


Kinetics and mechanism of the oxidation of furfural by benzimidazolium dichromate under non aqueous medium

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Abstract

The oxidation of furfural (2-furaldehyde), by benzimidazolium dichromate (BIDC) in dimethyl sulfoxide, leads to the formation of 2-furoic acid. The reaction is first order with respect to BIDC and hydrogen-ion. However, Michaelis–Menten type kinetics was observed with respect to furfural. The formation constants of furfural-BIDC complexes and the rates of their decomposition have been evaluated at different temperatures. Thermodynamic parameters of the complex formation and activation parameters for the decomposition of the complexes have been calculated. The deuterium isotope effect observed in the oxidation of furfural ($k_H/k_D = 6.23$ at 298 K) indicated an α -C-H bond cleavage in the rate-determining step. The reaction has been studied in 19 organic solvents. The analysis of the solvent effect showed that the role of cation-solvation is major. Based on the kinetic data, analysis of the solvent effect and the result of some non-kinetic parameters, a mechanism involving rate-determining oxidative decomposition of the complex, through hydride-ion transfer via a cyclic transition state, to give the corresponding product is suggested.

Keywords

kinetics, mechanism, oxidation, furfural, benzimidazolium dichromate

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Introduction

In synthetic organic chemistry, selective oxidation of organic compounds under non-aqueous conditions is an important transformation. For this purpose a number of different chromium (VI) have been reported¹⁻⁵. A new Cr(VI) derivative - benzimidazolium dichromate (BIDC) was reported in 1998⁶. This new compound is more efficient for quantitative oxidation of several organic substrates and has certain advantages over similar oxidizing agents in terms of the amount of oxidant and solvent required, short reaction time and high yields. Since BIDC is neither light sensitive nor hygroscopic, therefore, it is more stable and stored easily as compared to other Cr(VI) derivatives. It is reported⁶ to convert allylic and benzylic alcohols to corresponding carbonyl compounds with 75–98% yield from BIDC.

We get interested in the kinetics and mechanistic study of the oxidation by BIDC and a few reports have already been emanated from our laboratory⁷⁻¹³. The kinetics of oxidation of furfural have been studied in presence of acid by many reagents such as 1-Bromobenzimidazole (BBI)¹⁴, Imidazolium dichromate (IDC)⁹, Quinolinium dichromate (QDC)¹⁰, Quinolinium chlorochromate (QCC)²⁰, quinolinium fluorchromate (QFC)²¹ Nicotinic dichromate (NDC)¹⁹, Isonicotinium dichromate (INDC)²⁰, Chromic acid²¹, N-bromonicotinamide (NBN) and N- Chloronicotinamide (NCN)²² in binary mixture of acetic acid and water medium. In recent years some reports of oxidation of furfural over AuPd/Mg(OH)₂ under basic conditions²³ and with hydrogen peroxide using sulfated zirconia²⁴ have been published. Furfural base-free oxidation over Au-Pd embedded bimetallic nanoparticles²⁵, has also been reported.

In the oxidation of heteroaldehydes there exists clear feasibility of the reaction taking place either at the carbonyl function or at heteroatom. For the purpose of establish the site of reaction in the oxidation of heteroaldehyde, we have focused attention on oxidation of furfural and some substituted furfurals. A study of literature appears that there may be no report on the kinetic and mechanism of the oxidation of furfural by BIDC. In this paper, we report the oxidation kinetics of furfural by BIDC in dimethyl sulfoxide (DMSO) as solvent. Mechanistic aspects are discussed.

Experimental

Materials

BIDC was prepared by the reported method⁶ and its purity was checked by an iodometric method. Furfural (Sigma-Aldrich) was distilled and the fraction collected at 162°C was used. Other substituted furfurals were also purified by distillation under reduced pressure. Deuterated furfural (furfural-D₄) is available with high degree of purity and used as supplied. The solvents were purified by the reported methods²⁶. Among the solvents, CS₂ is a flammable liquid and toxic. Toluene *p*-sulphonic acid (TsOH) was used as a source of hydrogen ions. The solutions of TsOH were standardized by titrating them against standard alkali.

Product analysis

The oxidation of furfural leads to formation of 2-furoic acid. In this experiment, furfural (9.6 gm, 0.1 mol), TsOH (19.02 gm, 0.1 mol), and BIDC (4.54 gm, 0.01 mol) were composed to 100 ml in DMSO and it was then kept in the dark under nitrogen for a day to make sure the completion of reaction. The solution was rendered alkaline and evaporated to dryness under lower pressure. The residue was extracted three times with diethyl ether. The ether extract was dried with anhydrous

Na_2SO_4 . The product of oxidation was obtained after complete removal of ether. It was analysed by TLC, IR (KBr) and its melting point. The yield of the product formed was 84–89%.

