Kinetics and mechanism of oxidation of furfural by isonicotinium dichromate

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Cinética y mecanismo de oxidación del furfural por el dicromato isonicotínico

Cinètica i mecanisme d'oxidació del furfural per el dicromat isonicotínic

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RESUMEN

La cinética de oxidación del furfural por el dicromato isonicotínico (INDC) se ha estudiado en un medio de ácido acético-agua al 50% *(v/v)* en presencia de ácido perclórico a 303ºK. La reacción es de primer orden en la concentración de dicromato isonicotínico, furfural e ion hidrógeno. La velocidad de oxidación aumenta al disminuir la constante dieléctrica del disolvente, lo que sugiere una interacción ion-dipolo. El incremento de la resistencia iónica por la adición de perclorato de sodio no tiene ningún efecto en la constante de velocidad. No existe polimerización con el acrilonitrilo y se ha comprobado la ausencia de radicales libres. El ácido furoico se ha identificado como el producto de oxidación. La velocidad de la reacción se ha llevado a cabo a cuatro temperaturas distintas y se han calculado los parámetros de activación. A partir de los resultados cinéticos observados, se ha propuesto un mecanismo adecuado a la normativa.

Palabras clave: Cinética; oxidación; parámetros de activación.

SUMMARY

The kinetics of oxidation of furfural by isonicotinium dichromate (INDC) has been studied in a 50% *(v/v)* acetic acid- water medium in the presence of perchloric acid at 303 K. The reaction is first order each in [isonicotinium dichromate], [furfural] and hydrogen ion concentration. The rate of oxidation increases with decrease in dielectric constant of solvent suggests ion-dipole interaction. Increase in ionic strength by the addition of sodium perchlorate has no effect on the rate constant. There is no polymerization with acrylonitrile and absence of free radical was proved. Furoic acid has been identified as the product of oxidation.The rate of the reaction has been conducted at four different temperatures and activation parameters were calculated. From the observed kinetic results, a suitable mechanism with rate law has been proposed.

Key words: Kinetics; oxidation; activation parameters.

RESUM

La cinètica d'oxidació del furfural per el dicromat isonicotínic (INDC) s'ha estudiat en un mitjà de àcid acètic – aigua al 50% *(v/v)* en presència d'àcid perclòric à 303ºK. La reacció es de primer ordre en la concentració de dicromat isonicotínic, furfural e ió hidrogen. La velocitat d'oxidació augmenta quan disminueix la constant dielèctrica del dissolvent, i això suggereix una interacció ió-dipol. L'increment de la resistència iònica per la adició de perclorat de sodi no te cap efecte en la constant de velocitat. La polimerització amb l'acrilonitril no existeix i s'ha comprovat l'absència de radicals lliures. L'àcid furoic ha sigut identificat com el producte d'oxidació. La velocitat de la reacció ha tingut lloc a quatre temperatures diferents i s'han calculat els paràmetres d'activació. A partir dels resultats cinètics observats, s'ha proposat un mecanisme adient amb la normativa.

Paraules clau: Cinètica; oxidació; paràmetres d'activació.

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INTRODUCTION

Chromium compounds have been used in aqueous and non aqueous medium for the oxidation of a variety of organic compounds[1]. Chromium especially, Cr (VI) reagents have been proved to be versatile reagents and capable of oxidizing almost all the oxidisible organic functional groups[2-4]. Numerous reagents and experimental procedures have been developed to carry out this transformation[5]; in particular reagents containing chromium (VI) reactive species are widely used for the oxidation of alcohols to carbonyl compounds[6-7]. Kinetics of oxidation of furfural by imidazolium dichromate in aqueous acetic acid has already been studied[8]. However, the kinetics of oxidation of furfural by isonicotinium dichromate has not been reported. Moreover, isonicotinium dichromate is not hygroscopic and also not suffered from photosensitivity. Isonicotinium dichromate is isomer of nicotinium dichromate. Carboxyl group is on the 4-position in isonicotinium dichromate. It is a new, mild, efficient and stable reagent which is able to work as oxidizing reagent. Hence, in the present investigation, the oxidation of furfural by isonicotinium dichromate in aqueous acetic acid medium and the corresponding mechanistic aspects are reported.

EXPERIMENTAL

Materials

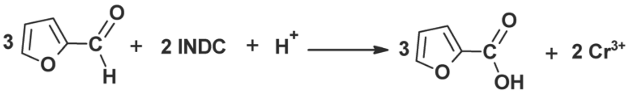
Isonicotinium dichromate was prepared by literature method[9] as nicotinium dichromate. Furfural was distilled and the fraction collected at 162 °C. Acetic acid was purified[10] by standard method and the fraction distilling at 118 °C was collected. All other chemicals used were of AnalaR grade. The solutions were prepared in triple distilled water.

