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Studies on the Kinetics of Benzyltrimethylammonium fluorochromate Oxidation of Substituted Benzaldehydes in aqueous Acetic Acid Medium

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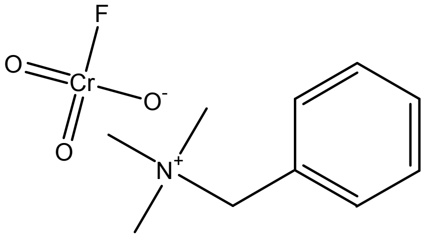
ABSTRACT : The kinetics of oxidation of benzaldehyde (BA) by Benzyltrimethyl ammonium fluorochromate (BTMAFC) in protic solvent system has been studied at 303K. A unit order dependence of the reaction with respect to [BTMAFC], [BA] and [H^+] ions has been observed. The reaction has been found to be catalysed by H^+ ions. To study the effect of structure reactivity relationships, some *para*-substituted benzaldehydes were subjected to oxidation by BTMAFC at four different temperatures and thermodynamic parameters were calculated. The Exner plot showed that all the *para*-substituted benzaldehydes are oxidized by the same mechanism. The Hammett plot is linear with positive ρ values. The products of the oxidation are the corresponding acids. From the observed kineic results a suitable mechanism has been proposed.

Keywords: Benzyltrimethylammonium fluorochromate, oxidation, kinetics, Benzaldehyde

1. INTRODUCTION

A number of new chromium(VI) containing compounds with heterocyclic bases have been developed recently (1-4). Kinetics of oxidation of substituted benzaldehydes by various oxidizing agents have been well studied (5-11). However, the kinetics of oxidation of substituted benzaldehydes by BTMAFC, a Cr (VI) reagent has not yet been studied. This prompted us to under take the present investigation. The structural formula of BTMAFC is shown in the following figure.



Benzyltrimethyl ammonium fluorochromate

$$[\,(C_6H_5CH_2)\,(CH_3)_3\,N\,]\,CrO_3F$$

2. EXPERIMENTAL

2.1 Materials and Reagents

All benzaldehydes used were of AnalaR Grade (E Merck, Germany), the solid benzaldehydes were used as such and the liquid benzaldehydes were used after vacuum distillation. Acetic acid was purified by standard method and the fraction distilling at 118°C was collected.

2.2 Preparation of Benzyltrimethylammonium fluorochromate:

To a solution of 15g (150 m mol) CrO_3 in 12mL water, placed in a 100 mL polythene beaker, 15mL (300 m mol) 40% HF is added with stirring. An orange red solution is obtained. The reaction mixture is then cooled in an ice-bath (0-5°C). Benzyltrimethyl ammonium bromide (35.7g, 155 m mol) is added portion-wise, with stirring. An orange soft solid, in a greenish liquid is obtained. To this mixture, 30mL CH_2Cl_2 is added. The orange organic phase is decanted and the solvent is distilled off. A reddish orange gel is separated (12) and stored in the refrigerator (92% yield)

$$[(C_6H_5CH_2)(CH_3)_3N]Br + CrO_3 \xrightarrow{40\ \%\ HF} [(C_6H_5CH_2)(CH_3)_3N]CrO_3F \quad (1)$$

(Benzyltrimethyl ammonium bromide)

Benzyltrimethyl ammonium
fluorochromate (**BTMAFC**)

This reagent has many advantages over similar oxidizing agents including ease of preparation, involving a simple cationic exchange; high yields of oxidizing species; good selectivity. BTMAFC is highly soluble in many solvents like dichloromethane, N,N-dimethyl formamide, acetonitrile, acetic acid, chloroform and acetone. It is less soluble in hexane, toluene, benzene and very slightly soluble in ethyl acetate and water. Its melting point range was found to be 55-58°C.

