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# Kinetics and Mechanism of Oxidation of Aromatic Acetals by Acidic Pyridinium Chlorochromate

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The kinetics of oxidation of aromatic acetals by pyridinium chlorochromate (PCC) have been studied. The reaction is first order each in [PCC] and [Acetal]. With an increase in the amount of acetic acid in its aqueous mixture, the rate increases. The reaction does not induce polymerisation of acrylonitrile. The presence of electron-withdrawing substituents in the benzene ring enhances the rate of oxidation. The rate of oxidation depends on the nature of alkyl group. The reaction rates have been studied at different temperatures and the activation parameters calculated.

## INTRODUCTION

Acetals are synthetically useful *gem*-dialkoxy compounds. The oxidation of aliphatic and aromatic acetals with several oxidants[1] yielded corresponding esters as products. Among halochromates of nitrogen containing heterocyclic cationic compounds, pyridinium chlorochromate (PCC) is a versatile oxidizing agent. A number of reports on the oxidation of several substrates by PCC are available in literature.[2] However, the kinetics of oxidation of acetal by PCC has not been investigated. Kinetics of several aromatic acetals with different substituents in the benzene ring and alcohol moieties have been studied in order to throw more light on mechanistic aspects.

## RESULTS AND DISCUSSION

The reaction was found to be first order with respect to PCC. The plot of log absorbance *vs.* time is linear (r = 0.99) indicating first order dependence on [PCC]. Further, the first order rate constants did not vary with initial concentration of PCC. The rate increases steadily with increase in [Acetal]. The plot of log $k_{obs}$ *vs.* log [Acetal] (Fig. 1A) is linear (r = 0.99) with a unit slope. These observations lead to the conclusion that the order with respect to acetal is unity. The second order rate constants ($k_2$) are found to be constant. Hence the reaction between acetals and PCC is governed by the simple rate expression:

$$\frac{-d[PCC]}{dt} = k_{obs}[Acetal][PCC]$$

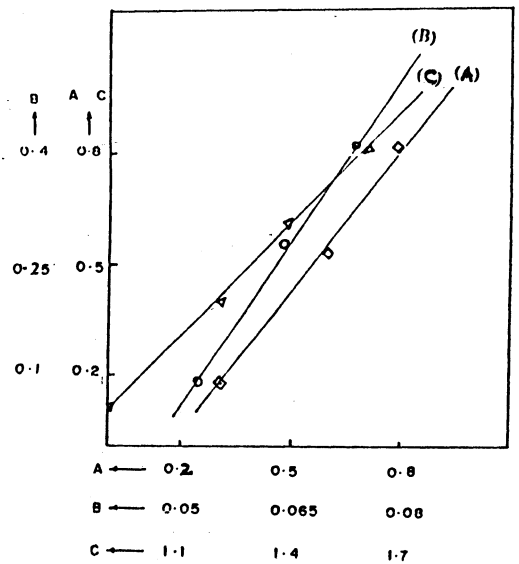
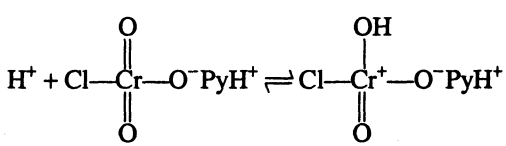



Fig. 1 Plot of 2 + log [acetal] *vs.* 4 + log $k_{obs}$ (A)
1/D *vs.* 4 + log $k_{obs}$ (B)
4 + log $[H^+]$ *vs.* 4 + log $k_{obs}$ (C)

The rate of acid catalyzed oxidation of acetal decreases with an increase in the dielectric constant of the medium. The plot of log $k_{obs}$ *vs.* inverse of dielectric constant is linear (Fig. 1B) with a positive slope ($r = 0.99$) suggesting an interaction between a positive ion and a dipole.[3] This leads to the conclusion that protonated PCC is involved in the rate determining step:[2]



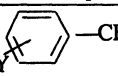

The acid catalyzed nature of this reaction is confirmed by the increase in the rate of oxidation (Fig. 1C) by the addition of *p*-toluenesulphonic acid (PTSA).

