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Effect of Substituents on the Kinetics of the Oxidation of Benzyl Chloride Using Acid-Dichromate

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Kinetics of the oxidation of benzyl chloride and some of its *para*-substituted derivatives by acid-dichromate have been investigated in acetic acid-water mixture. The reaction shows first order dependence on the concentrations of the oxidant as well as the substrate. The reaction is acid catalyzed and shows fractional order with respect to sulphuric acid concentration. The product of oxidation is the corresponding benzaldehyde. Electron releasing substituents accelerate the reaction, whereas electron withdrawing groups retard the rate. The rate data obey the Hammett's relationship. The reaction constant ρ is negative. Isosbestic point was found at 297 nm. The reaction does not induce polymerization of acrylonitrile. The effect of solvent composition shows that the rate increases with an increase in the polarity of the solvent. Activation parameters have been evaluated and a mechanism consistent with the kinetic results has been proposed.

Key Words: Benzyl chloride, Oxidation, Kinetics, Acid-dichromate.

INTRODUCTION

Benzylic halides can be converted to aldehydes using a variety of oxidants such as dimethyl sulphoxide, hexamethylenetetramine, trimethylamine oxide, different chromium(VI) species, *etc.*[1]. Capsule membrane supported phase transfer catalyzed (CM-PTC) oxidation of benzyl chloride using hydrogen peroxide gives benzaldehyde as the major product[2]. According to another report benzyl chloride can be oxidized to benzaldehyde using titanium silicates having Bronsted acidity in the presence of hydrogen peroxide and water[3].

Gopalan and Subbarayan[4] have reported the kinetics of chromic acid oxidation of benzyl chloride in aqueous acetic acid. Yadav *et al.*[5] have investigated the kinetics and mechanism of liquid-liquid phase transfer catalyzed oxidation of benzyl chloride to benzaldehyde using chromate

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salts. In this paper, the effect of substituents on the kinetics of oxidation of benzyl chloride using acid-dichromate is reported.

EXPERIMENTAL

Benzyl chloride (Merck sample) was purified by distillation under reduced pressure. *p*-Nitro, *p*-chloro and *p*-methyl derivatives of benzyl chloride were obtained from Lancaster and were used as supplied. AnalR grade potassium dichromate (Glaxo) was used and its solution prepared in doubly distilled water. Glacial acetic acid (100 %) indifferent to chromic acid GR (Merck) was used. All other chemicals used were either AnalR or GR grade.

The [substrate] was always taken in sufficient excess over [dichromate] so that observed kinetics were pseudo-first order. Reactions were conducted at constant acidity and ionic strength. The course of the reaction was followed iodometrically by withdrawing aliquots of the reaction mixture at definite intervals of time. The pseudo-first order rate constants, k_{obs}, were determined from the slopes of the linear plot of log [dichromate] against time.

Study of the stoichiometry showed that 3 mol of benzyl chloride consumed 1 mol of dichromate. The product analysis was carried out under kinetic conditions. Aldehydes formed were detected using TLC and characterized as their 2,4-DNP derivatives. Benzoic acid was not detected in the reaction mixture. The overall reaction may be represented by the following empirical equation

$$3PhCH_2Cl + Cr_2O_7^{2-} + 8H^+ \rightarrow 3Ph-CHO + 2Cr^{3+} + 4H_2O + 3HCl$$

Rate constants were determined for benzyl chloride and its derivatives at different temperatures ranging from 328 to 348 K and activation parameters were computed. Effect of change in the concentrations of substrate, oxidant, H^+ and salt and the effect of solvent polarity were studied at 333 K. Successive absorption spectra were taken at definite time intervals.

RESULTS AND DISCUSSION

Effect of change in [substrate] and [oxidant] are shown in Table-1. The k_{obs} values remained almost constant when the [dichromate] was varied. This shows first order dependence of the rate on the [oxidant]. When the [substrate] was varied, the log k_{obs} *vs.* log [substrate] plot was linear (r = 0.9998) with a positive slope of almost unity (0.9474) indicating first order dependence of the rate on the [substrate].

Reaction rates were determined at different [H^+] (Table-2). Plot of log k_{obs} *vs.* log [H^+] was linear (r = 0.9985) with a slope of +0.3304, indicating a fractional order dependence of the rate on the [H^+].

