Asian Journal of Chemistry Vol. 20, No. 5 (2008), 3866-3874

Kinetics and Mechanism of the Oxidation of Substituted Benzyl Alcohols by Pyrazinium Dichromate

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Pyrazinium dichromate oxidizes benzyl alcohol and substituted benzyl alcohols to the corresponding aldehydes in dimethyl sulfoxide and in the presence of acid. The rate of the reaction is dependent on the concentrations of the substrate, pyrazinium dichromate and acid. The oxidation of α,α-dideuteriobenzyl alcohol exhibits a substantial primary kinetic isotope effect ($k_H/k_D = 6.61$ at 303 K). Polymerization of acrylonitrile is not induced in this reaction. From the kinetic data, the activation parameters have been calculated. The analysis of the dependence of the kinetic isotope effect on temperature indicated that the reaction involves a symmetrical cyclic chromate ester in the rate-determining step. A suitable mechanism has been proposed.

Key Words: Kinetics, Mechanism, Oxidation, Substituted Benzyl alcohols, Pyrazinium dichromate.

INTRODUCTION

The chromium-based reagents are widely used and powerful oxidation reagents for the oxidation of alcohols to the corresponding carbonyl compounds[1,2]. A number of new Cr(VI) reagents together with special reaction conditions have been developed. Anhydrous conditions are more conducive to complexation of substrates with Cr(VI) species and therefore to mild oxidation. The most significant Cr(VI) oxidants are quinolinium fluorochromate (QFC)[3], pyridinium chlorochromate (PCC)[4], pyridinium dichromate (PDC)[5], pyridinium fluorochromate (PFC)[6], quinolinium chlorochromate (QCC)[7] and pyrazinium dichromate (PzDC)[8]. The author is interested in the synthesis and kinetics of reactions of complexed Cr(VI) species[9] and reported the kinetics and mechanism of oxidation of benzyl alcohol by potassium chlorochromate (KCC)[10], quinolinium chlorochromate (QCC)[11] and quinoxalinium dichromate (QxDC)[12]. There seems to be no report on the kinetics of oxidation of primary benzylic alcohols by pyrazinium dichromate (PzDC). In this paper, the kinetics and mechanism of this oxidation of 11 primary

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benzylic alcohols by pyrazinium dichromate (PzDC) in DMSO as solvent are reported. The mechanistic aspects are also discussed.

EXPERIMENTAL

The oxidant, pyrazinium dichromate (PzDC) was prepared by the reported method and its purity was checked by spectral analysis[8]. All the alcohols were commercial products (Fluka or Aldrich) and purified by either recrystallization or distillation. *p*-Toluenesulphonic acid (TsOH) was used as a source of hydrogen ions. DMSO and dichloromethane (CH_2Cl_2) were purified by the usual methods[13]. α,α-Dideuteriobenzyl alcohol was purchased from Isotec Inc. (USA). Its isotopic purity was ≥ 98 %.

The product analysis was carried out under kinetic conditions. In a typical experiment, benzyl alcohol (0.51 mL, 0.005 mol) and PzDC (0.37 g, 0.001 mol) were dissolved in 10 mL of DMSO and the solution was allowed to stand for 24 h to ensure completion of the reaction. Most of the solvent was removed by distillation under reduced pressure. The residue was then treated with an excess of a freshly prepared saturated solution of 2,4-dinitrophenylhydrazine in 1.5 M H_2SO_4 and kept overnight in a refrigerator. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol and weighed again. The product was identical (mp and mixture mp) to an authentic sample of the DNP of benzaldehyde. The yields of DNP before and after recrystallization were 68 and 60 %.

Kinetic measurements: The reactions were performed under pseudo-first-order conditions, keeping a large excess (10-fold or greater) of the alcohols with respect to PzDC. The reactions were carried out at constant temperature (± 0.3 K) and were followed by monitoring the decrease in [PzDC] at 375 nm on a Shimadzu UV-160A visible double-beam spectrophotometer. The pseudo-first-order rate constant, k_1, was evaluated from the linear plots of ln [PzDC] *versus* time. The values of the rate constants reported were the means of two or more runs and were reproducible to within ± 3 %.

