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Oxidation of some para- substituted Benzyl alcohols by Pyridinium Dichromate -Kinetics and Mechanism

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ABSTRACT

The kinetics of oxidation of some para-substituted benzyl alcohols by PDC have been studied in DMSO spectrophotometrically acidified with TsOH. From good linear Eyring plots $\Delta H^{\#}$ and $\Delta S^{\#}$ are calculated. The reaction has unit dependence on each [PDC], $[H^+]$ and [Alcohol]. Electron-releasing substituent accelerates the reaction, whereas electron-withdrawing groups retard the reaction, and the rate data obey Hammett's relationship. PDC is acting as two-electron transfer oxidant. A mechanism implicating the prior acid-catalyzed formation of dichromate ester followed by cyclic intermediate is proposed.

Introduction

The kinetics and mechanism of oxidation reactions of Chromium (V1) have been fairly well studied. Chromic acid is one of the most versatile of the available oxidizing agents reacting with diverse kinds of organic substrates. The mechanism of oxidation varies with the nature of the Chromium (V1) species and the solvent used. The development of Cr (V1) reagents [1] for the oxidation of organic substrates continues to be a subject of interest. We have been interested in the kinetic and mechanistic studies of the reactions of Chromium (V1) species [2]. The reagent employed in this investigation, Pyridinium dichromate (PDC) has emerged as a very useful and versatile oxidant [3] which is clearly deserving of widespread application. Substituent effects on the kinetics of organic reactions in solution are useful tools to probe reaction mechanisms. These tools have been applied to study the oxidation of different organic molecules in aqueous [4] and non-aqueous [5] solvents. Kinetics of oxidation of benzyl alcohol by various oxidising reagents has been studied [4b,6-9] but not using Pyridinium dichromate (PDC) as oxidising agent in non-aqueous solvent. We report herein the kinetics of oxidation of some para- mono substituted benzyl alcohols by PDC in DMSO as a solvent.

Experimental

Materials and reagents

PDC was prepared by the method described in the literature [1d]. Benzyl alcohol, substituted benzyl alcohols, p-toluene sulphonic acid and dimethyl sulphoxide (E. Merck) were used. The procedure used for the purification of alcohols has been described earlier [10]. Due to non aqueous nature of the solvent, Toluene p-sulphonic acid is used as a source of hydrogen ions. Solvent (DMSO) was purified by the usual method [11].

Kinetic measurements

The pseudo first order conditions were attained by maintaining a large excess (x 10 or more) of the alcohol over PDC. The solvent was DMSO, unless specified otherwise. The reaction mixture was prepared by mixing the requisite amount of substrate, p- toluene sulphonic acid solution and DMSO and allowed to stand in a thermostatic bath for a sufficient length of time. Adding solution of the oxidant started the reaction. The reactions were followed, at constant temperature (±0.1K), by monitoring the decrease in [PDC] spectrophotometrically at 350 nm using a digital UV/Visible spectrophotometer model 167. No other reactant or product has any significant absorption at this wavelength.

Product analysis

The product analysis was carried out under kinetic conditions. In a typical experiment, benzyl alcohol (0.05 mol) and PDC (0.005 mol) were made up to 50 cm^3 in DMSO and kept for 20 h to ensure completion of the reaction. The solution was then treated with excess (200 cm^3) of saturated solution of 2, 4-DNP in 2M HCl and was kept overnight in a refrigerator. The precipitated 2,4 dinitrophenyl hydrazone was filtered off, dried, weighed and recrystallized from ethanol and melting point was then determined. The DNP was found identical (m.pt. and mixed m.pt.) with the DNP of benzaldehyde. Similar experiments were performed with other substituted benzyl alcohols also.

Results and Discussion

Oxidation of benzyl alcohol and some para- mono substituted benzyl alcohols by PDC has been conducted in non-aqueous medium (DMSO) at 303 K, under the pseudo-first order conditions. The rates and other experimental data were obtained for all the alcohols. Since the results are similar, only representative data are reproduced here in the subsequent pages.

Stoichiometry

Oxidation of benzyl alcohols by PDC results in the formation of corresponding benzaldehydes. Analysis of products and the stoichiometric determinations indicate the following overall reaction:

$$3ArCH_2OH + 2Cr\ (VI) \longrightarrow 3ArCHO + 2Cr\ (III) + 2H^+ + H_2O$$

Effect of oxidant concentration

The reactions were found to be first order with respect to PDC. The individual kinetic runs were strictly first order to PDC.

