VI) from wastewater. This new technique has emerged as a new promising and pervasive in future technological industry. Moreover, the formed diketo-pectate as coordination biopolymeric oxidation precursor was found to possess high affinity for chelation with the Cr(III) formed as well as with polyvalent metal ions existed in the solution. Hence, this oxidation product can be used as a chelating agent for removal of toxic and undesired heavy metal ions from contaminated matters such as in water, soil or environment. The reduction kinetics of chromic acid by pectin (PEC) in aqueous solutions has been investigated, spectrophotometrically. A kinetic evidence for formation of 1:1 coordination biopolymer intermediate complexes between pectin and Cr (VI) was revealed. The route and nature of electron-transfer in the rate-determining step has been examined and discussed. The kinetic parameters have been evaluated and a tentative reaction mechanism consistent with the kinetic results obtained is discussed.

KEYWORDS: Pollution, Pectin, Natural polymers, Chromate (VI), Reduction, Cheating agents, Kinetics, Mechanisms.

I. INTRODUCTION

Chromium (VI) is well established carcinogen and mutagen as well as reduces the plant growth and cause skin inflammation, mammals and eczemas in fish. Therefore, the distribution of Cr(VI) in water, soil and environment from the chemical weathering such as the chemical manufacturing facilities, cooling towers, steel mills, and chrome plating facilities has become a serious problem faces the human health around the universe. The need for drinkable and pure water sources has become a major challenge. The environmental fate of chromium is controlled by many techniques including, precipitation-dissolution, adsorption-desorption and oxidation-reduction methods. The danger of environmental contamination depends on the oxidation state of the existed chromium ion [1].

Plants are the most important source of human survival. Plant carbohydrates involving polysaccharides are ideal candidates for therapeutics with immunomodulatory, antitumor and wound-healing action. Therefore, pectin as polysaccharide have received much attention in the last decade owing to its potential applications such as in cleaning up the industrial wastes, pharmaceutical industries, food industry as thickening and gelling agents [2-5].

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Preliminary experiments showed that pectin is a strong reducing agent of chromium (VI) in aqueous solutions. The reduction process indicated the existence of complex kinetics in which the pseudo-first-order plots showed curves of sigmoidal nature consisting of two distinct stages throughout the entire course of reaction.

In view of the above aspects and our interest on the reduction of oxidizing agents such as permanganate ion cerium (IV) and hexacyanoferrate(III), hexachloroiridate (IV) oxidants by polysaccharide substrates as natural polymer reducing agents [6-12], therefore, the reduction of chromium(VI) by pectin polysaccharide from insoluble toxic hexavalent state to trivalent state, Cr(III), which has high tendency to form removable insoluble complexes seems to be of great significant. This work aims to remediate wastewater from both toxic chromium(VI) and heavy metal ions with shedding more light on the reduction pathway in terms of the reactive species, nature of electron-transfer and the transition states in the rate-determining.

II. EXPERIMENTAL

Materials

All materials used were of analytical grade. Distilled water was redistilled from alkaline permanganate and degassed by bubbling through nitrogen, boiling and cooling under nitrogen atmosphere.

Pectin (PEC) as polysaccharide is the methyl ester of pectic acid consisting of long chains of D-galacturonic acid units in a linear block copolymer structure. The D-galacturonic acid residue are linked together by alpha-(1,4)-glycosidic linkages [9].

Apple pectin used was (BDH) and was used without further purification. Different concentrations of pectin (PEC) were prepared as described elsewhere [12]. The process was performed by stepwise addition of the sample reagent to deionized water whilst rapidly stirring the solution to avoid the formation of lumps, which swell with difficulty. The viscosity was measured using Ubbelohde viscometer 4% pectin solution in water at 20 °C. The inherent and reduced viscosities were found to be 0.62 dl g⁻¹ and 2.16 dl g⁻¹, respectively

Kinetic Measurements

The kinetic measurements were conducted under pseudo-first-order conditions where the PEC was present in a large excess over that of chromic acid concentration at a constant ionic strength of 2.0 mol dm⁻³. The experimental conditions and the procedure of measurements were the same as described earlier [6-8]. The course of reaction was followed by recording the decrease in absorbance of chromic acid at its absorption maximum, 350 nm, as a function of time. It was verified that there is no interference from other reagents at this wavelength. The absorbance measurements were made in a thermostated cell compartment at the desired temperature within ± 0.05 °C on a Shimadzu UV-2101/3101 PC automatic scanning double-beam spectrophotometer fitted with a wavelength program controller using cells of pathlength 1cm. The spectral changes during the progress of oxidation reaction are shown in Fig. 1.

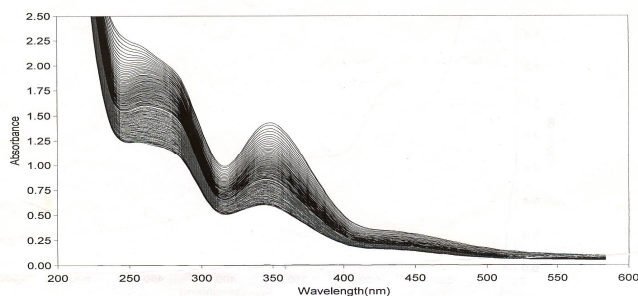


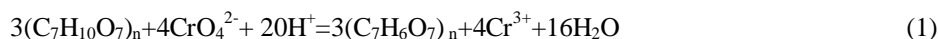
Fig. 1. Spectral changes (200–500 nm) in the oxidation of pectin by chromic acid in aqueous perchloric acid during the reaction progression.

[Cr^{VI}] = 7.0 × 10⁻⁴, [PEC] = 2.0 × 10⁻², [H⁺] = 1.0 and I = 2.0 mol dm⁻³ at 40 °C.

