

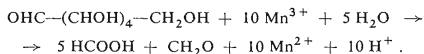
## OXIDATION OF GALACTOSE BY MANGANESE(III) SULPHATE\*

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Galactose was found to be oxidized by manganese(III) sulphate according to the equation



The kinetics of the reaction was studied and its mechanism suggested. A procedure was worked out for indirect titrimetric determination of galactose based on its oxidation with excess manganese(III) sulphate and potentiometric retitration of the unreacted reagent with iron(II) sulphate.

As part of a systematic study of oxidation of organic substances by trivalent manganese compounds, the present work deals with the reaction of galactose with manganese(III) sulphate. So far, attention has been paid to the oxidation of glucose by the diphosphate complex of trivalent manganese<sup>1</sup> and of glucose and saccharose by manganese(III) acetate<sup>2</sup>; neither of the reactions, however, has found analytical use. Information concerning the oxidation of related organic substances by compounds of trivalent manganese can be found in the reviews<sup>3,4</sup>; details of reactions of monosaccharides with other oxidants are given in the monographs<sup>5-7</sup>, references to their analytical applications, in the monographs<sup>8,9</sup>.

## EXPERIMENTAL

## Reagents and Apparatus

Solutions of manganese(III) sulphate of various concentrations in systems of sulphuric acid and manganese(II) sulphate were prepared as described previously<sup>10</sup>. The titre of 0.1M iron(II) sulphate was determined daily using dichromate. Solutions of galactose of various concentrations were prepared by dissolving a precisely weighed amount of the substance of reagent grade purity in distilled water and diluting to 1 litre. Their titre was checked periodatometrically<sup>11</sup>. Aqueous system of 100 µg formaldehyde per 1 ml of solution containing, in addition, sulphuric acid and manganese(II) sulphate in concentrations 4.8 and 0.8 mol l<sup>-1</sup>, respectively, was obtained by dilution of the stock solution with distilled water and addition of the appropriate amounts of sul-

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phuric acid and manganese(II) sulphate. The titre of the formaldehyde stock solution was determined by the sulphite method<sup>12</sup>. 10% aqueous solution of chromotropic acid and saturated solution of 2,4-dinitrophenylhydrazine in 2M hydrochloric acid were also used. All the chemicals used were of reagent grade purity.

The potentiometric titrations were carried out by means of a TTT 1c valve voltmeter and an ABU 1b automatic burette (both Radiometer, Copenhagen) using a system of a platinum indicating electrode and a saturated calomel reference electrode. The polarographic measurements were performed by employing an OH 102 polarograph (Radelkis, Budapest) in an all-glass thermostated vessel using a mercury dropping indicating electrode and a saturated calomel reference electrode. The solutions were freed from oxygen by nitrogen stream. The spectrophotometric measurements were carried out on a Specord UV VIS instrument (Zeiss, Jena) using cells of the optical path length 1 cm.

### Study of the Reaction Stoichiometry

*Consumption of the oxidant.* For monitoring the time course of consumption of manganese(III) sulphate, 5 ml of 0.01M galactose solution was added to 20 ml of a 0.05M manganese(III) sulphate solution containing sulphuric acid and manganese(II) sulphate in concentrations 6 and 0.1 mol  $\cdot$  l<sup>-1</sup>, respectively. After stirring, the reaction mixture was allowed to stand at room temperature and after a preselected time period the unreacted manganese(III) sulphate was determined by potentiometric titration with 0.1M iron(II) sulphate. A blank experiment was run in parallel, and the consumption of the oxidant (in mol per 1 mol of galactose) was calculated from the difference in the consumptions in the blank experiment and the determination.

*Detection of the formaldehyde formed.* 15 ml of 0.01M galactose solution was added to 60 ml of the above-mentioned 0.05M manganese(III) sulphate solution. After 60 minutes' standing at room temperature, the unreacted oxidant was removed by adding 1 g of oxalic acid. 80 ml of saturated solution of 2,4-dinitrophenylhydrazine was then added, the precipitate separated was collected, washed, and dried, and its melting point was determined.

