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Oxidation of gum arabic by soluble colloidal MnO_2

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Abstract—In the present work, the oxidative degradation of gum arabic by colloidal manganese dioxide (MnO_2) was carried out. Monitoring the disappearance of the MnO_2 spectrophotometrically at 375 nm was used to follow the kinetics. The oxidation obeyed fractional-order kinetics with respect to the [gum arabic]. Effect of various experimental parameters such as the initial colloidal [MnO_2], [$HClO_4$], temperature, and complexing agents ($P_2O_7^{4-}$, F^-, and Mn^{2+}) for the oxidation of gum arabic was studied. The reaction was acid catalyzed. Addition of $P_2O_7^{4-}$, F^-, and Mn^{2+} ions enhances the rate of oxidation significantly. Gum arabic adsorbs onto the surface of the colloidal MnO_2 through the equatorial –OH groups of the rhamnose moiety, and the complex breaks down into products. The Arrhenius equation was valid for the oxidation kinetics between 40 and 60 °C. To explain the observed kinetic results, a suitable mechanism and rate law for the reaction taking place at the surface of the colloidal particle has been proposed. The reducing nature of gum arabic is found be due to the presence of –OH group in the skeleton.

Keywords: Colloidal manganese dioxide; Oxidation; Gum arabic; Pyrophosphate; Fluoride

1. Introduction

Additives having various functional and interactive properties have been in use in foods for maintaining as well as enhancing certain specific qualities. These additives could be broadly classified into preservatives, nutrients, flavoring agents, coloring agents, texturizing agents, emulsifying agents, protective colloids, etc. Traditionally, natural polymers (water-soluble polysaccharides) like gum arabic have been in use for various food items. The chemistry of gum arabic in terms of their applications has come a long way, and its industrial uses are unlimited.[1–3] Gum arabic (completely water soluble) is a multifunctional hydrocolloid that features a highly branched arabino-galactam protein complex. Elucidation of structural features of gum arabic has been the subject of a large number of investigations.[3–5] It has been established that gum arabic is a highly branched polysaccharide consisting of a main chain of β-(1→3)-linked galactose residues with (1→6)-linked ramified side chains containing galactose, arabinose, rhamnose, and glucuronic acids.[1,2,6] Chemical and spectroscopic studies showed that the polysaccharide gum from *Acacia glomerosa* (physicochemical data and sugar composition are very close to gum arabic from *Acacia senegal*) gum consists of a (1→3)-β-galactopyranosyl backbone. Rhamnose is present as terminal residues.[4]

It has been reported that gum arabic stabilizes the colloidal manganese dioxide in solution and has a strong tendency to adsorb on the surface of colloidal MnO_2.[7,8] Perez-Benito et al.[9,10] pointed out that addition of gum arabic resulted in a definite decrease in the oxidation rate of formic and oxalic acids by colloidal MnO_2. Same type of behavior was also found in the colloidal MnO_2 oxidation of citric and malic acids.[11,12] Recently, we have observed that colloidal MnO_2 was unstable in presence of gum arabic.[13] As far as we know, no investigation has been carried out regarding the reactions involving gum arabic as a reactant in the presence

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of colloidal MnO_2. In view of our recent results of D-fructose (monosaccharide) oxidation by colloidal MnO_2, it was thought of interest to investigate the oxidation of gum arabic by colloidal MnO_2 with a view to having an insight into the role played by the polysaccharide.

2. Experimental

2.1. Materials

Potassium permanganate, gum arabic, sodium thiosulfate, sodium pyrophosphate, sodium fluoride, and manganese(II) chloride (all E. Merck, India, 99%) were used without further purification. Perchloric acid ($HClO_4$, Fisher, 70% reagent) was used for $[H^+]$. Double-distilled, deionized, and CO_2-free water was used throughout the studies.