Kinetic measurements

The kinetic studies were carried out under pseudo-first order conditions in 50% *(v/v)* aqueous acetic acid with the concentration of the furfural in large excess compared to that of the oxidant. All reactant solutions were placed in a thermostated water bath for one hour to attain a temperature of 30 °C. Appropriate quantities of the reagent solutions were mixed in a 250cm^3 conical flask already placed in the thermostated bath. The reaction rate was followed by measuring the decrease in absorbance at 470nm for upto 80% of the reaction by systronics UV-visible spectrophotometer. The reaction was completed when the isonicotinium dichromate solution turned from yellow to green. The reactions were followed by determining the concentration of the unreacted INDC, for known intervals of time. The pseudo-first order rate constants k_1 computed from the linear plots of log absorbance *versus* time by the least squares method were reproducible within ±3 %.

Stoichiometry and product analysis

The reaction mixture containing an excess of oxidant over furfural were kept at room temperature in the presence of perchloric acid for 24 h. Estimation of the unreacted oxidant showed that three mole of furfural consumed two mole of the oxidant.



Furfural (0.1 mole) and INDC (0.1 mole) were mixed together with perchloric acid in 50% (v/v) aqueous acetic acid. The reaction mixture was set aside for about 24 h to ensure completion of the reaction. It was then evaporated and extracted with ether. The ether layer was dried over anhydrous sodium sulphate and then evaporation of the ether layer gave the liquid product. The liquid product was confirmed as furoic acid by Infra-red, Gas-Chromatography- Mass spectra (IR,GC- MS).

RESULTS AND DISCUSSION

Oxidation of furfural by isonicotinium dichromate has been conducted in 50% acetic acid and 50% water medium at 303 K under pseudo-first order conditions and the observed results were discussed in the following pages.

The order of the reaction with respect to isonicotinium dichromate was found to be unity as shown by the linearity of log absorbance *verses* time plots. (Table I). At constant concentrations of substrate and perchloric acid, the increase in concentration of isonicotinium dichromate did not affect the rate of reaction (Table. I) The linear constancy in the value of k_1 irrespective of the concentration of the isonicotinium dichromate confirms the first order dependence on isonicotinium dichromate. The varying the concentration of fufural at 303 K and keeping all other reactant concentration as constant and the rates were measured (Table I). The rate of oxidation increased progressively on increasing the concentration of furfural. The plot of log k_{obs} *versus* log [furfural] gave the slope of 0.89(r= 0.999), shows that the oxidation reaction was first order with respect to furfural.

The reaction was followed with different concentrations of perchloric acid and keeping all the concentrations as constant and rate were measured(Table I). The rate of the reaction increases with the increasing the concentration of H$^+$. A plot of log k_{obs} *versus* log [H$^+$] gave a straight line with a slope of 0.86 which indicates first order with respect to hydrogen ion concentration. The change in ionic strength by the addition of sodium perchlorate has no effect on the rate constant (Table I) indicating the involvement of a neutral molecule in the rate determining step.

Table I. *Rate constant for the oxidation of furfural by isonicotinium dichromate at 303 K.*

[Furfurall]× 10^1 *mol dm^{-3}*	[INDC] ×10^3 *mol dm^{-3}*	[HClO$_4$] ×10^1 *mol dm^{-3}*	[NaClO$_4$] ×10^4 *mol dm^{-3}*	[ACOH-H$_2$O] (% v/v)	[AlCl$_3$] ×10^4 *mol dm^{-3}*	k_{obs} × 10^4 *s^{-1}*
3.0-5.0	3.0	0.5	-	50	-	1.23-2.04
4.5	3.0-4.5	0.5	-	50	-	1.66-1.60
4.5	3.0	0.5-2.0	-	50	-	1.66-4.10
4.5	3.0	0.5	0-7.5	50	-	1.66-1.59
4.5	3.0	0.5	-	50-65	-	1.66-3.01
4.5	3.0	0.5	-	50	0-7.5	1.66-0.23

