

ORIGINAL RESEARCH PAPER

## UNCATALYZED OXIDATION OF L(-)ARABINOSE BY ACIDIC MANGANESE (VII). OPTIMIZATION, STOICHIOMETRY, ACTIVATION FUNCTIONS AND MECHANISM

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**Abstract:** The uncatalyzed oxidation of L(-)arabinose by manganese (VII) in acidic medium of H<sub>2</sub>SO<sub>4</sub> and constant ionic strength (using potassium nitrate) were investigated kinetically. The change in concentration of manganese (VII) was followed using spectrophotometric method. The study showed that the reaction rate increases by raising the concentration of L(-)arabinose, manganese (VII) and H<sup>+</sup> and is independent of salt concentration.

The optimum condition of the reaction (highest rate value) found at 0.02 M of L(-)arabinose, 0.0003 M of manganese (VII), 0.5 M of H<sup>+</sup> and 0.5 M of KNO<sub>3</sub>. Findings from stoichiometry measurements revealed that one mol of arabinose consumed two mol of manganese (VII). The temperature influence on the reaction was carried under constant experimental conditions, it was found that the rate of the reaction enhanced by raising the temperature. The activation energy of the reaction was evaluated and found to be 22.74 kJ·mol<sup>-1</sup>. Activation functions namely, frequency factor, free energy change and the entropy change of the uncatalyzed oxidation were also evaluated at various temperatures. Spot test analysis of the uncatalyzed reaction products revealed the presence of formic acid supporting the proposed mechanism. Reaction rate law was established and it was in strong agreement with the experimental results.

**Keywords:** *activation energy, ionic strength, pseudo-first order, spectrophotometric method, spot analysis*

## INTRODUCTION

Carbohydrates are a major source of energy which is compared with fuel by many investigators [1 – 9]. The study of the carbohydrates and their derivatives has greatly enriched chemistry, particularly with respect to the role of molecular shape and conformation in chemical reactions [10]. The biological and economic of the carbohydrates and mainly of mono and di-saccharides were highly dependable for the study of their bio and physiochemical properties and reactivities [1, 11 – 16] their microbiological and physiological activities depend largely on their redox behavior [17, 18].

Potassium permanganate is widely used as an oxidizing agent in synthetic as well as in analytical chemistry and also as a disinfectant [19, 20]. It has been used in the determination of content of pharmaceutical formulation [21, 22], as oxidizing agent for removal of organic molecules and heavy metals from the nuclear wastes [23] and in the estimation of ascorbic acid [24]. During oxidation by permanganate, it is evident that the Mn(VII) in permanganate is reduced to various oxidation states in acidic, alkaline and neutral media. Consequently, the mechanism by which this multivalent oxidant oxidizes a substrate depends not only on the substrate but also on the medium [25].

Sugars may be oxidized in both acidic and basic environments, and this topic has been extensively studied in the literature [17, 26 – 28]. *N*-bromosuccinamide and potassium iodate, for example, may be chelated by transition metal ions in both acidic and basic environments (e.g., Os(VIII) [8], Pd(II) [29, 30], Ru(VIII) [6], ruthenate ion [3], Mn(VII) [31, 32], Hg(II) [33, 34].

Odebunmi and Owalude [35] investigated the rate at which alkaline permanganate anion oxidized glucose, galactose, fructose, maltose, and sucrose.

The kinetics of potassium permanganate's oxidation of D-glucose, D-sorbitol, and D-mannitol in  $\text{NaHCO}_3/\text{NaOH}$  have been investigated by Okoro and Odebunmi [8]. Kumar [36] investigated the effects of alkaline potassium bromated on the ruthenium (III) catalyzed oxidation of D-galactose and lactone. Salt (KCl) was demonstrated to have a beneficial impact, and the authors reported a zero-order rate concerning sugar content and a first-order rate in potassium bromide and ruthenium(III). Based on experimental results, a rate law and an appropriate mechanism are provided. Many oxidants, including Ti(III) [37], V(V) [6], and Cr(VI) [38, 39], have been studied for their ability to oxidize various mono- and disaccharides. Sugars are oxidized catalytically by transition metal ions [11], inorganic acids [14], organometallic complexes [17], and enzymes [40 – 44] in both acidic and alkaline conditions. Data is abundant, but the correlation is challenging because of differences in the reaction conditions [41].

The significance of this investigation lies in the fact that there has been no intensive work reported in connection with the oxidation potential of  $\text{KMnO}_4$  towards sugars in acidic medium in order to clarify the mechanism and create a rate law.