2.2. Kinetic procedure

The reaction was initiated by adding the required quantity of gum arabic to a thermally equilibrated mixture of colloidal MnO_2, perchloric acid, and other reagents. The progress of the reaction was followed spectrophotometrically by measuring the absorbance of the remaining colloidal MnO_2 at known time intervals at 375 nm using a Bausch & Lomb Spectronic-20 spectrophotometer. The pseudo-first-order conditions were maintained with a large excess of reductant over oxidant concentrations. The kinetic runs were carried out up to ca. 80% completion, and the pseudo-first-order rate constants were obtained from the slopes of log $(A)_{375}$ versus time plots. The results were reproducible to within ±4% with average linear regression coefficient, $r \geqslant 0.998$. Other details are described elsewhere.[14,15]

3. Results and discussion

3.1. Preparation and characterization of colloidal MnO_2

The oxidizing solution (i.e., the water soluble colloidal manganese dioxide) was prepared by addition of $Na_2S_2O_3$ to a permanganate solution. The resulting solution was dark brown and perfectly transparent and stable for several weeks. The absorption spectrum of the reaction mixture ($KMnO_4 = 5.0 \times 10^{-4}$ mol dm^{-3} and $Na_2S_2O_3 = 1.88 \times 10^{-4}$ mol dm^{-3}) consists of a single broad band in the whole visible region. The wavelength, 375 nm, was chosen to confirm the fulfillment of the Beer–Lambert law. A calibration graph was constructed between absorbance (375 nm) and concentration of colloidal MnO_2. The law is obeyed for the concentration range used in the present investigations. The effect of adding different electrolytes ($MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$, LiCl, NaCl, KCl, $CdCl_2$, $CuCl_2$, NH_4Cl, $MnCO_3$, $Pb(NO_3)_2$, and $FeSO_4$) in the transparent solution of water-soluble colloidal MnO_2 have also been studied. In presence of these electrolytes the precipitation of manganese dioxide occurs, which suggests that the soluble manganese(IV) species is present in the form of colloidal particles of manganese dioxide. The negative logarithm of the minimum electrolyte concentration required for the precipitation of MnO_2 is plotted against the cationic radius (Fig. 1). These results are in good agreement with the observations of other investigators.[8]

3.2. Product analysis

For the oxidation product of gum arabic, qualitative analysis of the oxidized reaction mixture was performed. After ensuring completion of the reaction, the oxidized reaction mixture was treated with alkaline hydroxylamine solution. The presence of lactone was tested by the ferric chloride–hydrochloric acid blue test.[16] The reaction mixture was also neutralized with barium carbonate. The addition of $FeCl_3$ solution, followed by phenol, resulted in the appearance of a bright-yellow color indicating that the aldonic acid is formed in the oxidation of gum arabic. Apparently, the lactone, which is formed in the rate-determining step, is hydrolyzed to the aldonic acid in neutral medium in a fast step.[17] Under the kinetic conditions, qualitative identification of the reaction product was carried out by paper chromatography.[17–19] The lactone was identified against an authentic sample (1,4-D-rhamnolactone) using 4:1:5 *n*-butanol–acetic acid–water eluent. A three-stage dip of $AgNO_3$, NaOH, and $Na_2S_2O_3$ was used to visualize the paper chromatograms.

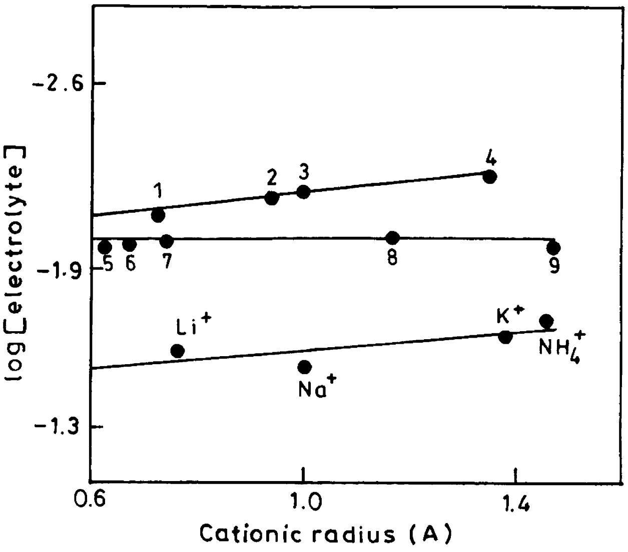


Figure 1. Plots of log[electrolyte] versus cationic radius. Experimental conditions: $MgCl_2$ (1); $CdCl_2$ (2); $CaCl_2$ (3); $BaCl_2$ (4); $FeSO_4$ (5); $MnCO_3$ (6); $CuCl_2$ (7); $SrCl_2$ (8) and $Pb(NO_3)_2$ (9).