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Further, the pseudo-first order rate constant, k_{obs}, was independent of initial concentration of PDC. The reaction rate increases linearly with an increase in the concentration of benzyl alcohols **(Table 1)**. The rate can be expressed as:

$$-d\,[PDC] / dt = k\,[PDC]$$

Table 1. Rate constant for the oxidation of p-methoxy benzyl alcohol by PDC at 303 K

[PDC] 10^3 mole dm^{-3}	**[Alcohol] 10^2 mole dm^{-3}**	**[TsOH] 10^2 mole dm^{-3}**	**k_{obs} x 10^5 s^{-1}**
0.4	2.0	3.0	111.19
1.2	2.0	3.0	113.60
2.0	2.0	3.0	111.50
2.4	2.0	3.0	114.30
3.0	2.0	3.0	112.81
2.0	1.6	3.0	84.26
2.0	2.0	3.0	111.50
2.0	4.0	3.0	220.68
2.0	6.0	3.0	329.08
2.0	8.0	3.0	436.42
2.0	2.0	1.0	40.93
2.0	2.0	2.0	79.80
2.0	2.0	3.0	114.08
2.0	2.0	4.0	161.06
2.0	2.0	5.0	199.99

Effect of substrate

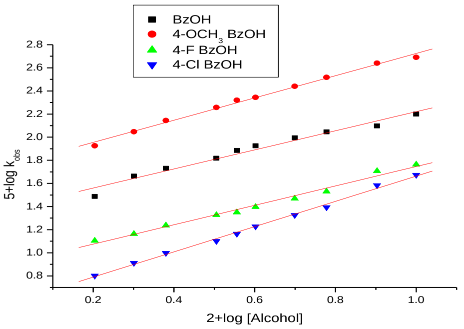
The rate of oxidation increases on increasing the concentration of substrate (substituted benzyl alcohols), the results from exploratory experiments, which are summarised in **Table 2**; indicate the reaction to be first order with respect to the substrate. Plot of log k_{obs} versus log [substrate] is a straight line in all the cases with slope 0.83, 0.96, 1.10 and 0.84 for benzyl alcohol, p-methoxy benzyl alcohol, p-chloro benzyl alcohol and p-fluoro benzyl alcohol respectively. Plot of $1/k_{obs}$ *versus* 1/[Substrate] gave linear line passing through origin or very small intercepts nearly zero suggest that the rate does not obey Michaelis-Menten type kinetics.

Table 2. Variation of rate with substrate concentration

[Substrate] × 10^2 M	**$k_1 \times 10^5$ (sec^{-1})**			
	BzOH	**p-methoxy BzOH**	**p-chloro BzOH**	**p-fluoro BzOH**
1.6	30.70	84.26	6.34	12.72
2.0	46.00	111.50	8.17	14.56
4.0	84.40	220.68	16.90	24.86
5.0	98.70	275.20	21.20	29.42
6.0	111.30	329.08	24.77	33.86
8.0	125.21	436.42	38.37	50.90
10.0	158.01	490.70	47.22	58.06

[PDC] = 2×10^{-3} M; [TsOH] = 3×10^{-2} M; Temperature = 303 K; Solvent = DMSO 100%

Figure 1. Variation of rate with substrate concentration



Effect of p-toluene sulphonic acid concentration

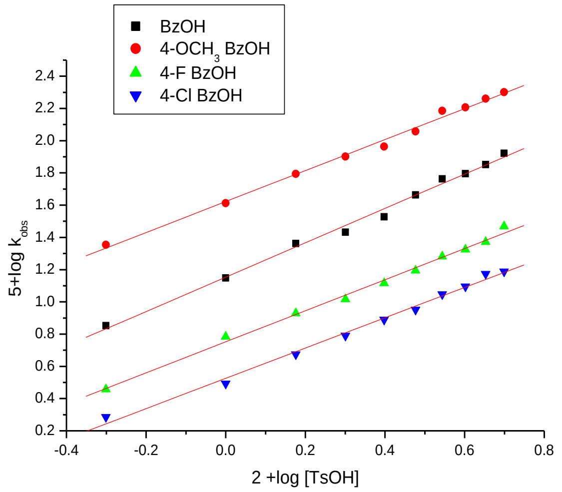
The effect of hydrogen ion concentration on the rate of the oxidation was studied by varying [H^+] while keeping the concentration of other reactants constant. A steady increase in oxidation rate with increase in the acidity of the medium suggests the formation of protonated PDC. The plot of log k_{obs} against log [H^+] is linear with slopes 1.06, 0.96, 0.94 and 0.96 respectively for benzyl alcohol, p-methoxy benzyl alcohol, p-chloro benzyl alcohol and p-fluoro benzyl alcohol **(Table 3).**

