

Kinetic Study of Oxidation of Organic Compounds by Halo Chromates

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ABSTRACT: The kinetics and oxidation of different organic compounds by halochromates in DMSO leads to the formation of corresponding oxoacids. The reaction was found to be of first order. The reaction followed Michaelis-Menten type of kinetics with respect to the hydroxy acids. Polymerization of acrylonitrile showed no effect on the rate of the α -reaction. Primary kinetic isotope effect ($k_H/k_D = 6.83$ at 25°C) was observed due to the oxidation of organic compounds. The solvent isotope effect was not observed. The reaction was catalyzed by the hydrogen ions. The hydrogen ion dependence has the following form: $k_{obs} = a + b [H^+]$. Reaction was analysed by using Kamlet's and Swain's multiparametric equations. We have tried to propose a suitable mechanism for the reaction.

I. INTRODUCTION

Varied class of organic compounds in which a hydroxyl group and a carboxylic group is present can be oxidised. Some of the important members are glycolic acid obtained from sugarcane, lactic acid obtained from milk, malic acid obtained from apple, citric acid obtained from citrus fruits like lemon and orange), tartaric acid obtained from grape wine and mandelic acid obtained from bitter almonds. These AHA (alpha hydroxy acids) and their derivatives have a wide application in various fields like biological, vital, cosmetic and organic synthesis. These are very important in the organic synthesis of aldehydes via oxidative cleavage of bonds. Many research work on kinetic study of catalytic oxidation of glycolic acids by PMS (1), oxidation of glycolic acid by hexamethylenetetramine-Bromine in glacial acetic acid medium (Tinsay et al), oxidation of hydroxy butyric acid salts by Ditelluratocuprate (III) in alkaline medium (Shan et al), induced electron transfer reaction in Pentaammine cobalt(III) complexes by QDC (2), Qx.BC (2) and oxidation of some alpha hydroxy acids by TEAFC (3), TEACC (4) as well as by PDC (5), oxidation of hydroxy acids by PFC, cobalt bounded and unbounded oxidation by 4-(DMA)PDC (6) has been reported. But still less work has been done in non-aqueous solvent. So, it is important to study kinetic and mechanistic aspects of these organic compounds in non-aqueous solvents for more detailing and characterization of these compounds.(5)

Hexavalent form of Chromium has been proved to be very effective reagent capable of oxidizing many oxidizable functional group. A lot of research has been done and many mild and selective oxidising agents have been prepared so far the oxidation of many of the organic compounds (7).

II. MATERIALS AND METHODS

We have prepared Morpholinium Fluoro Chromate by the known reported methods (6) and we have checked its purity by an iodometric method. earlier (5) The preparation of different α hydroxy acid like glycolic acid(GA), malic acid(MA), lactic acid (LA), mandelic acid(MLA) and some of the substituted mandelic acid have been described earlier(4) and α Deuteriated mandelic acid (PhCD (OH)COOH or DMA) was prepared by the method reported by Kemp and Water(7). The purity of MFC was found to be $95 \pm 5\%$ by NMR spectra. PTS or p-Toluene Sulfonic Acid) was used as source of hydrogen ions due to non-aqueous condition of the solvent. Solvent purity was checked by the usual reported methods (5).

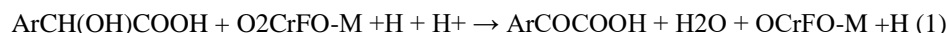
We have used UV-Vis spectrophotometer model (AIMIL India model MK2) for caring out our max at 352 nm. Thermostat experiments. λ_{max} 352 nm was selected as MFC showed (absorbance) water bath was used for maintaining constant temperature conditions and other common laboratory equipment's were also used during the investigations.

By taking a large excess (*15 times or more) of hydroxy acids over MFC pseudo first order constants were achieved. We used DMSO as non-aqueous solvent. We kept the temperature constant to 303 (± 0.1) 303K). The decrease in the MFC concentration were observed by monitoring spectrophotometrically at 352nm for up to 80% of the reaction. A graph was plotted between of log [MFC] against time and pseudo-first order rate constant k_1 was evaluated from linear least square from the graph. The second order rate constant k_2 was obtained from relation $k_2 = k_1 / [HA]$. All experiments were carried out in the absence of PTS except those where effect of H^+ concentration was studied. (6)

The product analysis was carried out under kinetic conditions i.e. with an excess of α -hydroxy acids was taken over MFC and made up to 50 ml in DMSO and kept in the dark for approximately 24hrs to ensure the completion of the reaction. The solution was then treated with an excess (200 ml) of a saturated solution of 2, 4-dinitrophenylhydrazine in 2mol/dm³HCl and kept for 24 hours in a refrigerator. The precipitate of 2, 4-dinitrophenylhydrazone (DNP) was first filtered then dried and weighed. It was recrystallized from ethanol and weighed again. The weights of the DNP before and after recrystallization were determined. The DNP was found identical (m.p. and mixed m.p.) with the DNP of α hydroxy acids. The oxidation state of chromium in the product which was an oxo acid, in a completely reduced reaction mixtures was determined by an iodometric method and was 3.92 ± 12 .