2.3 Kinetic Measurements

The reactions were followed under pseudo-first-order conditions by maintaining a large excess (x 15 or greater) of the benzaldehyde over BTMAFC. The temperature was kept constant to ± 0.1K. The reactions were followed by monitoring the decrease in the concentration of BTMAFC spectrophotometrically at 372 nm by using Simadzu U.V / Visible spectrophotometer with recording facilities for up to 80% of the reaction. No other reactant or product has any significant absorption at this wavelength. The pseudo-first-order rate constants, k_{obs}, were evaluated from the linear plots of log [BTMAFC] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within ± 4%. Correlation analysis were carried out using Microcal Origin (Version 6.1) computer software.

2.4 Product analysis

Product study was made under mineral acid catalysed conditions in benzaldehyde. Keeping concentration of BTMAFC in excess over benzaldehydes, the two solutions were mixed and perchloric acid was also added in 50% acetic acid – 50% water mixture. The reaction mixture was set aside for about 24h to ensure completion of the reaction. The reaction mixture was then evaporated and extracted with ether. The ether layer was washed with water many times. The ether layer was then kept on a water bath for the evaporation of ether and cooled in ice bath to obtain the product (m.p.121°C). The product was dissolved in benzene and a careful TLC analysis was done with benzoic acid and benzaldehyde as references. Only one spot corresponding to benzoic acid was obtained. Formation of benzoic acid was further confirmed by mixing the product with pure benzoic acid and noting that there was no change in the melting point.

2.5 Stoichiometric studies

Stoichiometric analysis showed that 3 mol of aldehyde consumed 2 mol of BTMAFC in accordance with Eq (2) to give the corresponding carboxylic acid.

$$3ArCHO + 2BTMAFC + H^+ \longrightarrow 3ArCOOH + 2Cr(III) \ldots\ldots\ldots\ldots (2)$$

3. RESULTS AND DISCUSSION

The title reaction was studied in 50% acetic acid - 50% water medium at 303 K, under the pseudo-first-order conditions. The observed pseudo-first-order rate constants (k_{obs}) are given in Table 1.

3.1 Effect of varying substrate concentration

The concentration of BTMAFC was varied in the range 6.80×10^{-4} to 3.40×10^{-3} mol dm^{-3} and keeping all other reactant concentrations as constant and the rates were measured (Table 1). The near constancy in the value of k_1 irrespective of the concentration of the BTMAFC confirms the first order dependence on BTMAFC.

The substrate benzaldehyde was varied in the range of 1.00×10^{-2} to 2.5×10^{-2} mol dm^{-3} at 303 K and keeping all other reactant concentrations as constant and the rates were measured (Table 1). The rate of oxidation increased progressively on increasing the concentration of benzaldehyde, indicating first order dependence with substrate. The plot of log k_{obs} *versus* log [BA] gave the slope of 0.9827 (r = 0.997) (Fig. 1) shows that this oxidation reaction was first order with respect to [BA]. The second order rate constant k_2 is invariant supporting the first order dependence on [BA].

3.2 Effect of varying perchloric acid concentration

The perchloric acid concentration was varied in the range of 0.15 to 0.75 mol dm^{-3} and keeping the concentrations of all other reactant concentrations as constant and the rates were measured (Table 1). The increase in [$HClO_4$] in the oxidation reaction increases the rate of the reaction and shows a direct first order dependence on [$HClO_4$]. A plot of log k_1 against log [H^+] is linear. Change in ionic strength by the addition of $NaClO_4$ has no effect on the rate constant.

3.3 Effect of varying solvent composition

The effect from solvent composition on the reaction rate was studied by varying the concentration of acetic acid from 40% to 70%. The pseudo-first-order rate constants were estimated for the oxidation reactions of all of the substituted benzaldehydes, with BTMAFC in the presence of prechloric acid at a constant ionic strength. The reaction rate is increases markedly with the decrease in the proportion of acetic acid in the medium (Table 1). The decrease in the dielectric constant of the medium with increase in the rate of the reaction suggests that the involvement of an ion and a neural molecule in the rate-determining step.