III. RESULTS

Stoichiometry

Since this reaction seems to be of considerable complexity, determination of the stoichiometry of the overall reaction is of a great importance. Reaction mixtures containing known of different initial concentrations of the reactants were equilibrated for about 48 h at room temperature in a set of experiments. The unreacted chromic acid was estimated periodically until it reached a constant value, i.e. reaction completion. A stoichiometric ratio of ($[\text{chromic acid}]_{\text{consumed}}/[\text{PEC}]_0$) was found to be 1.33 ± 0.1 mol. This result conforms to the following stoichiometric overall reaction,



where $\text{C}_7\text{H}_{10}\text{O}_7$ and $\text{C}_7\text{H}_6\text{O}_7$ represent the pectin and its corresponding keto- derivative form, respectively. The reaction product was separated and identified by elemental analysis and spectral data. The product was identified by the reaction with 2,4-dinitrophenylhydrazine and hydroxyl amine to afford the formation of the corresponding 2,4-dinitrophenylhydrazone and dioxime, respectively, as described elsewhere [13, 14]. The decay of the band at 3450 cm^{-1} and the enhancement the band at 1700 cm^{-1} would suggest the transformation of secondary alcohols (-OH) to its corresponding keto (C=O) groups. The IR spectra of the reactants and products are shown in Fig. 2.

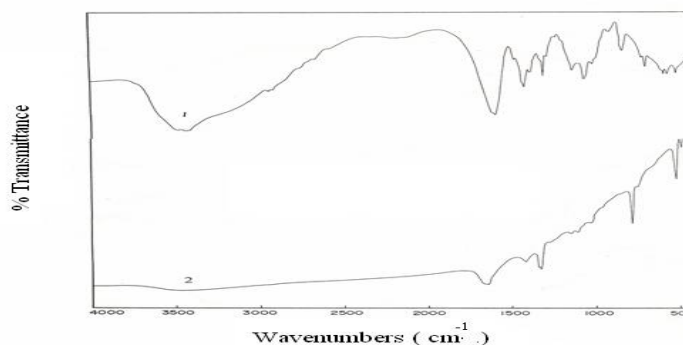


Fig.2. FTIR spectra of the reactants and products; (1) pectin; (2) ketoderivative.

Reaction-Time Curves

Reaction time curves were found to be of sigmoidal nature throughout the entire course of reaction. The initial rates were relatively fast in the early stage (autoacceleration period), followed by a slow stage which became linear over longer time periods (induction period) as shown in Fig. 3. As the reaction is of autocatalytic nature, the oxidation kinetics may obey the rate-law expression $(A_\infty - A_t) = B_0 e^{-k_f t} + P_0 e^{-k_s t}$ where k_f and k_s are the pseudo first-order rate constants for the fast and slow stages. A_t and A_∞ are the absorbance at time t and infinity, while B_0 and P_0 represent the absorbance change for the slow and fast reacting species, respectively. The pseudo first-order rate constants (k_f and k_s) were calculated by the least-squares method and are summarized in Table 1. The rate constants, k_s , listed in Table 1, were obtained by drawing a straight line through the slow-time linear portion of the first-order plot and extrapolating the line back to zero time (B_0). Again, the rate constants, k_f , for the autoacceleration period were obtained from plots of $-\ln[(A_t - A_\infty) - (A_t' - A_\infty)]$ vs. time. The quantity $(A_t - A_\infty)$ represents the experimental point and $(A_t' - A_\infty)$ represents the extrapolated point at time t' [9-12,15,16].

Dependence of Reaction Rates on [Chromic acid] and [PEC]

The gradual decrease in absorbance of chromic acid with time (Fig. 1) as well as the pseudo first-order plots (Fig. 3) may indicate that the reaction is first-order in chromic acid concentration. This first-order dependency was confirmed for the two reaction stages not only from the linear portions of the pseudo-first-order plots (Fig. 3) but also

from the independence of the observed pseudo first-order rate constants obtained on different initial concentrations of chromic acid and constants of all other reagents. The $[\text{CrO}_4^{2-}]$ was varied in the range of $(2-9) \times 10^{-4}$, $[\text{PEC}] = 2 \times 10^{-2}$, $[\text{H}^+] = 1.0$ and $I = 2.0 \text{ mol dm}^{-3}$ at various temperatures.

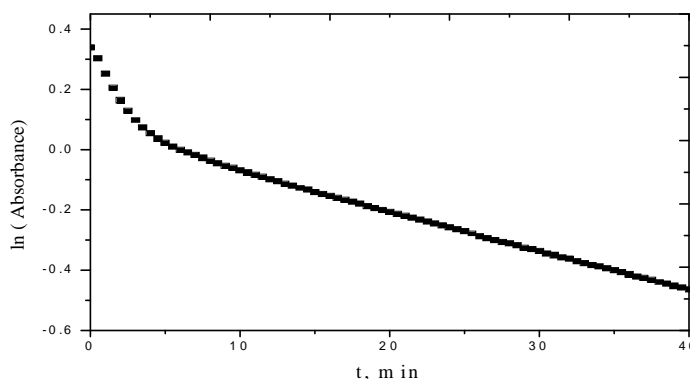


Fig. 3. Plots of pseudo-first-order rate constants for the oxidation of pectin by chromic acid in aqueous perchloric acid. $[\text{Cr}^{\text{VI}}] = 7.0 \times 10^{-4}$, $[\text{H}^+] = 2.0$ and $I = 2.0 \text{ mol dm}^{-3}$ at 45°C .

The order with respect to PEC was deduced from the kinetic measurements at several $[\text{PEC}]_0$ and fixed chromic acid concentration. The non-constancy obtained for the second-order rate constants derived from dividing the observed pseudo-first-order rate constants k_{obs} (where k_{obs} represents to either of k_f and k_s) by $[\text{PEC}]_0$ indicating that the reaction is fractional-order in PEC concentration.. When these values were plotted against the $[\text{PEC}]$, curvature lines passing through the origin were obtained on contrary to that observed elsewhere [5]. Again, when the values of $1/k_f$ or $1/k_s$ were plotted against $1/[\text{PEC}]$, straight lines with positive intercept on $1/k_f$ or $1/k_s$ axes, respectively, were obtained as shown in Fig. 4. Such dependence of the rate constants on the pectin concentration was found to exhibit the Michaelis-Menten kinetics for formation of 1:1 intermediate complexes between the substrate and the oxidant.

