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Kinetics and Mechanism of Oxidation of Methanol by Benzyl Triethyl Ammonium Chloro Chromate in aqueous acetic acid medium – catalyzed by 1,10-phenanthroline

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ABSTRACT

Kinetics of oxidation of Aliphatic Primary alcohol, methanol by Benzyl Triethyl Ammonium Chloro Chromate (BTEACC) has been studied in acetic acid medium. The reaction shows first order dependence with respect to [BTEACC] and [Methanol] and fractional order dependence with respect to $[H^+]$ and [Phen]. The rate of oxidation decreases with increase in dielectric constant of solvent which suggests ion-dipole interaction. Activation parameters have been evaluated. Finally a mechanism consistent with the observed result has been proposed and discussed.

Keywords: Methanol, BTEACC, Oxidation, Kinetics, Mechanism, 1,10-phenanthroline.

INTRODUCTION

The selective oxidation of alcohols to the corresponding aldehydic compounds is a frequently used transformation in organic synthesis [1]. Among them chromium (VI) containing reagents have been extensively studied [2]. In this work we report the kinetics of oxidation of methanol by BTEACC at different temperatures and the mechanistic aspects are discussed and a probable mechanism has been proposed.

MATERIALS AND METHODS

All chemicals were used of 'AnalarR' grade. The methanol was used after their distillation by proper method and purity checked by their boiling point. The solution of perchloric acid was prepared by diluting known volume of acid in water and standardized using phenolphthalein as an indicator. BTEACC is prepared by earlier reported method and its purity was checked by iodometric method [3].

Kinetic Measurement

Rate measurement was carried out at constant temperature in aqueous acetic acid medium. The course of reaction was followed iodometrically and the rate constant (k_1) was obtained from linear plot of log titre versus time by the least square method.

Stoichiometry

The reaction mixture containing an excess of the oxidant over methanol were kept at room temperature for sufficient length of time under the conditions employed for the kinetic run. Estimation of unchanged oxidant showed that one mole of methanol consumed one mole of BTEACC. The product formaldehyde obtained was identified by IR spectroscopy.

RESULTS AND DISCUSSION

Effect of oxidant and substrate concentration on reaction rate

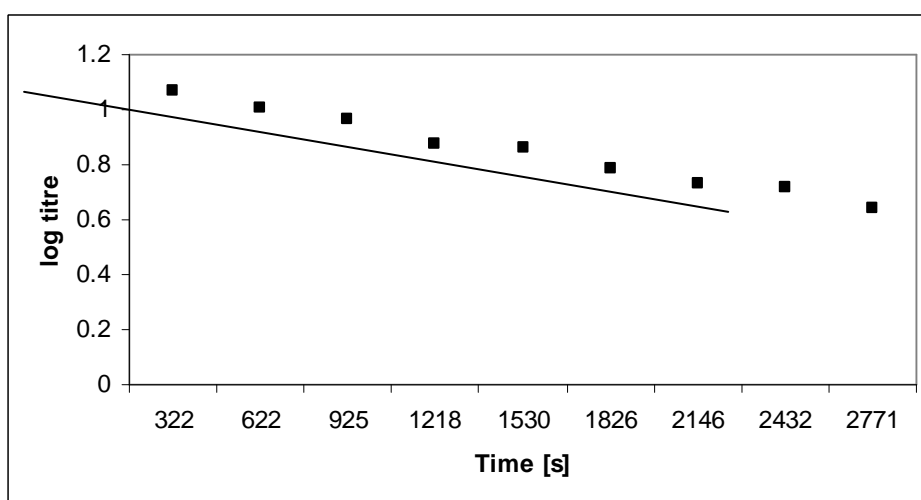
The oxidation of methanol by BTEACC was investigated at several concentrations of oxidant [BTEACC] and the substrate [methanol] (Table 1). The values of pseudo-first order rate constant k_1 were evaluated from the plot of log titre versus time following least square method. The plot of log titre versus time was linear (Fig.1) indicating the first order dependence on concentration of [BTEACC]. The plot of $\log k_1$ versus \log [substrate] is a straight line with slope equal to one. This shows that the reaction is first order with respect to methanol (Fig.2).