The goals of the present study were to determine the stoichiometry, activation functions, and mechanism of the uncatalyzed oxidation of L(-)-arabinose by manganese (VII) in an acidic medium of  $\text{H}_2\text{SO}_4$  and constant ionic strength and to develop the rate law to describe the route of the reaction.

## MATERIALS AND METHODS

All chemicals were of analytical grade and were used without further purification. Potassium permanganate (99-100 %) as source of manganese (VII), L(-)arabinose (99 %), sulfuric acid (95-98 %), potassium nitrate (99 %) were supplied from Sigma Aldrich CO LTD. All solutions were prepared using deionized double distilled water.

All experiments used to investigate the uncatalyzed oxidation of L(-)arabinose by acidic manganese (VII) were carried out at room temperature. The course of the reaction was followed spectrophotometrically by observing the change in absorbance of manganese (VII) as a function of time using the Jasco Model V570 UV/VIS (180-1100 nm) spectrophotometer (JASCO International Co, Tokyo, Japan).

The temperature range 303 K-323 K was used to investigate the effect of temperature on the uncatalyzed reaction.

### The absorption maxima ( $\lambda_{\max}$ )

The maximum absorption wavelength of manganese (VII) was determined from its aqueous solution absorption spectra ( $\lambda_{\max}$ ).

### Stoichiometry

Stoichiometric measurements were carried by taking different sets of reaction mixtures containing different amounts of L(-)arabinose and manganese (VII) at constant concentration of  $[H^+]$  and a constant ionic strength, in all sets always the concentration of manganese (VII) is much greater than L(-)arabinose, these different sets were allowed to react at room temperature for 72 hours, and finally the remaining [manganese (VII)] in each set was estimated.

### Spot test analysis of the uncatalyzed reaction products

It was found that when manganese (VII) reacts with sulfuric acid the following reaction takes place [14].



The oxygen formed [O], reacts with sugar (arabinose) to form a corresponding acid. Hence,



Adding 1,8-dihydronaphthalene-3,6-disulfonic acid (chronotropic acid) to the different mixtures of [manganese (VII)]:[arabinose] proved the existence of formic acid in the reaction products.

### Spectrophotometric measurements

#### *KMnO<sub>4</sub> dependence*

The process was investigated at different starting manganese (VII) concentrations ranging from 0.00005 M to 0.0004 M to see if the addition of potassium permanganate

increased, decreased, or had no influence on the pace of the uncatalyzed reaction. The temperature was steady at 303 K, while the concentrations of arabinose and sulfuric acid were steady at 0.02 M and 0.1 M, respectively. In addition, spectrophotometric recordings of absorbance were made at 60-second intervals to track the progress of the reaction.

#### ***Arabinose dependence***

Researcher examined the impact of arabinose doses ranging from 0.01 M to 0.05 M. Constants of 0.0001 M for manganese (VII) and 0.1 M for sulfuric acid was used. The room was maintained at a steady 303 K.

#### ***H<sub>2</sub>SO<sub>4</sub> dependence***

By keeping the concentrations of arabinose (0.02 M), manganese (VII) (0.0001 M), and 303 K constant, the effect of hydrogen ion concentration was investigated.

#### ***KNO<sub>3</sub> dependence***

The effect of salt concentration was studied by changing the concentration of potassium nitrate (0.3-1.1 M) at a constant concentration of arabinose 0.02 M, manganese (VII) 0.0001 M and at a temperature of 303 K.

#### ***Temperature dependence***

Keeping the concentrations of manganese (VII), arabinose, sulfuric acid, and potassium nitrate constant while varying the temperature from 303 K to 323 K allowed for a study of the temperature dependency. According to the published methods [45, 46], the activation energy (E<sub>a</sub>) and other activation functions were calculated.