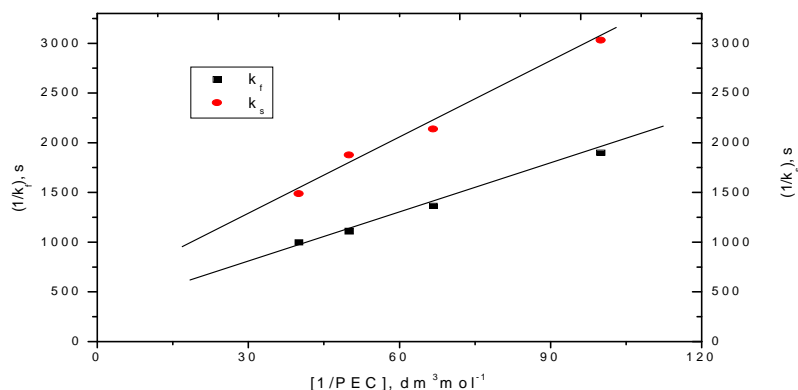


Fig. 4. Reciprocal Michaelis-Menten plot for the oxidation of pectin by chromic acid in aqueous perchloric acid. $[\text{Cr}^{\text{VI}}] = 7.0 \times 10^{-4}$, $[\text{H}^+] = 1.0$ and $I = 2.0 \text{ mol dm}^{-3}$ at 40°C .

From the Lineweaver-Burk plot, the Michaelis-Menten constant (K_m) was calculated and found to be 0.24×10^2 and $0.21 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}$ where the maximum rates (γ_{max}) were found to be 1.0×10^{-3} and $6.73 \times 10^{-4} \text{ s}^{-1}$ for the autoacceleration and induction periods, respectively. The observed large values for K_m indicated the fast formation of the intermediate complexes throughout the entire course of the oxidation process.

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Again, some kinetic runs were performed by using dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) as an oxidant in order to examine the effect of variation of the oxidant conformation on the oxidation rates. The kinetic results are summarized in Table 2.

Dependence of Reaction Rates on $[\text{H}^+]$

Kinetic measurements were performed in $\text{HClO}_4\text{-NaClO}_4$ solutions with different hydrogen ion concentrations and constants of ionic strength and temperature in order to clarify the influence of $[\text{H}^+]$ on the reaction rates as well as to elucidate a suitable reaction mechanism. An increase in the acid concentration was found to accelerate the oxidation rates of both the autoacceleration and induction periods indicating that the oxidation process is acid-catalyzed in both two stages. The results are summarized in Table 1. When the values of the rate constants (k_f and k_s) were plotted against the $[\text{H}^+]$, straight lines with positive intercepts on $1/\text{rate}$ axes were observed which is opposite to that reported earlier [5].

Table 1. Dependence of pseudo-first order of the rate constants (k_f and k_s) on $[\text{H}^+]$ and [PEC] reactants in the oxidation of pectin by chromic acid in aqueous perchlorate solutions. $[\text{Cr}^{\text{VI}}]=7 \times 10^{-4}$ and $I = 2.0 \text{ mol dm}^{-3}$ at 40°C .

$[\text{H}^+]^a$ mol dm^{-3}	$k_{\text{obs}}, \text{s}^{-1}$		10^2 [PEC] ^b , mol dm^{-3}	$k_{\text{obs}}, \text{s}^{-1}$	
	$10^3 k_f$	$10^4 k_s$		$10^3 k_f$	$10^4 k_s$
1.0	1.026	5.33	1.0	0.56	3.30
2.0	1.93	6.30	2.5	1.0	6.737

a: $[\text{PEC}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$

b: $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$

Moreover, some kinetic runs were performed using sulfuric and hydrochloric acids as a source of hydrogen ions in order to examine the influence of the nature of acids on the reaction rates. The kinetic results are summarized in Table 2.

Table 2. Effect of variation of both added mineral acids and Cr (VI) on the oxidation rates of the induction period in the oxidation of pectin by chromic acid in acid perchlorate solutions. $[\text{PEC}] = 2.0 \times 10^{-2}$, $[\text{Ox}] = 7.0 \times 10^{-4}$, $[\text{H}^+] = 1.0$ and $I = 2.0 \text{ mol dm}^{-3}$ at 40°C .

Acid	$10^4 k_s, \text{s}^{-1}$	$[\text{Cr}^{\text{VI}}]$	$10^4 k_s, \text{s}^{-1}$
HClO_4	5.33	K_2CrO_4	5.33
H_2SO_4	8.67	$\text{K}_2\text{Cr}_2\text{O}_7$	2.08
HCl	6.83		

Dependence of Reaction Rates on Ionic Strength

To shed some lights on the reactive species in the rate-determining step, the influence of the ionic strength on the reaction rates was examined. Kinetic runs were performed at constant $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$ as NaClO_4 concentration was increased to 2.5 mol dm^{-3} . The values of k_f and k_s were found to increase with increasing the ionic strength. Plots of $\ln k_f$ and k_s against $I^{0.5}$ according to the Debye-Hückel relationship gave good straight lines with positive slopes as shown in Fig. 5. The ionic strength dependence was qualitatively as expected when considering the charges involved. This means that the reaction takes place between two negative charge ions or between a positive ion and neutral molecule [17].