Stoichiometry

The oxidation of furfural leads to the formation of the corresponding carboxylic acid. For stoichiometry determination, B IDC (0.005 mol) and furfural (0.001 mol) were composed to 100 ml in DMSO in the presence of 1.0 mol L^{-1} TsOH. To ensure the completion of the reaction the solution was allowed to stand for a day. Spectrophotometrically at 372 nm the residual B IDC was measured. Various observations with different concentrations of furfural showed that the reaction indicated 3:2 stoichiometry, *i.e.* three mol of furfural were consumed with two mol of B IDC. The outcomes with furfural are shown in Table 1. B IDC is reduced to Cr^{III} and participating in the reaction as a 3-electron oxidant.

Kinetic measurements

The pseudo-first-order conditions were carried out at constant temperature (± 0.1) for all kinetic runs, by maintaining a large excess of the furfural (10 fold or greater) over B IDC. The reaction was carried out under DMSO solvent, unless specified. The progress of reaction was studied by monitoring the consumption of B IDC at 372 nm for up to 80% of the reaction. The Beer's law is valid for all concentration range used in our experiments. The rate constant, k_{obs} , was evaluated from the linear ($r^2 > 0.996$) plots of $\log[\text{B IDC}]$ against time. The values observed were the mean of two or more than two runs (reproducibility $\pm 3\%$). As the measures of the goodness of fit, we have used coefficient of determination (R^2 or r^2), standard deviation (SD) and Exner's parameter²⁷, ψ , in correlation analysis.

Results

The stoichiometric determination indicated the following overall reactions for the oxidation of furfural.

Test for free radicals

The oxidations of furfurals by B IDC, under atmosphere of nitrogen, the induced polymerization of acrylonitrile was not observed. In blank experiments, with the absence of substrate, no observable consumption of B IDC was noticed. The rate of oxidation had no effect on addition of acrylonitrile

Table 1. Stoichiometry of the oxidation of furfural by B IDC.

10^3 [B IDC] (mol L^{-1})	10^3 [furfural] (mol L^{-1})	10^3 [Residual B IDC] (mol L^{-1})	Consumed B IDC] [furfural]
5.0	1.0	4.31	0.69
5.0	2.0	3.72	0.64
5.0	3.0	3.02	0.66
			Mean = 0.66 ± 0.05

Table 2. Rate constants for the oxidation of furfural by B IDC at 308 K $[H^+] = 1.0 \text{ mol dm}^{-3}$.

[Furfural] (mol L ⁻¹)	10 ³ [B IDC] (mol L ⁻¹)	10 ⁴ <i>k</i> _{obs} (s ⁻¹)			
		Furfural	5-Methyl furfural	5-Bromo furfural	5-Nitro furfural
0.010	0.5	2.3	2.53	1.9	1.4
0.025	0.5	5.5	6.11	4.5	3.4
0.045	0.5	9.4	10.6	7.8	5.8
0.060	0.5	12.0	13.6	9.9	7.5
0.090	0.5	16.9	19.0	14.0	10.5
0.150	0.5	25.1	28.3	20.7	15.6
0.250	0.5	35.0	39.9	29.0	21.9
0.150	0.8	25.6	27.9	21.2	15.4
0.150	1.0	24.7	27.4	20.9	16.0
0.150	1.5	24.3	28.8	21.5	15.8
0.150	2.0	25.2	28.1	20.4	15.1
0.250	0.5	35.8 ^a	39.5 ^a	28.6 ^a	21.6 ^a
0.250	0.5	34.4 ^b	40.6 ^b	29.4 ^b	22.2 ^b

^ac (acrylonitrile) = 0.001 mol L⁻¹.

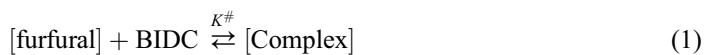
^bc (acrylonitrile) = 0.005 mol L⁻¹.

(Table 2). The reaction was executed in the presence of 0.005 mol L⁻¹ of 2,6-di-*t*-butyl-4-methylphenol (butylated hydroxytoluene or BHT) to additional confirmation of the absence of one electron oxidation during course of the reaction. The BHT did not show any considerable change and observed nearly quantitatively.

Rate laws

The reactions were found to be of first order with respect to B IDC. In individual kinetic runs, plots of log[B IDC] versus time were linear ($r^2 > 0.996$). Further, the pseudo-first-order rate constants do not depend on the initial concentration of B IDC (Table 2). The order with respect to furfural was less than one (Table 2). A plot of k_{obs} versus [furfural] is shown in Figure 1. The downward curvature of the plots suggests the existence of a complex. A plot of $1/k_{obs}$ versus $1/[furfural]$ was linear with an intercept on the rate ordinate (Figure 2). Thus, a Michaelis–Menten type kinetics was observed with respect to furfural. This leads to the postulation of following overall mechanism and rate law:

The dependence of k_{obs} on the concentration of furfural and substituted furfurals was calculated at non-identical temperatures and with the help of double reciprocal plots using Equation (4), the values of K^\ddagger and k_2 were determined. The thermodynamic parameters for establishment of complex and the activation parameters for their breaking down were calculated from the values of K^\ddagger and k_2 respectively, at non-identical temperatures (Tables 3 and 4).