Table 1 : Effect of varying [BA], [BTMAFC], [$HClO_4$], Solvent composition and temperature on the reaction rate.

[BTMAFC] x 10^3 mol.dm^{-3}	[BA] x 10^2 mol.dm^{-3}	[$HClO_4$] mol.dm^{-3}	Solvent(v/v) AcOH-H_2O	Temperature K	k_{obs} x 10^4 s^{-1}
0.68	2.0	0.45	50-50	303	2.75
1.36	2.0	0.45	50-50	303	2.82
2.04	2.0	0.45	50-50	303	2.76
2.72	2.0	0.45	50-50	303	2.80
3.40	2.0	0.45	50-50	303	2.74
1.36	1.0	0.45	50-50	303	1.36
1.36	1.5	0.45	50-50	303	2.06
1.36	2.5	0.45	50-50	303	3.46
1.36	3.0	0.45	50-50	303	3.98
1.36	2.0	0.15	50-50	303	0.94
1.36	2.0	0.30	50-50	303	1.80
1.36	2.0	0.60	50-50	303	3.56
1.36	2.0	0.75	50-50	303	4.66
1.36	2.0	0.45	40-60	303	3.38
1.36	2.0	0.45	60-40	303	2.04
1.36	2.0	0.45	70-30	303	1.68
1.36	2.0	0.45	50-50	298	1.96
1.36	2.0	0.45	50-50	308	3.70
1.36	2.0	0.45	50-50	313	4.88

