

OXIDATION OF FURFURAL BY IMIDAZOLIUM DICHROMATE IN ACID MEDIUM

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ABSTRACT

The kinetics of oxidation of furfural by imidazolium dichromate has been studied in 60% acetic acid – water (v/v) medium. The order of the reaction is found to be one with respect to oxidant and substrate. The order with respect to hydrogen ion concentration is two. Increase in ionic strength as well as dielectric constant decrease the rate of the reaction. The reaction does not induce the polymerization of acrylonitrile. The retardation of the rate by the addition of Mn^{2+} ions confirms that a two electron transfer process is involved in the reaction. The reaction rates have been determined at different temperatures and the activation parameters calculated and a suitable mechanism has been proposed.

Key words : Kinetics, Oxidation, Imidazolium dichromate, Activation parameters

INTRODUCTION

Imidazolium dichromate (IDC), one of the Cr (VI) compound, is reported to be neutral and mild selective reagent for the oxidation of allylic and benzylic alcohols to the corresponding carbonyl compounds. Kinetics of oxidation of some organic substrates^{1–3} by imidazolium dichromate have already been reported. It appears that no work has been done on furfural oxidation by IDC from kinetic view point. This prompted us to investigate the oxidation of furfural by IDC in aqueous acetic acid medium.

EXPERIMENTAL

Materials and methods: IDC was prepared by the method⁴ and its purity was checked iodometrically. 2-Furaldehyde (furfural) was distilled and the fraction collected at 162°C was used. Glacial acetic acid was purified by literature procedure⁵. All other chemicals used were of AnalaR grade. Triple distilled water was used throughout.

Kinetic measurements: The reaction was carried out under pseudo–first order conditions ($[FAL] \gg [IDC]$) in 60% (v/v) aqueous acetic acid containing perchloric acid. The reaction was followed by estimating the unchanged IDC by standard iodometric procedures. The pseudo–first order rate constants (k_{obs}) were evaluated from the linear plots of $\log [IDC]$ versus time by the least square method and these were reproducible within $\pm 2\%$.

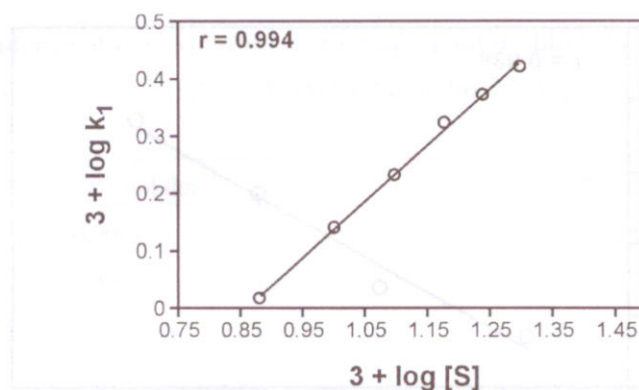
Stoichiometry and product analysis: The reaction mixtures containing an excess of the oxidant over furfural were kept at room temperature for sufficient time under the conditions employed for the kinetic runs. Estimation of the unchanged oxidant showed that one mole of oxidant reacts with one mole of furfural. After about 70% completion of the actual kinetic runs, reaction mixture was ether extracted, ether was evaporated and the residue was analysed by thin layer chromatography, and its melting point. Furoic acid was found to be the product formed in the reaction.

RESULTS AND DISCUSSION

The kinetics of oxidation of furfural by IDC was investigated at several initial concentrations of the reactants. The oxidation of furfural by IDC proceeds smoothly at 300 K in aqueous acetic acid medium. The reaction was found to be first-order with respect to the oxidant as evidenced by a good linearity in the plot of $\log [\text{IDC}]$ vs time. The pseudo-first order rate constants were found to be independent of the initial concentration of IDC. The reaction was found to be first order in substrate as evidenced by the unit slope of the plot of $\log k_{\text{obs}}$ vs. $\log [\text{FAL}]$ (Fig.1) ($r = 0.994$). The second order rate constants obtained by dividing the pseudo-first order rate constant by the respective substrate concentration were found to be constant indicating the first order dependence on substrate (Table 1).