$$\text{Rate} = \left[\frac{k_2 K^\ddagger (\text{furfural})(\text{B IDC})_t}{1 + K^\ddagger (\text{furfural})} \right] \quad (3)$$

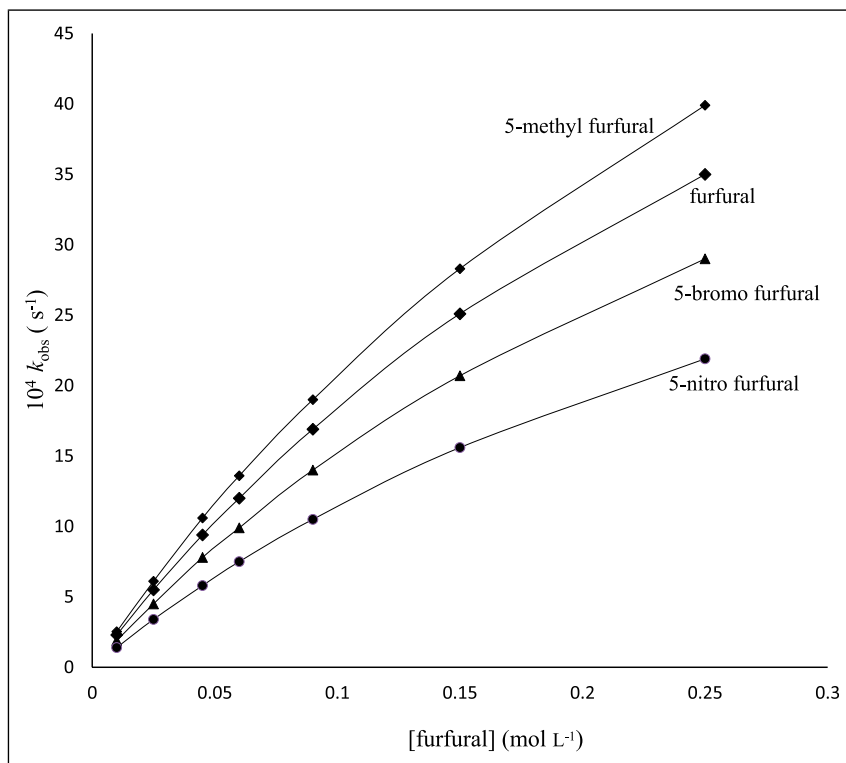


Figure 1. A plot of $10^4 k_{\text{obs}}$ versus $[\text{furfural}]$. $[\text{BIDC}] = 0.0005 \text{ mol L}^{-1}$; $[\text{H}^+] = 1.0 \text{ mol L}^{-1}$; temperature 308 K

$$\left(\frac{\text{Rate}}{(\text{BIDC})_t} \right)^{-1} = \frac{1}{k_{\text{obs}}} = \frac{1}{k_2 K^{\#} [\text{furfural}]} + \frac{1}{k_2} \quad (4)$$

$$[\text{BIDC}]_t = [\text{Complex}] + [\text{BIDC}]$$

Spectral analysis

Inspection of the spectra of BIDC and BIDC+furfural showed that there is a definite increase in the absorbance of BIDC on addition of furfural (Figure 3).

Kinetic isotope effect

To establish the importance of the cleavage of $\alpha\text{-C-H}$ bond in the rate-controlling step, the oxidation of deuterated furfural (furfural- D_4) was studied with BIDC. The findings (Tables 3 and 4) showed that the formation constants of the complexes of normal and deuterated furfural are nearly close but the rates of their decomposition indicated a primary isotope effect ($k_{\text{H}}/k_{\text{D}} = 6.23$ at 298 K). In the oxidation of benzaldehyde by BIDC¹², nearly similar value of primary kinetic isotope effect of *ca.* Six was obtained. Further, in the present study, the value of kinetic isotope effect decreases with an increase in temperature.