$10^3[\text{MnSO}_4], \text{mol dm}^{-3}$	0.0	1.0	4.0	8.0
$10^4 k_{obs}, \text{s}^{-1}$	5.3	3.0	2.3	1.2

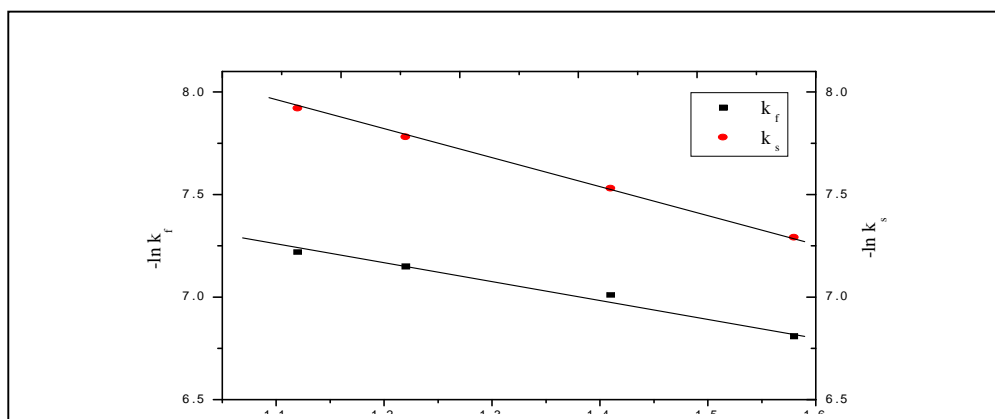


Fig. 5. Ionic strength dependency of the rate constants in the oxidation of pectin by chromic acid in aqueous perchloric acid. $[\text{Cr}^{\text{VI}}] = 7.0 \times 10^{-4}$, $[\text{PEC}] = 2.0 \times 10^{-2}$, $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$ at 40°C .

Polymerization Test

Since this oxidation reaction seems to be of complementary type, the possibility of formation of free-radicals was examined by adding 10% (v/v) of acrylonitrile to the partially oxidized reaction mixtures. A polymeric suspension was noticeable after a lapse of 20 min on warming. Black experiments from which either CrO_4^{2-} or PEC were excluded gave no detectable polymerization during this time. This result indicates the intervention of free-radical during the entire course of oxidation reaction.

Influence of the Manganous Ions on the Rates

In order to check the involvement or absent of Cr^{IV} as an intermediate during the progress of oxidation reaction, the effect of addition of manganous ions to the reaction mixture has been examined [18,19]. The reaction rates were found to decrease linearly with increasing the added Mn^{+2} ions. The experimental results are summarized in Table 3.

Table 3. Effect of added salts on the rate constants of the induction period in the oxidation of pectin by chromic acid in aqueous perchloric. $[\text{Cr}^{\text{VI}}] = 7.0 \times 10^{-4}$, $[\text{PEC}] = 2.0 \times 10^{-2}$, $[\text{H}^+] = 1.0$ and $I = 2.0 \text{ mol dm}^{-3}$ at 40°C .

In general, two reaction mechanisms for electron-transfer in the redox reactions which involve chromium (VI) as an oxidant may be suggested. The first one corresponds to successive one-electron-transfer mechanism, $\text{Cr}^{\text{VI}} \rightarrow \text{Cr}^{\text{V}} \rightarrow \text{Cr}^{\text{IV}} \rightarrow \text{Cr}^{\text{III}}$, in a sequence. The second mechanism involves a simultaneous two-electron changes, $\text{Cr}^{\text{VI}} \rightarrow \text{Cr}^{\text{IV}} \rightarrow \text{Cr}^{\text{II}}$, in a single step. This means that both one-electron transfer and two-electron changes may be considered for the oxidation of pectin by chromium (VI) with formation of either Cr^{V} or Cr^{IV} transient species, respectively [18-20]. The involvement of chromium (IV) as an intermediate in those redox reactions has generated much debate in the past [20]. Therefore, the influence of addition of manganous ion on the oxidation rates is considered as good evidence to determine the involvement of such chromium (IV) as an intermediate during the reaction progress. This is because Mn (II) has been recognized as frequently tool for trapping of Cr (IV) intermediate.

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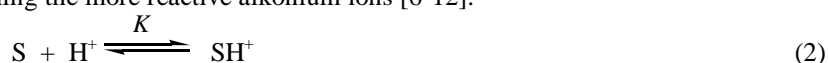
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IV. DISCUSSION

The oxidation of apple pectin by chromium (VI) has been investigated, elsewhere [21]. It reported that the oxidation process was of selective nature in which the oxidation process occurring by the break of C-C bond in – (H) C (OR)-CO₂H moieties rather than C-H cleavage of the terminal hemiacetals. So, the oxidation reaction affords the formation of CO₂/HCO₂H and oxidized pectin in the oxidation process. Two mechanisms for electron-transfer were suggested, depending on the pH of the medium. The first one corresponds to one-electron transfer with formation of chromium (V) as transient species, whereas the other involves simultaneous two-electron changes with formation of chromium (IV) as the transient species. Unfortunately, the influence of some variables such as the ionic strength and temperature on the oxidation rates had not been examined. Therefore, details information on the reactive species, nature of electron-transfer and the transition states in the rate-determining step still remains not completed and poor understood.

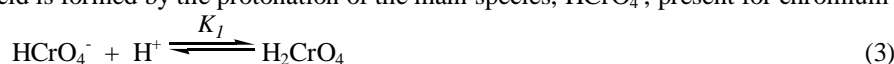
The reaction time-curves showed that the kinetics of the cited redox reaction is complex. This fact may be attributed to the variety species of chromium (VI) in acid solution, the presumed passage of chromium through transient unstable species of oxidation numbers (V) and (IV) as well as the tendency of the formed chromium (III) to form variety of complexes with the oxidation products, all combine to give systems of considerable complexity [22].

The hydrogen ion dependence of the rate constants indicated that the oxidation reaction is acid-catalyzed in both two stages. This means that at least one or both reactants are subjected to protonation process prior to the rate-determining steps. It is well known that polysaccharides (S) involving pectin substrate have a high tendency to protonate in acidic solutions forming the more reactive alkonium ions [6-12].



where S and SH⁺ represent PEC and its protonated form, whereas *K* is the protonation constant of pectin substrate.

On the other hand, considering the values of the protolytic and hydrolytic equilibrium constants for chromium (VI) in aqueous perchlorate solutions [19,23,24], it may reasonable to assume that the main reactive chromium (VI) ions are H₂CrO₄ species since the quantity of the dimeric form is negligible small under our experimental conditions. Again, using the reported values for the protonation constants (*K*) of chromic acid [25-27], the formed H₂CrO₄ was found to be in the range 80 -95 % of the total analytical concentration of Cr (VI) used under our experimental conditions. Chromic acid is formed by the protonation of the main species, HCrO₄⁻, present for chromium (VI) [6,7] as follows,



where *K*₁ is the protonation constant of chromic acid.

