



Kinetic studies on the oxidation of benzyl alcohol by hypochlorite in aqueous acetic medium

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ABSTRACT

Kinetics of the oxidation of benzyl alcohol by hypochlorite ion has been studied in acetic acid-water medium. The reaction showed first order dependence on both [substrate] and [oxidant]. The reaction failed to induce the polymerisation of added acrylonitrile which rules out the involvement of any radical intermediate during the reaction. The rate of reaction is found to decrease with increase in dielectric constant of the medium. Benzaldehyde was obtained as the product with high yield and no traces of benzoic acid were detected. Thermodynamic parameters were determined and a suitable mechanism is proposed in concordance with the obtained results.

Keywords: Benzyl alcohol, hypochlorite, kinetics, mechanism

INTRODUCTION

Oxidation of organic compounds using different oxidising agents is of great significance synthetically [1-2]. Permanganate and chromate ions are extensively used for the oxidation primary and secondary alcohols in a selective manner to get corresponding aldehydes [3-4]. There are lot of reports on the kinetic studies of oxidation alcohols using permanganate and chromate [5-10]. But reports on the use of hypochlorite as an oxidant for the oxidation of alcohols and kinetic studies on such oxidation are scanty and hence we carried out this work [11-13]. Hypochlorite ions are very cheap, less toxic and an environment friendly oxidant that can be employed for selective oxidation of alcohols. Benzaldehyde is an important starting compound for the manufacture of various compounds like dyes, odorants, flavours, perfumes etc.

The present paper deals with the kinetics of the selective oxidation of benzyl alcohol in aqueous acetic acid medium with hypochlorite. Stoichiometry of the reaction, product analysis, effect of [oxidant] and [substrate], effect of dielectric constant of the medium, effect of temperature on the oxidation are carried out. Thermodynamic parameters like energy of activation (E_a), enthalpy of activation (ΔH^\ddagger), entropy of activation (ΔS^\ddagger) and free energy of activation (ΔG^\ddagger) were calculated and a suitable mechanism is proposed based on the experimental observations.

EXPERIMENTAL SECTION

Analar grade sodium hypochlorite (Merck, India) was used as such and acetic acid was purified by refluxing with potassium dichromate for six hours and then distilled [14-15]. Analar benzyl alcohol (Merck India) was purified by distillation and doubly distilled water was used.

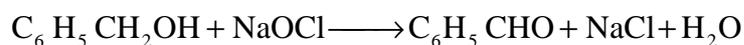
The stoichiometry of the reaction was established by equilibrating known excess concentration of hypochlorite ion with known amount of benzyl alcohol. Product analysis was carried out by stirring excess hypochlorite with benzyl alcohol in 20% aqueous acetic acid medium for about six hours at room temperature. The obtained solution is treated with sodium metabisulphite and then extracted with ether. A saturated solution of 2,4-dinitrophenylhydrazine

in HCl was added to the organic layer and kept overnight in refrigerator. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, recrystallised from ethanol, dried and weighed. The obtained product after purification was identified by determining its melting point and by infra red and UV-Visible spectral analyses.

Kinetic investigation was carried out at desired temperatures in a thermostat with an accuracy of $\pm 0.1^\circ\text{C}$ by maintaining pseudo first order condition by keeping $[\text{benzyl alcohol}] \gg [\text{hypochlorite}]$. A known volume of exactly known concentration of hypochlorite in 20% aqueous acetic acid was equilibrated. The reaction was initiated by adding required volume of previously thermostated benzyl alcohol in acetic acid to the hypochlorite solution. The reaction mixture was stirred well and aliquots were withdrawn at regular intervals and the concentration was determined iodometrically upto 90% completion of the reaction. The experiments were repeated and pseudo first order rate constants, k_{obs} were computed from the linear least square plots of $\log [\text{hypochlorite}]$ versus time.

RESULTS AND DISCUSSION

Stoichiometry of the oxidation was established by equilibrating known excess concentration of hypochlorite with known amount of alcohol. It was found that one mole of benzyl alcohol reacts with one mole of hypochlorite.