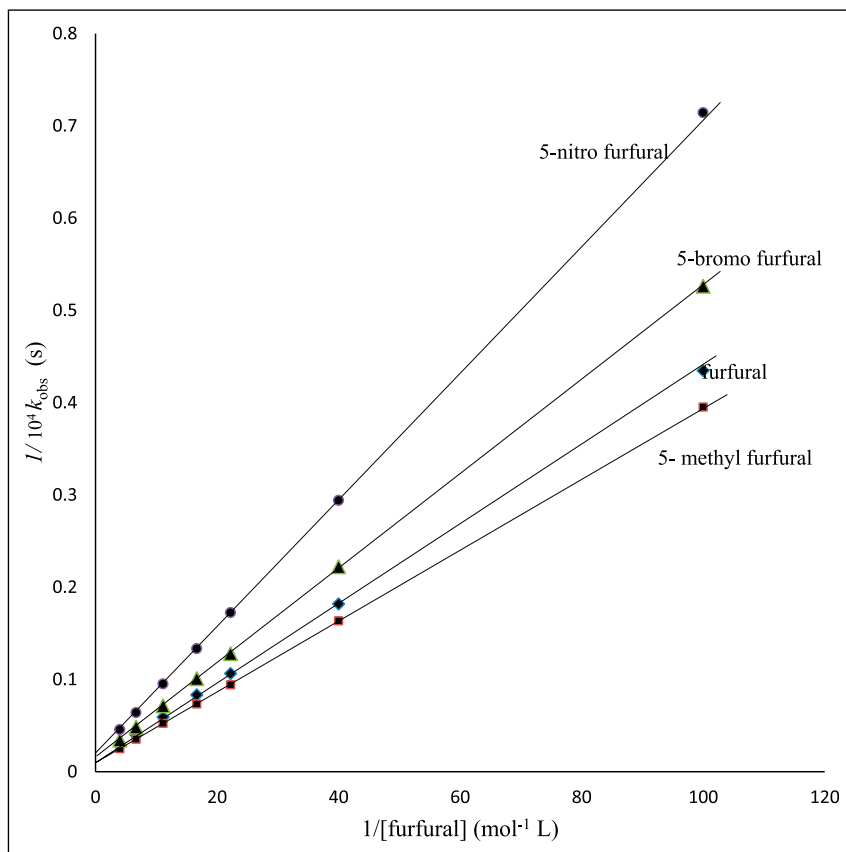


Figure 2. A plot of $1/(10^4 k_{obs})$ versus $1/[furfural]$. $[BIDC] = 0.0005 \text{ mol L}^{-1}$; $[H^+] = 1.0 \text{ mol L}^{-1}$; temperature 308 K.

Effect of acidity

The rates of oxidation favoured with an increase in acidity and the dependence is of the form: $\text{Rate} = k' [H^+]$ (Table 4). For all furfurals, order with respect to $[H^+]$ is one (Figure 4). A plot of $\log k_{obs}$ versus $\log[H^+]$, for all furfurals, exhibited the slope >0.96 and $r^2 > 0.99$.

There was no particular reaction without toluene *p*-sulphonic acid (TsOH). The dependence of the reaction rate on the concentration of furfurals were studied at three different acidities, *i.e.* $[H^+] = 0.2, 0.6, 1.0$ and 1.6 mol L^{-1} (Table 5). It was observed that formation constant, K^\ddagger , does not change considerably with the acid concentration, however, the rate of decomposition of complex, k_2 , increases linearly. Similar observations have been observed in the oxidation of aliphatic aldehyde by BIDC¹¹.

Effect of substituents

The kinetics of oxidation of some 5-substituted furfurals were studied in DMSO medium in presence of TsOH. The effect of substituent on rate is explained on the basis of resonating structures of furfural.

Table 3. Formation constants and thermodynamic parameters of furfural-BIDC complexes.

Subst	K (L mol ⁻¹)				ΔH_f	ΔS_f	ΔG_f
	298 K	308 K	318 K	328 K	kJ mol ⁻¹	J mol ⁻¹ K ⁻¹	kJ mol ⁻¹
Furfural	3.29	2.68	2.23	1.86	-17.89±0.05	42±0.16	-5.45±0.04
5-Methyl furfural	3.12	2.52	2.08	1.58	-20.59±0.86	-52±2.76	-5.35±0.67
5-Bromo furfural	3.24	2.67	2.16	2.16	-19.76±0.57	-49±1.83	-5.45±0.45
5-Nitro furfural	3.08	2.56	2.21	1.82	-16.50±0.41	-38±1.33	-5.29±0.32
furfural-D ₄	3.32	2.76	2.18	1.91	-17.9±0.64	-42±2.06	-5.47±0.50

Table 4. Rate constants of decomposition of furfural-BIDC complexes and their activation parameters.

Subst	10 ³ k ₂ (s ⁻¹)				ΔH^*	ΔS^*	ΔG^*
	298 K	308 K	318 K	328 K	kJ mol ⁻¹	J mol ⁻¹ K ⁻¹	kJ mol ⁻¹
Furfural	4.61	8.72	14.6	25.2	43.1±0.57	-88±1.84	69.21±0.45
5-Methyl furfural	5.24	10.32	16.76	29.6	43.66±1.07	85±3.45	68.87±0.84
5-Bromo furfural	4.12	7.24	12.61	21.4	42.14±0.28	-92±0.91	69.54±0.22
5-Nitro furfural	3.42	5.62	10.82	19.03	44.58±1.55	-86±4.95	70.1±1.20
Furfural-D ₄	0.74	1.48	2.61	4.79	47.63±0.60	-88±1.93	73.75±0.47
k _H /k _D	6.23	5.89	5.59	5.26	—	—	—

In these structures fifth carbon atom of furfural is an electron-deficient center. Therefore, the rate of oxidation is accelerated by electron donating substituent and retarded by electron withdrawing substituent at fifth carbon of furfural. The order of reactivity is as follows: 5-methyl > 5-Hydrogen > 5-Bromo > 5- Nitro

Solvent effect. 19 organic solvents were used to study the oxidation of furfural by BIDC. The solubility of the reactants and the reaction of BIDC with primary and secondary alcohols restricted the selectivity of solvents. With the selected solvents there was no reaction. For all the solvents kinetics was almost similar. The corresponding values of $K^{\#}$ and k_2 , are mentioned in Table 6.