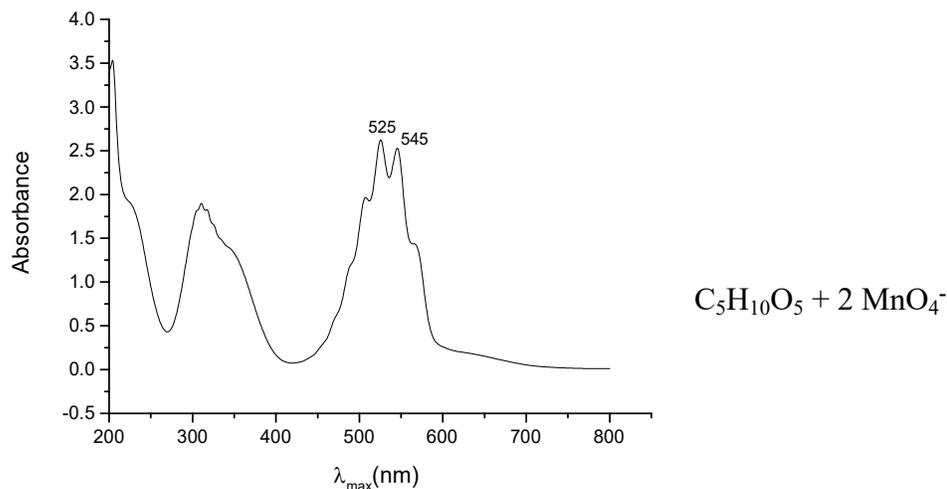
### **Proposed mechanism and rate law**

In an acidic medium, the stable reduction product of potassium permanganate is the manganate ion [MnO<sub>4</sub><sup>-</sup>], i.e., Mn<sup>+7</sup>, which reacts with arabinose to form a complex. This complex eventually forms the aldonic acid in the presence of a nucleophile [14].

## **RESULTS AND DISCUSSION**

### **The absorption maxima (λ<sub>max</sub>)**

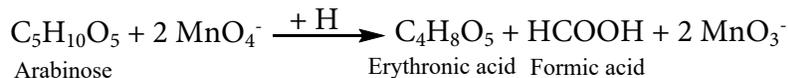
The spectrum of manganese (VII) shows two maxima, one at 525 nm for manganese dioxide (MnO<sub>2</sub>), a reduction product of MnO<sub>4</sub><sup>-</sup> and the other at 545 nm for MnO<sub>4</sub><sup>-</sup>, the maxima at 545 nm was considered as λ<sub>max</sub> (Figure 1).



**Figure 1.** The maximum absorption ( $\lambda_{max}$ ) of  $KMnO_4$  as source of manganese (VII)

### Stoichiometry

Since two moles of manganese (VII) are used up for every mole of arabinose, the following stoichiometric equations for the uncatalyzed redox reaction can be written:



### Product qualitative analysis

Since the sugar combines with the oxygen created in the process to make the acid, we have:



The development of a violet pink color proved that formic acid had been produced.

### Spectrophotometric measurements

#### *Manganese (VII) dependence*

Absorbance was determined after every 60 seconds (Table 1).

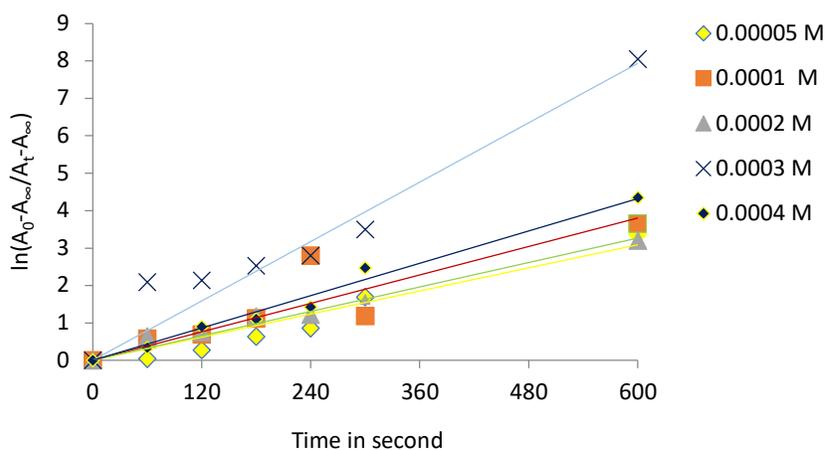
**Table 1.** Manganese (VII) dependence

Time [s]	0.00005 M	0.0001 M	0.0002 M	0.0003 M	0.0004 M
0	0.0931	0.0902	0.4817	0.7409	0.9093
60	0.0927	0.0752	0.4546	0.6721	0.9026
120	0.0904	0.0731	0.4509	0.6716	0.8954
180	0.0878	0.067	0.4415	0.6686	0.8936
240	0.0866	0.0578	0.4408	0.6671	0.8914
300	0.0839	0.0663	0.4351	0.6647	0.8877
600	0.0818	0.0557	0.4235	0.6623	0.8857

From the slope of the  $\ln A_0 - A_\infty / A_t - A_\infty$  with time (Table 2, Figure 2), the values of the rate constants (Table 3) were calculated. The findings demonstrate that the reaction follows first-order kinetics concerning manganese (VII).