The product of oxidation was ascertained to be benzaldehyde from the formation of corresponding 2,4-dinitrophenylhydrazone and the yield was found to be nearly 90%. The oxidation reaction was carried out at room temperature and there was no further oxidation to benzoic acid. The recrystallised sample of product in the form of 2,4-dinitrophenylhydrazone was characterized by its melting point and was found as $239 \pm 2^\circ\text{C}$. The obtained result of melting point was compared with the values of authentic sample and found to have excellent similarity. This showed that the product obtained may be benzaldehyde. This was further confirmed by IR and UV-Visible spectral analysis of the product in the form of 2,4-dinitrophenylhydrazone.

The infra red absorption spectrum was recorded from KBr pellets using Jasco FT-IR 4100 spectrophotometer (Japan) and is shown in Figure 1.

The IR spectrum showed sharp peaks at 3287 cm^{-1} (N-H stretching), 3090 cm^{-1} (Aromatic C-H stretching), 1744 cm^{-1} (C=O stretching), 1620 cm^{-1} (C=C stretching), 1516 cm^{-1} (Ar-NO₂ asymmetric stretching), 1329 cm^{-1} (Ar-NO₂ symmetric stretching), and 1136 cm^{-1} (C-NH stretching). Presence of all these peaks leads to the conclusion that the product formed may be 2,4-dinitrophenylhydrazone of benzaldehyde. Furthermore this spectrum was compared with the IR spectrum of 2,4-dinitrophenylhydrazone of pure benzaldehyde and found to have excellent similarities.

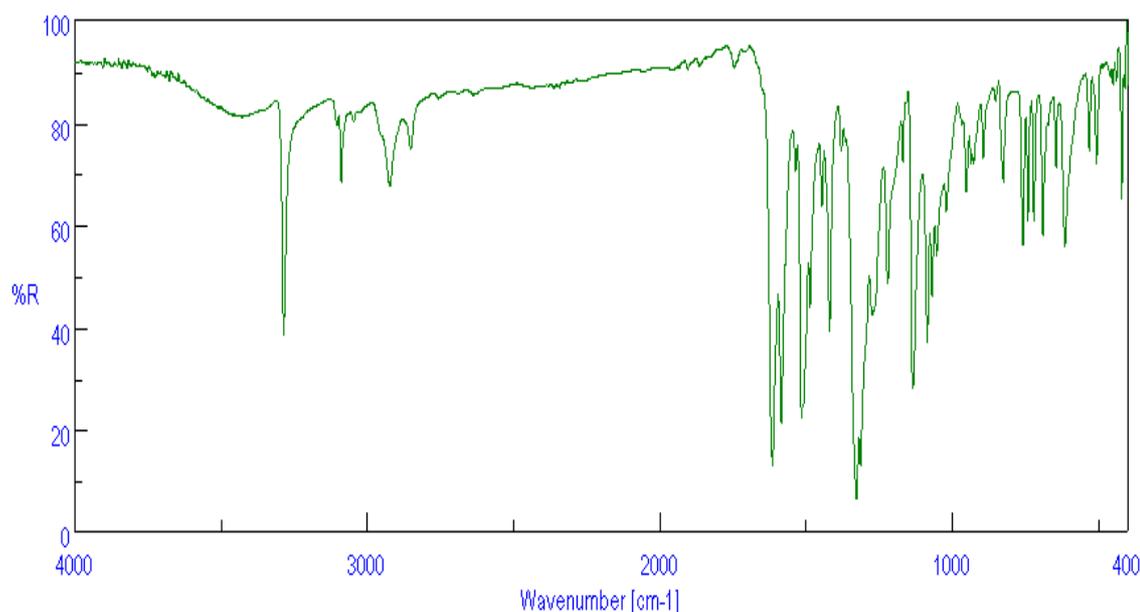


Figure 1: IR spectrum of 2,4-dinitrophenylhydrazone of product

UV-Visible absorption of the product obtained on the oxidation of benzyl alcohol was recorded by Hitachi U-3000 UV-Visible spectrophotometer using 1 cm quartz cell and spectrograde ethanol (Merck, India) as solvent and is given in Figure 2

In the UV-Visible spectrum of 2,4-dinitrophenylhydrazone of the product on the oxidation of benzyl alcohol showed intense peaks at 235 nm and 353 nm and were assigned to π - π^* and n - π^* transition of the aromatic compound. The UV-Visible spectrum of the obtained product was compared with the UV-Visible spectrum of 2,4-dinitrophenylhydrazone of pure benzaldehyde and gave excellent similarities. All the above analyses, viz., melting point determination, IR and UV-Visible spectral studies showed that the product formed on the oxidation of benzyl alcohol by hypochlorite is benzaldehyde.