III.RESULTS AND DISCUSSION

The oxidation of different alpha hydroxy acids like glycolic acid, malic acid, lactic acid and mandelic acid were carried out by MFC in the DMSO at 30°C, under pseudo first order conditions. For all the hydroxy acids rate and other experimental data's were obtained. . Since the results were similar, only representative data are reproduced here. The results obtained are discussed in the following paragraphs. The stoichiometric studies of the oxidation of different α -hydroxy acids by MFC were carried out with the excess of oxidant i.e. MFC. The unreacted concentration of Cr (VI) was determined iodometrically after nine half-lives when reaction was near to completion. The $[H^+]$ and ionic strength was maintained at 30 ± 0.2 °C. The difference in concentration of oxidant [MFC] was measured and then stoichiometry was calculated from the ratio between reacted [oxidant] and [substrate]. The amount of reduced chromium (VI) was also calculated from the decrease in the absorbance spectrophotometrically. Product analysis and stoichiometric results determination indicates overall reaction could be written as below



It is clear from the above equation that MFC undergoes a two electron change. This is in compliance with the earlier observations with PCC (Corey and Boger 1978) and other halochromates(7)

p-Toluene Sulfonic acid (TsOH) was used as a source of hydrogen ions due to non-aqueous conditions. The H^+ dependence has the following form as shown in the equation (2). $k_{obs} = a + b [H^+]$ (2) The values of a and b, for p-methyl mandelic acid, are $7.12 \pm 0.18 \times 10^{-4} s^{-1}$ and $12.7 \pm 0.54 \times 10^{-4} lit^3 / mol/s$ respectively ($r^2 = 0.9987$). Table 2 represents the effect of H^+ concentration of P-Mandelic acid by MFC.

Due to the absence of the effect of added acrylonitrile on the reaction rate, the possibility of a one – electron oxidation, leading to the formation of free radicals was ruled out. The presence of a considerable kinetic isotope effect in the oxidation of mandelic acid confirms the cleavage of the α -CH bond in the rate-determining step. The large negative value of reaction constant (-1.86 at 30°C) points to a highly electron deficient carbon centre in the transition state. The transition state thus has a highly electron deficient carbon centre, supported by the solvent effect. Cation-solvating power of the solvents plays a great role in the formation of a carbocationic transition state. Therefore, the correlation analysis of the effect of substituent and solvents on the oxidation of mandelic acid supports the mechanism involving a hydride-ion transfer through a cyclic chromate ester. (8)

IV.CONCLUSION

We have shown that a study of dependence of the kinetic isotopic effect on the temperature can be applied to resolve this problem. The data for protio- and deuterio-mandelic acids, fitted to the familiar expression $k_H/k_D = A_H/A_D \exp(E_a/RT)$ shows a direct correspondence with the properties of a symmetrical transition state in which the activation energy difference (E_a) for k_H/k_D is equal to the zero-point energy difference for respective C-H and C-D bonds (≈ 6.83 kJ/mol) and frequency factors and entropies of activation of the respective reactions are nearly equal. It is documented evidence against

the occurrence of concerted one-step biomolecular processes by hydrogen transfer takes place in a cyclic manner. Involving six electrons and, formation of chromate ester in a fast pre-equilibrium and then a decomposition of the ester in a subsequent slow step via a cyclic concerted symmetrical transition state leading to the product (9).

The observed negative entropy of activation also supports a polar transition state. Just like the oxidation of α hydroxy acid by PFC and QCC, MFC also exhibits similar Michaelis Menten kinetics with respect to hydroxy acids. The rate laws, H⁺ dependence and kinetic isotope effect are similar to both the above cases. The reaction is proposed to proceed through a hydride – ion transfer via chromate ester in the rate determining step (9). Hydride ion transfer is also supported by cation – solvating power of the solvents. Both protonated and deprotonated forms of MFC are reactive oxidizing species.

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