Table 1. Dependence of the oxidation rate on IDC and furfural at 300 K

$[\text{H}^+] = 1 \text{ mol dm}^{-3}$		60% Acetic acid–water (v/v)	
$[\text{IDC}] 10^3 (\text{mol dm}^{-3})$	$[\text{FAL}] 10^2 (\text{mol dm}^{-3})$	$k_1 10^4 (\text{s}^{-1})$	$k_2 = k_1 / [\text{FAL}] 10^2$ (litre $\text{mol}^{-1} \text{s}^{-1}$)
1.50	1.00	13.26	—
2.00	1.00	13.65	—
2.50	1.00	12.98	—
3.00	1.00	13.41	—
3.50	1.00	13.52	—
4.00	1.00	13.48	—
2.00	0.75	10.53	14.04
2.00	1.00	13.65	13.65
2.00	1.25	16.98	13.58
2.00	1.50	20.89	13.93
2.00	1.75	23.44	13.39
2.00	2.00	26.30	13.15

Figure 1. A Plot of $\log k_1$ vs. $\log [S]$

There was no appreciable change in the rate with change of ionic strength indicating the involvement of a neutral molecule in the rate determining step⁶. The effect of acidity was studied by varying the concentration of perchloric acid and the rate constants were found to increase with the increase in the concentration of perchloric acid. Plot of $\log k_1$ vs. $\log [H^+]$ gave a straight line with the slope of two indicating that the protonated species of the reactant is involved in the slow step⁷ (Table 2) (Fig. 2).

Table 2. Dependence of the oxidation rate on ionic strength and $[H^+]$ at 300 K

[IDC]= 2.0×10^{-3} mol dm ⁻³ [FAL]= 1.0×10^{-2} mol dm ⁻³ 60% acetic acid–water (v/v)			
[KNO ₃] 10 ⁴ (mol dm ⁻³)	k_1 10 ⁴ (s ⁻¹)	[HClO ₄] (mol dm ⁻³)	k_1 10 ⁴ (s ⁻¹)
0.00	13.65	0.88	11.75
2.50	13.73	1.00	13.65
3.75	13.35	1.13	18.62
5.00	13.46	1.25	23.64

The rate of acid-catalysed oxidation of furfural decreases with an increase in the dielectric constant of the medium. A plot of $\log k_1$ vs. inverse of dielectric constant is linear with a positive slope (Fig. 3) suggesting an interaction between a positive ion and a dipole. This also confirms the involvement of protonated Cr (VI) species in the rate determining step (Table 3).

The reaction mixture, when allowed to stand with acrylonitrile does not induce polymerisation, suggesting the absence of free radical mechanism. On the other hand, the addition of Mn^{2+} ions retarded the reaction rate showing the two electron transfer process in the reaction (Table 4). The rate constants were measured at three different temperatures (Table 5) and the activation parameters have been calculated from the linear Eyring's plot of $\log k_2$ vs. $1/T$ by the least-squares method.

$$\Delta H^\ddagger = 22.50 \text{ kJ mol}^{-1} ; \Delta S^\ddagger = -142.49 \text{ J K}^{-1} \text{ mol}^{-1}; \Delta G^\ddagger = 65.25 \text{ kJ mol}^{-1} \text{ at } 300 \text{ K}$$