Table 3. Variation of rate with p-toluene sulphonic acid concentration

[TsOH] × 10^2 M	**$k_1 \times 10^5$ (sec^{-1})**			
	BzOH	**p-methoxy BzOH**	**p-fluoro BzOH**	**p-chloro BzOH**
1.0	14.06	40.93	6.08	3.11
1.5	23.01	62.23	8.49	4.72
2.0	27.04	79.80	10.38	6.17
2.5	33.65	91.83	13.06	7.76
3.0	46.06	114.08	15.62	8.94
3.5	57.94	153.11	19.14	11.15
4.0	62.37	161.06	21.13	12.46
4.5	71.12	182.39	23.51	14.93
5.0	83.37	199.99	29.42	15.45

[PDC] = 2×10^{-3} M; [Alcohol] = 2×10^{-2} M; Temperature = 303 K; Solvent = DMSO 100%

Figure 2. Variation of rate with TsOH concentration



Effect of solvent

At fixed [H^+], the rate of oxidation of benzyl alcohol and substituted benzyl alcohols with PDC increases with decrease in polarity of solvent. In other words an increase in rate with decrease in dielectric constant of solvent (DMSO and Acetone) is observed. This is due to polar character of the transition state as compared to the reactants. According to Scatchard [12] the logarithm of the rate constant of a reaction between ions should vary linearly with the reciprocal of the dielectric constant, if reaction involves ion-dipole type of interaction **(Table 4).**

Effect of temperature

The rate of oxidation of benzyl alcohol and substituted benzyl alcohols was determined at different temperature **(Table 5)** and the reactions obey Arrhenius equation. Energy of activation was calculated by slopes of straight line obtained plotting log k_{obs} versus 1/T. The activation parameters for benzyl alcohol, p-methoxy benzyl alcohol, p-chloro benzyl alcohol and p-fluoro benzyl alcohol were calculated **(Table 5).** The value of isokinetic temperature is 441.25 K. However, according to Exner [13] an isokinetic relationship between the calculated values of activation enthalpies and entropies is often vitiated by random experimental error.

Table 4-Variation of rate with solvent composition concentration

Acetone % v/v	D-1 /2D+1	Mole Fraction of DMSO	(1/D) x 10^3	BzOH	p-methoxy BzOH	p-chloro BzOH	p-fluoro BzOH
	$k_1 \times 10^5$ (sec^{-1})						
00	24.60	1.00	21.2	43.26	112.80	8.63	16.74
10	23.31	0.90	22.4	49.32	132.11	9.48	18.38
20	22.03	0.81	23.8	58.27	164.20	10.19	20.52
30	20.72	0.71	25.4	62.40	200.10	11.62	22.63
40	19.41	0.61	27.2	83.02	251.80	12.68	26.42
50	18.08	0.51	29.3	102.00	326.80	15.78	32.18

[Alcohol] = 2 x 10^{-2}; [TsOH] = 3x10^{-2}; [PDC] = 2×10^{-3} M; T= 303 K

Exner plot between log k_{obs} at 303 K and log k_{obs} at 313 K was linear (R^2=0.985) **(Figure 5).** The value of isokinetic temperature evaluated from Exner's plot is 441.25 K. The linear isokinetic correlation implies that all the alcohols are oxidized by the same mechanism and the changes in the rate are governed by changes in both the enthalpy and entropy of activation.

Table 5- Variation of rate with Temperature and Activation Parameters

Temp. (K)	$k_1 \times 10^5$ (sec^{-1})			
	BzOH	p-methoxy BzOH	p-fluoro BzOH	p-chloro BzOH
303	46.06	113.84	15.93	8.26
308	64.48	128.89	26.42	13.44
313	84.80	167.42	39.62	17.48
318	122.06	224.10	51.28	26.98
323	158.50	300.20	68.74	36.42
$\Delta Ea^{\#}$ (KJ mol^{-1})	50.60	40.40	58.43	59.98
$\Delta S^{\#}$ (J mol^{-1} K^{-1})	-83.68	-110.03	-67.41	-67.00
$\Delta G^{\#}$ (KJ mol^{-1})	75.96	73.74	78.85	80.28
$\Delta H^{\#}$ (KJ mol^{-1})	48.08	37.88	55.91	57.46