3.3. General considerations

It is well known that stability of colloidal MnO_2 depends strongly on the pH of the reaction medium, and the water-soluble colloidal MnO_2 can exist in neutral aqueous medium.[9,10] Therefore, choice of the best conditions for the kinetic experiments is a crucial problem that we address first. In order to examine the effects of variables, experiments were tried at 3.7×10^{-4} mol dm^{-3} of $HClO_4$. Figure 2 shows the deviation from the linearity in the plot of log (absorbance) against time as a function of temperature. It is clear that oxidation kinetics proceeds in two stages, that is, an initial fast stage, followed by relatively slow step (Tables 1 and 2). The time at which the deviation commenced was found to decrease with an increase in temperature.

3.4. Order in [$HClO_4$]

The reaction rate was found to increase with increasing [$HClO_4$]. The induction period was not observed at lower [$HClO_4$] ($\leqslant 5.5 \times 10^{-4}$ mol dm^{-3}). At higher [$HClO_4$] ($\geqslant 7.4 \times 10^{-4}$ to 14.8×10^{-4} mol dm^{-3}), the rate during the second reaction (slow stage) increased gradually with increasing [$HClO_4$]. This indicates that $HClO_4$ catalyses the rate of the induction as well as slow-stage reaction pathways. These results are summarized in Table 1. A plot of k_{obs1} against [$HClO_4$] at constant [gum arabic] shows a nonlinear relationship with positive intercept on the y-axis, indicating acid-independent and acid-dependent reaction paths (Fig. 3). The plot of log k_{obs1} versus log [$HClO_4$] resulted in two straight portions with slopes = 0.8 and 0.0, suggesting that the reaction is fractional and zero-order dependence with respect to [$HClO_4$]. Therefore, the reaction follows different order kinetics with respect to [$HClO_4$]: it is fractional and zero for the [$HClO_4$] in the range of 1.8×10^{-4} to 11.1×10^{-4} and 11.1×10^{-4} to 14.8×10^{-4} mol dm^{-3}, respectively. On the other hand, the plot of k_{obs1} versus [$HClO_4$] is linear passing through the origin (extrapolating the measured k_{obs1} at [$HClO_4$] = 0.0 mol dm^{-3}), which indicates that first-order dependence on [$HClO_4$] exists in the range of 3.7×10^{-4} to 9.3×10^{-4} mol dm^{-3}.

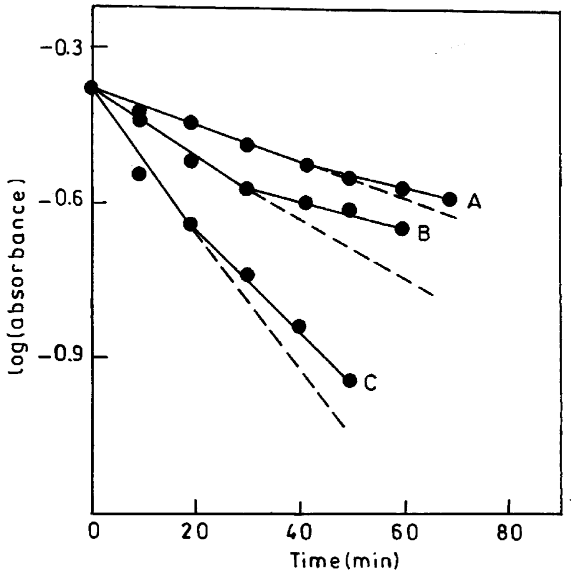


Figure 2. Plots of log(absorbance) versus time for the oxidation of [gum arabic] = 9.0×10^{-2} g dm^{-3} by colloidal [MnO_2] = 5.0×10^{-5} mol dm^{-3} in the presence of [$HClO_4$] = 3.7×10^{-4} mol dm^{-3} at different temperatures A(40 °C), B(50 °C) and C(60 °C).