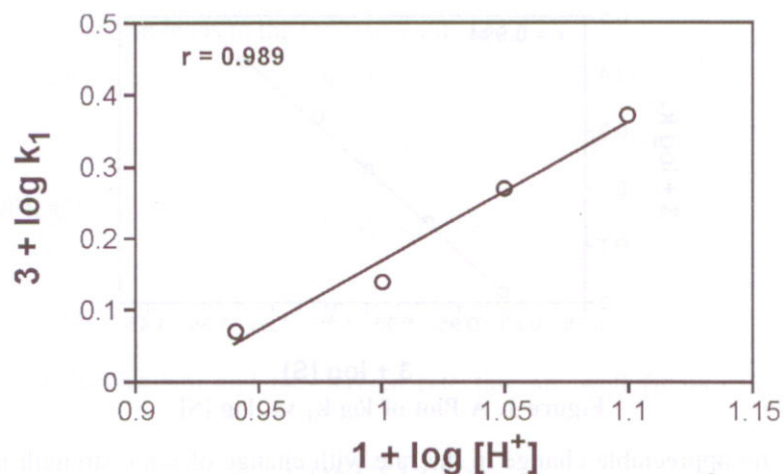


Figure 2. A Plot of $\log k_1$ vs. $\log [H^+]$

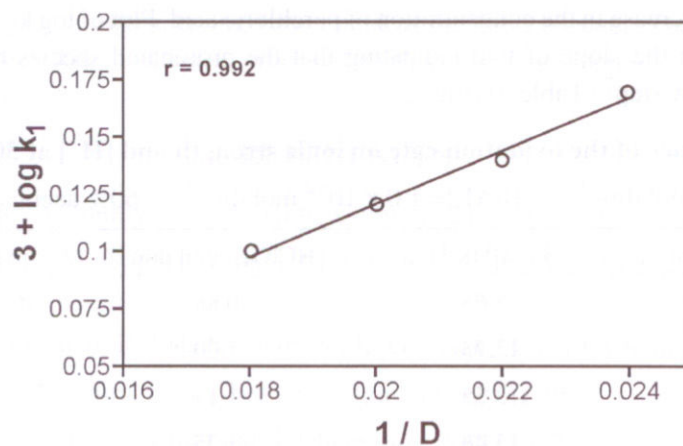


Figure 3. A Plot of $\log k_1$ vs. $1/D$

Table 3. Effect of concentration of solvent on reaction rates at 300 K in acid media

$[IDC] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[FAL] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[H^+] = 1 \text{ mol dm}^{-3}$

Acetic acid–water (% v/v)	Dielectric constant	$k_1 \text{ } 10^4 (\text{s}^{-1})$
50	56.0	12.63
55	50.8	13.18
60	45.5	13.65
65	42.0	14.79

Table 4. Dependence of the oxidation rate on manganese sulphate at 300 K

[IDC] = 2.0×10^{-3} mol dm $^{-3}$; [FAL] = 1.0×10^{-2} mol dm $^{-3}$; [H $^{+}$] = 1 mol dm $^{-3}$;
60% Acetic acid–water (v/v)

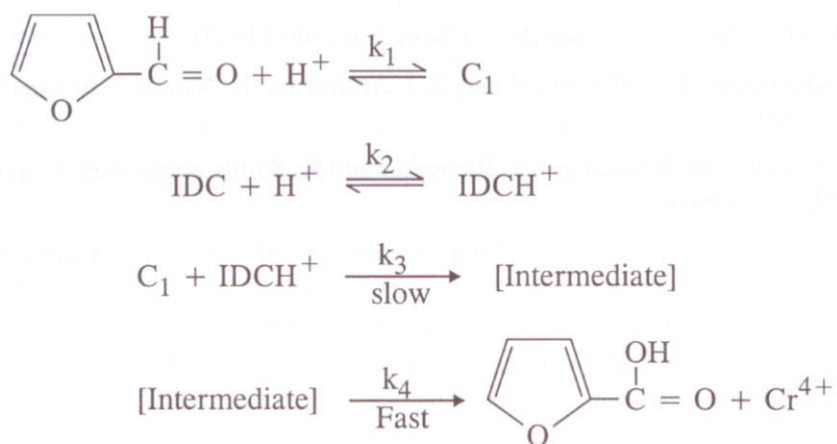
[MnSO $_4$] 10^4 (mol dm $^{-3}$)	k_1 10^4 (s $^{-1}$)
0.00	13.65
2.50	12.14
3.75	12.05
5.00	11.99

Table 5. Dependence of the oxidation rate on temperature

[IDC] = 2.0×10^{-3} mol dm $^{-3}$; [FAL] = 1.0×10^{-2} mol dm $^{-3}$; [H $^{+}$] = 1 mol dm $^{-3}$;
60% Acetic acid–water (v/v)

Temperature (K)	k_1 10^4 (s $^{-1}$)
300	13.65
313	28.61
323	47.22

Mechanism and rate law. It is clear that the reaction has first order dependence on oxidant, substrate and second order dependence on [H $^{+}$] ion. The ionic strength of the medium has a negligible effect on the reaction rate, but it increases with decreasing dielectric constant of the medium. Based on the above facts, the following mechanism has been proposed for the oxidation of furfural by imidazolium dichromate (scheme 1).

**(Scheme I)**

The above mechanism leads to the following rate law,

$$\begin{aligned}
 \text{Rate} &= k_3 [\text{IDCH}^+] [\text{C}_1] \\
 &= k_3 K_2 K_1 [\text{IDC}] [\text{H}^+] [\text{S}] [\text{H}^+] \\
 \frac{d[\text{IDC}]}{dt} &= k_3 K_2 K_1 [\text{IDC}] [\text{H}^+]^2 [\text{S}] \\
 k_{\text{obs}} &= K_1 K_2 k_3 [\text{S}] [\text{H}^+]^2
 \end{aligned}$$

The proposed mechanism and the derived rate law are well fit into the experimental observations.

CONCLUSION

The oxidation of furfural by imidazolium dichromate in aqueous acetic acid medium leads to the formation of a complex giving furoic acid as the final product. The reaction follows simple order kinetics. The mechanism proposed for this oxidation kinetics is in accordance with the observed facts.

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Accepted : 9.6.2003