Since, addition of manganese (II) to the reaction mixture was found to decrease the oxidation rate (Table 4).

Table 4. The values of the apparent rate constants *k*_a' (*k*_a' = *k*_a*KK*₁*K*₂) and *k*_b' (*k*_b' = *k*_b*KK*₃)

Temp., °C	35	40	45
Rate constant			
10 ² <i>k</i> _a ' , dm ⁹ mol ⁻³ s ⁻¹	4.45	5.40	6.13
10 ² <i>k</i> _b ' , dm ⁶ mol ⁻² s ⁻¹	8.60	8.91	9.20

Experimental error ± 4 %

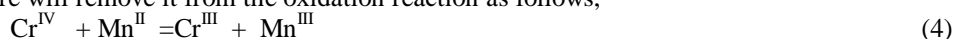
Such a behavior was observed in most oxidation of organic substrates by this oxidant in which chromium (IV) was suggested as the transient species [27,29]. Although, the formed manganese (III) is a strong competitor oxidant to chromic acid and, hence, is capable to oxidize the protonated substrate, its oxidation is comparably negligible small. This fact can be explained by the unstability of Mn (III) which undergoes a rapid disproportionation under our experimental conditions of the hydrogen ion used [30]. The estimated redox potentials of Cr^{VI}/Cr^{III} (E° = 1.33 V) and Mn^{III}/Mn^{II} (E° = 1.51V) couples indicated that the oxidation of Mn^{II} byCr^{VI} is unfavorable based on the

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thermodynamic grounds [31,32]. Therefore, if chromium (IV) intermediate is involved, the addition of Mn^{+2} to the reaction mixture will remove it from the oxidation reaction as follows,

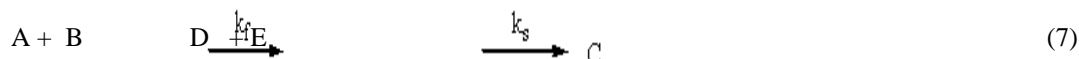


On the other hand, no spectrophotometric evidence was observed for formation of chromium (V) at 700 nm, its maximum wavelength, on using chromic acid as a reference cell. This fact may support the formation of Cr^{IV} as transient species intermediate for reduction of chromium (VI) rather than the formation of Cr^V species.

In view of the above interpretations and our experimental results, two reaction mechanisms may be suggested for oxidation of pectin by chromic acid. The first one corresponds to the existence of either two parallel reactions [30]

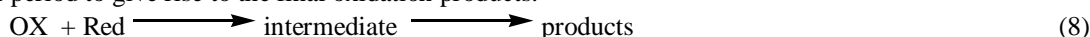


or two- consecutive first-order reactions as follows



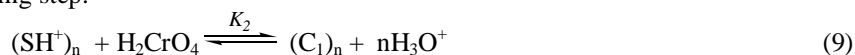
where the symbols k_f and k_s represent to the observed pseudo-first-order rate constants in the two stages, A and B ; D and E are their respective reactants, respectively and C is the product.

The second mechanism involves fast formation of an intermediate complex with the occurrence of electron-transfer process in the autoacceleration period, followed by a slow decomposition of such intermediate in the final induction period to give rise to the final oxidation products.

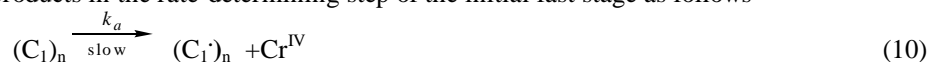


The second mechanism may be excluded in terms of the perturbation in the spectrum of chromic acid during the progress of reaction changes (Fig.1) as well as the dependence of the observed pseudo-first-order rate constants on both PEC substrate and hydrogen ion concentrations in both two stages. Hence, the former mechanism may be considered as the most suitable one for oxidation of pectin substrate by chromic acid. However, the two-parallel reactions-path is the more predominant mechanism; the two-consecutive first-order reaction-path could not be completely excluded.

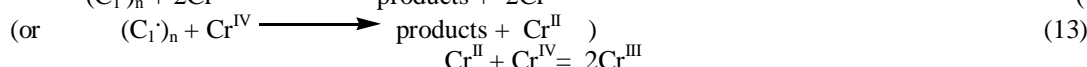
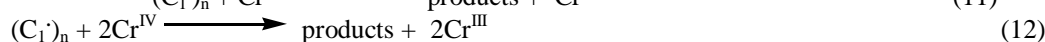
In a such two-parallel reaction-path mechanism, the protonated species of pectin substrate is firstly attacked by chromic acid oxidant to form the coordination biopolymer intermediate complex $(C_1)_n$ with abstraction of hydronium ions prior to the rate-determining step.



Then, a transfer of electrons from pectin to the oxidant occurs forming a radical substrate $(C_1\cdot)$ and chromium (IV) as initial oxidation products in the rate-determining step of the initial fast stage as follows



The substrate radical $(C_1\cdot)$ formed is rapidly oxidized by either Cr^{IV} or picking up a further chromic acid molecule to give rise to the oxidation product as in Eqs. (11-13),



The change of the rate constant with the change in the substrate and hydrogen ion concentrations can be expressed by the following rate-law equation

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$$\text{Rate} = \frac{(k_a K K_1 K_2 [H^+][\text{PEC}])[\text{OX}]}{1 + K_1 [H^+] + K K_1 K_2 [H^+][\text{PEC}]} \quad (14)$$

Under our experimental conditions of presence of a large excess of [PEC] over that of chromic acid concentration, the rate-law expression is

$$\text{Rate} = k_{\text{obs}} [\text{OX}] \quad (15)$$

where k_{obs} is the observed pseudo-first-order rate constant which corresponds to either k_f or k_s rate constants. Comparing both Eq. (14) and Eq. (15) and rearrangement, one concludes that

$$\frac{1}{k_f} = \frac{[H^+]^{-1}}{k_a K K_1 K_2 [\text{PEC}]} + \frac{1}{k_a K K_2 [\text{PEC}]} + \frac{1}{k_a} \quad (16)$$

Equation (16) required that plots of $1/k_f$ ($k_f = k_{\text{obs}}$) vs $1/[\text{PEC}]$ at constant $[H^+]$ to be linear with positive intercepts on $1/k_f$ axis as was experimentally observed (Fig.4). Again, at constant [PEC] plots of $1/k_f$ vs $1/[H^+]$ were found to be linear with positive intercepts on $1/k_f$ axes as shown in Fig. 6.