**Table 2.** Values of  $\ln A_0 - A_\infty / A_t - A_\infty$  for manganese (VII) dependence

Concentration of manganese (VII) [M]	0.00005	0.0001	0.0002	0.0003	0.0004
$\ln(A_0 - A_{600} / A_0 - A_{600})$	0	0	0	0	0
$\ln(A_0 - A_{600} / A_{60} - A_{600})$	0.036039936	0.570544858	0.626677536	2.081989314	0.33393309
$\ln(A_0 - A_{600} / A_{120} - A_{600})$	0.273040522	0.684489118	0.753342341	2.134357299	0.889120827
$\ln(A_0 - A_{600} / A_{180} - A_{600})$	0.633043256	1.116156598	1.173513597	2.523822066	1.094383953
$\ln(A_0 - A_{600} / A_{240} - A_{600})$	0.856186808	2.799021979	1.213178853	2.795755782	1.420780537
$\ln(A_0 - A_{600} / A_{300} - A_{600})$	1.682865381	1.180105323	1.612880257	3.488902962	2.468099531
$\ln(A_0 - A_{600} / A_{600} - A_{600})$	3.35	3.65	3.20	8.05	4.35
NB: $A_{600} = A_\infty$					



**Figure 2.** The effect of manganese (VII) concentration

**Table 3.** Rate constants values for manganese (VII) dependence

Concentration of manganese (VII) [M]	0.00005	0.0001	0.0002	0.0003	0.0004
The slope = k	0.0051	0.0063	0.0054	0.0132	0.0072

**Arabinose dependence**

Absorption was measured at 60 second intervals (Table 4).

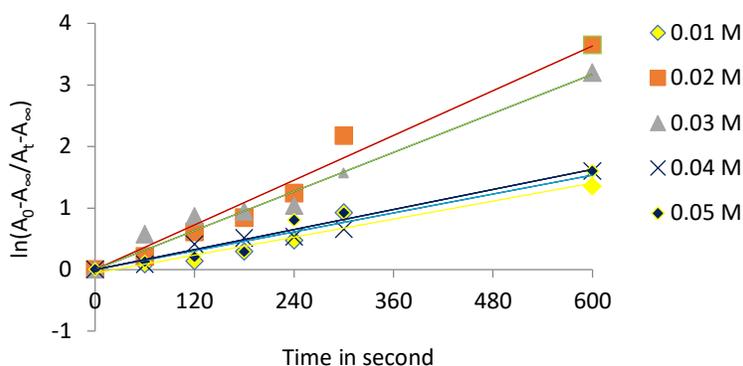
**Table 4.** Arabinose dependence

Time [s]	0.01 M	0.02 M	0.03 M	0.04 M	0.05 M
0	0.2505	0.1896	0.2313	0.2296	0.2565
60	0.2461	0.1874	0.2214	0.226	0.2518
120	0.2434	0.1844	0.2182	0.2145	0.2491
180	0.2363	0.1831	0.2175	0.2115	0.2466
240	0.2296	0.1815	0.2167	0.211	0.2346
300	0.2169	0.1795	0.2134	0.208	0.2327
600	0.1949	0.1782	0.2087	0.1845	0.2169

From the slope of the line depicting  $\ln A_0 - A_\infty / A_t - A_\infty$  with time (Table 5, Figure 3), the values of the rate constants (Table 6) were calculated. These findings demonstrate that the reaction rate is proportional to the concentration of arabinose and follows first-order kinetics concerning arabinose.

**Table 5.** Values of  $\ln A_0 - A_\infty / A_t - A_\infty$  for arabinose dependence

Concentration of arabinose [M]	0.01	0.02	0.03	0.04	0.05
$\ln(A_0 - A_\infty / A_t - A_\infty)$	0	0	0	0	0
$\ln(A_0 - A_{600} / A_{60} - A_{600})$	0.082443669	0.214409871	0.576347913	0.083188819	0.126342289
$\ln(A_0 - A_{600} / A_{120} - A_{600})$	0.136619403	0.609064063	0.866658108	0.407684865	0.206862666
$\ln(A_0 - A_{600} / A_{180} - A_{600})$	0.29490232	0.84437815	0.943198185	0.513045381	0.287682072
$\ln(A_0 - A_{600} / A_{240} - A_{600})$	0.471443514	1.239690887	1.038508365	0.531737514	0.805264479
$\ln(A_0 - A_{600} / A_{300} - A_{600})$	0.927140748	2.171249091	1.570387398	0.651881825	0.918819178
$\ln(A_0 - A_{600} / A_{600} - A_{600})$	1.35	3.65	3.2	1.6	1.6
NB: $A_{600} = A_\infty$					



**Figure 3.** The effect of arabinose concentration

**Table 6.** Rate constants values for arabinose dependence

Concentration of arabinose [M]	0.01	0.02	0.03	0.04	0.05
The slope = k	0.0023	0.0061	0.0053	0.0026	0.0027

### *H<sub>2</sub>SO<sub>4</sub> dependence*

Absorbance was determined after every 60 seconds (Table 7).