Table 1. Values of rate constants (k_{obs}) for the oxidation of gum arabic by colloidal MnO_2 at 40 °C under different conditions

10^4 [$HClO_4$] (mol dm^{-3})	10^2 [gum arabic] (g dm^{-3})	10^5 [MnO_2] (mol dm^{-3})	10^4 k_{obs1} (s^{-1})	10^4 k_{obs2} (s^{-1})
1.8	9.0	5.0	0.8	n.o.[a]
3.7	9.0	5.0	1.2	n.o.
5.5	9.0	5.0	1.3	n.o.
7.4	9.0	5.0	1.9	1.3
9.3	9.0	5.0	2.3	1.6
11.1	9.0	5.0	2.3	1.7
13.0	9.0	5.0	2.3	2.0
14.8	9.0	5.0	2.4	2.1
3.7	1.0	5.0	0.5	n.o.
3.7	2.0	5.0	0.5	n.o.
3.7	3.0	5.0	0.5	n.o.
3.7	4.0	5.0	0.7	n.o.
3.7	5.0	5.0	0.7	n.o.
3.7	6.0	5.0	0.9	n.o.
3.7	7.0	5.0	1.1	n.o.
3.7	10.0	5.0	3.4	n.o.
3.7	9.0	6.0	0.8	n.o.
3.7	9.0	7.0	0.6	n.o.
3.7	9.0	8.0	0.5	n.o.
3.7	9.0	9.0	0.3	n.o.

[a] n.o. = not observed.

Table 2. Values of the rate constants and activation parameters (E_a, $\Delta H^{\#}$ and $\Delta S^{\#}$) for the oxidation of [gum arabic] = 9.0×10^{-2} gdm^{-3} by [MnO_2] = 5.0×10^{-5} mol dm^{-3} in [$HClO_4$] = 3.7×10^{-4} mol dm^{-3}

Temperature (°C)		10^4 k_{obs1} (s^{-1})	10^4 k_{obs2} (s^{-1})
40		1.2	n.o.[a]
50		2.3	1.5
60		4.0	1.9
Activation parameters:			
E_a (kJ mol^{-1})	54		
$\Delta H^{\#}$ (kJ mol^{-1})	51		
$\Delta S^{\#}$ (J K^{-1} mol^{-1})	−77		

[a] n.o. = not observed.

3.5. Order in [gum arabic]

Table 1 contains pertinent data regarding the reaction studied as a function of [gum arabic] between 1.0×10^{-2} and 10.0×10^{-2} gdm^{-3} at constant [$HClO_4$] = 3.7×10^{-4} mol dm^{-3}, [MnO_2] = 5.0×10^{-5} mol dm^{-3}

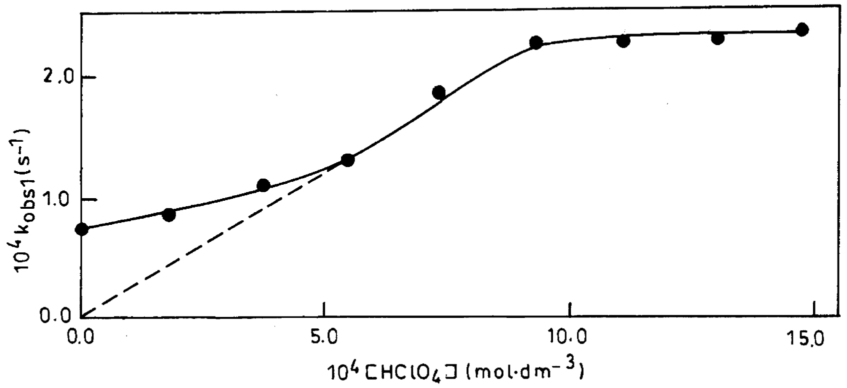


Figure 3. Effect of $[HClO_4]$ on the rate constants (k_{obs1}) for the oxidation of [gum arabic] = 9.0×10^{-2} g dm^{-3} by colloidal $[MnO_2]$ = 5.0×10^{-5} mol dm^{-3} at 40 °C.