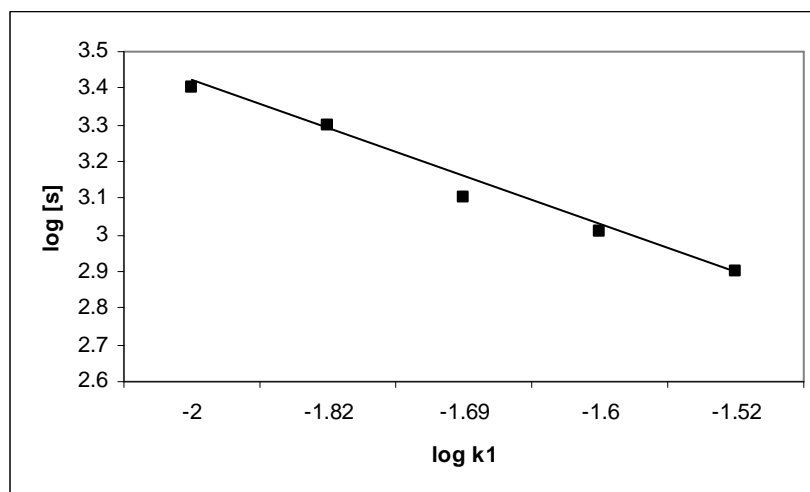
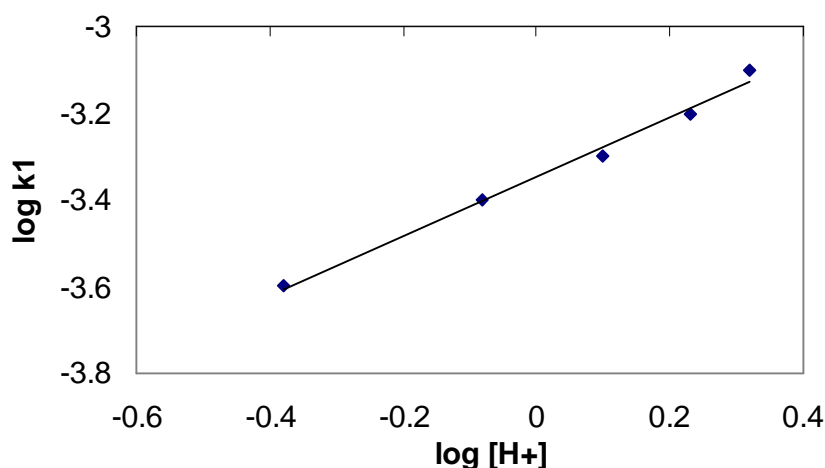
Effect of Perchloric acid

The effect of hydrogen ion concentration on the rate of oxidation was studied by varying $[H^+]$ while keeping the concentration other reactant constant. A steady increase in the oxidation state with increase in the acidity of the medium suggests the formation of protonated BTEACC in the rate determining step [4]. The plot of $\log k_1$ against $[H^+]$ is linear with slope 0.69 (Fig.3). Therefore order with respect to H^+ is fractional order. The protonated chromium (VI) species is likely to be better electrophile and oxidant compared to the neutral one.

Table 1 - Effect of varying reactant concentration on reaction rate at 303K

[OX] mol dm ⁻³	[CH ₃ OH] mol dm ⁻³	[H ⁺] mol dm ⁻³	[Catalyst] mol dm ⁻³	$k \times 10^4 \text{ s}^{-1}$
0.001	0.01	1.26	0.01	3.96
0.001	0.015	1.26	0.01	5.30
0.001	0.02	1.26	0.01	8.29
0.001	0.025	1.26	0.01	9.62
0.001	0.03	1.26	0.01	10.63
0.001	0.015	0.42	0.01	2.57
0.001	0.015	0.84	0.01	4.43
0.001	0.015	1.26	0.01	5.30
0.001	0.015	1.68	0.01	6.30
0.001	0.015	2.10	0.01	7.90
0.001	0.015	1.26	0.0025	2.88
0.001	0.015	1.26	0.005	3.55
0.001	0.015	1.26	0.0075	4.47
0.001	0.015	1.26	0.0100	5.30
0.001	0.015	1.26	0.0125	5.48
0.00025	0.015	1.26	0.01	3.52
0.00050	0.015	1.26	0.01	3.53
0.00075	0.015	1.26	0.01	5.70
0.00100	0.015	1.26	0.01	5.30
0.00125	0.015	1.26	0.01	3.80

**Fig.1 log titre versus time**

Fig.2 log k₁ versus log [s]Fig. 3 log k₁ versus log [H⁺]

Effect of solvent composition

The rate of oxidation of methanol with BTEACC at fixed ionic strength and H⁺ was determined in different solvent compositions (CH₃COOH). The reaction rate increases with the increase in the percentage of acetic acid. This shows that decreasing dielectric constant increases the rate of the reaction. This is due to polar character of transition state as compared to reactant. According to Scatchard [5] the logarithm of the rate constant of the reaction between ions should vary linearly with the reciprocal of the dielectric constant if reaction involves ion-dipole type of interaction as shown in the Table-2.