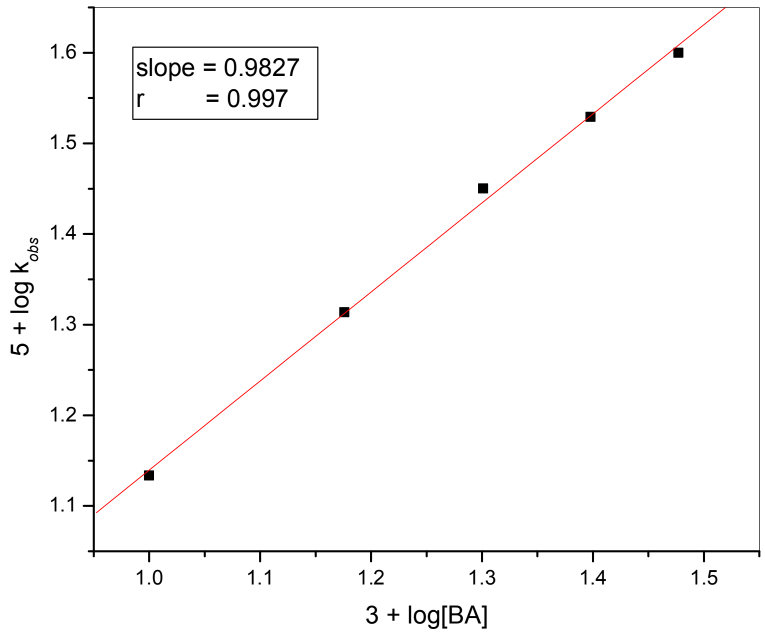


Fig. 1. Plot of log [BA] versus log k_{obs}

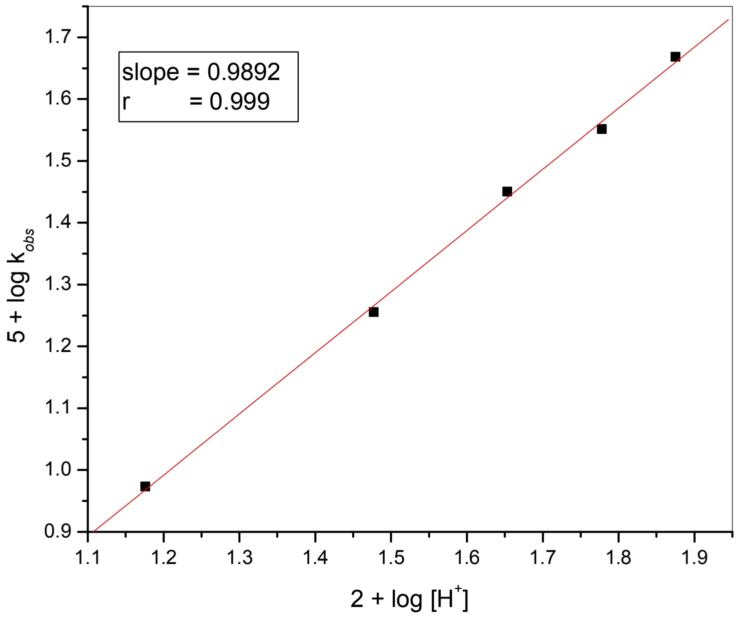


Fig. 2. Plot of log [H$^+$] versus log k$_{obs}$

3.4 Mechanism and Rate law

Based on the present experimental observations and from the reports of previous work (13), an initial two electron transfer with the formation of chromium (IV) has been formulated. Chromium (IV) reacts with an aldehyde molecule to form an aryl radical and Cr(III). The radical formation has been tested with the monomer acrylonitrile when a polymer precipitated in methanol under nitrogen atmosphere. Aryl radical reduces BTMAFC to Cr(V) which further reacts with another aldehyde molecule by a two electron transfer to form Cr(III). The involvement of intermediate valance states of chromium in the reaction has been tested with the induced oxidation by Mn (II). The reaction proceeds with the formation of a monochromate ester as the intermediate (Scheme 1). Since the rate of the reaction is he decomposition of the monochromate ester, the rate law given as

Rate = $K_1 K_2 k_3$ [BA] [BTMAFC] [H$^+$]

3.5 Structure reactivity correlation

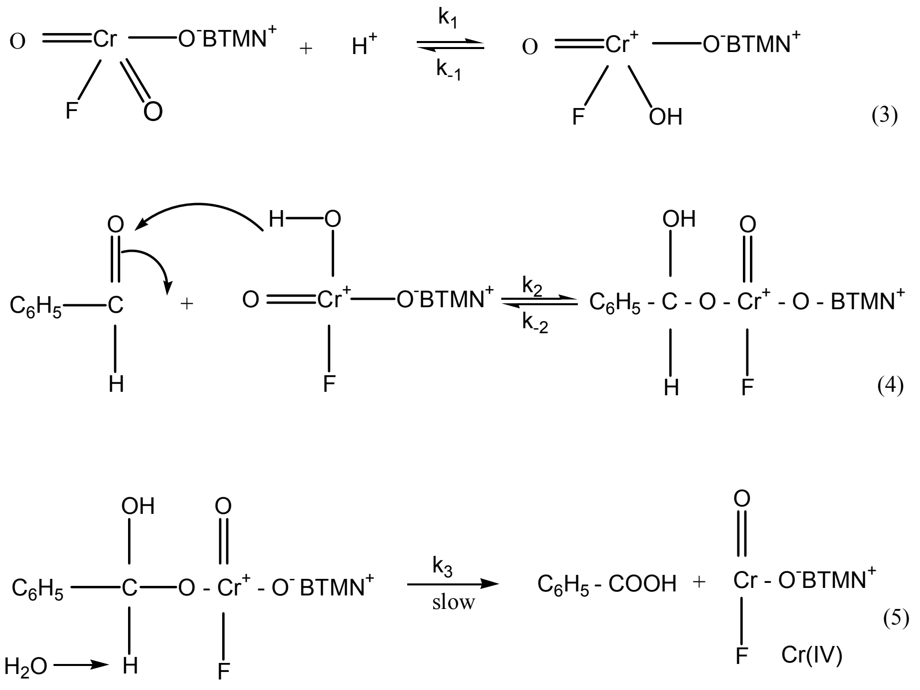
In order to study the effect of structure on reactivity, some *para*-substituted benzaldehydes were subjected to oxidation kinetics by BTMAFC at four different temperatures *viz.*, 298, 303, 308 and 313 K in 50% – 50% (v/v) acetic acid – water medium in presence of perchloric acid. Substrate effect reveals that *para*-substituted benzaldehydes also first order dependence.