and temperature = 40 °C. Plot of k_{obs1} versus [gum arabic] at constant $[H^+]$ is nonlinear passing through the origin (Fig. 4). However, log k_{obs1} versus log [gum arabic] is linear with slope 0.65, indicating fractional-order dependence of the rate on [gum arabic]. Thus, the rate equation experimentally found was

$$\upsilon = -\frac{d[MnO_2]}{dt} = \{k'_I + k''_{II}[H^+]^{0.8}\}[MnO_2][\text{gum arabic}]^{0.65} \quad (1)$$

3.6. Order in colloidal $[MnO_2]$

The effect of $[MnO_2]$ on the reaction rate was studied at constant [gum arabic], $[HClO_4]$ and temperature. It was observed that k_{obs1} decreased as the initial colloidal $[MnO_2]$ increased (Table 1). It is well established that pseudo-first-order rate constants are independent of the initial reactant concentration. The abnormal behavior is due to possible coagulation (flocculation) of the colloidal particles of MnO_2. This type of ambiguity was also observed in many permanganate and colloidal MnO_2 reactions.[10–12,20]

3.7. Effect of temperature

In order to calculate the values of activation parameters, the reaction was studied at 40, 50, and 60 °C at [gum arabic] = 9.0×10^{-2} g dm^{-3}, $[MnO_2] = 5.0 \times 10^{-5}$ mol dm^{-3} and $[HClO_4] = 3.7 \times 10^{-4}$ mol dm^{-3}. Plots of log(absorbance) versus time were deviate from the linearity (Fig. 2). Finally, k_{obs1} was found to increase with temperature; these data are presented in Figure 5 in an Arrhenius-type fashion. The value of a activation energy (E_a) for the oxidation of gum arabic by colloidal MnO_2 was calculated from the slope of Figure 5 plot, and the result has been

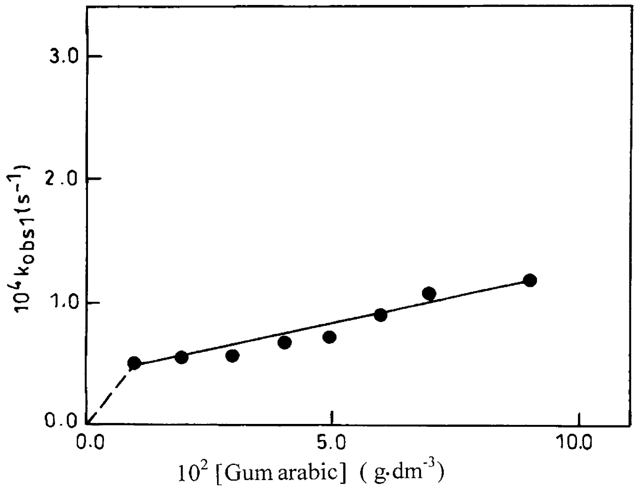


Figure 4. Effect of [gum arabic] on the rate constants (k_{obs1}) for the oxidation of gum arabic by colloidal $[MnO_2] = 5.0 \times 10^{-5}$ mol dm^{-3} in presence of $[HClO_4] = 3.7 \times 10^{-4}$ mol dm^{-3} at 40 °C.

