KINETICS AND MECHANISM OF OXIDATION OF D(+) GLUCOSE BY POTASSIUM PERMANGANATE

By

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The kinetics of oxidation of D(+) glucose by potassium permanganate has been studied in aqueous phosphoric acid solution. The reaction has been found to obey first order kinetics in substrate and in oxidant, both. Various hypotheses for the mechanism of acid catalysis have been tested. The energy and entropy of activation have been determined as 11.4 and 13.4 kcal/mole and −29.3 and −24.1 e.u. for the two stages of the reaction, respectively. A mechanism consistent with the experimental data has been proposed.

Potassium permanganate has been known as a versatile oxidising agent and the kinetics of oxidation of various organic substrates have been studied by earlier workers [1—4]. However, careful survey of the literature reveals that oxidation of aldohexoses by potassium permanganate has received little attention [5]. The present paper deals with the kinetic study of the oxidation of D(+) glucose by permanganate.

Experimental

Reagents

D(+) glucose, potassium permanganate and other chemicals used were of S.M. 'GR' grade. Doubly distilled water was used to prepare all solutions. The reaction vessels were coated with black paint to exclude any photochemical effect. Potassium permanganate solution was prepared by the method of Vogel [6].

Kinetic Measurements

The requisite amount of D(+) glucose and phosphoric acid were taken in the reaction flask and kept in a thermostat at the desired temperature within the range of ±0.1 °C. The flask of potassium permanganate was also kept in the thermostat. Requisite volume of permanganate was then rapidly mixed. The kinetics of the reaction was followed by estimating unreacted permanganate iodometrically.

Results and discussion

Dependence on oxidant concentration

The reaction was studied at different temperatures and concentrations of substrate, oxidant and phosphoric acid. It was observed that at constant concentration of substrate and phosphoric acid, the value of pseudo-first order rate constant is not affected by the change in concentration of the oxidant, hence, the order with respect to oxidant is unity.

Dependence on substrate concentration

The plot of rate constant against concentration of $D(+)$ glucose gives a straight line not passing through origin, thus showing that the order of reaction with respect to substrate is one and also that, there is a kinetic evidence for the intermediate complex formation between substrate and permanganate [7]. The results are summarised below in Table I.

Table I

Variation of rate with concentration of $D(+)$ glucose

$[KMnO_4] = 6.66 \times 10^{-4}$ M   [Phosphoric Acid] $= 2.50$ M
Temperature $= 30$ °C

$[D(+)\ glucose] \times 10^3$ M	$k_1 \times 10^2$ min.$^{-1}$	$k_2 \times 10^2$ min.$^{-1}$
4.00	1.37	0.67
5.00	1.52	0.85
6.66	2.05	1.08
10.00	2.85	1.50
20.00	5.12	2.66

Dependence on acid concentration

Increase in phosphoric acid concentration also increase the rate of oxidation of $D(+)$ glucose. $HMnO_4$ is considered as the active oxidising species in this case based on the fact that the rate of oxidation is directly proportional to the substrate concentration indicating that $HMnO_4$ oxidises the substrate directly [8].

Further in an attempt to correlate the rate of oxidation with acid concentration, various hypotheses for the mechanism of acid catalysis were tested. In this case, either of two Zucker — Hammett plots [9], are linear, indicating that reaction is acid catalysed, but however, no straight line of these plots in the present case, produces the ideal slope of unity. In view of these departure of ideal slope values from unity, applicability of Bunnett's hypothesis [10] and Bunnett Olsen l.f.e.r. [11] were tested. The values of $-H_0$ and log a_{H_2O}, corresponding to given acid concentration have been taken from PAUL and LONG [12] and BUNNETT [13], respectively.

The values of Bunnett parameters ω and Φ were found to be -2.08 and -0.22 for first stage and $+5.36$ and $+0.57$ for second stage, respectively.

Activation parameters

The reaction was studied at different temperatures to evaluate activation parameters. The results are summarised in Table II.
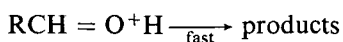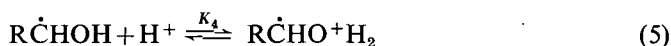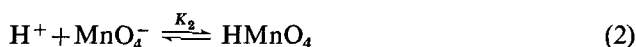
Table II

Activation parameters

[D(+) glucose] = 6.66×10^{-3} M   [Phosphoric Acid] = 2.5 M

[KMnO$_4$] = 6.66×10^{-4} M

Stage	Temp. coeff.	$\Delta E^{\neq}$ kcal/mole	$\Delta S^{\neq}$ cal mole^{-1}K^{-1}	pZ litres mole^{-1}min.$^{-1}$
First	2.00	11.4	−29.3	3.93×10^6
Second	2.00	13.4	−24.1	5.38×10^7

Primary salt effect was not observed, but a linear plot of log k against ionic strength was obtained at higher concentration of added neutral salts. This indicates that the reaction involves both the neutral species or a neutral molecule and an ion in the rate determining step.

Stoichiometry of the reaction was also studied. It was observed that two equivalents of permanganate were consumed by one equivalent of D(+) glucose. Carbon dioxide has been detected by usual lime water method. Formic acid and formaldehyde were detected as the reaction products [14]. The induced reduction of mercuric chloride by the reaction mixture indicates the participation of free radicals [15].

The information gained from the experimental data leads to the following probable mechanism, which explains the observed results very well. In the following treatment 'S' stands for the substrate.

$$S + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} SH^+ \tag{1}$$

$$H^+ + MnO_4^- \underset{}{\overset{K_2}{\rightleftharpoons}} HMnO_4 \tag{2}$$

$$SH^+ + HMnO_4 \underset{}{\overset{K_3}{\rightleftharpoons}} [Complex] \tag{3}$$

$$[Complex] \xrightarrow[slow]{k_1} R\dot{C}HOH + HCHO + HMnO_4^- \tag{4}$$

$$R\dot{C}HOH + H^+ \underset{}{\overset{K_4}{\rightleftharpoons}} R\dot{C}HO^+H_2 \tag{5}$$

$$R\dot{C}HO^+H_2 + HMnO_4 + H_2O \xrightarrow[slow]{k_2} RCH = O^+H + HMnO_4^- + H_3^+O \tag{6}$$

$$RCH = O^+H \xrightarrow[fast]{} products$$

Rate expression for this mechanism has been developed as

$$-\frac{d[MnO_4^-]}{dt} = K_s[S][MnO_4^-] + K_s'[S][MnO_4^-] \tag{8}$$

where $k_s = \dfrac{k_1 K_1 K_2 K_3 [H^+]^2}{1 + K_2[H^+]}$ and $k_s' = \dfrac{k_2 K_2 K_4 [H_2O][H^+]^2}{1 + K_2[H^+]}$.

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КИНЕТИКА И МЕХАНИЗМ ОКИСЛЕНИЯ D(+) ГЛЮКОЗЫ ПЕРМАНГАНАТОМ КАЛИЯ

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Изучено окисление D(+) глюкозы перманганатом калия в водных растворах фосфорной кислоты. Найдено, что реакция первого порядка как относительно субстрата, так и окислителя. Рассмотрены различные гипотезы для механизма кислотного катализа. Рассчитаны энергия и энтропия активации, соответственно для двух стадий равны: 11,4, 13,4 ккал/моль и $-29,3$, $-24,1$ энтропийных единиц. Предложен механизм, согласующийся с экспериментальными данными.