Discussion

Conductivity measurements have been carried out at 308 K to determine the state of BIDC in our reaction conditions. It was noticed that DMSO has very low conductivity and the inclusion of BIDC in DMSO shows insignificant variation in the conductivity value. Therefore, under our reaction conditions, BIDC can be considered as non-ionised and does not break up as dichromate and benzimidazolium ions. The rate of oxidation does not alter on addition of benzimidazolium ion, also favours the postulation that BIDC remains as non-ionised^{13, 28}. reported the crystal structure study of BIDC, supports the non-ionic character of the oxidant in the reaction system. Two benzimidazolium rings attached with the dichromate ion via. Hydrogen bonds. BIDC forms a number of hydrogen bonds with the hydrogen donor (N-H) and hydrogen acceptor (O) in the molecule. Further, an intermolecular hydrogen bridge is unusually formed between two adjacent dichromate ions. By these hydrogen bridges the molecules are combined into infinite chains which controlled the

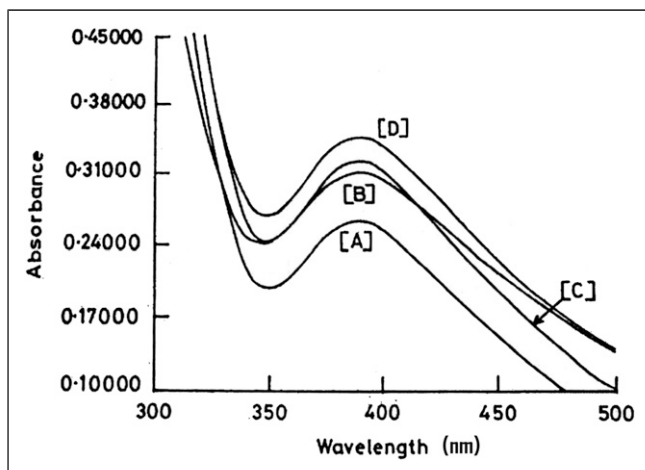


Figure 3. UV-VIS spectra of [A] 0.0005 mol L⁻¹ BIDC, [B] 0.0005 mol L⁻¹ BIDC + 0.001 furfural, [C] 0.0005 mol L⁻¹ BIDC + 0.015 furfural, [D] 0.0005 mol L⁻¹ BIDC + 0.025 furfural. Solvent: DMSO, temperature: 298 ± 1 K.

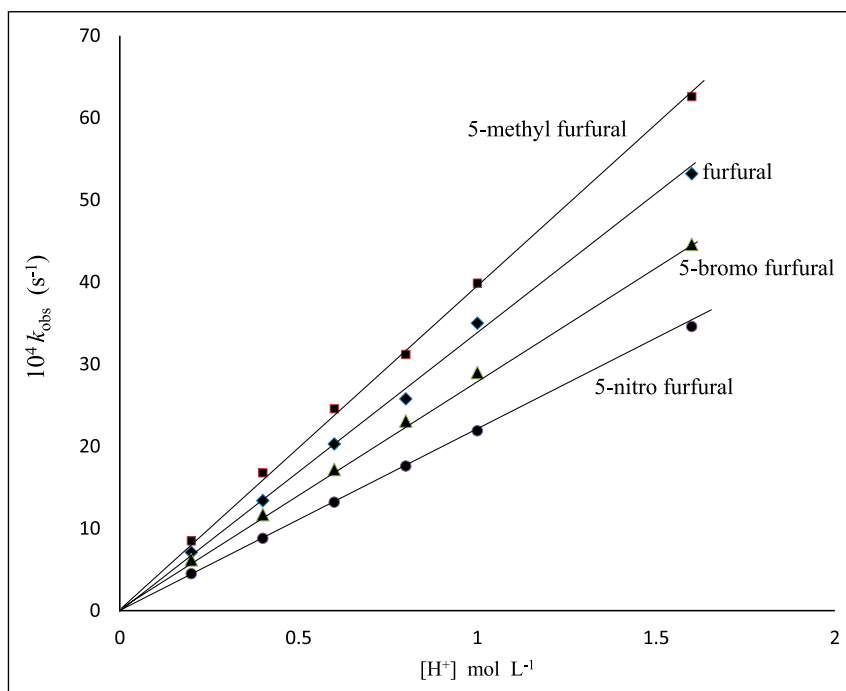


Figure 4. A plot of $10^4 k_{\text{obs}}$ versus $[\text{H}^+]$ at 308 K. $[\text{BIDC}] = 0.0005 \text{ mol L}^{-1}$ $[\text{furfural}] = 0.025 \text{ mol L}^{-1}$; temperature 308 K.

Table 5. Dependence of reaction rate of furfurals on hydrogen ion concentration. [Furfurals] = 0.025 mol L⁻¹; [BIDC] = 0.0005 mol L⁻¹; Temperature 308K.