*Determination of the formaldehyde formed.* A modification of the chromotropic acid method was used<sup>15</sup>. For obtaining the calibration plot, portions of 1.0, 1.2, 1.4, 1.6, 1.8, and 2.0 ml of solution containing 100  $\mu$ g formaldehyde in 1 ml and sulphuric acid and manganese(II) sulphate in concentrations 4.8 and 0.08 mol l<sup>-1</sup> were placed in ground-in test tubes. To each of them were added 1 ml of 10% aqueous solution of chromotropic acid and, after shaking, 10 ml of concentrated sulphuric acid. The test tubes were heated for 30 min on boiling water bath, and after cooling down to ambient temperature, their contents were transferred quantitatively into 100 ml volumetric flasks and diluted to volume with distilled water. The absorbances of the solutions were measured in 1 cm cells at 570 nm. In the experiments with galactose, 5 ml of 0.02M galactose was added to 20 ml of 0.075M manganese(III) sulphate solution in 6M sulphuric acid and 0.1M manganese(II) sulphate. After 60 minutes' standing at room temperature, the excess reagent was removed with 1 g of oxalic acid, 1 ml of the solution was transferred into a ground-in test tube, and further was proceeded as in the case of the calibration curve plotting. The absorbance was measured at 570 nm and the amount of the formaldehyde formed was read from the calibration graph.

### Study of the Reaction Kinetics

10 ml of a fresh solution of galactose in a system containing sulphuric acid and manganese(II) sulphate and, occasionally, perchloric acid or sodium sulphate, was thermostated in the polaro-

graphic vessel and freed from oxygen by nitrogen purging. One ml of 0.01M manganese(III) sulphate solution in a system of sulphuric acid and manganese(II) sulphate, also thermostated and freed from oxygen, was added by means of a microsyringe, and the scanning was activated. Nitrogen was supplied for additional 30 s to ensure good mixing of the solution; then the bubbling was discontinued and nitrogen was brought above the solution level. The concentration of trivalent manganese was determined polarographically applying the voltage of 0 V, at which — as has been verified — the current is directly proportional to the manganese(III) sulphate concentration. The initial concentrations of the components were calculated from the concentrations of the substances in the galactose and manganese(III) sulphate solutions.

#### Detection of Free Radicals as Intermediates

The procedure was analogous to that used in<sup>13</sup>. To a stirred mixture of 50 ml of 0.01M galactose and 50 ml of acrylonitrile was slowly added 100 ml of 0.05M manganese(III) sulphate in sulphuric acid (6 mol l<sup>-1</sup>) and manganese(II) sulphate (0.1 mol l<sup>-1</sup>) system. The polymer separated was collected on an S 4 glass filter, washed with water and dried in a desiccator, and its infrared spectrum was scanned in a nujol mull.

## RESULTS

### Reaction Stoichiometry

The time dependence of the consumption of the oxidant was found as follows:

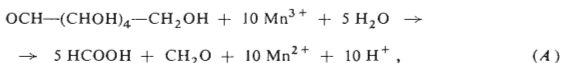
Time, min	5	30	60	90	120	240	1 200
Degree of oxidation, mol/mol	8.65	9.84	9.98	9.97	9.98	10.10	10.05

These data indicate that in the conditions applied, the reaction proceeds quantitatively and stoichiometrically, 10 mol of the oxidant being taken up per 1 mol of galactose.

The melting point of the isolated 2,4-dinitrophenylhydrazone was 166–167°C, which agrees well with that of the authentic formaldehyde derivative (167–168°C) as well as with the tabulated data<sup>14</sup>.

By spectrophotometric determination of the formed formaldehyde with chromotropic acid, 660 µg of galactose was found to give rise to 110 µg of formaldehyde, which corresponds to the formation of 1 mol of formaldehyde from 1 mol of galactose.

These facts give evidence that galactose is oxidized by manganese(III) sulphate according to the equation



the products being subject to no further oxidation.