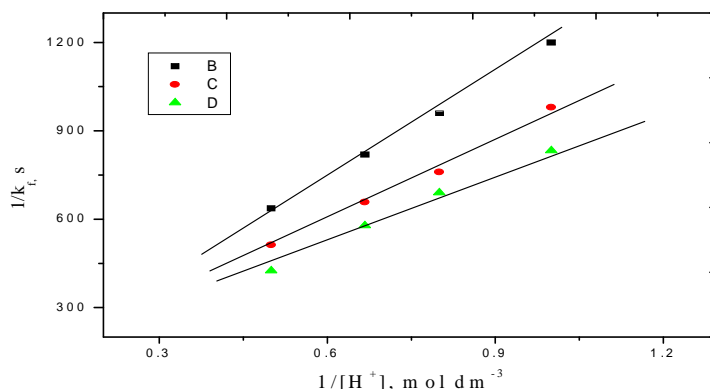
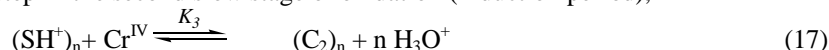


Fig.6. Plots of $1/\text{rate}$ vs $1/[H^+]$ in the oxidation of pectin by chromic acid in aqueous perchlorate solutions. $[\text{Cr}^{\text{VI}}] = 7 \times 10^{-4}$, $[\text{PEC}] = 2 \times 10^{-2}$, $I = 2.0 \text{ mol dm}^{-3}$ at various temperatures.

The values of the elementary reaction (k_a) and the protonation constants (K_1) of chromic acid can be evaluated from the slopes and intercepts of the above two plots. These values were calculated by the least-squares method and found to be $2.73 \times 10^{-3} \text{ s}^{-1}$ and $0.1 \text{ dm}^3 \text{ mol}^{-1}$, respectively, at 40°C .

The value of the protonation constant (K_1) obtained was found to be in good agreement to that reported elsewhere [19,25-27] which may support the suggested mechanism for oxidation of pectin by chromic acid. Unfortunately, the values of the elementary reactions (k_a) and the protonation constants could not be calculated at various temperatures since the dependence of the reaction rates on the substrate concentration was studied at only 40°C . Therefore, the apparent rate constant k_a' (where $k_a' = k_a K K_1 K_2$) were calculated by the least-squares method and are summarized in Table 4. The activation parameters of the apparent rate constants were calculated by the method of least-squares and found to be $E^\ddagger = 26.12 \text{ kJmol}^{-1}$, $\Delta H^\ddagger = 23.51 \text{ kJmol}^{-1}$, $\Delta S^\ddagger = -194.64 \text{ Jmol}^{-1}\text{K}^{-1}$, $\Delta G^\ddagger = 81.52 \text{ kJmol}^{-1}$, $A = 1.21 \times 10^3 \text{ mols}^{-1}$ (within experimental errors $\pm 4\%$).

On the other hand, the chromium (IV) formed in Eq. (10) will attack the center of a further protonated pectin substrate to form the coordination biopolymeric intermediate complex $(C_2)_n$ with abstraction of hydronium ions prior to the rate-determining step in the second slow stage of oxidation (induction period),

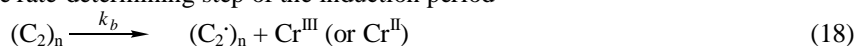


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Then, an electron-transfer process occurs to give a further substrate radical $(C_2)_n$ and the reduced chromium ions as initial oxidation products in the rate-determining step of the induction period



A such substrate radical formed $(C_2)_n$ is rapidly oxidized by picking up further oxidant molecules (either Cr^{IV} or Cr^{VI}) to give rise to the oxidation product in the second slow-stage of oxidation (induction period).

In a similar manner to that followed in the autoacceleration period, the change of the rate constants with the change in the hydrogen ion and substrate concentrations can be deduced. Considering that the chromium (IV) concentration equals to that of initial chromium (VI) concentration, the corresponding rate-law expression can be written as follows,

$$\frac{1}{k_s} = \frac{[H^+]^{-1}}{k_b K K_3 [PEC]} + \frac{1}{k_b K_3 [PEC]} + \frac{1}{k_b} \quad (19)$$

According to Eq. (19), plots of $1/k_s$ ($k_s = k_{obs}$) at constant $[H^+]$. Against $1/[PEC]$ as well as $1/k_s$ vs. $1/[H^+]$ at constant $[PEC]$ gave good straight lines with positive intercepts on $1/k_s$ axes from which the rate constant of the final slow stage can be evaluated. The value of the rate constant of the elementary reaction (k_b) was found to be $1.89 \times 10^{-3} \text{ s}^{-1}$ at 40°C . The values of k_b could not be evaluated at other temperatures since the dependence of the rate constants on the $[PEC]$ was performed at only 40°C . Hence, the values of the apparent rate constants k_b^{app} (where $k_b^{\text{app}} = k_b K K_3$) were considered. The values of the activation parameters of the apparent rate constants (k_b^{app}) were calculated from the Arrhenius and Eyring equations using the least-squares method and found to be $E_a^\ddagger = 5.46 \text{ kJmol}^{-1}$, $\Delta H^\ddagger = 2.93 \text{ kJmol}^{-1}$, $\Delta S^\ddagger = -256.04 \text{ Jmol}^{-1}\text{K}^{-1}$, $\Delta G^\ddagger = 79.24 \text{ kJmol}^{-1}$, $A = 0.73 \text{ mols}^{-1}$ (within experimental errors $\pm 4\%$).