The second order rate constants at four different temperatures are given in the Table 2 and the activation parameters in Table 3.

It is interesting to note that the reactivity decreases in the order *p*-NO_2 > *p*-CN > *p*-Cl> *p*-H > *p*-CH_3 > *p*-OCH_3 for the substituents.

The activation parameters were calculated from k_2 at 298, 303, 308 and 313 K using the van't Hoff plot by the method of least squares and are presented in Table 2. The reaction is neither isoenthalpic nor isoentropic but complies with the compensation law also known as the isokinetic relationship. The isokinetic temperature is the temperature at which all the compounds of the series react equally fast. Also, at the isokinetic temperature, the variation of substituent has no influence on the free energy of activation. In an isoentropic reaction, the isokinetic temperature lies at infinite and only enthalpy of activation determines the reactivity. The isokinetic temperature is zero for an isoenthalpic series, and the reactivity is determined by the entropy of activation (14). The operation of the isokinetic relationship is tested by plotting the logarithms of rate constants at two different temperatures ($T_2 > T_1$) against each other according to Eq (9).

log k (at T_2) = a + b log k (at T_1)………. (9)



$$C_6H_5\text{-}CHO + Cr(IV) \xrightarrow{\text{fast}} C_6H_5\text{-}CO^{\cdot} + Cr(III) \qquad (6)$$

$$C_6H_5\text{-}CO^{\cdot} + BTMAFCH^{+} \xrightarrow{\text{fast}} C_6H_5\text{-}COOH + Cr(V) \qquad (7)$$

$$C_6H_5\text{-}CHO + Cr(V) \longrightarrow C_6H_5\text{-}COOH + Cr(III) \qquad (8)$$

(Scheme - 1)

Table 2: Second-order rate constant for the oxidation of substituted benzaldehydes by BTMAFC at different temperatures.

Substituents	**10^2 k_2 (dm^3 mol^{-1} s^{-1})**			
	298K	**303K**	**308K**	**313K**
H	0.98	1.41	1.85	2.44
p–OCH_3	0.35	0.53	0.75	1.12
p–CH_3	0.55	0.81	1.01	1.42
p–Cl	1.82	2.31	2.95	3.53
p–CN	5.80	7.20	9.20	11.20
p–NO_2	7.20	9.05	11.20	13.50

[BA] = 2.0×10^{-2} mol dm^{-3} ; [BTMAFC] = 1.36×10^{-3} mol dm^{-3}
[$HClO_4$] = 0.45 mol dm^{-3} ; AcOH – H_2O = 50% - 50% (v/v)

Table 3: Activation parameters for the oxidation of substituted benzaldehydes by BTMAFC

Substituents	E_a (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$-\Delta S^{\#}$ (J K^{-1} mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1}) (303K)	r
H	45.93	44.15	135.07	85.07	0.998
p–OCH_3	58.04	56.94	100.84	87.49	0.960
p–CH_3	48.36	45.01	136.97	86.51	0.975
p–Cl	38.33	32.11	170.43	83.75	0.996
p–CN	35.13	31.87	161.68	80.85	0.975
p–NO_2	33.72	30.03	165.98	80.32	0.997

[BA] = 2.0×10^{-2} mol dm^{-3} ; [BTMAFC] = 1.36×10^{-3} mol dm^{-3}
[$HClO_4$] = 0.45 mol dm^{-3} ; AcOH – H_2O = 50% - 50% (v/v)