RESULTS AND DISCUSSION

Since the results were similar, with regard to the rate laws and other experimental data, only representative data are reproduced for benzyl alcohol (BA). The oxidation of the alcohols by PzDC resulted in the formation of the corresponding aldehydes.

Rate laws: Under pseudo-first-order conditions the pseudo-first order plots of log[PzDC] *vs.* time at different initial concentrations of PzDC (0.001 to 0.008 mol dm^{-3}) are all linear with nearly the same slope indicating a first-order dependence of the rate on the PzDC concentration (Table-1).

Further, the pseudo-first-order rate constants were independent of the initial concentration of PzDC at constant substrate concentration. In order to know the effect of the concentration of the alcohol on the rate of oxidation, the k_{obs} values were determined at different concentrations of alcohols in the range 0.04 to 0.20 mol dm^{-3} (Table-1). The reaction rate increases linearly with an increase in the concentration of alcohol (Table-1). Thus, the reaction is first order with respect to the alcohol as well. The plot of $1/k_1$ *vs.* 1/[BA] at 30 °C is linear with no intercept on the $1/k_1$ axis. This indicates the absence of a preformed complex or a complex whose formation constant is too low to be kinetically determined.

TABLE-1
RATE CONSTANTS FOR THE OXIDATION OF BENZYL ALCOHOL (BA) BY PYRAZINIUM DICHROMATE (PzDC) IN THE PRESENCE OF ACID AT 303 K

BA (M)	PzDC × 10^3	10^4 (k_1/s^{-1})	10^3 (k_2/s^{-1} M^{-1})
0.04	3.0	10.90	27.25
0.06	3.0	16.13	26.88
0.08	3.0	20.82	26.03
0.10	3.0	26.42	26.42
0.12	3.0	32.07	26.73
0.15	3.0	40.31	26.87
0.20	3.0	52.16	26.08
0.06	1.0	16.02	–
0.06	2.0	16.09	–
0.06*	3.0	16.17	–
0.06	4.0	16.45	–
0.06	5.0	16.16	–
0.06	6.0	16.00	–
0.06	7.0	16.13	–
0.06	8.0	16.62	–

*Contained 10^{-3} M acrylonitrile. [H^+] = 0.05 M; T = 303 K

The oxidation was found to be acid-catalyzed. The k_{obs} values determined at increasing concentrations of *p*-toluene sulphonic acid (TsOH) in the range 0.05-0.25 mol dm^{-3}, increase (Table-2). The linear increase in the oxidation rate with acidity suggests the involvement of a protonated Cr(VI) species in the rate determining step, which is a stronger oxidant and electrophile than an unprotonated Cr(VI) species. There have been earlier reports suggesting the involvement of such Cr(VI) species in chromic acid oxidation[14] and protonated Cr(VI) species have been observed in the presence of TsOH acid in nitrobenzene-dichloromethane mixtures[15].

TABLE-2
DEPENDENCE OF THE REACTION RATE ON ACIDITY*

[TsOH]/M	0.05	0.07	0.10	0.20	0.25
10^4 k_1 s^{-1}	16.13	22.46	32.76	64.54	80.89

*[BA] = 0.06 M; [PzDC] = 0.003 M; T= 303 K

Effect of solvent composition: The rate of acid-catalyzed oxidation of benzyl alcohol (BA) was studied in solutions containing varying proportions of DMSO and CH_2Cl_2 (Table-3). Permittivity (D) values for DMSO-CH_2Cl_2 were estimated from the dielectric constants of the pure solvents[16] and are recorded in Table-3. It can be seen that the solvent effect on reactivity is quite significant. A plot of log k_1 against the inverse of permittivity is linear with a positive slope. This suggests an ion-dipole interaction in agreement[17] with the observation that in the presence of an acid, the rate-determining step involves a protonated Cr(VI) species.