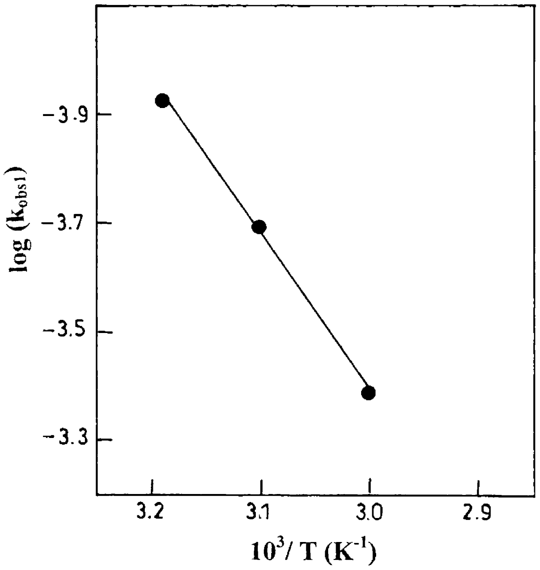


Figure 5. Arrhenius plot for the oxidation of [gum arabic] = 9.0×10^{-2} g dm^{-3} by colloidal $[MnO_2] = 5.0 \times 10^{-5}$ mol dm^{-3} in the presence of $[HClO_4] = 3.7 \times 10^{-4}$ mol dm^{-3}.

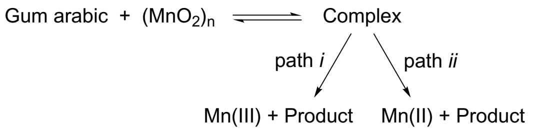
listed in Table 2 along with other parameters (entropy of activation ($\Delta S^{\#}$) and enthalpy of activation ($\Delta H^{\#}$)).

3.8. The mechanism

In the light of the observed experimental data, we assume that oxidation kinetics proceed by two routes: (i) a one-step one-electron oxidation and (ii) a one-step two-electron oxidation (Scheme 1).

In order to confirm the involvement of Mn(III) as an intermediate (path (i)), the effects of sodium pyrophosphate and sodium fluoride (range: 2.0×10^{-4} to 20.0×10^{-4} mol dm^{-3}) were studied under the same experimental conditions of [gum arabic] = 9.0×10^{-2} g dm^{-3}, [$HClO_4$] = 3.7×10^{-4} mol dm^{-3} and [MnO_2] = 5.0×10^{-5} mol dm^{-3} at 40 °C. Under these conditions the rate constants increased continuously with increase in [$P_2O_7^{4-}$] or [F^-] (Fig. 6). The increase in the k_{obs1} with increasing complexing agents indicates that Mn(III) is formed during the course of colloidal MnO_2 reduction.[20–23] Therefore, the possibility for path (i) in Scheme 1 cannot be ruled out completely. Further, to observe the formation of any stable Mn(III)–$P_2O_7^{4-}$ species, some experiments monitoring absorbance at 470 nm were also performed. All attempts at 470 nm were unsuccessful to detect any buildup of Mn(III) during the course of the reaction.

In order to confirm the second stage (*vide supra*), i.e., the oxidation of intermediate product(s) of gum arabic, the effect of Mn(II) (a reduction product of MnO_2) was evaluated under the same experimental condition of [gum arabic] = 9.0×10^{-2} g dm^{-3}, [$HClO_4$] = 3.7×10^{-4} mol dm^{-3} and [MnO_2] = 5.0×10^{-5} mol dm^{-3} at 40 °C. The rate constants, obtained as a function of Mn(II), were found to increase with increasing [Mn(II)]. These results are shown in Figure 6. The reduction of colloidal MnO_2 by Mn(II) has also been reported by several investigators.[13,20,23] Therefore, the exact dependence of rate constant on externally added Mn(II) concentrations cannot be predicted.



Scheme 1.