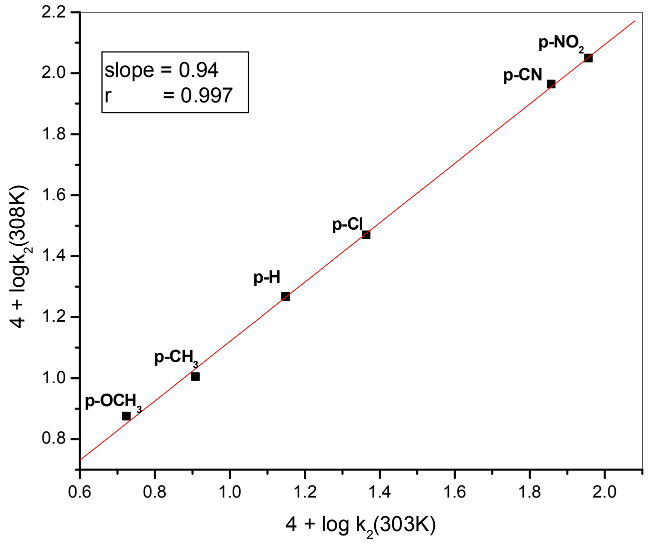


Fig. 3. Exner plot between log k_2 (308 K) versus log k_2 (303 K)

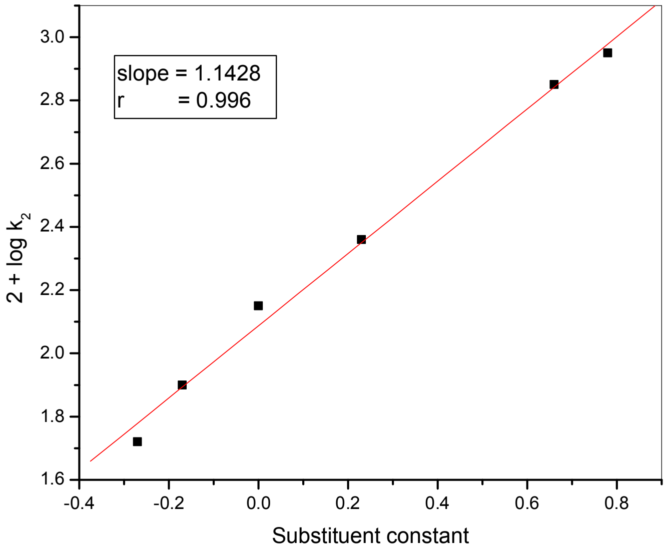


Fig. 4. Hammett Plot (at 303 K) for the oxidation of BA by BTMAFC

3.6 Isokinetic temperature

In the present study, linear plots imply the validity of the isokinetic relationship. A representative plot is shown in Fig. 3 (slope = 0.94, r = 0.999, isokinetic temperature = 415 K). The operation of isokinetic relationship reveals that all the substituted benzaldehydes examined follow a common mechanism.

3.7 Hammett plot

The Hammett plot is also linear (r = 0.996, SD = 0.06) with $\rho = +1.1428$ at 303K. According to Hammett reaction with positive ρ values are accelerated by electron withdrawal from benzene ring, whereas those with negative ρ values are retarded by electron withdrawal from benzene ring (15). In this oxidation reactions, the electron withdrawing group increases the rate and the electron donating group decreases the rate. These observations supporting the positive ρ value obtained from the Hammett plot

Conclusions: The oxidation of benzaldehyde by BTMAFC is an acid catalysed reaction and yields the corresponding benzoic acid as the product. The reaction is first order each in [Substrate], [Oxidant] and [H^+]. The stoichiometry was found to be 3 mol of aldehydes consuming 2 mol of BTMAFC. The negative values of $\Delta S^{\#}$ provided support for the formation of a rigid activated complex.

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