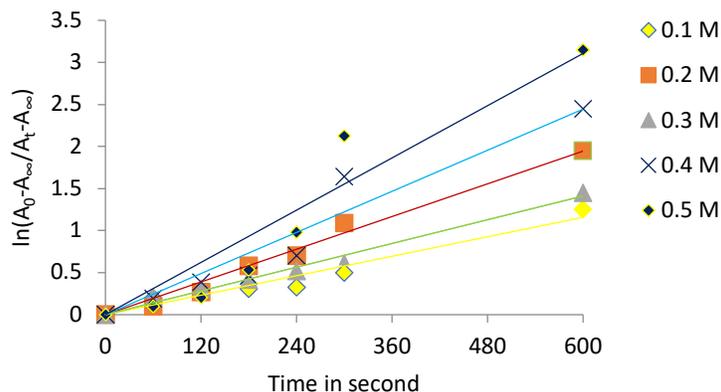
**Table 7.** H<sub>2</sub>SO<sub>4</sub> dependence

Time [s]	0.1 M	0.2 M	0.3 M	0.4 M	0.5 M
0	0.1775	0.1832	0.2052	0.2192	0.2231
60	0.1627	0.171	0.1898	0.2131	0.2221
120	0.1593	0.152	0.1835	0.208	0.2211
180	0.1557	0.1248	0.1773	0.2062	0.2186
240	0.1545	0.1163	0.172	0.2015	0.2163
300	0.1449	0.0952	0.166	0.1909	0.2135
600	0.0947	0.0507	0.1231	0.1841	0.2122

From the slope of the  $\ln A_0 - A_\infty / A_t - A_\infty$  versus time curves (Table 8, Figure 4), the rate constant values (Table 9) were calculated, showing that the reaction rate is proportional to the  $H^+$  concentration.

**Table 8.** Values of  $\ln A_0 - A_\infty / A_t - A_\infty$  for  $H_2SO_4$  dependence

Concentration of $H_2SO_4$ [M]	0.1	0.2	0.3	0.4	0.5
$\ln(A_0 - A_{600} / A_0 - A_{600})$	0	0	0	0	0
$\ln(A_0 - A_{600} / A_{60} - A_{600})$	0.196920356	0.096594022	0.207733064	0.1909053	0.096228032
$\ln(A_0 - A_{600} / A_{120} - A_{600})$	0.248213651	0.268496234	0.306948912	0.384322672	0.202711512
$\ln(A_0 - A_{600} / A_{180} - A_{600})$	0.305554197	0.581167113	0.415257108	0.462623522	0.532464799
$\ln(A_0 - A_{600} / A_{240} - A_{600})$	0.3254224	0.703006949	0.51816062	0.701730924	0.977775816
$\ln(A_0 - A_{600} / A_{300} - A_{600})$	0.500413035	1.091093456	0.649066191	1.641278518	2.126398525
$\ln(A_0 - A_{600} / A_{600} - A_{600})$	1.25	1.95	1.45	2.45	3.15
NB: $A_{600} = A_\infty$					



**Figure 4.** The effect of  $H_2SO_4$  concentration

**Table 9.** Rate constants values for  $H_2SO_4$  dependence

Concentration of $H_2SO_4$ [M]	0.1	0.2	0.3	0.4	0.5
The slope = k	0.0019	0.0032	0.0024	0.0041	0.0052

***KNO<sub>3</sub> dependence***

Absorbance was determined after every 60 seconds (Table 10).