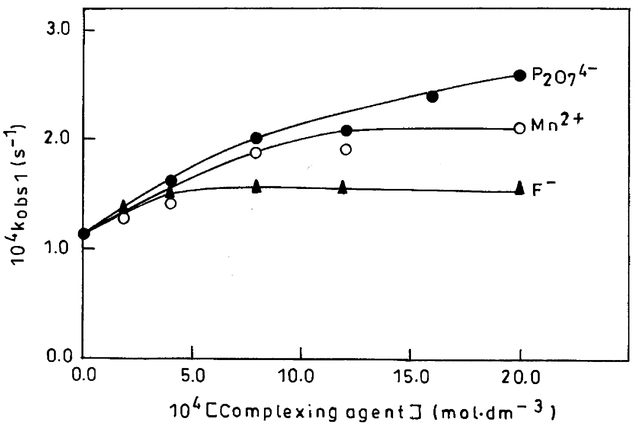


Figure 6. Effect of [$P_2O_7^{4-}$] (●), [Mn^{2+}] (○) and [F^-] (▲) on k_{obs1} for the oxidation of [gum arabic] = 9.0×10^{-2} g dm^{-3} by colloidal [MnO_2] = 5.0×10^{-5} mol dm^{-3} in the presence of [$HClO_4$] = 3.7×10^{-4} mol dm^{-3}.

An aqueous solution of sugar is an equilibrium mixture of α and β anomers. Gum arabic is water-soluble polysaccharide, which has rhamnose as its terminal residues. It has been established in the oxidation of aldoses by metal ions that the anomer having OH-1 equatorial undergoes faster oxidation than the corresponding anomer having OH-1 axial.[24–26] Despite uncertainty of the exact oxidation site for the complicated structure of gum arabic, the rhamnose unit can at least be considered with some degree of reliability. Therefore, the reaction is presumed to follow the fast adsorption of gum arabic onto the surface of the colloidal MnO_2 through hydroxy groups (Eqs. 2 and 5). The adsorption is similar to the oxidation of organic acids[9–12] and monosaccharide[13] by colloidal MnO_2. In the rate-determining step (Eqs. 3 and 6), the complex B/C breaks leading to the formation of products (Scheme 2).

After the slow two-electron step, reactions (7) to (8) may follow (this is understandable in view of the fact that disproportionation reaction (8) is fast). The complete rate law for the reaction is given by

$$\begin{aligned} v &= -\frac{d[MnO_2]}{dt} \\ &= k'_I + k''_{II}[(H^+)_s]^{0.80}[MnO_2][(\text{gum arabic})_s]^{0.65} \end{aligned} \quad (10)$$

where k_I and k_{II} represent the rate constants corresponding to acid-independent and acid-dependent path, [$(H^+)_s$] and [(gum arabic)$_s$] stand for the concentrations of hydrogen ion and gum arabic adsorbed on the colloid surface, respectively. Considering Scheme 2, the rate law (10) can be written as Eq. 11.

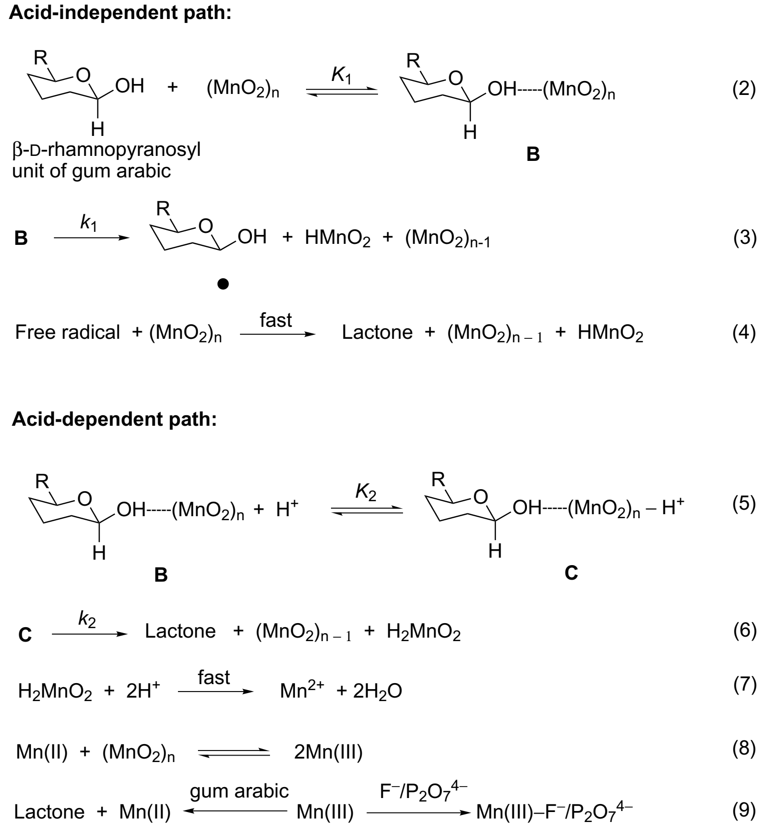
$$k_{obs1} = \frac{(k_1K_1 + k_2K_1K_2[(H^+)_s])[(\text{gum arabic})_s]}{1 + (K_1 + K_2K_1)[(H^+)_s][(\text{gum arabic})_s]} \quad (11)$$

