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# The effect of solvent on the kinetics of the oxidation of benzaldehydes by quinolinium chlorochromate in aqueous organic solvent media

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*Abstract*: The kinetics of the oxidation of benzaldehyde and *para*-substituted benzaldehydes by quinolinium chlorochromate in water-dimethylformamide mixtures has been studied under pseudo-first-order conditions at 25±0.2 °C. The operation of non-specific and specific solvent-solute interactions was explored by correlating the rate data with solvent parameters through a correlation analysis technique. Both electron-releasing and electron-withdrawing substitutents enhance the rate of oxidation and the Hammett plot shows a break in the reactivity order indicating the applicability of a dual mechanism.

Keywords: kinetics, solvent effect, structural effect, benzaldehyde, oxidation.

#### INTRODUCTION

In the last few years we have been interested in the study of solvent effects in electron transfer reactions.<sup>1–4</sup> The main conclusion from these studies is that the reactivity is influenced by preferential solvation of the reactants and/or transition state through non-specific and specific solvent-solute interactions. Furthermore, it has been established that the technique of correlation analysis may be successfully used to separate and quantify the effect of such solvent-solute interactions on reactivity.

The mechanistic pathways of the oxidation of organic compounds including substituted benzaldehydes by various Cr(VI) oxidants have been reviewed recently.<sup>5</sup> It was observed that, either the formation of a complex from the reactants or its decomposition to products were proposed as the rate determining step in the oxidation of benzaldehydes by Cr(VI) oxidants. Furthermore, these studies were often carried out in solvent mixtures containing water and protic, hydrogen bond donor (HBD) solvents such as acetic acid, *t*-butanol, *etc.* Hence, an attempt has been made to study the kinetics of the oxidation of *para*-substituted benzaldehydes by quinolinium chlorochromate (QCC) in water-DMF (aprotic, non-HBD solvent) mixtures, with the aim of obtaining a better insight into the mechanism of the reaction.

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### EXPERIMENTAL

All the chemicals and solvent used were of analytical grade. The solid benzaldehydes were used as received and the liquid aldehydes were vacuum distilled before use. Quinolinium chlorochromate (QCC) was prepared by a reported method<sup>6</sup> and its purity was checked by the iodometric method. The reactions were carried out under pseudo-first-order conditions by keeping an excess of the substrate over QCC. The progress of the reactions was followed by estimating the unreacted oxidant iodometrically at  $25.0\pm0.2$  °C. The rate constants were determined by the least squares method, from the linear plots of log [QCC] *versus* time. Duplicate runs showed that the rate constants were reproducible to within  $\pm 3$  %. The stoichiometry and product analysis were carried out as reported earlier.<sup>4</sup> Correlation analyses were carried out using Microcal Origin (version 3.5) computer software. The adequacy of the fit was discussed using the correlation coefficient and standard deviation (*sd*).

### RESULTS AND DISCUSSION

The kinetics of the oxidation of benzaldehyde and *para*-substituted benzaldehydes by QCC has been studied in various water-DMF mixtures (30-90 % v/v DMF) at 25.0 $\pm$ 0.2 °C. The observed pseudo-first-order rate constants ( $k_{obs}$ ) are given in Table I. A probable mechanism consistent with the kinetic and non-kinetic observations is given below.

 $QCC + H^+ \rightleftharpoons QCCH^+$  $QCCH^+ + Ar-CHO \rightleftharpoons [complex]$  $[complex] \rightarrow Product$ 

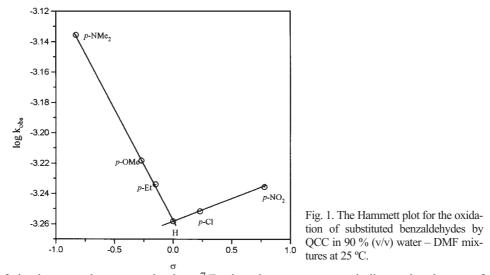
TABLE I. Pseudo-first-order rate constants  $(10^4 k_{obs}/s^{-1})$  for the oxidation of *para*-substituted benzaldehydes by QCC in water-DMF mixtures at 25.0±0.2 °C.