[Substrate] = 2×10^{-2} M; [PDC] = 2×10^{-3} M; [TsOH] = 3x10^{-2}

Figure 3. Variation of rate with solvent composition

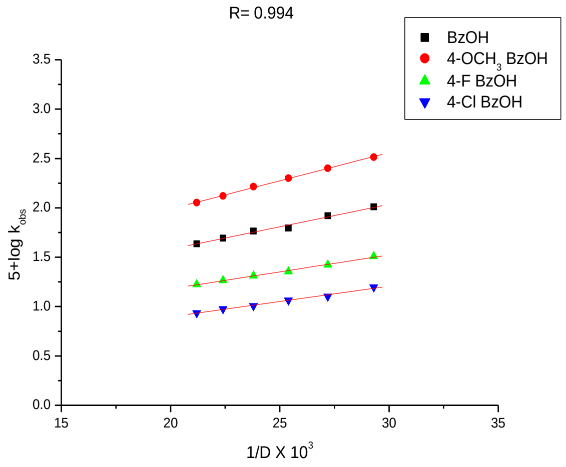


Figure 4. Variation of rate with temperature

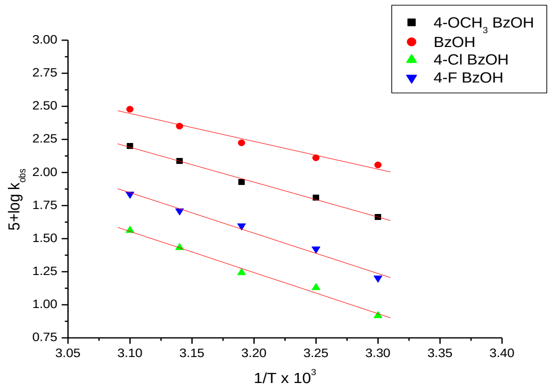
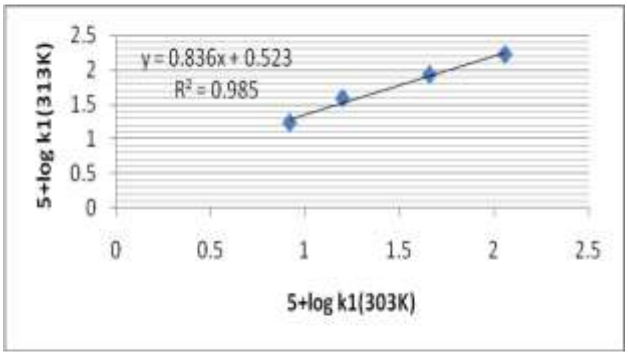


Figure 5. Exner's plot for aromatic alcohols



Discussion

Kinetics of the oxidation of benzyl alcohol and some para-substituted benzyl alcohols by PDC was investigated at several initial concentrations of the reactants. At low concentrations of PDC and when substrates are in large excess, the reaction is found to be first order in PDC. A plot of log k_{obs} *v/s* log [Substrate] gave a straight-line with slope ≈ 1 showed first order dependence over substrate.

A study increase in the rate of oxidation with an increase in the acidity of the medium suggests the formation of protonated PDC. The plot of log k_{obs} against log [H^+] is linear with a slope of nearly one. Since protonation of benzyl alcohol and mono-substituted benzyl alcohols is less probable it is more likely that the proton is used by the oxidant. Many workers have suggested protonated PDC [14]. The protonated PDC and alcohol combine to give intermediate, which was also indicated by increase in rate with decrease in dielectric constant of reaction medium. In this oxidation Zucker-Hammett [15] plot (log k_1 v/s H_0) and Bunnett-Olsen [16] plot (log k_1+H_0 v/s log [H^+] + H_0) doesn't fit. This suggests that the solvent is not acting as proton abstractor.

The Hammett [17] plot of k_1 *versus* σ is linear **(Figure 6)** with a reaction constant (ρ) = - 1.34 [$\rho < 0$, the reaction builds positive charge (or loses negative charge)] in the case of aromatic alcohols supporting the result that the electron releasing groups accelerate the reaction and the electron withdrawing group retard the reaction. Hammett plot is not perfectly linear. For instance, a curve may show a sudden change in slope, or ρ value. In such a case, it is likely that the mechanism of the reaction changes upon adding a different substituent. Other deviations from linearity may be due to a change in the position of the transition state. In such a situation, certain substituents may cause the transition state to appear earlier (or later) in the reaction mechanism [18].