TABLE-1
EFFECT OF [SUBSTRATE] AND [OXIDANT] ON THE REACTION RATE
Solvent = 60 % HOAc, T = 333 K, μ = 0.15 M, $[H^+]$ = 0.5 M

$[PhCH_2Cl] \times 10^2$ (mol dm^{-3})	[dichromate] $\times 10^3$ (mol dm^{-3})	$k_{obs} \times 10^5$ (s^{-1})	$k_2 \times 10^3$ (dm^3 mol^{-1} s^{-1})
2.50	2.00	3.733	1.493
3.75	2.00	5.426	1.447
5.00	2.00	7.182	1.436
6.25	2.00	8.882	1.421
5.00	1.00	7.635	1.527
5.00	1.50	7.345	1.469
5.00	2.00	7.182	1.436
5.00	2.50	7.052	1.410

TABLE-2
EFFECT OF $[H^+]$ ON THE REACTION RATE
[S] = 5 × 10^{-2} M, [oxidant] = 2 × 10^{-3} M, Solvent = 60 % HOAc
μ = 0.15 M, T = 333K

$[H^+]$ M	0.250	0.375	0.500	0.625	0.750
$k_{obs} \times 10^5$ (s^{-1})	5.814	6.593	7.182	7.838	8.372

Study of the solvent effect showed that the rate increases with increase in the dielectric constant (D) of the solvent (Table-3). Plot of log k_{obs} *vs.* 1/D is linear (r = 0.9939) with a negative slope indicating the possibility of an interaction between a negative ion and a dipole[6].

TABLE-3
EFFECT OF SOLVENT POLARITY ON THE REACTION RATE
[S] = 5 × 10^{-2} M, [oxidant] = 2 × 10^{-3} M, μ = 0.15 M, T = 333K

% of HOAc (v/v)	40	50	60	70
Dielectric constant (D)	47.0	39.8	32.0	24.5
$k_{obs} \times 10^5$ (s^{-1})	26.460	14.800	7.182	3.041

Study of the effect of added salt, showed that the rate slightly decreases with increase in the ionic strength (Table-4).

TABLE-4
EFFECT OF ADDED SALT ON THE REACTION RATE
[S] = 5 × 10^{-2} M, [oxidant] = 2 × 10^{-3} M, $[H^+]$ = 0.5 M
Solvent = 60 % HOAc, T = 333K

$[Na_2SO_4] \times 10^2$ M	0.000	1.250	2.500	5.000
$k_{obs} \times 10^5$ (s^{-1})	8.162	7.689	7.372	7.182

Successive scans at definite intervals gave the isosbestic point at 297 nm, indicating the formation of a single product. The failure to induce polymerization of acrylonitrile, points against a one-electron oxidation, giving rise to free radicals.

Determination of rate constants for different *para*-substituted benzyl chlorides showed that electron donating groups enhance the rate while electron withdrawing groups retard the rate (Table-5). The rate data correlate well with Hammett's σ values (r = 0.9911) and the reaction constant is negative (ρ = -1.711).

TABLE-5
RATE CONSTANTS FOR THE OXIDATION OF BENZYL CHLORIDES
$[S] = 5 \times 10^{-2}$ M, [oxidant] = 2×10^{-3} M, $[H^+] = 0.5$ M
Solvent = 60 % HOAc, μ = 0.15 M, T = 333K