DMF %	Substituents in benzaldehyde						
	None	<i>p</i> -OMe	<i>p</i> -Et	<i>p</i> -NMe <sub>2</sub>	<i>p</i> -Cl	p-NO <sub>2</sub>	
30	1.02	1.57	1.26	2.12	Insoluble	2.09	
40	1.65	1.91	1.79	2.49	Insoluble	2.46	
50	2.45	2.56	2.51	2.80	Insoluble	2.77	
60	3.30	3.43	3.26	3.72	3.40	3.68	
70	3.79	3.96	3.91	4.34	3.79	3.83	
80	4.48	4.42	4.69	5.59	4.50	5.02	
90	5.52	6.05	5.84	7.32	5.60	5.81	

[Ar-CHO] = 0.02 M; [QCC] = 0.001 M; [ClCH<sub>2</sub>COOH] = 0.5 M

## Structure-reactivity correlation

Structural variation studies give a very good insight into the nature of the transition state and the mechanism of a reaction. The perusal of data given in Table I indicates that both electron-releasing and electron-withdrawing substitutents in the ring accelerate the rate of oxidation. The plot of log  $k_{obs}$  versus the Hammett's substituent constant,  $\sigma$ , shows two distinct lines (statistical data are given in Table II), for groups comprising of electron-releasing and electron-withdrawing substituents, converging at a point. A representative plot is shown in Fig. 1. The concave nature of the plot indicates that the reaction occurs by two competing mechanisms, with the susceptibility to the effect of the substituents dif-



fering between the two mechanisms.<sup>7</sup> Further, the concave curve indicates that the rate of complex formation, a process which is facilitated by the presence of electron-releasing groups, is competing with the rate of its decomposition to products, a reaction which is accelerated by the presence of electron-withdrawing groups. Due to this competition, the Hammett plot shows a break. Such anomalous curves have been reported in the oxidation of benzaldehydes by phenyliodosyl acetate<sup>8</sup> and trichloroisocyanuric acid.<sup>9</sup>

TABLE II. Reaction constants for the oxidation of *para*-substituted benzaldehydes by QCC in water-DMF mixtures at 25.0 $\pm$ 0.2 °C

DMF % (v/v)	Electron donating substituents			Electron withdrawing substituents		
	r	sd	ρ	r	sd	ρ
30	0.958	0.045	-0.360	1	0	0.399
40	0.999	0.003	-0.214	1	0	0.222
50	0.999	0.001	-0.070	1	0	0.068
60	0.963	0.009	-0.069	0.999	0.001	0.061
70	0.998	0.002	-0.069	0.958	0.001	0.006
80	0.999	0.001	-0.114	0.967	0.010	0.068
90	0.999	0.001	-0.147	0.999	0.002	0.029

r – correlation coefficient; sd – standard deviation and  $\rho$  – reaction constant

Hammett<sup>10</sup> predicted that, in general, a reaction constant is linearly related to the reciprocal of the relative permittivity ( $\varepsilon_r$ ) of the medium. However, data recorded in Table I reveals that, in the present study there is a marked deviation in the relationship between  $\rho$ and  $\varepsilon_r$ . This may be due to the fact that the  $\rho$  values, like the log  $k_{obs}$  values for the given reactants, are influenced by both non-specific and specific solvent effects.<sup>10</sup> This is an indication of the existence of specific and non-specific solvent-solute interactions.

#### Solvent-reactivity correlation

Solvent effects on the rates of reactions are as important as structural effects. The observed pseudo-first-order rate constants,  $k_{obs}$ , (Table I) are remarkably sensitive to the composition of the mixed solvent and increase with increasing mole fraction of DMF in the mixture. The effect of solvent on the reactivities may be understood from the stand point of a specific solvation effect and a non-specific solvation effect. This kind of dual dependency of reactivity on the composition of the solvent is illustrated by the Kamlet-Taft's<sup>11</sup> solvatochromic comparison method through Eq. (1). This method may be used to unravel, quantify, correlate and rationalize multiple interacting solvent effects on reactivity. Thus, the rate data were correlated with the solvatochromic parameters in the form of the following Linear Solvation Energy Relationship (LSER).