Effect of substituents on the rate of oxidation has been studied. There are two types of substituents. The acetals were prepared from the number of *para*- and *meta*-substituted benzaldehydes with different primary alcohols. The rate of oxidation depends on the substituents in the benzene ring and also alcohol moieties. The rate of oxidation is moderately accelerated by electron withdrawing substituents and retarded by electron-releasing ones (Table-1). Although the plot of log $k_{obs}/k_H$ *vs.* $\sigma$ gives a satisfactory correlation ($r = 0.97$), a better correlation is obtained with $\sigma^+$ ($r = 0.99$) with a low positive $\rho$ value (0.42). A small $\rho$ often means that the mechanism of this reaction involves a radical intermediate or some

other mechanism with little charge separation. The oxidation of acetal by PCC in an atmosphere of nitrogen failed to induce polymerisation of acrylonitrile, Thus the involvement of one electron oxidation leading to the formation of radical intermediate is unlikely in this oxidation. The negative salt effect indicates the presence of transition state[4], which may be less polar than the reactants.

TABLE-1
RATE CONSTANTS AND ACTIVATION PARAMETERS FOR PCC OXIDATION OF AROMATIC ACETALS

Solvents: AcOH—$H_2O$ (4 : 1), [PCC] = $1.00 \times 10^{-3}$ mol $dm^{-3}$
[ACETAL] = $1.00 \times 10^{-2}$ mol $dm^{-3}$

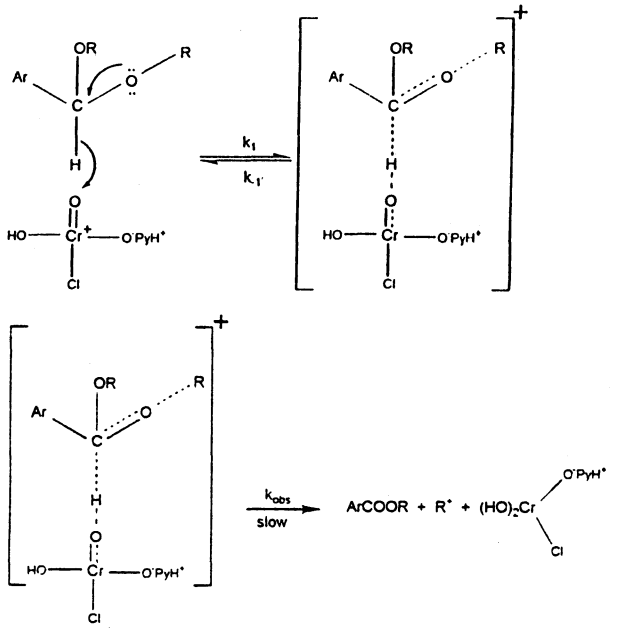
|  —CH(OR)$_2$ | $K_{obs} \times 10^4$ $s^{-1}$ | | | $\Delta H^{\#}$ | $\Delta S^{\#}$ | $\Delta G^{\#}$ |
|---|---|---|---|---|---|---|
| R = n-butyl; Y = | 313 K | 323 K | 333 K | kJ $mol^{-1}$ | kJ $mol^{-1}$ | kJ $mol^{-1}$ |
| *p*-$NO_2$ | 2.3 | 3.5 | 4.6 | 27.6 | –180.9 | 84.2 |
| *m*-$NO_2$ | 2.1 | 3.2 | 4.2 | 27.6 | –182.3 | 84.2 |
| *m*-Cl | 1.7 | 2.6 | 3.4 | 27.6 | –183.9 | 85.2 |
| *p*–Cl | 1.4 | 2.2 | 2.9 | 27.7 | –185.4 | 85.7 |
| *p*-Me | 0.8 | 1.2 | 1.7 | 30.2 | –182.0 | 87.2 |
| *p*-OMe | 0.5 | 0.8 | 1.1 | 31.8 | –181.0 | 88.4 |
| Y = H, R = n-propyl | 0.7 | 1.0 | 1.4 | 27.6 | –201.7 | 90.7 |
| iso-butyl | 1.0 | 1.5 | 2.0 | 27.7 | –188.3 | 86.6 |
| n-butyl | 1.2 | 1.8 | 2.4 | 27.7 | –186.8 | 86.1 |
| iso-amyl | 1.5 | 2.3 | 3.0 | 27.6 | –185.0 | 85.6 |
| benzyl | 5.5 | 8.2 | 11.1 | 27.6 | –174.0 | 82.2 |