Table 2 - Variation of rate with solvent composition

[CH₃OH] = 0.015 mol dm⁻³

[H⁺] = 1.26 mol dm⁻³

Temperature = 303K

[CAT] = 0.01 mol dm⁻³

[OX] = 0.001 mol dm⁻³

SOLVENT COMPOSITION %	k ₁ x 10 ⁴ (s ⁻¹)
30	4.82
35	5.30
40	6.79
45	7.20

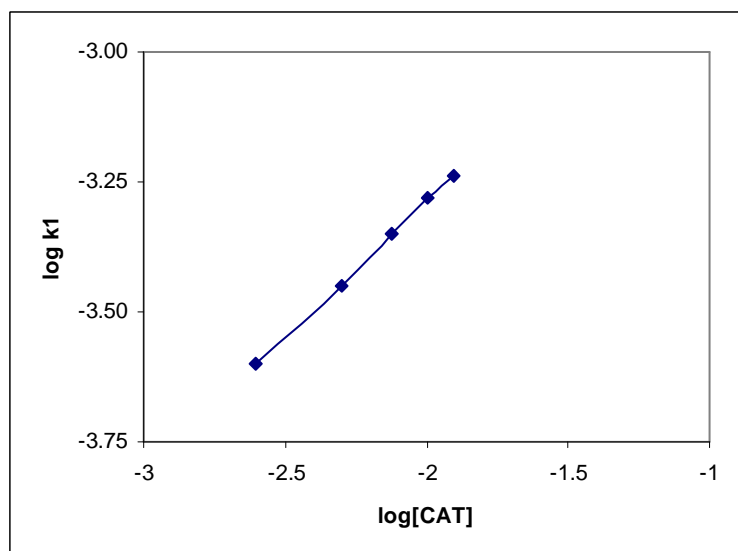


Fig.4 log [CAT] Vs. log k₁

Effect of Catalyst:

The reaction rate of oxidation of methanol by BTEACC was also studied by varying the concentration of catalyst 1,10-phenanthroline. The catalytic pathway in methanol has a non integral kinetic order (<1) as shown in Figure 4. Here we examine the oxidation kinetic investigation in the presence of the complexing agent 1,10-phenanthroline, since it can form a very reactive complex with Cr(VI) [6] and Cr(V) [7]. The catalysis by 1,10-phenanthroline may be explained as due to a more favourable electron transfer through its pi-electron cloud [8]. Generally the added catalyst stabilizes the end product and thereby accelerates the reaction.

Effect of temperature

To determine the activation parameter, the reaction was carried out at three different temperatures (30, 40 and 50 degrees) at constant hydrogen ion concentration, oxidant, catalyst and alcohol concentration. The energy parameters were computed using the slope and the intercept of $\ln k/T$ versus $1/T$.