Oxidation rates are increased by para electron donor substituents because these polar groups increase the electric potential near Chromium atoms, thus facilitating their reduction in oxidation state. Since the converse mode of action applies to electron-acceptor substituents, this mechanism proposal is consistent with the experimentally observed negative Hammett reaction constants.

The presence of electron withdrawing groups in the benzyl alcohol ring retards the rate of reaction. These electrons withdrawing group destabilizes the carbocation by making the ring more positive. This result in raising the energy of the carbocation, its transition state, the activation energy and the reaction rate is slowed down. Due to the more charge the stability of the carbocation decreases in turn again raising the energy of the carbocation, its transition state and the activation energy and the reaction rate is thus slowed down. Thus the benzyl alcohol ring contains groups which are more electron withdrawing have slower rate, than the benzyl alcohol ring contains groups which are electron donating.

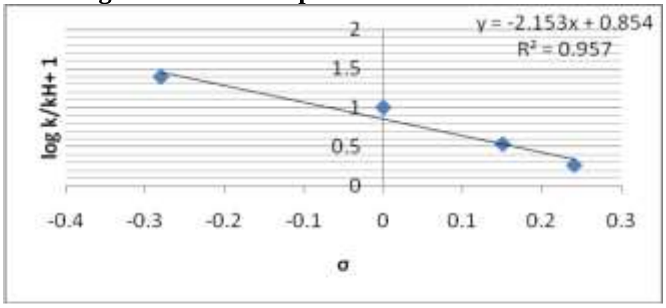
p- Chloro and p- Fluoro substituted benzyl alcohol shows only inductive effect and there is no resonance effect. Chloro and Fluoro substituted benzyl alcohol react slower than benzyl alcohol, so the order compare to benzyl alcohol is,

BzOH > p- F BzOH > p- Cl BzOH

p- Methoxy substituted benzyl alcohol is electrons donating group. p- methoxy group show a +R effect but a -I effect. In this cases where resonance effect is possible, methoxy group is activating in p- position in benzyl alcohol. So it reacts faster than other substituted groups compare to fluoro and chloro substitution. According to Hammett values the order for electron withdrawing nature is

p- OCH_3 BzOH > BzOH > p- F BzOH > p- Cl BzOH

Figure 6. Hammett plot for aromatic alcohols



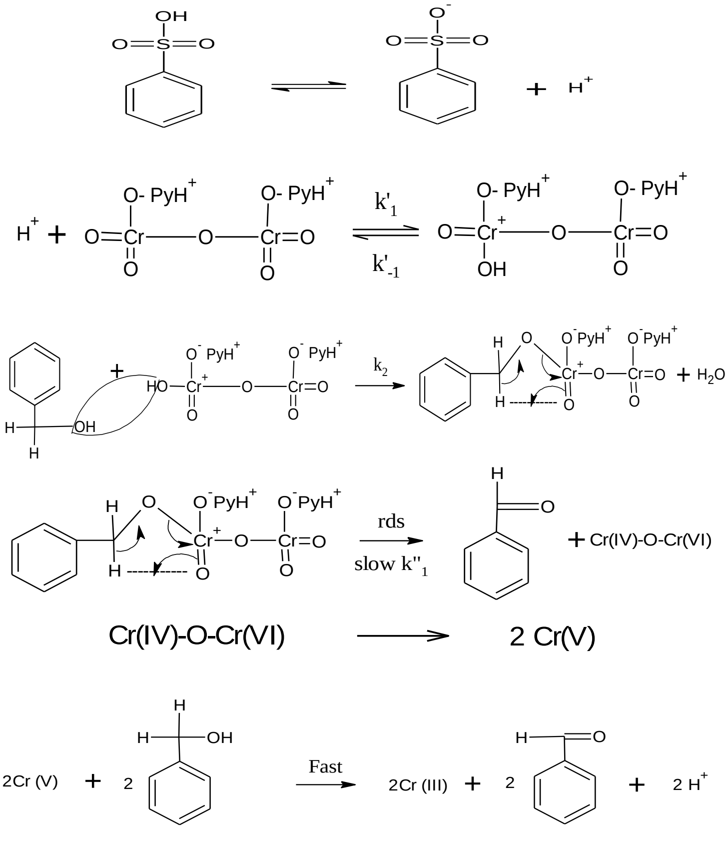
The thermodynamic parameters are mentioned in **Table 5**. The negative value of entropy comes under a category of slow reaction according to the Glasstone [19]. In these oxidation processes, negative values of entropy also suggested that activated state showed more polarity than reactant.