$$\log k = A_0 s \,\pi^* + a \,\alpha + b \,\beta \tag{1}$$

where  $\pi^*$  is an index of the solvent dipolarity/polarizability, which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect,  $\alpha$  is the solvent HBD (hydrogen bond donor) acidity,  $\beta$  is the HBA (hydrogen bond acceptor) basicity of the solvent in a solute to solvent hydrogen bond and  $A_0$  is the regression value of the solute property in reference to the solvent cyclohexane. The regression coefficients *s*, *a* and *b* measure the relative susceptibilities of the solvent dependent solute property log *k* to the indicated solvent parameter. The rates of oxidation for all the compounds studied show good correlation (0.962 < R < 0.987,  $0.925 < R^2 < 0.974$ , 0.04 < sd < 0.10) with the solvent *via* the above LSER. The correlation results were obtained for all the benzaldehydes studied except *p*-Cl compound for which the number of data was not sufficient for multiple regression analysis. Since the results are similar, only representative data for the *p*-NMe<sub>2</sub> compound is given in Eq. (2).

$$\log k_{\rm obs} = 9.17 + 23.19 \,\pi^* - 23.13 \,\alpha - 39.59 \,\beta \tag{2}$$

$$(N=7, R=0.987, R^2=0.974, sd=0.04 \text{ and } \psi=0.21)$$

Such a good correlation, with an explained variance of *ca*. 97 %, indicates the existence of non-specific and specific solvent-solute interactions. From the values of the regression coefficients, the contribution of each parameter, on a percentage basis, to reactivity were calculated<sup>12</sup> and are listed in Table III.

The observation of this multiple regression analysis leads to the following preliminary conslusions. i) The rate of the reaction is strongly influenced by specific solute-solvent interactions as indicated by the percentage contributions of the  $\alpha$  and  $\beta$  parameters. ii) The negative sign of the coefficients of  $\alpha$  and  $\beta$  terms suggest that the specific interactions between the reactants and the solvent, through HBD and HBA properties, is more than that between the transition state and the solvent. iii) Furthermore, the negative signs of the coefficients of  $\alpha$  and  $\beta$  terms indicate that a decrease in both the HBD and HBA property of the medium will accelerate the rate of oxidation. In the present study the rate of reaction in-

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creases with increasing mole fraction of DMF (a typical HBA solvent) in the mixture, contrary to the results of the oxidation of benzaldehydes by QCC in aqueous acetic acid medium,<sup>13</sup> where there is a decrease in the rate with increasing mole fraction of acetic acid (a typical HBD solvent) in the mixture. This may be due to the fact that the reaction occurs by two competing mechanisms (as evidenced by structural variation studies), the susceptibility to the effect of solvent differ between the two mechanisms.

Solvent parameters	Substituents in benzaldehyde						
	None	<i>p</i> -OMe	<i>p</i> -Et	<i>p</i> -NMe <sub>2</sub>	<i>p</i> -Cl	p-NO <sub>2</sub>	
α	25	26	25	26	#	27	
β	43	42	45	47	#	25	
$\pi^*$	32	31	30	27	#	48	

TABLE III. Percentage contributions of Kamlet-Tafts's solvatochromic parameters to the reactivity

<sup>#</sup>Number of data is not sufficient for multiple regression analysis

To conclude, the correlation analysis technique may be used to separate and quantify the specific and non-specific solvational effects on the title reaction. Using the above method the significance of those solvent-solvent-solute interactions on the reactivity has been established. From the regression coefficients, information on the solvent-reactant and the solvent-transition state interactions is obtained. Further structural and solvent variation studies indicate the applicability of a dual mechanism in the studied reaction.

#### ИЗВОД

# УТИЦАЈ РАСТВАРАЧА НА КИНЕТИКУ ОКСИДАЦИЈЕ БЕНЗАЛДЕХИДА ХИНОЛИНИЈУМ ХЛОРОХРОМАТОМ У СМЕШАМА ОРГАНСКОГ РАСТВАРАЧА И ВОДЕ

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Проучавана је оксидација бензалдехида и *para*-супституисаних бензалдехида хинолинијум-хлорохроматом у смешама воде и диметилформамида под условима за реакцију псеудо-првог реда на 25±0,2 °C. Дејство неспецифичних и раставарач-растворак специфичних интеракција разматрано је на основу корелације података о брзинама реакција и параметара растварача техником корелационе анализе. И електрон-донорски и електрон-акцепторски супституенти повећавају брзину оксидације, при чему Наттеt-ов дијаграм показује прелом у редоследу реактивности указујући на двојни механизам.

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