### Reaction Kinetics

*Dependence of the reaction rate on the manganese(III) sulphate concentration.* The time dependence of the limiting diffusion current of trivalent manganese was measured for the initial concentrations  $C_{\text{Mn(III)}} = 0.91 \text{ mmol l}^{-1}$ ,  $C_{\text{C}_6\text{H}_{12}\text{O}_6} = 9.10 \text{ mmol l}^{-1}$ ,  $C_{\text{Mn(II)}} = 0.1 \text{ mol l}^{-1}$ ,  $[\text{H}^+] = 5.9 \text{ mol l}^{-1}$ ,  $[\text{HSO}_4^-] = 6.1 \text{ mol l}^{-1}$ . (The  $[\text{HSO}_4^-]$  and  $[\text{H}^+]$  values were calculated based on the known concentrations of sulphuric acid and manganese(II) sulphate assuming a complete dissociation of the former to the 1st degree.) In these conditions, the concentrations of all of the components except trivalent manganese can be regarded as constant during the reaction. The plot of  $\ln I_t$  vs  $t$  (where  $I_t$  is the limiting diffusion current of trivalent manganese in time  $t$ ) was a straight line, hence in the conditions applied the reaction under study is a 1st order reaction with respect to manganese(III) sulphate. The slope of the straight line,  $\text{tg } \alpha$ , afforded the pseudo-first order rate constant  $k' = -\text{tg } \alpha = 0.26 \text{ min}^{-1}$ .

*Dependence of the reaction rate on the galactose concentration.* In the same manner and in the same conditions as above, the pseudo-first order rate constant was calculated applying a 10–30 fold excess of galactose with respect to trivalent manganese. The values obtained were as follows:

$C_{\text{C}_6\text{H}_{12}\text{O}_6}, \text{ mmol l}^{-1}$	4.5	9.1	13.6	18.2	22.7	27.3
$k', \text{ min}^{-1}$	0.14	0.26	0.45	0.53	0.63	0.77

With regard to the nature of this dependence, the inverse rate constant was plotted against the inverse total concentration of galactose. A straight line was obtained with the slope of  $0.032 \text{ min mol l}^{-1}$  and  $1/k'$  intercept of  $0.25 \text{ min}$ .

*Dependence of the reaction rate on the concentration of hydrogensulphate ions.* Again in the same manner, the pseudo-first order rate constant was measured for various concentrations of sulphuric acid, the hydrogen ion concentration being held constant at  $5.9 \text{ mol l}^{-1}$  by adding perchloric acid. The following dependence was established:

$[\text{HSO}_4^-], \text{ mol l}^{-1}$	2.1	3.1	4.1	5.1	6.1
$k', \text{ min}^{-1}$	0.59	0.45	0.35	0.30	0.26

The inverse rate constant was plotted against the  $\text{HSO}_4^-$  ion concentration to give a straight line with the slope of  $0.56 \text{ min l mol}^{-1}$  and the  $1/k'$  intercept of  $0.5 \text{ min}$ .

*Dependence of the reaction rate on the concentration of hydrogen ions.* The pseudo-first order rate constant was determined also in dependence on the hydrogen ion concentration; the concentration of hydrogensulphate ions was held constant

at the level of  $6.1 \text{ mol l}^{-1}$  by adding sodium sulphate. The values were as follows:

$[\text{H}^+]$ , $\text{mol l}^{-1}$	0.9	1.9	2.9	3.9	4.9	5.9
$k'$ , $\text{min}^{-1}$	0.104	0.129	0.150	0.170	0.200	0.256

The dependence of  $k'$  on the concentration of  $\text{H}^+$  ions gives a straight line plot, with the slope of  $23.8 \text{ l mol}^{-1} \text{ min}^{-1}$  and the  $k'$  intercept of  $0.082 \text{ min}^{-1}$ .

*Dependence of the reaction rate on the concentration of manganese(II) ions.* The pseudo-first order rate constant was determined for different concentrations of manganese(II) ions, added in the form of manganese(II) sulphate. The concentration of  $\text{HSO}_4^-$  ions was held at a constant value of  $6.1 \text{ mol l}^{-1}$  by using additions of zinc sulphate, which does not affect the reaction rate. The following values were measured:

$C_{\text{Mn(II)}}$ , $\text{mol l}^{-1}$	0.02	0.04	0.06	0.08	0.10
$k'$ , $\text{min}^{-1}$	0.35	0.32	0.30	0.28	0.26

The inverse rate constant was plotted against the manganese(II) ion concentration. A straight line was obtained, with the slope of  $1.30 \text{ min l mol}^{-1}$  and the  $1/k'$  intercept of 2.6 min.