TABLE-3
DEPENDENCE OF THE REACTION RATE ON
SOLVENT COMPOSITION*

DMSO: CH_2Cl_2 (%, v/v)	100:0	70:30	60:40	50:50	40:60	30:70
D	46.70	35.40	31.60	27.80	24.00	20.24
10^4 k_1/s^{-1}	16.13	20.36	25.36	33.40	41.64	50.15

*[PzDC] = 0.003 M; [BA] = 0.06 M; [TsOH] = 0.05 M; T = 303 K

Effect of temperature: The rates of oxidation of all the benzyl alcohols were determined at different temperatures and it was observed that the rate increased with an increase in temperature (Table-4). From the linear plots of log k, against the reciprocal of temperature, the activation energy was calculated. The activation parameters were calculated (Table-5) using the Eyring equation and the Gibbs equation[18].

Kinetic isotope effect: To ascertain the importance of the cleavage of the α-C-H bond in the rate-determining step, the oxidation of α,α-dideuteriobenzyl alcohol was studied at four different temperatures (Table-4). The reaction showed the presence of a substantial primary kinetic isotope effect ($k_H/k_D = 6.61$ at 303 K).

Induced polymerization of acrylonitrile: The oxidation of benzyl alcohol, by PzDC, in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. Further, the addition of acrylonitrile had no effect on the rate (Table-1). Thus, a one-electron oxidation giving rise to free radicals is unlikely.

TABLE-4
TEMPERATURE DEPENDENCE OF THE OXIDATION OF SUBSTITUTED BENZYL ALCOHOLS BY PzDC

No.	Substituents	10^4 k_1/s^{-1}			
		298 K	303 K	308 K	313 K
1	*p*-OMe	24.98	32.88	52.50	57.21
2	*p*-Me	19.75	25.32	38.74	50.68
3	*m*-Me	15.42	18.62	30.91	36.12
4	H	11.12	16.13	21.42	31.81
5	*m*-OMe	19.33	12.92	17.45	24.86
6	*p*-Cl	7.14	9.21	13.61	18.75
7	*p*-Br	5.92	8.22	10.86	17.08
8	*m*-Cl	4.60	5.34	8.85	11.62
9	*m*-Br	3.16	4.50	6.91	10.43
10	*p*-NO_2	1.38	1.95	2.70	3.83
11	$phCD_2OH$	1.67	2.44	3.35	5.12

[PzDC] = 0.003 M; [Alcohol] = 0.06 M; [TsOH] = 0.05 M

TABLE-5
ACTIVATION PARAMETERS OF THE OXIDATION OF SUBSTITUTED BENZYL ALCOHOLS BY PzDC

Substituent	ΔH^* (kJ mol^{-1})	ΔS^* (J mol^{-1} K^{-1})	ΔG_{298}^* (kJ mol^{-1})
p-OMe	44.0 ± 0.3	147 ± 1.0	87.8 ± 0.4
p-Me	48.3 ± 0.2	135 ± 0.5	88.5 ± 0.3
m-Me	45.1 ± 0.2	148 ± 0.5	89.2 ± 0.3
H	51.3 ± 0.1	130 ± 0.5	90.0 ± 0.2
m-OMe	46.5 ± 0.7	147 ± 2.5	90.3 ± 1.0
p-Cl	48.7 ± 0.2	142 ± 0.5	91.0 ± 0.3
p-Br	51.5 ± 0.1	134 ± 0.5	91.4 ± 0.2
m-Cl	48.4 ± 0.1	147 ± 0.5	92.2 ± 0.2
m-Br	60.1 ± 0.7	110 ± 2.0	92.9 ± 0.9
p-NO_2	50.7 ± 0.2	149 ± 0.5	95.1 ± 0.3
$phCD_2OH$	55.5 ± 0.8	132 ± 3.0	94.8 ± 1.2

Correlation analysis of reactivity: A Hammett plot[19] of log k_1 *vs.* σ was drawn (Fig. 1) to correlate structure-reactivity for these reactions. The rate increased with electron-donating groups and decreased with respect to electron-withdrawing groups. The results showed lower rates with respect to electron-withdrawing groups and higher rates with electron-donating groups (Table-4). Electron-donating substituents stabilize a transition state having a carbocation centre by resonance. This facilitates the bond-breaking process in the transition state. On the other hand, an electron-withdrawing