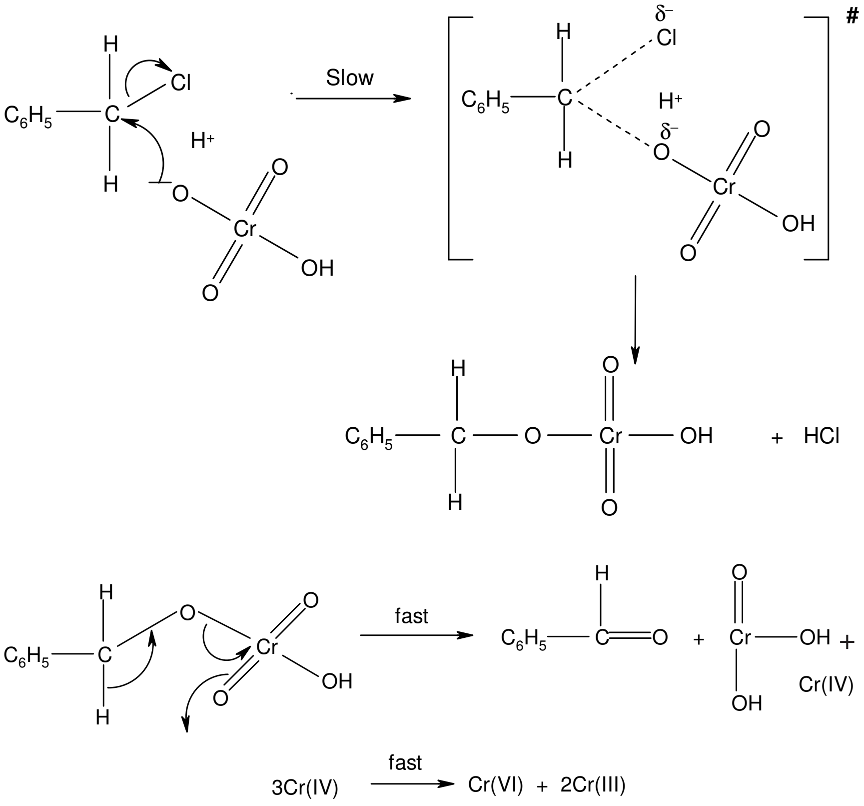
Substituent	$k_2 \times 10^4$ dm^3 mol^{-1} s^{-1}				
	328 K	333 K	338 K	343 K	348 K
p-NO_2	–	0.813	1.538	2.912	4.366
p-Cl	3.928	6.452	10.980	18.600	–
H	8.388	14.360	22.540	39.000	–
p-CH_3	28.880	41.640	60.120	84.040	–

The activation parameters are given in Table-6. $\Delta H^{\#}$ *vs.* $\Delta S^{\#}$ plot is linear (r = 0.9897). The isokinetic temperature computed from the isokinetic plot is 425 K. The correlations were tested and found genuine by applying Exner's criterion. Plot of log k_2 at 333 K against log k_2 at 343 K is linear (r = 0.9989). The isokinetic temperature calculated from the slope of Exner's plot is 424 K. A linear isokinetic relationship is a necessary condition for the validity of linear free energy relationships. It also implies that all reactions so correlated follow similar mechanism[7].

TABLE-6
ACTIVATION PARAMETERS FOR THE OXIDATION OF BENZYL CHLORIDES
$[S] = 5 \times 10^{-2}$ M, [oxidant] = 2×10^{-3} M, $[H^+] = 0.5$ M,
Solvent = 60 % HOAc, μ = 0.15 M, T = 333 K

Substituent	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (JK^{-1} mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
p-NO_2	107	-3.5	108
p-Cl	94	-23.0	102
H	92	-24.0	100
p-CH_3	64	-98.0	97

It has been proved by several authors[8] that under the pH used in this study the active Cr(VI) species is the acid chromate ion, $HCrO_4^-$. It may be assumed that, $HCrO_4^-$ attacks the benzyl chloride molecule resulting in the formation of a chromate ester in a rate controlling slow step[9]. Then the chromate ester decomposes in a fast step to give the aldehyde and Cr(IV). The Cr(IV) being unstable disproportionates into Cr(VI) and Cr(III) (**Scheme-I**).



Scheme-I

It can be shown that the breaking of C–Cl bond, liberating Cl^- is involved in the rate determining step. Study of the substituent effect had shown that, electron releasing groups enhance the rate and electron withdrawing groups retard the rate. Electron donating groups repel the electron pair of the C–Cl bond and hence aid its breaking. Electron withdrawing groups have an opposite effect. Further, the rate of the reaction increases considerably with increase in polarity of the solvent. The k_{obs} value increased from 3.041×10^{-5} s^{-1} to 2.646×10^{-4} s^{-1} (a nine-fold increase) when the dielectric constant of the solvent was increased from 24.5 to 47. An increase in the polarity of the medium can facilitate the breaking of the polar C–Cl bond[10]. Therefore, the first step, *i.e.*, the formation of chromate ester should be the rate determining step.

The negative $\Delta S^{\#}$ values indicate the formation of a transition state which is ordered and solvated.

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