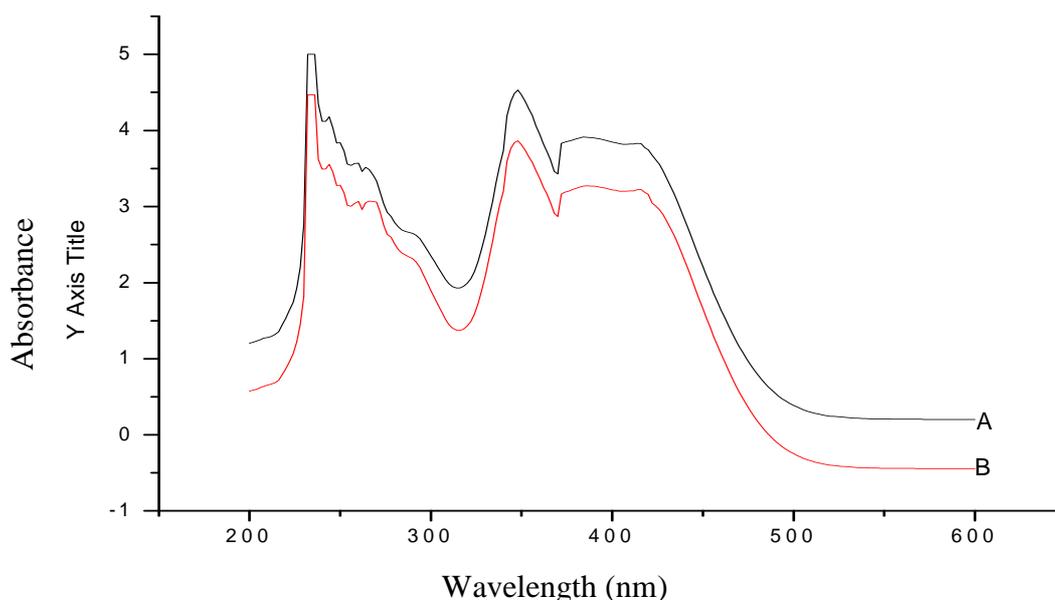


Figure 2 : UV-Visible spectrum of **A: 2,4-dinitrophenylhydrazone of pure benzaldehyde** **B: 2,4-dinitrophenylhydrazone of product on the oxidation of benzyl alcohol**

The oxidation of benzyl alcohol was carried out with different initial concentrations of the oxidant and substrate in 20% aqueous acetic acid medium at 303 K. The effect of [oxidant] and [substrate] on oxidation is given in Table 1. The plot of \log [hypochlorite] versus time was found to be linear at various [oxidant]. This proved that the reaction is first order with respect to [oxidant]. This was again confirmed from the constancy in the values of specific rates (k_{obs}) for the different [oxidant] for a given concentration of the substrate. The effect of [substrate] on the rate of oxidation was studied by taking different initial concentrations of the substrate and the observed rate constant increased linearly with the increase in [substrate]. Further, the second order rate constants k_2 , were found to be constant indicating the first order dependence of the reaction with respect to [benzyl alcohol]. The first order dependence on [substrate] was further confirmed by the plot of $\log k_{\text{obs}}$ versus \log [substrate] which is linear with a slope of unity.

Table 1: Effect of [oxidant] and [substrate] on the rate of oxidation of benzyl alcohol
Temperature - 303 K Medium - 20% aq. HOAc (v/v)

[NaOCl] $\times 10^3$ (mol dm ⁻³)	[PhCH ₂ OH] $\times 10^1$ (mol dm ⁻³)	$k_{\text{obs}} \times 10^4$ (s ⁻¹)	$k_2 \times 10^4$ (dm ³ mol ⁻¹ s ⁻¹)
2.5	1.0	9.58	95.83
5.0	1.0	9.43	94.33
7.5	1.0	9.96	99.67
10	1.0	9.30	93.00
10	1.0	9.30	93.00
10	1.25	11.03	88.17
10	1.5	13.43	89.50
10	1.75	14.88	85.00

The effect of dielectric constant of the medium on the oxidation of benzyl alcohol was carried under pseudo first order condition, by varying the percentage of acetic acid and is given in Table 2. The reaction rate is found to

increase with decrease in dielectric constant of the medium. The plot of $\log k_2$ versus $1/D$ where D is the dielectric constant is linear with a negative slope and is in accordance with Amis equation [16].