where $k'_I = k_1K_1$, $k''_{II} = k_2K_1K_2$.

Under our experimental conditions ([$HClO_4$] = 1.8×10^{-4} to 14.8×10^{-4} mol dm^{-3}), acid-independent path can be neglected in comparison to acid-dependent path. Therefore, Eq. 11 simplifies to Eq. 12.

$$k_{obs1} = \frac{k_2K_1K_2[(H^+)_s][(\text{gum arabic})_s]}{1 + K_2K_1[(H^+)_s][(\text{gum arabic})_s]} \quad (12)$$

The derived rate law clearly accounts for the fractional-order dependence on [gum arabic] as well as [H^+].



Scheme 2.

3.9. Application of adsorption isotherm

In general, the Freundlich adsorption isotherm has been used to explain the adsorption of a solute onto a solid adsorbent in solution. It was assumed that a dynamic equilibrium exists between the adsorbed molecules and the free molecules. It has also been established that redox reactions of colloidal MnO_2 proceed through the adsorption of reductant on the surface of the colloidal particles. According to the Freundlich isotherm,[9] the concentration of a species adsorbed on the colloid surface is directly proportional to the concentration of that species in the bulk solution raised to a certain exponent; hence, using the Freundlich adsorption isotherm for Eqs. 2 and 5, we get

$$[(\mathrm{H}^+)_\mathrm{s}] = \alpha[\mathrm{H}^+]^\beta \tag{13}$$

$$[(\text{gum arabic})\mathrm{s}] = \alpha'[\text{gum arabic}]^{\beta'} \tag{14}$$

where α, β and α', β' are the Freundlich adsorption parameters for hydrogen ion and gum arabic, respectively, whereas $[H^+]$ and [gum arabic] represent the concentrations of the corresponding species present in the bulk solution. Substitution of $[(H^+)_s]$ and $[(\text{gum arabic})_s]$ from Eqs. 12 and 14 in Eq. 10 gives

$$\upsilon = \{k'_\mathrm{I}\alpha' + k''_\mathrm{II}\alpha\alpha'[\mathrm{H}^+]^\beta\}[\mathrm{MnO_2}][\text{gum arabic}]^{\beta'} \tag{15}$$

Thus, we may safely conclude that Eq. 15 is in good agreement with the observed kinetic results. Freundlich exponents $\beta = 0.8$ and $\beta' = 0.65$ satisfactorily explain one of the requirements of the Freundlich isotherm, that is, the exponent must be a number in the 0–1 interval.[27]

4. Conclusions

The important finding of this study is the oxidation/decomposition of gum arabic by colloidal MnO_2 in aqueous medium. Oxidation of this water-soluble polysaccharide could probably be explained due to the reducing nature of the sugar moieties. We are unaware of any precedence in the redox chemistry of this system. A perusal of the literature revealed that gum arabic stabilizes the colloidal MnO_2 in solution. To examine the nature of any protective colloid, it is necessary to study the oxidizing as well as reducing properties in detail. To the best of our knowledge, this is the first evidence showing the oxidative decomposition of gum arabic in presence of colloidal MnO_2. These studies can be used to resolve the differences of existing opinions regarding the role of gum arabic in the protection of colloidal solutions.

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