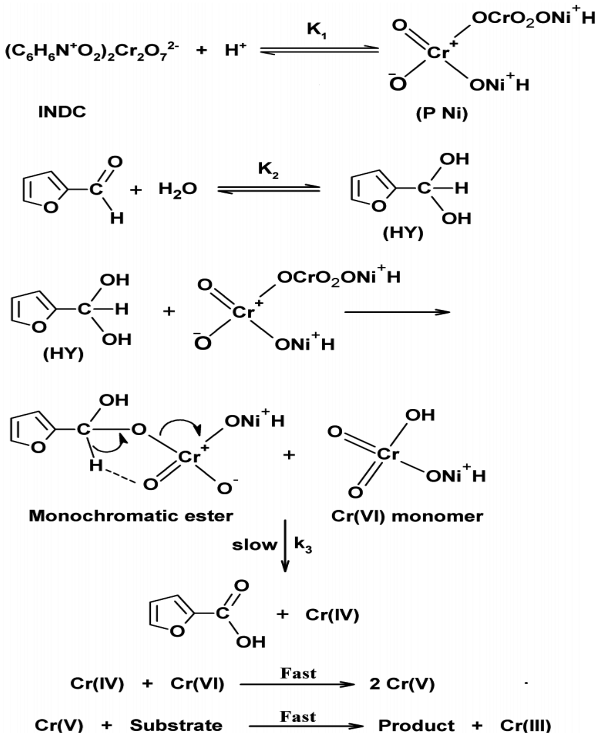
The effect of solvent composition on the reaction rate was studied by varying the concentration of acetic acid 50%-65%. The reaction rate increases with the increase in the proportion of acetic acid in the medium. When the acetic acid content increases in the medium, the acidity of the medium is increased where as the dielectric constant of the medium is decreased suggesting ion-dipole interaction[11,12] The clear mixture containing furfural and isonicotinium dichromate when allowed to stand with a drop of acrylonitrile[13] no turbidity is formed suggesting the non involvement of free radicals in this reaction.

The rate constants were measured at four different temperature and the activation parameters were computed from a plot of ln k_2 / T *versus* 1 / T of the Eyring's equation[14] and it was found to be linear[15]. This negative value of entropy of activation *($\Delta S^{\#}$)* indicates a polar transition state with extensive charge separation which promotes high degree of solvation of the transition state compared to the reactants. The rate constant and thermodynamic parameters are tabulated in Table II.

Table II. *Dependence of rate constant on temperature and activation parameters*

Temperature (K)	k_1 x 10^4 (s^{-1})	Activation Parameters
303	1.66	$\Delta H^{\#}$ =20.68 kJ mol $^{-1}$
308	1.84	$\Delta S^{\#}$ = -126.404 JK^{-1} mol^{-1}
313	2.06	$\Delta G^{\#}$ = 58.93 kJ mol^{-1} at 303 K
318	2.44	Ea = 23.20 kJ mol^{-1} at 303 K

[INDC] = 3.0× 10^{-3} mol dm^{-3} [$HClO_4$] = 0.5×10^{-1} mol dm^{-3}
[Furfural]= 4.5×10^{-1} mol dm^{-3} AcOH –H_2O = 50 -50 %(v/v)



Scheme I

Mechanism and Rate law

The order with respect both INDC and furfural was first order. The addition of sodium perchlorate or acrylonitrile had an insignificant effect on the rate of the reaction. The observed stoichiometry for the reaction was 3:2 and the oxidation product is furoic acid.Based on the experimental results, a probable mechanism and rate law for the oxidation of furfural by isonicotinium dichromate is given below.

The mechanism of reactions for the oxidation of furfural by INDC in an acid medium is shown in scheme I. In acid medium, the oxidant INDC is converted to the protonated bimetallic chromium(VI) species (P Ni) in the acid range used for the present investigation, the protonated INDC would have the Cr(VI) existing mainly as $Cr_2O_7^{2-}$. The substrate is converted to the hydrated form (HY). The reaction of the hydrated form (HY) of the substrate with the protonated INDC resulted in the formation of the monochromatic ester which under decomposition in the rate determining step gives the product. In order to know whether the reaction follows a three electron transfer process, the rate of the reaction was followed with various initial concentrations of $AlCl_3$ at constant concentration of substrate, oxidant and perchloric acid. The rate decreases, it is as an evidence for a three electron transfer process in this reaction. Based on the experimental results, the mechanism shown in Scheme I.

The rate law has been derived as follows

$$\frac{-d\,[INDC]}{dt} = k_3\,[E] = k_3\,[HY]\,[PINDC]$$

Where
[PINDC] = K_1[INDC] [H^+]
[HY] = K_2 [s] [H_2O]
Substitute the values of [PINDC] and [HY]
The following equation was obtained

$$\frac{-d\,[INDC]}{dt} = K_1K_2k_3\,[S]\,[INDC]\,[H^+]$$

From this rate expression, it is clear that the reaction exhibited a first order dependence with respect to the concentrations of each furfural, isonicotinium dichromate and H^+.

CONCLUSION

The oxidation of furfural by INDC is of first order with respect to INDC, furfural and H^+. Under the employed experimental conditions, furfural is oxidized to furoic acid. The stoichiometry was found to be three mole of furfural consuming two mole of isonicotinium dichromate. The negative entropy of activation suggests the formation of the complex in the slow step.

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