*Dependence of the reaction rate on temperature.* Again in the same manner and in the same conditions, the temperature dependence of the pseudo-first order rate constant was established for the range of  $20-40^\circ\text{C}$ . The data are given in Table I.

The plot of  $\log k'$  vs  $1/T$ , where  $T$  is the absolute temperature, is a straight line with the slope  $\text{tg } \alpha = -4.25 \cdot 10^3 \text{ deg}$ , which yields the activation energy of the reac-

TABLE I

Dependence of the rate of reaction ( $A$ ) on temperature. Initial concentrations:  $C_{\text{Mn(III)}} = 0.91 \text{ mmol l}^{-1}$ ,  $C_{\text{C}_6\text{H}_{12}\text{O}_6} = 9.1 \text{ mmol l}^{-1}$ ,  $[\text{H}^+] = 5.9 \text{ mol l}^{-1}$ ,  $[\text{HSO}_4^-] = 6.1 \text{ mol l}^{-1}$ ,  $C_{\text{Mn(II)}} = 0.1 \text{ mol l}^{-1}$

$T$ K	$k'$ $\text{min}^{-1}$	$10^3/T$ $\text{K}^{-1}$	$\log k'$	$T \log k'$ K
293.16	0.26	3.41	-0.580	-169.9
298.16	0.48	3.35	-0.319	-95.1
303.16	0.82	3.30	-0.090	-27.2
308.16	1.29	3.25	+0.111	+34.2
313.16	2.00	3.19	+0.310	+97.0

tion,  $E = -2.303 R \lg \alpha = 81.4 \text{ kJ mol}^{-1}$ . The values of  $T \log k'$  were also plotted against the absolute temperature to give a straight line with the slope of  $\lg \alpha = 13.5$ , which — equated with  $\log A$  — yields the frequency factor value of  $A = 3.16 \cdot 10^{13} \text{ min}^{-1}$ .

*Free radicals as reaction intermediates.* Based on their ability to initiate radical polymerization of acrylonitrile, free radicals were proved to form during the reaction; the infrared spectrum of the polymer exhibits bands due to the stretching vibrations of OH groups.

#### *Analytical Application of the Reaction*

Taking into account the fact that the rate of oxidation of galactose by manganese(III) sulphate increases with increasing acidity and decreases with increasing concentration of manganese(II) ions, a procedure is suggested for the determination of galactose with this reagent as given below. Lower concentrations of manganese(II) ions should be avoided because of the lowered stability of the reagent<sup>10</sup>, higher concentrations of sulphuric acid could not be applied because of the poor solubility of manganese(II) sulphate in concentrated sulphuric acid.

*Procedure:* 5 ml of aqueous solution containing 4–14 mg of galactose is added to 20 ml of 0.05M manganese(III) sulphate in a solution containing also sulphuric acid and manganese(II) sulphate in concentrations 8 and 0.04 mol l<sup>-1</sup>, respectively. The mixture is shaken and allowed to stand for 2 h at room temperature. The unreacted reagent is then determined by potentiometric titration with 0.1M iron(II) sulphate solution. A blank experiment is run in parallel, and the amount of the substance is calculated from the difference in the consumption of iron(II) sulphate in the blank experiment and in the determination.

One ml of 0.1M iron(II) sulphate corresponds to 1.802 mg of galactose. The accuracy and the reproducibility of the determination are apparent from the data of Table II.

#### DISCUSSION

Based on the reaction kinetics established and on the analogy with the oxidation of monosaccharides with periodic acid<sup>16,17</sup>, a mechanism can be suggested for the oxidation of galactose with manganese(III) sulphate, involving a reversible formation of a complex of the oxidized substance with the oxidant, which in the rate-determining step decomposes giving rise to a free radical of the type  $\text{HOCH}_2\text{—}(\text{CHOH})_3\text{—}\overset{\cdot}{\text{C}}\text{HOH}$  and a  $\overset{+}{\text{C}}\text{H=O}$  ion. The former than is rapidly oxidized to  $\text{HOCH}_2\text{—}(\text{CHOH})_3\text{—CHO}$ , and the  $\overset{+}{\text{C}}\text{HO}$  ion reacts with water to yield HCOH. This step