In line with previous research on the ester mechanism for similar oxidation reactions [9a,14b,20] the formation of five-member cyclic ground and transition states stabilised by intramolecular hydrogen bonds linking an oxygen atom from the inorganic moiety to an α-hydrogen in the organic counterpart was suggested.

Mechanism

A hydrogen abstraction mechanism leading to the formation of free radical is unlikely in view of the failure to induce polymerization of acrylonitrile and no effect of the radical scavenger on the reaction rate. This also confirms that the Cr (VI) of PDC act as two-electron transfer agent. The prior acid-catalysed formation of dichromate ester followed by cyclic intermediate is suggested. This mechanism is also supported by the major role of cation-solvating power of the solvent. Bordwell [21] has documented very cogent evidence against the occurrence of concerted one-step bimolecular process by hydrogen transfer and it is evident that in the present study also the hydrogen transfer does not occur by an acyclic bimolecular process.

para- toluene sulfonic acid acts as a proton donating agent. Solvent DMSO acts as weak nucleophile it helps to dissociate H^+ ion from TsOH [22]. The order with respect to TsOH is unity. So it releases only one proton which reacts with PDC. The proton which is released by the TsOH reacts with PDC to form protonated PDC which behaved as a dipole. The benzyl alcohol or its substituted molecule reacts with the protonated PDC to form an intermediate cyclic dichromate ester [C] (transition state) which is indicated by negative entropy of activation ($\Delta S^{\#}$). The formation of intermediate dichromate molecule is stabilised by intramolecular hydrogen bond. The cyclic dichromate ester intermediate undergoes intramolecular proton transfer to form the corresponding aldehyde. A C-H bond break in this step is the rate determining step which is also supported by the value of Energy of activation ($\Delta Ea^{\#}$) ranges approximately between 50-60 KCal/mole. The values for the free energy of activation ($\Delta G^{\#}$) were nearly constant, indicating that the same mechanism operates for all the alcohols. This gives Cr(IV)-O-Cr(VI) i.e. two electron transfer. This rearranges to give Cr (V) which further oxidize alcohol by two electron transfer and give end product as Cr (III) and aldehyde in a fast step.



Rate Law

Rate = -d [PDC] / dt = k_1" [C]

d [H^+PDC] / dt = k'$_1$ [PDC] [H^+] – k'$_{-1}$ [H^+PDC] = 0

k'$_1$ [PDC] [H+] = k'$_{-1}$ [H^+PDC]

R = k_1" k_2 [ArOH] [H^+PDC]

$R = k_1'' k_2 [ArOH] . (k'_1 / k'_{-1}) [H^+] [PDC]$

$R = k_{obs} [PDC] = k_1'' [PDC]$

Where, $k_{obs} = k_1'' k_2 [ArOH] . k'_1 / k'_{-1} [H^+] = k_1''$

$k_1'' = k_s [ArOH] [H^+]$

where, $k_s = k_1''. k_2. k'_1 / k'_{-1}$ i.e. Specific rate constant.

$k_s = k_1'' / [ArOH] [H^+]$

This rate law and suggested probable mechanism is consistent with all the observed experimental results suggesting that the reaction proceeds via the formation of a dichromate ester.

Concluding Remarks

In summary, from the analysis of chemical data for oxidation rates of benzyl alcohol (BzOH) and its para-substituted compounds using pyridinium dichromate in DMSO solution in presence of p-toluene sulphonic acid (TsOH), we have gathered evidence that strongly supports the following detailed mechanism proposal.

i. The main oxidising species are protonated PDC, the kinetics being first order with respect to PDC, BzOH and TsOH.
ii. TsOH is a catalyst in the formation of intermediate protonated PDC.
iii. Both deprotonated and protonated forms of PDC are the reactive oxidising species.
iv. The formation of intermediate dichromate ester molecule is stabilised by intramolecular hydrogen bonds.
v. The oxidative, rate-determining step is initiated by the change in oxidation state from VI to IV taking place in chromium atoms.
vi. Oxidation rates are increased by para electron-donor substituents because these polar groups increase the electric potential near chromium atoms, thus facilitating their reduction in oxidation state. Since the converse mode of action applies to electron-acceptor substituents, this mechanism proposal is consistent with the experimentally observed negative Hammett reaction constants.
vii. Absence of polymerization in presence of acrylonitrile confirms two-electron transfer process.

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