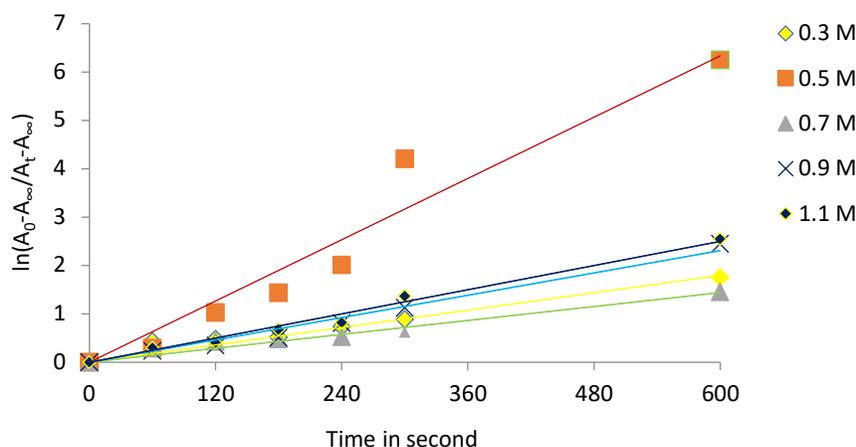
**Table 10.**  $KNO_3$  dependence

Time [s]	0.3 M	0.5 M	0.7 M	0.9 M	1.1 M
0	0.2077	0.1988	0.2054	0.204	0.1798
60	0.1988	0.1971	0.1992	0.1947	0.173
120	0.198	0.1945	0.197	0.1908	0.171
180	0.1973	0.1937	0.1962	0.1862	0.1667
240	0.1944	0.193	0.1955	0.1791	0.1649
300	0.1927	0.1922	0.1943	0.1737	0.1599
600	0.1821	0.1921	0.1812	0.1591	0.1531

Straight lines were also shown for the  $\ln A_0-A_\infty/A_t-A_\infty$  versus time data (Table 11, Figure 5), suggesting that the reaction rate is insensitive to changes in salt content (Table 12).

**Table 11.** Values of  $\ln A_0-A_\infty/A_t-A_\infty$  for  $KNO_3$  dependence

Concentration of $KNO_3$ [M]	0.3	0.5	0.7	0.9	1.1
$\ln(A_0-A_\infty/A_t-A_\infty)$	0	0	0	0	0
$\ln(A_0-A_{600}/A_{60}-A_{600})$	0.4271836	0.29266961	0.29598088	0.232092	0.293944
$\ln(A_0-A_{600}/A_{120}-A_{600})$	0.4762732	1.02663879	0.42634269	0.348121	0.399863
$\ln(A_0-A_{600}/A_{180}-A_{600})$	0.5212969	1.4321039	0.47830243	0.504904	0.674594
$\ln(A_0-A_{600}/A_{240}-A_{600})$	0.7329931	2.00746804	0.5260931	0.808706	0.816564
$\ln(A_0-A_{600}/A_{300}-A_{600})$	0.8817384	4.20469262	0.6137404	1.123416	1.367741
$\ln(A_0-A_{600}/A_{600}-A_{600})$	1.75	6.25	1.45	2.45	2.55
NB: $A_{600} = A_\infty$					



**Figure 5.** The effect of  $KNO_3$  concentration

**Table 12.** Rate constants values for  $KNO_3$  dependence

Concentration of $KNO_3$ [M]	0.3	0.5	0.7	0.9	1.1
The slope = k	0.003	0.0106	0.0024	0.0038	0.0042

### Temperature dependence

From the slope of the plots of  $\ln A_0-A_\infty/A_t-A_\infty$  versus time (Table 13, Figure 6), the rate constant values (Table 14) were determined, suggesting that the reaction rate rises with increasing temperature.