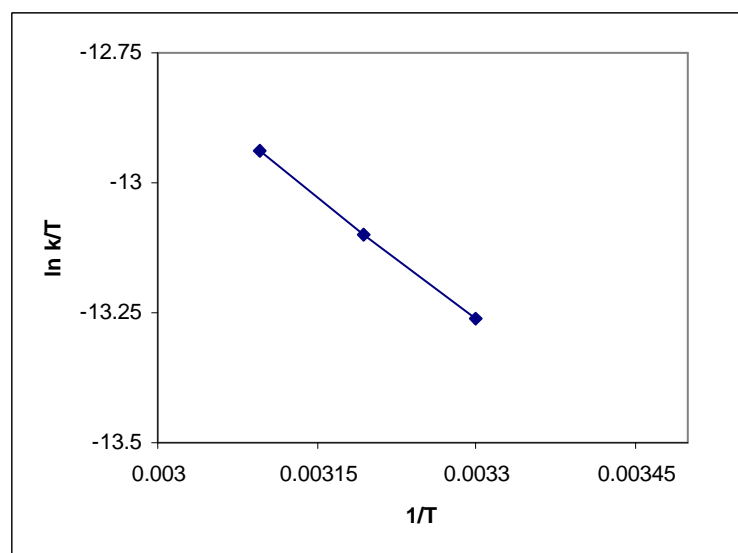


Fig. 5 ln k/T vs. 1/T

Table 3 - Variation of rate with temperature

[CH₃OH] = 0.015 mol dm⁻³
 [H⁺] = 1.26 mol dm⁻³
 AcOH – Water 35% – 65%

[CAT] = 0.01 mol dm⁻³
 [OX] = 0.001 mol dm⁻³

T	k ₁ x 10 ⁴ s ⁻¹
303K	5.30
313K	6.42
323K	7.75

ΔH[#] = 13.01 kJ/mole; Δs[#] = -264.88 J/K/mole; ΔG[#] = 93.27 kJ/mol

Effect of ionic strength, MnSO₄ and Acrylonitrile on reaction rate

The effect of ionic strength was studied by varying the NaClO₄ concentration in the reaction medium. The ionic strength of the reaction was varied from 2.50 x 10⁻⁴ to 10 x 10⁻⁴ mol dm⁻³ and keeping all other reactant concentration as constant. It was found that the rate constant increases with increase in concentration of NaClO₄ (Table 4). This suggests that the participation of an ion and a neutral molecule in the mechanistic step [9]. Addition of Manganous sulphate shows decrease in the rate of reaction. Depressed reactivity observed in the presence of Mn²⁺ clearly indicates the involvement of intermediate valence state of chromium particularly Cr(IV). Added acrylonitrile has no effect on the reaction rate indicating the absence of free radical pathway.

Table 4 - Effect of variation of [MnSO₄], [NaClO₄] and [acrylonitrile] on reaction rate at 303K.

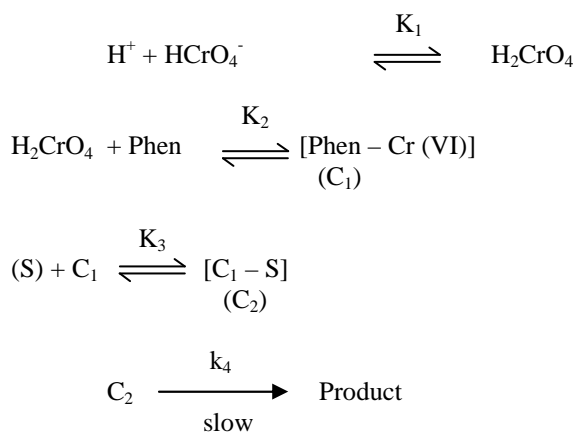
[MnSO ₄] x 10 ³ mol dm ⁻³	[NaClO ₄] x 10 ⁴ mol dm ⁻³	[Acrylonitrile] x 10 ⁴ mol dm ⁻³	k ₁ x 10 ⁴ s ⁻¹
2.50	-	-	5.09
5.00	-	-	4.79
7.50	-	-	4.56
10.00	-	-	4.07
-	2.50	-	4.38
-	5.00	-	4.72
-	7.50	-	4.98
-	10.00	-	5.11
-	-	2.50	4.08
-	-	5.00	4.19
-	-	7.50	4.52
-	-	10.00	4.62

DISCUSSION

The rate of oxidation increases on increasing the concentration of substrate [Methanol]. Plot of log k versus log [S] is linear with slope of unity. The rate of reaction increases with increasing [H⁺] concentration. Plot of log k₁ versus [H⁺] is a straight line with a Slope equal to 0.69 supports the idea that the protonated BTEACC may enhance the rate of oxidation. Increase in the percentage of acetic acid increases the rate, suggesting that medium of low dielectric constant favour the reaction. The rate of reaction increases with increase in temperature. The reactions are carried out in three different temperatures and thermodynamic parameters are evaluated. The entropy of activation is negative as expected for a bimolecular reaction. The larger negative values suggest that the transition state is less disordered than reactants [10].

The oxidation of methanol by BTEACC, in an atmosphere of Nitrogen failed to induce the polymerization of acrylonitrile. Further, an addition of a radical scavenger, acrylonitrile had no effect on reaction rate. With the above data and the proposed mechanism for Alcohols [11] the following suitable mechanism has been proposed, for the oxidation of methanol.

Mechanism



$$\begin{aligned}
 \text{rate} &= k_4\text{C}_2 \\
 &= K_3k_4[\text{C}_1][\text{s}] \\
 &= K_3k_4[\text{s}][\text{Phen}][\text{H}_2\text{CrO}_4] \\
 &= K_2K_3k_4[\text{s}][\text{Phen}][\text{HCrO}_4^-] \\
 &= \frac{K_1K_2K_3k_4[\text{s}][\text{Phen}][\text{HCrO}_4^-]}{\{1+K_1[\text{H}^+]\}} \\
 &= \frac{K_1K_2K_3k_4[\text{s}][\text{Phen}]}{\{1+K_1[\text{H}^+]\}}
 \end{aligned}$$

Scheme 1

CONCLUSION

Oxidation of primary alcohol by BTEACC catalyzed by 1,10-phenanthroline is an acid-catalyzed reaction. The oxidation yields the corresponding formaldehyde as product. The effect of ionic strength and solvent polarity suggest the participation of an ion and a neutral molecule in the mechanistic steps. Addition of Mn^{2+} shows catalytic activity in the oxidation reaction. The negative value of entropy adds additional support for the formation of the intermediate complex.

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