Table 2: Effect of dielectric constant of the medium on the rate of oxidation
 $[\text{NaOCl}] \times 10^3 = 10.0 \text{ mol dm}^{-3}$ $[\text{PhCH}_2\text{OH}] \times 10^1 = 1.0 \text{ mol dm}^{-3}$
 Temperature - 303 K

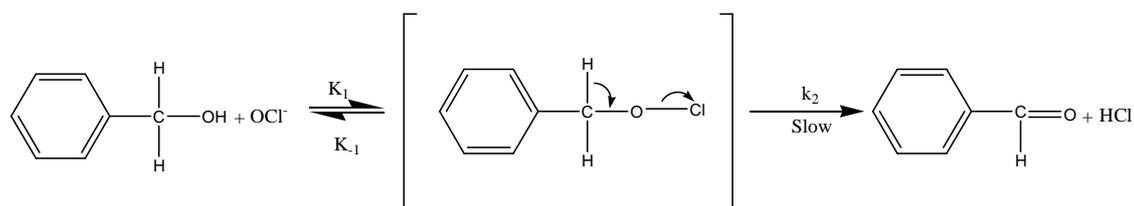
Acetic acid: water	Dielectric constant	$k_{\text{obs}} \times 10^4$ (s^{-1})	$k_2 \times 10^4$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
10 : 90	68	7.68	76.83
15 : 85	64.5	8.62	86.17
20 : 80	61	9.30	93.00
25 : 75	57.5	10.23	102.33

The effect of temperature on the rate of oxidation of benzyl alcohol using hypochlorite in 20% aqueous acetic acid (v/v) were studied in the temperature range 303 K to 318 K. The values of various thermodynamic parameters were calculated and presented in Table 3.

Table 3: Activation parameters for the oxidation of benzyl alcohol
 Medium - 20% aq. HOAc
 Temperature - 303 K

Substrate	$k_2 \times 10^4$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	E_a (kJ mol^{-1})	ΔH^\ddagger (kJ mol^{-1})	$-\Delta S^\ddagger$ ($\text{JK}^{-1} \text{mol}^{-1}$)	ΔG^\ddagger (kJ mol^{-1})
Benzyl alcohol	93	82.9	80.5	173.06	52.38

Based on the experimental evidences the proposed mechanism is as explained. A hydrogen abstraction mechanism leading to the formation of free radicals is ruled out in view of the failure to induce the polymerisation of added acrylonitrile. The reaction is first order with respect to [oxidant] and [substrate]. It is already established that such oxidation of alcohols exhibits a substantial primary kinetic isotopic effect [17-18]. This confirmed the cleavage of a α C-H bond in the rate determining step. The high negative value of ΔS^\ddagger shows the existence of a crowded transition state with hindered motion. Benzyl alcohol reacts with hypochlorite in acetic acid medium giving carbinol-hypochlorite complex by the elimination of water in a fast equilibrium. This complex then undergoes a slow rate determining decomposition involving the cleavage of C - H bond and O - Cl bond. The proposed mechanism is given in Scheme 1.



$$\text{Rate} = \frac{-d[\text{OCl}^-]}{dt} = k_2 [\text{C}_6\text{H}_5 \text{CH}_2 \text{OCl}]$$

$$= Kk_2 [\text{C}_6\text{H}_5 \text{CH}_2 \text{OH}][\text{OCl}^-]$$

$$\text{Where } K = \frac{K_1}{K_1 - 1}$$

Scheme 1

CONCLUSION

The selective oxidation of benzyl alcohol to benzaldehyde by hypochlorite involves the formation of carbinol - hypochlorite complex which on decomposition gives the product. So hypochlorite, which is a cheap, efficient and selective oxidant, can be used for the oxidation of other alcohols in a selective manner and kinetics of such reactions can be studied with ease.

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