[H ⁺] (mol L ⁻¹)	10 ⁴ k _{obs} (s ⁻¹)			
	Furfural	5-Methyl furfural	5-Bromo furfural	5-Nitro furfural
0.2	7.1	8.5	6.2	4.6
0.4	13.4	16.8	11.7	8.8
0.6	20.3	24.6	17.4	13.2
0.8	25.8	31.2	23.1	17.6
1.0	35.0	39.9	29.0	21.9
1.6	53.2	62.6	44.6	34.6

releasing procedure of dichromate ions to the reaction system and hence the compound acts as non-ionic in our reaction system.

Solvent effect

The data described in Table 6 represents that the equilibrium constant, K^\ddagger , is quite insensitive with change in solvent, however, k_2 , varies considerably. Hence, the rate constant of the decomposition of complexes, k_2 , in 18 solvents (CS₂ was not studied as the absolute span of the solvent parameters are unavailable), were correlated in terms of linear solvation energy relationship (LSER) of²⁹. But the correlations were irrelevant.

The solvent effect data were studied in connection with Swain's³⁰ equation (6), where ampere denotes the anion-solvating power of the solvent and B denotes the cation-solvating power and solvent-polarity is denoted by the term (A + B) where intercept term is denoted by C.

$$\log k = aA + B + C \quad (6)$$

The conclusion of the correlation analysis in respect of Swain's equation (6), individually with ampere and B, and with (A + B) are described as

$$\begin{aligned} \log k_2 &= 0.54 \pm 0.01 A + 1.73 \pm 0.03 B - 4.1 \\ R^2 &= 0.9999, sd = 0.003, n = 19, \psi = 0.01 \end{aligned} \quad (7)$$

$$\begin{aligned} \log k_2 &= 0.30 \pm 0.56 A - 2.92 \\ r^2 &= 0.0155, sd = 0.46, n = 19, \psi = 1.02 \end{aligned} \quad (8)$$

$$\begin{aligned} \log k_2 &= 1.68 \pm 0.09 B - 3.93 \\ r^2 &= 0.9484, sd = 0.10, n = 19, \psi = 0.23 \end{aligned} \quad (9)$$

$$\begin{aligned} \log k_2 &= 1.33 \pm 0.15 (A + B) - 4.07 \\ r^2 &= 0.8196, sd = 0.20, n = 19, \psi = 0.44 \end{aligned} \quad (10)$$

The observed results of solvent effect revealed a perfect correlation regarding Swain's equation³⁰ with both cation- and anion-solvating powers participating to the observed solvent effect. Although, the contribution of cation-solvation is greater, it alone contributes for ca. 95% of the data (A + B),

Table 6. Effect of solvent on the oxidation of furfural by BDC at 308 K.

Solvent	K (L mol ⁻¹)	10 ³ k ₂ (s ⁻¹)
Chloroform	2.32	2.40
1,2-Dichloroethane	2.73	2.97
Dichloromethane	2.27	2.84
DMSO	2.68	8.72
Acetone	2.84	2.68
Dimethylformamide	2.42	4.59
Butanone	2.16	1.98
Nitrobenzene	2.27	3.43
Benzene	2.21	0.99
Cyclohexane	2.12	0.1
Toluene	2.04	0.80
Acetophenone	2.36	3.74
Tetrahydrofurane	2.19	1.40
tert-Butyl alcohol	2.71	1.0
1,4-Dioxane	2.28	1.43
1,2-Dimethoxyethane	2.13	0.75
Ethyl acetate	1.98	1.07
Carbon disulfide	2.31	0.41
Acetic acid	2.06	0.42

represents the solvent polarity, explains *ca.* 82% of the data. Relative permittivities of the solvents were correlated with the data by considering the fact that *ca.* 82% of the data is contributed by (A+B). A plot of log k_2 versus 1/D, where D represents relative permittivity of the solvent, though, It is not linear ($r^2 = 0.5068$). This showed that the relative permittivity and solvent polarity, defined by³⁰ do not represent the same solvent characteristics.