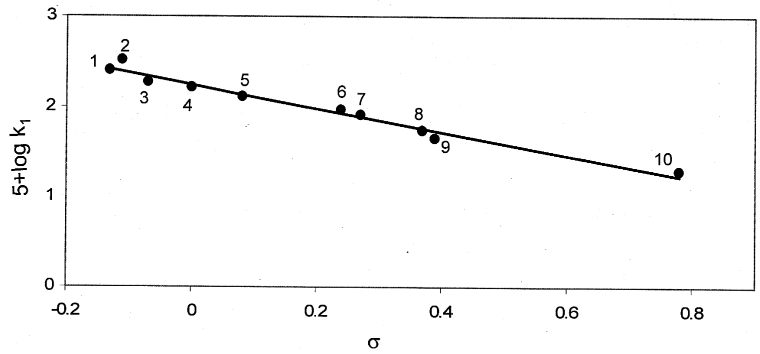


Fig. 1. Hammet plot for the PzDC oxidation of substituted benzyl alcohols (for numbering see Table-4)

substituent increases the capacity of the carbocation ion centre, suggesting the development of a loose or partial positive charge at the transition state, which in turn helps the bond-making process, thus leading to a decrease in rate. The negative ρ values indicate an electron-deficient transition state and increase with increase in temperature. The ρ values at temperatures 298, 303, 308 and 313 K are -1.32, -1.29, -1.32 and -1.24, respectively. Such values are not uncommon in hydride ion transfer mechanism[20]. The similarity of ΔG* values arises from changes in ΔH* and ΔS* values and stresses the probability that these oxidation reactions involve similar rate determining steps (Table-5). The high negative values of activation entropies support the assumption of a highly solvated transition state due to its increased polarity. They are also indicative of the bimolecular rate-determining step[21] as shown in **Scheme-I**.

$(C_4H_5N_2)_2Cr_2O_7 + TsOH \rightleftharpoons \text{Complex}$ K

$\text{Complex} + ArCH_2OH \longrightarrow ArCHO + Cr(IV) + TsOH$ k

$Cr(IV) + Cr(VI) \longrightarrow 2Cr(V)$ Fast [Ref. 14,35]

$2Cr(V) + 2ArCH_2OH \longrightarrow 2ArCHO + 2Cr(III) + 4H^+$ Fast [Ref. 14,35]

Scheme-I

The correlation between activation enthalpies and entropies of oxidation of the ten alcohols is fairly good. The value of the isokinetic temperature is 248 K. However, according to Exner[18] an isokinetic relationship between the calculated values of activation enthalpies and entropies is often vitiated by random experimental errors. Exner suggested an alternative method for establishing the isokinetic relationship. Exner's plot between log k_1 at 298 K and at 313 K was reasonably linear (Fig. 2). 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.

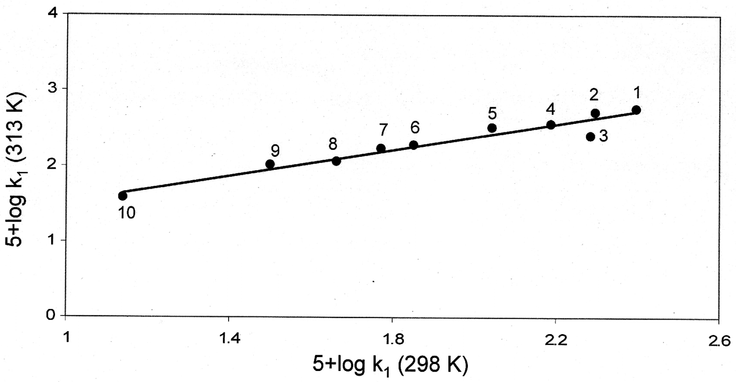


Fig. 2. Exner plot for the PzDC oxidation of substituted benzyl alcohols (for numbering see Table-4)