is triply repeated, giving successively rise to hydroxyaldehydes always one carbon shorter. The glycolaldehyde thus formed is ultimately oxidized<sup>18</sup> to formaldehyde and formic acid. The positive effect of H<sup>+</sup> ions on the reaction rate can be explained in terms of a reversible formation of the protonized form of galactose, preferably attacked by the trivalent manganese. The observed retardation by manganese(II) ions can be explained by the reversible formation of a galactose complex with bivalent manganese, associated with a decrease in the equilibrium concentration of free galactose in the system. The mechanism suggested can be represented by the equations

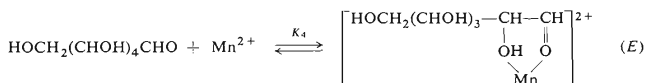
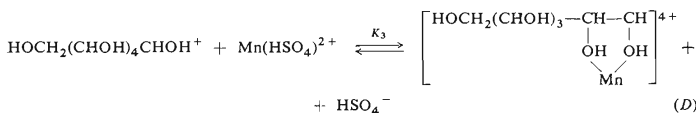
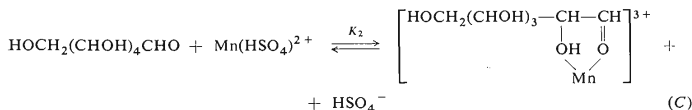
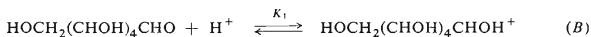
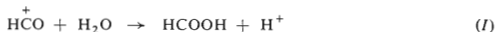
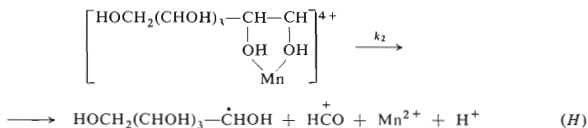
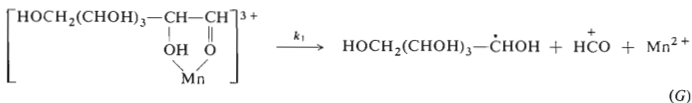
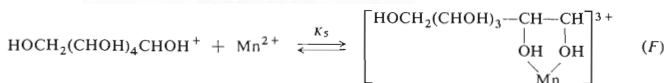


TABLE II

Accuracy and reproducibility of the indirect determination of galactose with manganese(III) sulphate

Added mg	Found <sup>a</sup> mg	Standard deviation mg
4.505	4.514	0.03
9.010	9.087	0.02
13.515	13.502	0.02

<sup>a</sup> Average of 7 determinations, from which the standard deviation was also evaluated.



$\text{OHCH}_2(\text{CHOH})_3\text{CHO}$  then is oxidized analogously to  $\text{OHCH}_2(\text{CHOH})_2\text{CHO}$  and further *via*  $\text{OHCH}_2(\text{CHOH})\text{CHO}$  as far as  $\text{OHCH}_2\text{CHO}$ , which in turn is oxidized to  $\text{CH}_2\text{O}$  and  $\text{HCOOH}$  by the mechanism described previously<sup>18</sup>.

The total concentrations of sulphuric acid, bivalent manganese, galactose, and trivalent manganese are given by the relations

$$C_{\text{HSO}_4^-} = [\text{HSO}_4^-] + [\text{Mn}(\text{HSO}_4)^{2+}] \quad (1)$$

$$C_{\text{Mn}^{2+}} = [\text{Mn}^{2+}] \quad (2)$$

$$C_G = [\text{MnG}^{2+}] + [\text{MnGH}^{3+}] + [G] + [\text{GH}^+] \quad (3)$$

$$C_{\text{Mn}^{3+}} = [\text{Mn}(\text{HSO}_4)^{2+}] + [\text{MnG}^{3+}] + [\text{MnGH}^{4+}], \quad (4)$$

where the  $C$ 's are the total analytical concentrations and the bracketed symbols are the equilibrium concentrations of the various species;  $G$  stands for galactose and  $\text{GH}^+$  for its protonized form.