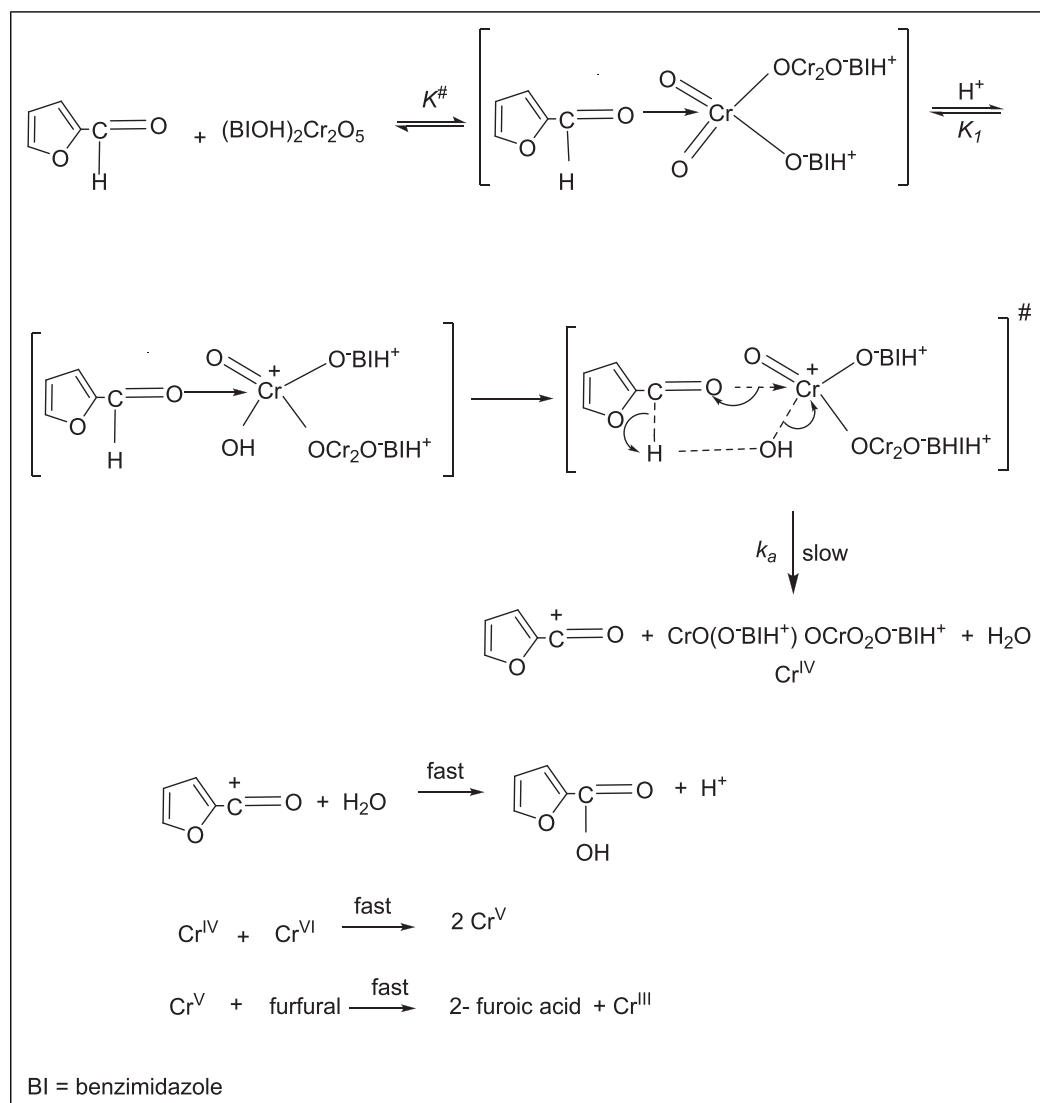
Mechanism

Considering the absence of any effect of acrylonitrile on the rate of reaction, it is unfavoured that free radical oxidation is operative in the present reaction³¹. BHT is a perfect trapping reagent for free radicals. However, BHT was recovered unchanged also goes in opposition to the existence of free radical oxidation. The formation constants of the complexes of normal and deuterated furfural are nearly same but the rates of their decomposition showed a primary kinetic isotope effect. This specifies that in furfural, the aldehydic C–H bond is cleaved in rate controlling step. Formation of electron-deficient reaction centre in the transition state is favoured by analysis of the solvent effect indicating major contribution of the cation-solvation on the rate of decomposition of the complex. It is supported by reactivity order of furfurals. Therefore, it is indicated that the removal of hydrogen as hydride-ion results in an electron-deficient species in rate controlling step. However, the observed Michaelis - Menten type kinetics with respect to furfural led to propose the formation of 1:1 complex by a nucleophilic attack of aldehydic oxygen on chromium in a fast pre-equilibrium (Scheme 1). The nature of complex suggested is similar to that reported in oxidation of aromatic aldehyde by BDC¹². The observed order of reactivity indicated that the electron-donating group at five position of furan ring, speed up the oxidation process. This is accounted in terms of an increase in

electron-availability at oxygen of the aldehydic group resulting in the facilitation of the complex formation. The observed acid-dependence of the reaction points to a fast reversible protonation of the intermediate complex proceeding to its disproportionation. A mechanism represented in account for the experimental results. Based on the proposed mechanism, rate law can be written as-

$$\text{Rate} = \frac{k_a K_1 K^\# [\text{BIDC}]_t [\text{Furfural}] [\text{H}^+]}{1 + K^\# [\text{Furfural}]} \quad (11)$$

With the help of Equations (4) and (11), we have, $k_2 = k_a K_1 [\text{H}^+]$.



Scheme 1. Mechanism of oxidation of furfural by BIDC.