The observed small activation energy value, E_a^\ddagger , is an indication of the lower energy barrier required for the formation of the activated complexes in the transition states. Therefore, the electrostatic attraction between the reactants does not need much energy to bring them together in order to form the activated complex. This is in good agreement with the values of Michaelis-Menten constants obtained. The observed large negatively values for ΔS^\ddagger may confirm the compactness of the intermediates rather than the reactants. It reported that the entropy of activation, ΔS^\ddagger , is negative for oxidation reactions that proceeding via complex formation of inner-sphere nature; while the values of ΔS^\ddagger for the outer-sphere mechanisms tend to be more positive [18,34,35]. Therefore, the observed negative values of ΔS^\ddagger obtained in the present investigation may exhibit reactions of inner-sphere mechanism. This means that the oxidation of PEC by chromic acid is more favorable to proceed by inner-sphere path of two-electron changes rather than by outer-sphere mechanism. In this context, it should be noted that there does not appear to be any experimental confirmation of outer-sphere two-electron transfer process [32-34]. Moreover, the positive values of ΔG^\ddagger obtained may confirm the non-spontaneity of the complexes formation in the rate-determining steps, as suggested by the cited proposed mechanism.

Here, it is clear that no cleavage of the C-C bond in $-(H)C(OR)-CO_2H$ moieties occurs during the oxidation of pectin substrate by chromic acid oxidation. The absence of any appreciable changes in the measured viscosities between the cited pectin substrate and its corresponding keto-derivative precursor as the oxidation product under our experimental conditions may confirm this fact. This result was found to be quite similar to that reported previously for oxidation of other polysaccharides by either chromic acid or permanganate ion as strong oxidants [6-12]. However, the possibility of C-O scission could not be ruled out.

On the other hand, two alternative reaction mechanisms have been taken into consideration for the present oxidation process. The first one was based on the assumption that the first fast part of reaction could not be considered for the true process of oxidation for the cited reaction, but it may due to the formation of an intermediate complex. If so, the pseudo-first-order rate constants can be evaluated from the linear portions of the slow second stage. Unfortunately, all attempts to make any spectrophotometric detection of such intermediate were failed either at lower temperatures or on using reference cells containing the same concentrations of the oxidant and the acid of the tested solutions. In addition, the results calculated for the formation constant of the intermediate complex were not encouraged. This result led us to exclude such a suggestion. The other mechanism was suggested on the basis of the presence of two competitive reactions, one of which is between the unprotonated reactants and the other is between the protonated species. The kinetic data did not fit the forms derived for the rate law-expressions in this mechanism.

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In view of the above interpretations and the experimental observations, a suitable reaction mechanism in good consistent with the observed kinetics may be suggested by Schemes I and II. It involves a rapid attack of chromic acid on the center of protonated pectin to form the coordination biopolymer complex intermediate (C_1)_n via two reaction-paths (A) and (B) prior to the first rate-determining step (Scheme I). Then, the intermediate complexes are decomposed in the rate-determining step of the autoacceleration period to give free-radical substrates and either Cr^{IV} (reaction-path A) or Cr^V (reaction-path B) as transient species as initial oxidation products for the reduction of Cr^{VI} ion oxidant. The substrate radicals are further oxidized very rapidly by further molecules of chromic acid oxidant or either Cr^{IV} and Cr^V species formed as transient species to give rise to the oxidation products. Reaction-path (B) may be excluded based on the results of the dependence of the reaction rate constants (k_f) on the added manganous ion concentration that indicated the involvement of Cr^{IV} rather than Cr^V intermediate species during the oxidation progress.

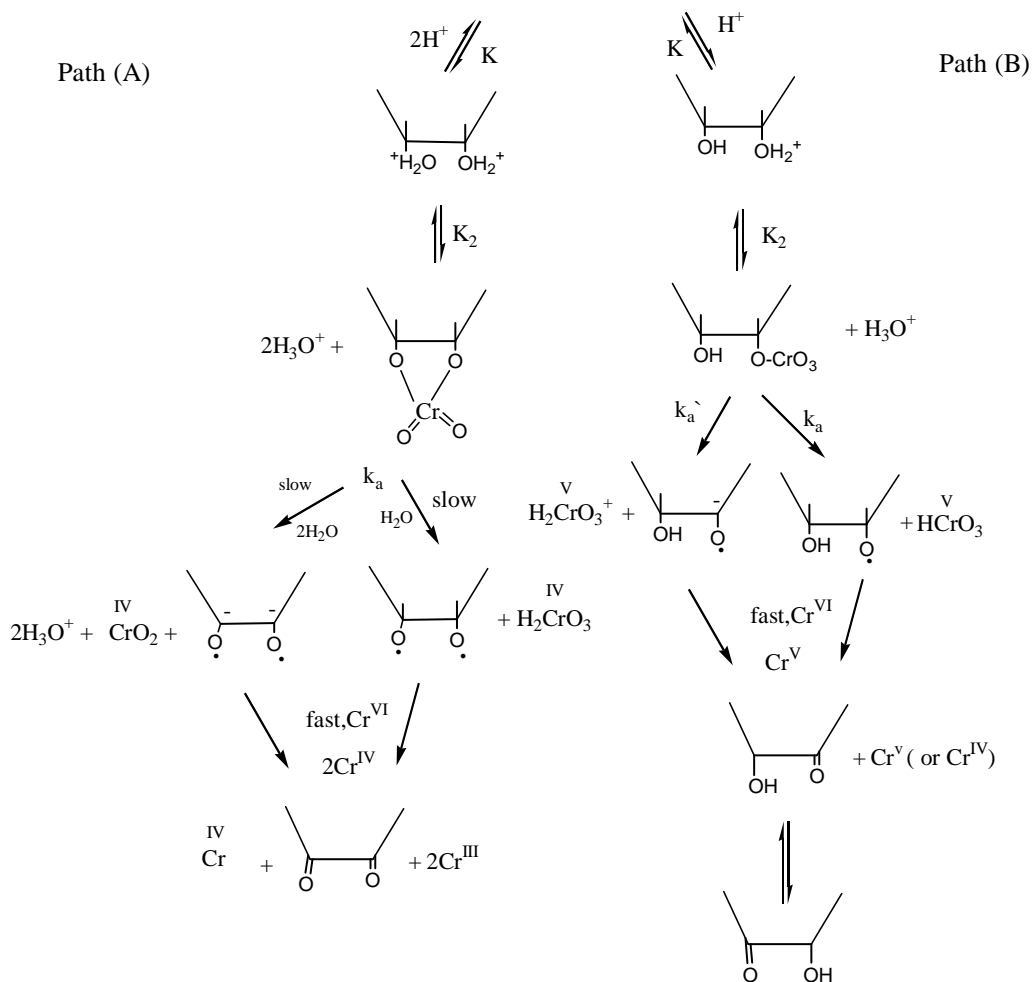
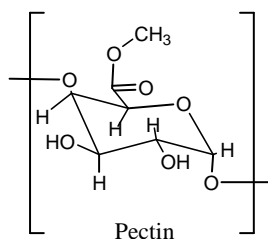
On the other hand, the Cr^{IV} species formed in reaction-path (A) will attack the center of a further protonated pectin molecule (Scheme II) via two reaction-paths either (C) or (D) to give coordination biopolymeric complexes (C_2) prior to the rate-determining step of the slow second stage of reaction. These complexes (C_2) are decomposed in the rate-determining step of the induction period as a result of electron transfer process from pectin to the oxidants forming the free-radical substrates (C_2^{\cdot}) and either Cr^{II} or Cr^{III} ions as initial oxidation products in the slow final stage of oxidation (induction period). The substrate radicals are rapidly oxidized by either chromic acid or Cr^{IV} oxidants to give rise to the oxidation product. Reaction-path (D) is unfavorable from the kinetic points of view based on the hydrogen ion dependence of the rate constants (k_s) observed in the induction period.

