Int. J. Chem. Sci. : 2 (1), 2004, 57–61

COMPARATIVE STUDY OF THE INDUCING POWER OF THE OXIDANTS $KMnO_4$ AND $K_2S_2O_8$ IN THE REDUCTION OF Hg (II) CHLORIDE BY MONOSACCHARIDES

H. K. GUPTA, P. K. MISHRA, B. KUMAR and VISHAL PATHAK[*]

[*]Chemistry Department, C. L. Jain (P.G.) College, FIROZABAD (U.P.), INDIA

ABSTRACT

A comparative study of the inducing power of the oxidants, permangnate and peroxodisuslphate was studied by monosaccharides (glucose/fructose) in the reduction of Hg (II) chloride. From a comparative angle, it may be suggested that permanganate rapidly oxidizes monosaccharides at a lower temperature range whereas peroxodisulphate requires a higher temperature range for oxidation.

Key words : Hg (II) chloride, Permanganate, Peroxodisulphate.

INTRODUCTION

Analytical studies showed, many years ago[1], that the addition of a trace of a strong oxidant activates certain organc compounds to reduce Hg (II) chloride. Recently, it was shown that the carbohydrates undergo oxidative degradation to reduce Hg (II) chloride. Sarbhai and Saxena[2,3] employed the oxidant, peroxodisulphate, as the inducing ion. However, the permanganate ion, which is a stronger oxidant than the peroxodisulphate ion under comparable conditions, has not been used as an inductor. This induced reaction has attracted little attention, though the permanganate oxidation of glucose has been investigated and the nature of the products and the steps of the mechanism are known with certainty[4]. Here, our main purpose is to make a comparative study of the inducing power, nature of the reaction products and other parameters of the two oxidants peroxodisulphate and permanganate in the induced reduction of Hg (II) chloride by monosaccharides (glucose and fructose).

EXPERIMENTAL

Chemicals of BDH (GR) and E. Merck (GR) were used and their solutions were prepared in redistilled water. The strength of each solution was determined by established methods[5].

The products of the reaction were then subjected to fractional separation. The volatile fractions were collected by distillation over the temperature range 99°–101°C. The non–volatile fraction remained in the reactin vessel was separated and identified by chromatographic and spot tests[6]. The quantitative investigations were spectrophotometrically estimated by Bousch and Lombs Spectronic 20.

RESULTS AND DISCUSSION

For a comparative study of the roles of the two inductors ($K_2S_2O_8$ and $KMnO_4$) the kinetic data of peroxodisulphate induced Hg (II) reduction reaction incorporated in the following tables is from the earlier work[2,3]. It was deemed necessary for a correct assessment of the difference in the rates, nature of the reaction products and other parameters required for a comparative study.

Investigations in the past have revealed that the mechanism of the induced reaction of Hg (II) by various organic compounds mainly depends upon the oxidant–organic compound reaction mechanism and that the oxidation products of the organic compound reduce Hg (II) to Hg (I). In view of this, it becomes imperative to compare the oxidation of the two monosaccharides by $K_2S_2O_8$ and $KMnO_4$ so as to gain an insight into the nature of the oxidation products and the extent of oxidation. This will not be a prelude to the principal reduction reaction.

Table 1, therefore, compares the reaction products, which have been indentified and a few which have been isolated in the oxidation of the monosaccharides–glucose and fructose by the two–oxidant peroxodisulphate and permanganate, under identical conditions of temperature, concentration and analysis procedure.

Table 1. Identified reaction products

Products	$KMnO_4$		$K_2S_2O_8$	
	Glucose	Fructose	Glucose	Fructose
Volatile	Formaldehyde, Formic acid	Formaldehyde, Formic acid	Formaldehyde, Formic acid	Formaldehyde, Formic acid
Non-volatile	D-Gluconic, D-Glucuronic, Saccharic acids	D-arabinoic, Glycollic & oxalic acids, Erythrose	D-Gluconic, D-Glucuronic acids	D-arabinoic, Glycollic acids, Erythrose
Gaseous	Carbon dioxide	Carbon dioxide	Carbon dioxide	Carbon dioxide
Residual	Manganese dioxide, calomel	Manganese dioxide, calomel	Potassium hydrogen sulphate, calomel	Potassium hydrogen sulphate, calomel

As regards the comparison of the kinetic parameters of glucose/fructose oxidation reaction, it is not possible, since the permanganate oxidation of glucose and fructose in neutral medium, could not be kinetically followed due to two reasons; firstly due to manganese dioxide precipitation and secondly, because of the instantaneous decolourisation of permanganate indicating an almost instantaneous disproportionation rate of Mn (VII).

Scrutiny of the different oxidation products enlisted in Table–1 reveals the extent to which the oxidation of glucose and fructose proceeds with each oxidant. It may be inferred that the two oxidants lead to a variety of compounds indicating both cleaved as well as uncleaved compounds of glucose and fructose. The oxidative cleavage of C–C bond produces the volatile and the gaseous compounds.

Potassium peroxodisulphate, which is a less potent oxidant than permanganate under comparable conditions, oxidizes to D–gluconic and D–glucoronic acid state only whereas potassium permanganate advances the oxidation to saccharic acid stage. It signifies the fact that oxidation of glucose proceeds at both the terminal groups.

In case of fructose, a similar series of products are obtained with both the oxidants. The nature of these products is almost identical signifying the C_2–C_3 rupture[7]. While with permanganate, fructose yields oxalic acid, with peroxodisulphate; glycollic acid is the end product.