Ampere hydride-ion transfer may occur either by a chromate ester or via an acyclic process. Kwart and Nickle [32] developed a method to analysis of the temperature dependence of the kinetic isotope effect, showed that the loss of hydrogen proceeds via a concerted cyclic mechanism. The data for ordinary and deuterated-furfural were expressed in a familiar manner

$$\frac{k_H}{k_D} = \frac{A_H}{A_D} \exp\left(-\frac{\Delta E_a}{RT}\right) \quad (12a)$$

or

$$\log\left(\frac{k_H}{k_D}\right) = \log\left(\frac{A_H}{A_D}\right) - \left(\frac{\Delta E_a}{2.303RT}\right) \quad (12b)$$

The activation energy difference for k_H/k_D is 4.59 kJ mol^{-1} which concluded by final results agrees with the zero-point energy gap for the C-H and C-D bonds (*ca.* 4.53 kJ mol^{-1}) and the entropy of activation (ΔS^*) of the respective reactions are almost same. This directly corresponds to the properties of a symmetrical transition state^{33,34}. Earlier, in the oxidation of benzaldehydes by B IDC¹², similar kinds of results have been noticed. Bordwell³⁵ has given strong evidence against the phenomenon of concerted one-step bimolecular process of hydrogen shifting. It is strongly recommended in the present reaction system that the hydrogen transfer does not take place by an acyclic bimolecular process. The truly symmetrical processes involving linear transfer of hydrogen are intrinsically concerted sigmatropic reactions characterized by transfer with a cyclic transition state³⁶. The shifting of two electrons in a cyclic system of the reaction was the next step of the reaction. This electrocyclic mechanism for the oxidation of furfural by B IDC involved six electrons, being a Hückel type $(4n+2)\pi$ electron system, is an allowed process³⁷. Hence, one can conclude that in the oxidation of furfural by B IDC, the hydride-ion shifting occurs via a cyclic transition state. The manner of electron transfer has to be set up. The first step includes the nucleophilic attack of aldehydic-oxygen electrons on electron-deficient chromium atom to form an intermediate complex. This complex goes.

Through unimolecular decomposition in the slow step. The transition state involves the bonding of hydrogen atom to both the OH group attached to chromium and the aldehydic-carbon. The electron flow in a cyclic transition state has been observed assuming that hydrogen is separated as hydride-ion. Therefore, the way of electron transfer occurs through the carbon-hydrogen-oxygen-chromium bond (Scheme 1). This would develop the initiation of carbocationic species by reverting back the nucleophilic attack of aldehydic oxygen. Similar kind of mechanism has noticed in the oxidation of aliphatic aldehydes by B IDC¹¹.

The proposed mechanism was favoured by the observed loss of entropy of activation. The two ends become highly solvated when the charge separation occurs in the transition state. In the transition state, this results in an immobilization of an immense number of solvent molecules, exhibited in the loss of entropy. The negative entropy also accounts for the effect of solvent.

Initially oxidation state of Chromium metal reduced from Cr(VI) to Cr(IV) and expected to react with another Cr(VI) to produced Cr(V) which is ultimately reduced in a fast step to produce Cr(III). Such a pattern of reactions in Cr(VI) oxidations is well established³⁸.

It is interesting here to compare the findings of the oxidation of the existing reaction with the results of oxidation of furfurals by other Cr(VI) complexes. The oxidation of furfural by IDC¹⁵, QCC¹⁷ and QFC¹⁸ in 60% acetic acid–water medium, exhibited first order with substrate and oxidant. However, order with respect to hydrogen ion concentration is two. The rate of oxidation increases with increase in percentage of acetic acid. The retardation of rate by addition of Mn^{+2} ions

conforms that a two electron transfer process is involved in the reaction. The kinetics of the oxidation of furfural by BBI¹⁴, QDC¹⁶ and INDC²⁰ in 50% (v/v) aqueous acetic acid leading to 2-furoic acid. The reaction was found to be first order with respect to each of oxidant, furfural and hydrogen ion. The oxidant was converted into the protonated dimetallic Cr(VI) species. The kinetic data are explained with reference to the aldehyde-hydration equilibrium. The observed results support a mechanistic pathway proceeding via a rate-controlling oxidative decomposition of the chromate ester of the aldehyde hydrate. However, Sekar et al. reported oxidation by chromic acid [18] in 70% (v/v) aqueous acetic acid exhibited first order with respect to each of oxidant, furfural and acid. Similar kind of kinetics was observed with NDC¹⁹ in 30% (v/v) aqueous acetic acid. The comparative study of oxidation kinetics of furfural by NBN and NCN²² in acetic acid medium exhibited first order with respect to substrate and inverse first order with respect to oxidant and hydrochloric acid. The reaction slowed down on adding one of the reaction products, nicotinamide (NA). The rate of oxidation increases with acetic acid percentage. Thus, it is noticed that the oxidation process depends on the nature of the oxidant and the reactions conditions.

Conclusions

The oxidation of furfural by BIDC in DMSO resulted in the formation of 2-furoic acid. The site of oxidation reaction was carbonyl function. The reaction exhibited first order kinetics with respect to hydrogen ion and oxidant. Michaelis–Menten type kinetics observed with furfural. A α -C-H bond breaking is indicated in rate controlling step. A mechanism involving the rate-controlling oxidative decomposition of complex through a hydride-ion transfer from furfural to oxidant to give end product is suggested.

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