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Autoacceleration period

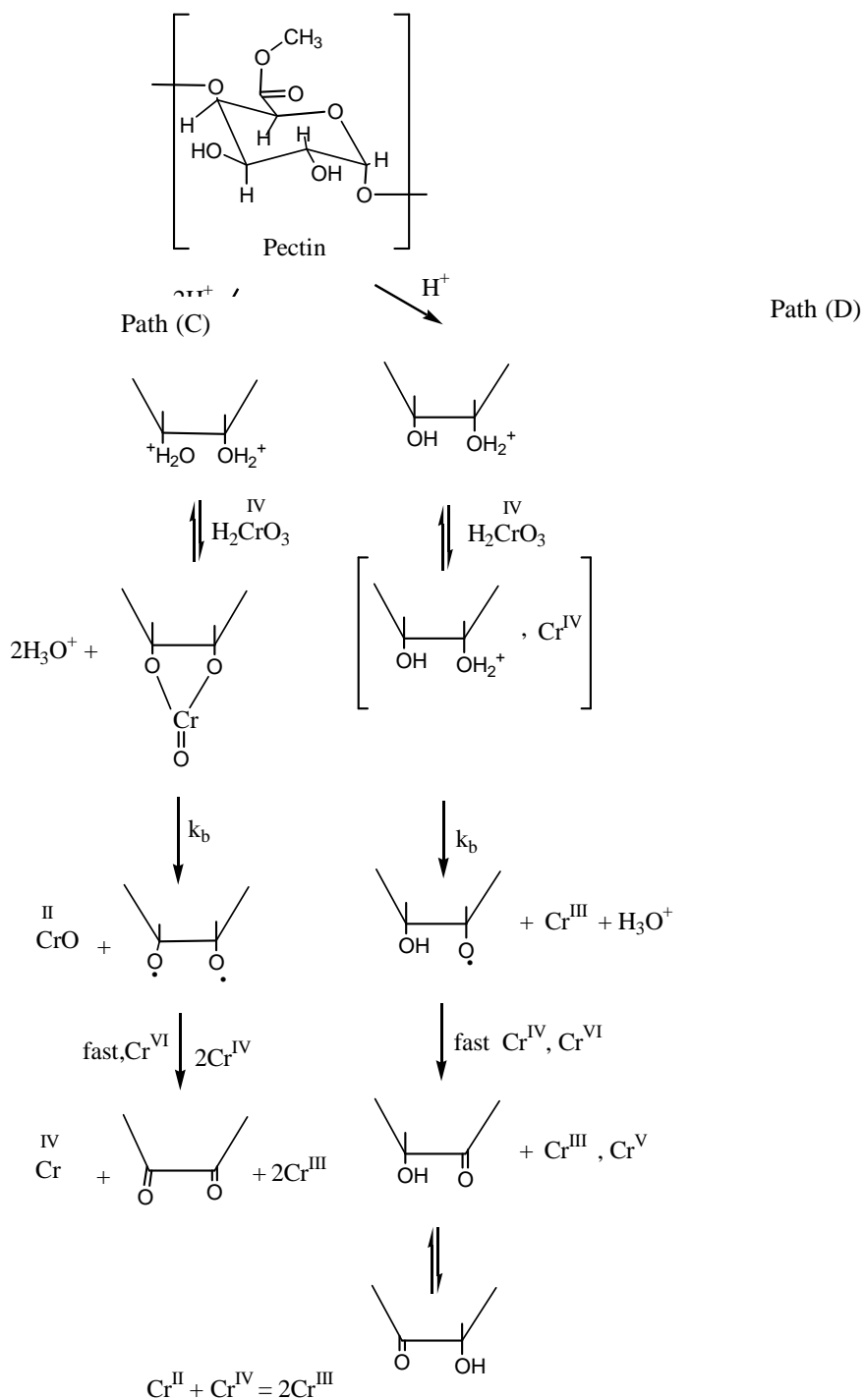


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Induction period



Scheme II

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