In the conditions applied, where the concentration of sulphuric acid exceeds substantially that of trivalent manganese, the term  $[\text{Mn}(\text{HSO}_4)^{2+}]$  in Eq. (1) can be neglected; the terms  $[\text{MnG}^{3+}]$  and  $[\text{MnGH}^{4+}]$  in Eq. (3) can be neglected as well, with regard to the fact that galactose is present in a molar excess of an order of magnitude with respect to trivalent manganese.



The equilibrium constants  $K_1$  through  $K_5$  of the reactions (B)–(F) are given by the relations

$$K_1[G][H^+] = [GH^+] \quad (5)$$

$$K_2[G][Mn(HSO_4)^{2+}] = [MnG^{3+}][HSO_4^-] \quad (6)$$

$$K_3[GH^+][Mn(HSO_4)^{2+}] = [MnGH^{4+}][HSO_4^-] \quad (7)$$

$$K_4[G][Mn^{2+}] = [MnG^{2+}] \quad (8)$$

$$K_5[GH^+][Mn^{2+}] = [MnGH^{3+}]. \quad (9)$$

Provided that the rate-determining step of the reaction is the decomposition of the complex of the oxidized substance or its protonized form with the oxidant, the reaction rate can be written as

$$v = -d[Mn^{3+}]/dt = nk_1[MnG^{3+}] + nk_2[MnGH^{4+}], \quad (10)$$

where  $n = 10$  is the number of electrons exchanged in the reaction.

Dividing Eq. (6) by Eq. (7) and substituting from Eq. (5) we obtain

$$[MnG^{3+}] = K_2[MnGH^{4+}]/(K_3K_1[H^+]). \quad (11)$$

Furthermore,  $[MnGH^{4+}]$  from Eq. (7) is

$$[MnGH^{4+}] = K_3[GH^+][Mn(HSO_4)^{2+}]/[HSO_4^-]; \quad (12)$$

$[GH^+]$  from Eqs (3), (5), (8) and (9) is

$$[GH^+] = K_1[G][H^+] = K_1C_G[H^+]/(K_4[Mn^{2+}] + K_1K_5[H^+][Mn^{2+}] + K_1[H^+] + 1) \quad (13)$$

and  $[Mn(HSO_4)^{2+}]$  can be expressed from Eqs (4)–(7), (13) as

$$\begin{aligned} [Mn(HSO_4)^{2+}] &= C_{Mn^{3+}} - K_2[G][Mn(HSO_4)^{2+}]/[HSO_4^-] - \\ &\quad - K_3[GH^+][Mn(HSO_4)^{2+}]/[HSO_4^-] = \\ &= C_{Mn^{3+}}HSO_4^-(K_4[Mn^{2+}] + K_1K_5[H^+][Mn^{2+}] + \\ &\quad + K_1[H^+] + 1)/\{[HSO_4^-](K_4[Mn^{2+}] + K_1K_5[H^+][Mn^{2+}] + \\ &\quad + K_1[H^+] + 1) + K_2C_G + K_1K_3C_G[H^+]\}. \end{aligned} \quad (14)$$

Substituting from the relations (11)–(14), (1), (2) into the equation for the reaction rate, (10), we obtain

$$v = n(k_1K_2/K_1K_3C_{H^+} + k_2)K_1K_3C_G C_{H^+} C_{Mn^{3+}} / \{C_{HSO_4^-} (K_4 C_{Mn^{2+}} + K_1K_5 C_{H^+} C_{Mn^{2+}} + K_1 C_{H^+} + 1) + K_2 C_G + K_1K_3 C_G C_{H^+}\} \quad (15)$$

which finally can be transformed into

$$v = nC_G(k_1K_2 + k_2K_1K_3C_{H^+}) C_{Mn^{3+}} / \{C_{HSO_4^-} (K_4 C_{Mn^{2+}} + K_1K_5 C_{H^+} C_{Mn^{2+}} + K_1 C_{H^+} + 1) + C_G(K_2 + K_1K_3C_{H^+})\}. \quad (16)$$

This relation is valid provided that the concentrations of the  $Mn^{2+}$  and  $HSO_4^-$  ions in the solution are in a high excess with respect to the concentration of galactose, which, in turn, is present in a sufficient excess with respect to trivalent manganese; these conditions have been met in all experiments.