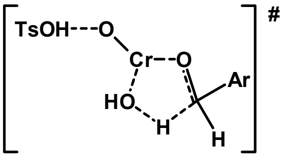
Mechanism: The oxidations have been performed in non-aqueous medium. Thus hydrolysis of dichromate may safely be ruled out. PzDC in the wave length region 375-320 nm exhibits stronger absorbance than $K_2Cr_2O_7$. This indicates that in solution PzDC does not dissociate to any appreciable extent. The fact that only TsOH brings about the oxidation points out an involvement of TsOH in the oxida-tion process. The UV-Vis spectrum clearly confirms the complex formation between oxidant and TsOH. Complex formation between imidazolium dichromate-TsOH[22], PzDC-TsOH[23], NDC-TsOH and INDC-TsOH[24] has already been reported. If the formation constant of the complex is small the oxidation is dependent on [TsOH]. The PzDC-TsOH complex is more reactive than other Cr(VI) species because since the complexation makes the oxidant a better electrophile. It behaves like a protonated Cr(VI) species, which is a stronger oxidant and electrophile[22].

An examination of the kinetic data obtained in the present investigation, showed that the rate of oxidation of the alcohols was dependent on the first powers of the concentrations for each reactant (substrate, oxidant and acid) (Table-1) and PzDC-TsOH is the likely oxidizing species.

The presence of a substantial primary kinetic isotope effect indicates that the rupture of the C-H bond occurs after the O-H bond cleavage creating a carbocation centre or a positive character in the transition state. The ρ values higher than -3 generally suggest a fairly large degree of carbonium character in the transition state[25]. The ρ value of -1.29 at 303 K found in the present study is indicative of a partial bonding. The negative value of the polar reaction constant together with the substantial deuterium isotope effect indicates that the transition state approaches a carbocation in character. Hence, the transfer of a hydride-ion from the alcohol to the oxidant is suggested.

The hyride-ion transfer may take place either by a cyclic process *via* an ester intermediate[26] or by an acyclic one-step bimolecular process[27]. Kwart and Nickel[26] have shown that the dependence of k_H/k_D on temperature can be successfully employed to determine whether the loss of hydrogen proceeds through a concerted cyclic process or by an acyclic one.

The data for protio- and deuterio- benzyl alcohols, fitted to the familiar expression, $k_H/k_D = A_H/A_D\ e^{-\Delta H^*/RT}$, show a direct correspondence with the properties of a symmetrical transition state in which activation-energy difference for protio and deuterio compounds are equal to the difference in the zero-point energy for the respective C-H and C-D bonds (*ca.* 4.5 kJ mol^{-1}) and the entropies of activation of the respective reactions are nearly equal[28,29]. Evidence against a hydrogen transfer occuring by a concerted one-step bimolecular process has been well documented by Bordwell[30]. It is evident that in the present study also the hydrogen transfer does not occur by an acyclic bimolecular process. It is well established that intrinsically concerted sigmatropic reactions characterized by a transfer of hydrogen in a cyclic transition state are the only symmetrical processes involving a linear hydrogen transfer[31]. Furthermore, a cyclic hydride-ion transfer in the oxidation of alcohols by Cr(VI) involves six electrons and, being a Hückel-type system, is an allowed process[32]. Therefore, one can safely conclude that in the oxidation of benzyl alcohols by PzDC, the hydride ion transfer occurs *via* a chromate ester. Formation of ester intermediates in the oxidation of hydroxy compounds is well documented[14]. Further, an intermolecular hydride transfer should normally lead to a correlation with σ^+ values[33]. Good correlation with Hammett's σ values is also in accordance with the ester mechanism. A mechanism depicted in **Scheme-II** accounts for the experimental results. Thus a transition state having a planar, cyclic symmetrical structure can be envisaged for the decomposition of the ester intermediate (**Scheme-II**). A linear transition state will certainly exhibit a larger isotope effect than a cyclic intermediate[34].



Scheme-II

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(*Received*: 4 October 2007; *Accepted*: 8 February 2008) AJC-6322