The rate of oxidation is more influenced by alcohol moieties present in the acetals. The Taft[5] polar plot of log $k_{obs}$ $\sigma^*$ is linear (0.98) with negative slope. The order of reactivity with respect to alcohol moiety is in the order of the stability of carbocation that may be formed during oxidation. This is also confirmed by the Taft polar plot. The plot of log $k_2$ (333 K) *vs.* log $k_2$ (313 K) is linear (r = 0.99) for all acetals showing that they undergo oxidation with similar mechanism.

The activation parameters have been computed from the plot of log $k_2$ *vs.* 1/T in the temperature range 313–333 K (r = 0.99). The existence of linear free energy relationship is confirmed by the plot of $\sigma^+$ *vs.* $\Delta G$ (r = 0.99) which also confirms that a single mechanism is operating throughout the series.[6]

Based on experimental finding acyclic bimolecular transition state may be proposed (Scheme-1). In this transition state hydride ion transfer, oxygen-alkyl cleavage and the formation of carbon-oxygen multiple bonds may be taking place simultaneously. The hydride ion transfer may take place due to the electron deficient nature of chromium ion in PCC. The chrominum ion in PCC is electron deficient because of the presence of chlorine and protonation. The cleavage of O—R bond is the driving force for the formation of C=O. The formation of

C=O may be made easier by the electron withdrawing groups in the benzene ring and delayed by electron donating groups. The proposed bimolecular transition state mechanism involves greater entropy loss as found experimentally. Contrary to acetal hydrolysis[7] during oxidation acetal oxygen-alkyl cleavage is preferred even when R is chosen deliberately so as to make $R^+$ a poor cation.




$$R^+ \xrightarrow{\text{Fast}} \text{Alkene} + H^+ \qquad R = n\text{-propyl, iso-butyl, } n\text{-butyl and iso-amyl}$$

$$R^+ + H_2O \xrightarrow{\text{Fast}} ROH + H^+ \qquad R = \text{benzyl}$$

Scheme-1

## EXPERIMENTAL

PCC was prepared by reported method.[2] Acetals were prepared by the reported procedure and characterized by IR and NMR spectra. Acetic acid was purified and distilled. The product analysis was carried out under kinetic conditions. The oxidation products of the corresponding esters were separated and characterized by IR and NMR spectra.

Kinetic measurements were studied under pseudo-first order conditions keeping a large excess of acetal over PCC. Temperature was kept constant with ±0.1 K. The required percentage of acetic acid was prepared using conductivity water. The reactions were followed calorimetrically (Erma AE11S). The pseudo first order rate constant ($k_{obs}$) were evaluated from least square method ($r = 0.99$). Duplicate kinetic reactions showed that the rate constants were reproducible within ±3%. The stoichiometric equation for the oxidation may be written as:

$$3ArCH(OR)_2 + 2PCC \longrightarrow 3ArCOOR + 3\ alkene + 3\ Cr(III)$$

R = n-propyl, n-butyl, iso-amyl, iso-butyl

$$3ArCH(OCH_2—C_6H_5)_2 + 2PCC + 3H_2O \longrightarrow 3ArCOOCH_2—C_6H_5 + 3C_6H_5CH_2OH + 2Cr(III)$$

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