Table 13. Temperature dependence

T	A	Time [s]	$A_0 - A_\infty$	$A_t - A_\infty$	$A_0 - A_\infty / A_t - A_\infty$	$\ln A_0 - A_\infty / A_t - A_\infty$
303 K	0.2547	0	0.0307	0.0307	1	0
	0.2519	60	0.0307	0.0279	1.100358423	0.09563597
	0.2419	120	0.0307	0.0179	1.715083799	0.53946194
	0.2354	180	0.0307	0.0114	2.692982456	0.9906493
	0.2312	240	0.0307	0.0072	4.263888889	1.45018163
	0.2253	300	0.0307	0.0013	23.61538462	1.46189839
	0.224	600	0.0307	0	$\infty$	1.55
308 K	0.2432	0	0.0069	0.0069	1	0
	0.242	60	0.0069	0.0057	1.210526316	0.19105524
	0.2418	120	0.0069	0.0055	1.254545455	0.22677332
	0.241	180	0.0069	0.0047	1.468085106	0.3839589
	0.238	240	0.0069	0.0017	4.058823529	1.40089316
	0.2371	300	0.0069	0.0008	8.625	1.41466496
	0.2363	600	0.0069	0	$\infty$	1.95
313 K	0.3296	0	0.293	0.293	1	0
	0.3155	60	0.293	0.2789	1.050555755	0.049319314
	0.273	120	0.293	0.2364	1.239424704	0.214647323
	0.2477	180	0.293	0.2111	1.387967788	0.327840654
	0.2421	240	0.293	0.2055	1.425790754	0.354726575
	0.199	300	0.293	0.1624	1.804187192	0.700110181
	0.0366	600	0.293	0	$\infty$	2.85
318 K	0.267	0	0.0369	0.0369	1	0
	0.2588	60	0.0369	0.0287	1.285714286	0.251314428
	0.2558	120	0.0369	0.0257	1.435797665	0.361720559
	0.2557	180	0.0369	0.0256	1.44140625	0.3656192
	0.251	240	0.0369	0.0209	1.765550239	0.568462392
	0.2393	300	0.0369	0.0092	4.010869565	1.389008067
	0.2301	600	0.0369	0	$\infty$	3.35
323 K	0.2712	0	0.0211	0.0211	1	0
	0.2661	60	0.0211	0.016	1.31875	0.276684318
	0.2653	120	0.0211	0.0152	1.388157895	0.327977613
	0.2633	180	0.0211	0.0132	1.598484848	0.469056211
	0.2557	240	0.0211	0.0056	3.767857143	1.326506443
	0.2545	300	0.0211	0.0044	4.795454545	1.5676685
	0.2501	600	0.0211	0	$\infty$	4.25

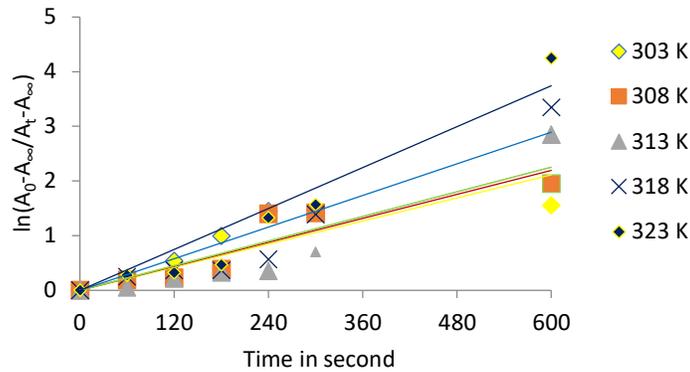


Figure 6. The effect of temperature

**Table 14.** Rate constants values for temperature dependence

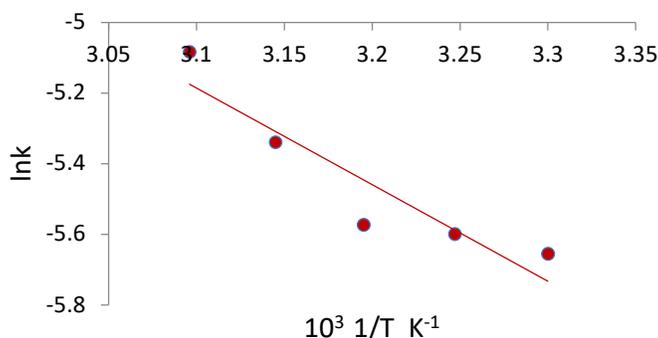
<b>Temperature [K]</b>	303	308	313	318	323
<b>The slope = k</b>	0.0035	0.0037	0.0038	0.0048	0.0062

Using the Arrhenius equation [47], the activation energy (E<sub>a</sub>) was determined from the slope of the plot of 1/Tx10<sup>3</sup> versus ln k (Table 15, Figure 7).

$$k = Ae^{-\frac{E_a}{RT}} \quad \text{or} \quad \ln k = \ln A - \frac{E_a}{RT}$$

**Table 15.** Values of 1/T x 10<sup>3</sup> and ln k

<b>T [K]</b>	<b>10<sup>3</sup> 1/T</b>	<b>10<sup>3</sup> k 1/sec</b>	<b>ln k</b>
303	3.300	3.50	-5.65499231
308	3.247	3.70	-5.59942246
313	3.195	3.80	-5.57275421
318	3.145	4.80	-5.33913936
323	3.096	6.20	-5.08320599