When all the components in the solution are in an excess of orders of magnitude with respect to trivalent manganese and, consequently, their concentrations remain practically constant, Eq. (16) can be written in the form

$$v = k' C_{Mn^{3+}}, \quad (17)$$

where

$$k' = nC_G(k_1K_2 + k_2K_1K_3C_{H^+}) / \{C_{HSO_4^-} (K_4 C_{Mn^{2+}} + K_1K_5 C_{H^+} C_{Mn^{2+}} + K_1 C_{H^+} + 1) + C_G(K_2 + K_1K_3C_{H^+})\}. \quad (18)$$

The direct proportionality (17) is in accordance with the experiment, in which the reaction under study was found to be 1st order with respect to trivalent manganese.

Eq. (18) can be re-arranged to the form

$$1/k' = C_{HSO_4^-} (K_4 C_{Mn^{2+}} + K_1K_5 C_{H^+} C_{Mn^{2+}} + K_1 C_{H^+} + 1) / nC_G(k_1K_2 + k_2K_1K_3C_{H^+}) + (K_2 + K_1K_3C_{H^+}) / n(k_1K_2 + k_2K_1K_3C_{H^+}). \quad (19)$$

For constant concentrations of  $Mn^{2+}$ ,  $H^+$ , and  $HSO_4^-$  ions, this relation is one of the type  $1/k' = (a_1/b_1)/C_G + c_1/b_1$ , where  $a_1$ ,  $b_1$ , and  $c_1$  are constants, and is in agreement with the experimentally found linear dependence of  $1/k'$  on  $1/C_G$ ; also, the validity of this relation is a corroboration of the assumption that the mechanism of the oxidation involves a reversible formation of the complex of galactose with trivalent manganese.

For constant concentrations of galactose and  $H^+$  and  $HSO_4^-$  ions, relation (19) is one of the type  $1/k' = (a_2/b_2) C_{Mn^{2+}} + c_2/b_2$ , where  $a_2, b_2$ , and  $c_2$  are constants. This relation, too, is in agreement with the experimentally found linear dependence of  $1/k'$  on  $C_{Mn^{2+}}$ .

If the concentrations of galactose and  $H^+$  and  $Mn^{2+}$  ions are held constant, Eq. (19) can be written as  $1/k' = (b_3/a_3) C_{HSO_4^-} + c_3/a_3$ , where  $a_3, b_3$ , and  $c_3$  are constants. Again, this relation is consistent with the experimentally established linear dependence of  $1/k'$  on  $C_{HSO_4^-}$ .

Finally, if the concentrations of galactose and of  $Mn^{2+}$  and  $HSO_4^-$  ions are assumed to be constant, Eq. (18) can be re-arranged

$$1/k' = \{C_{HSO_4^-}(K_4 C_{Mn^{2+}} + K_1 K_5 C_{H^+} + C_{Mn^{2+}}) + C_{HSO_4^-}(K_1 C_{H^+} + 1) + C_G K_2 + K_1 K_3 C_G C_{H^+}\} / n C_G (k_1 K_2 + k_2 K_1 K_3 C_{H^+}). \quad (20)$$

For a low degree of galactose protonation ( $K_1 < 1$ ), the terms involving  $K_1$  can be neglected in the numerator against  $C_{HSO_4^-}$  (which is as high as  $6.1 \text{ mol l}^{-1}$ ), so that we can write

$$1/k' = \{C_{HSO_4^-}(K_4 C_{Mn^{2+}} + 1) + K_2 C_G\} / n C_G (k_1 K_2 + k_2 K_1 K_3 C_{H^+}) = a_4 / (b_4 + c_4 C_{H^+}), \quad (21)$$

or  $k' = b_4/a_4 + (c_4/a_4) C_{H^+}$ , where  $a_4, b_4$ , and  $c_4$  are constants. The linear dependence of  $k'$  on  $C_{H^+}$  again has actually been observed.

An analogous mechanism can be assumed also for the oxidation of other aldoses by manganese(III) sulphate; the reaction rates will be, of course, different. This fact may be utilized for a kinetic analysis of mixtures of aldoses consisting in their oxidation by manganese(III) sulphate.

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