Thus, from a comparative angle, it may be suggested that while permanganate rapidly oxidizes glucose/fructose requiring a lower temperature range; peroxodisulphate requires a higher temperature range for oxidation to proceed and that too, to aldonic stage only. Saccharic acid is not produced when peroxodisulphate is the oxidant. Similarly, in case of fructose, oxalic acid is not produced with peroxodisulphate.

The product analysis data further reveal that only a small fraction of the total monosaccharide results in the C–C oxidative cleavage while the uncleaved compounds are the major end products. Surprisingly the C–C cleavage with the relatively mild oxidizing agent, ($K_2S_2O_8$), exceeds that obtained with the stronger one ($KMnO_4$). With peroxodisulphate, C–C cleavage approximates to 7–8% while with permanganate as the oxidant, it is limited to 1–2% only.

Further, it must be remembered that $OH^{\bullet}$ radical, through hydrogen abstracting, can also cleave the C–C bond[8]. This implies that an adequate stationary concentration of the $OH^{\bullet}$ radical is built up when peroxodisulphate is the oxidant. This seems more probable also seeing to the relative efficiencies of the following two reaction sequences that have been proposed as the oxidative reaction steps in the mechanism of $S_2O_8^{2-}$ and MnO_4^- oxidations, respectively.

$$SO_4^{\bar{\bullet}} + H_2O = HSO_4^- + OH^{\bullet} \qquad ...(1)$$

$$MnO_4^- + H_2O = MnO_4^{2-} + H^+ + OH^{\bullet} \qquad ...(2)$$

The quantitative data obtained for the reduction of Hg (II) chloride by monosaccharides, induced by two oxidants ($KMnO_4$ and $K_2S_2O_8$) under identical conditions of concentration and temperature are summarized in Table–2.

Table 2. Reduction of Hg (II) chloride by glucose/fructose induced by the two oxidants $KMnO_4$ and $K_2S_2O_8$.

Kinetic Parameters	Glucose		Fructose	
	$KMnO_4$	$K_2S_2O_8$	$KMnO_4$	$K_2S_2O_8$
Induction Period (mins.)	10.00	7.00	10.50	8.00
% reduction of Hg (II) chloride	36.50	40.20	46.25	50.00
10^5 IR (moles l^{-1} min^{-1})	1.58	2.29	2.31	2.49
Temp. Coefficient	1.58	2.52	1.62	1.51
Δ E (K. cals.)	10.40	28.90	10.90	9.41
Δ S (e.u.)	–48.48	+18.0	–46.88	–
Δ F (K. cals.)	26.54	–	26.51	–
Δ H (K. cals.)	9.74	–	10.24	–

Much can be learnt about the inducing power of the two oxidants on the reduction of Hg (II) chloride by monosaccharide and more quantitative conclusions can be readily drawn from Table–2. The following facts stand out from these quantitative data.

(i) Percentage reduction of Hg (II) chloride is greatest with peroxodisulphate as the inducing ion.

(ii) Associated period of induction of the reduction reaction is least with peroxodisulphate as the inductor.

(iii) Further, when peroxodisulphate is the inductor, the reduction rate is the highest. The order in which rate decreases is as follows:

$$\text{Rate with } S_2O_8^{2-} > \text{Rate with } MnO_4^-$$

From the mechanism point of view, each oxidants behaves differently; whereas permanganate ions directly attack the sugar molecule, peroxodisulphate first undergoes a fission (of the weak O–O bond) forming the sulphate free radical–ion. These energetic free radical–ions subsequently attack the monosaccharide molecule. Kinetic evidences show that the mechanism operative in each case seems to be distinctly different; while permanganate participates in a bimolecular reaction, peroxodisulphate does not. Chain initiation in the latter case is the homolytic cleavage of the peroxodisulphate ion. This in itself is an indication of a basic difference in the two types of mechanism, (A) and (B).

(A) $G + MnO_4^{-} = G^{\cdot} + MnO_3^{-} + OH^{\cdot}$ ...(3)

(B) $S_2O_8^{2-} = 2\,SO_4^{\cdot-}$ ...(4)

$G + SO_4^{\cdot-} = HSO_4^{-} + G^{\cdot}$ ...(5)

ACKNOWLEDGEMENTS

The authors wish to thank Dr. S. C. Singh, Principal, C.L. Jain (P.G.) College, Firozabad for providing the necessary facilities. The authors are also grateful to Dr. P. Pathak for the valuable suggestions.

REFERENCES

1. N. R. Dhar, J. Chem. Soc., **111**, 690 (1917).
2. K. P. Sarbhai and L. K. Saxena, J. Inorg. Nucl. Chem., **34**, 2563, (1972).
3. K. P. Sarbhai and L. K. Saxena, Agra Univ. J. Res. (Sci.), **24**, 175, (1975).
4. S. Abiya and T. J. Watanable, Pharm. Chem. (Japan), **64a**, 37 (1944).
5. A. I. Vogel, "Text Book of Quantitative Inorganic Analysis", Longmans Green and Co. Ltd., New York, (1961).
6. F. Feigl, "Spot Tests in Organic Analysis", 6th Edition, Elsevier Publishing Co., New York, (1960).
7. P. K. Mishra, K. K. Bhardwaj, B. Kumar and Vishal Pathak, Int. J. Chem. Sci., **1(2)**, 123 (2003).
8. M. C. R. Symons, "Reactivity of Hydroxyl Radicals", Peroxide Reaction Mechanism, p. 149.

Accepted : 12.1.2004