**Figure 7.** ln k versus 1/T for arabinose – manganese (VII) reaction

Using the following equations, both the entropy change of activation ( $\Delta S^\ddagger$ ) and the free energy change of activation ( $\Delta G^\ddagger$ ) (Table 16) were determined:

$$\Delta S^\ddagger = 2.303R \left( \log A - \log \frac{RT}{Nh} \right), \quad J \cdot K^{-1}$$

where  $R/N$  is the Boltzmann's gas constant  $1.3805 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$  and  $h$  is Planck's constant  $6.62 \times 10^{-34} \text{ Js}$ .

$$\Delta G^\ddagger = \Delta E_a - T\Delta S^\ddagger, \quad \text{kJ} \cdot \text{mol}^{-1}$$



So, to sum up, the whole rate law from (5-8):

$$\frac{-d[\text{manganese(VII)}]}{dt} = \frac{k_3 k_1 [\text{arabinose}] (k_2 + k_3) [\text{manganese(VII)}]_T}{[(k_2 + k_3) + k_1 [\text{arabinose}]] (k_2 + k_3)} \quad (9)$$

$$\frac{-d[\text{manganese(VII)}]}{dt} = \frac{k_3 k_1 [\text{arabinose}] [\text{manganese(VII)}]_T}{[(k_2 + k_3) + k_1 [\text{arabinose}]]} \quad (10)$$

The present research work follows the condition:

$$(k_2 + k_3) > k_1 [\text{arabinose}]$$

Hence above equations (9) and (10) reduce to,

$$\frac{-d[\text{MnO}_4^-]}{dt} = \frac{k_3 k_1 [\text{arabinose}] [\text{manganese(VII)}]_T}{(k_2 + k_3)} = k_1 [\text{arabinose}] [\text{manganese(VII)}]_T \quad (11)$$

where,

$$k = \frac{k_3 k_1}{(k_2 + k_3)}$$

The given equation demonstrates first-order kinetics as a function of arabinose and manganese (VII) ion concentration.

## CONCLUSIONS

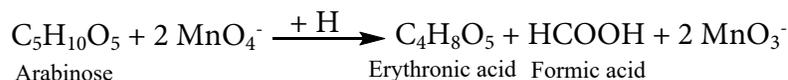
Potassium permanganate is highly reactive under certain conditions. In potassium permanganate ( $\text{Mn}^{+7}$ ) is reduced to ( $\text{MnO}_2$ ) ( $\text{Mn}^{+4}$ ). Under acidic conditions the following reaction was observed:



When combined with the hydrogen ion ( $\text{H}^+$ ), stoichiometric studies show that  $\text{MnO}_4^-$  is the active, reactive oxidizing specie in an acidic media.



This permanganic acid is a highly oxidative unstable inorganic acid that, with catalyst or alone, oxidizes the sugar arabinose by forming an unstable intermediate complex that ultimately yields aldehyde hydrate. This aldehyde hydrate is typically transformed into the corresponding carboxylic acid through reactions with  $\text{MnO}_3^-$  species. The oxidative property of manganese (VII) ions with organic reducing arabinose sugar in acidic media are the basis for the present investigation. It has been determined that erythronic and formic acids and their corresponding acid of arabinose are two necessary by-products.



Creating two manganese (VII) oxidative species in an acidic media may be responsible for the products. Reactive oxygen species are generated in the presence of an acid, which catalyzes erythronic and formic acids formation by breaking the C-C bond (VII). The proposed mechanism was used to confirm that the uncatalyzed reaction of manganese (VII) ions with arabinose sugar molecules in an acidic medium and at constant ionic strength exhibits first-order kinetics concerning arabinose and manganese

(VII) concentration and that the rate increases linearly with increasing acidity of the medium.

The optimum reaction condition was 0.02 M of L(-)arabinose, 0.0003 M of manganese (VII), 0.5 M of H<sup>+</sup> and 0.5 M of KNO<sub>3</sub>.

The influence of temperature on the reaction is usually expressed mathematically by introducing two parameters, one representing the intercept which is the frequency factor (A) found equal 26.88x10<sup>5</sup> s<sup>-1</sup> and the other is the slope of the straight line which is the activation energy E<sub>a</sub>, found equal 22.74 kJ·mol<sup>-1</sup>. Furthermore, the activation functions, entropy change (ΔS<sup>#</sup>), and free energy change (ΔG<sup>#</sup>) were also calculated at different temperatures. The solvated intermediate state, indicated by a negative value of ΔS<sup>#</sup>, lends credence to the idea that the solute and solvent have an electrostatic solid connection. In addition to slow kinetics, a negative activation entropy value shows the existence of substantially solvated transition intermediate states.

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