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Oxidation of Cinnnamic acid by Bipyridinium chlorochromate – Rate Determination at Various Concentration of Bipyridinium chlorochromate

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Abstract

The kinetics of oxidation of cinnamic acid by BPCC in aqueous acetic acid (50%-50% v/v) in the presence of sulphuric acid has been studied. In order to arrive at a correlation between the synthetic efficacy and structure of reagent, the kinetics of oxidation of cinnamic acid with BPCC has been carried out in aqueous acetic acid. The reaction exhibit first order dependence on both the oxidant and substrate concentrations. In this part we have studied oxidation of cinnnamic acid by bipyridinium chlorochromate and determined rate at various concentration of bipyridinium chlorochromate.

Keywords: BPCC, Cinnamic Acid, Correlation, First Order, Mechanism

1. Introduction

A great variety of compounds containing chromium (VI) have proved to be versatile reagents capable of oxidising almost every oxidisable organic functional group[1]. Chromic acid is the most popular reagent of this type used in organic chemistry for well over a century. In the last two decades, however a number of new chromium (VI) containing reagents together with special reaction condition have been developed to improve the selectivity of oxidation and to deal with complex, highly sensitive compounds[1a-1f].

1.1 Chemistry of Chromium (VI)

One of the most important chromium (VI) derivatives is chromium trioxide. It may be obtained as an orange-red highly poisonous precipitate on adding sulphuric acid to aqueous solution of sodium or potassium dichromate, or on evaporating the water from a reaction mixture of sodium dichromate dihydride and concentrated sulphuric acid. The structure of chromium trioxide has been determined by X-ray analysis[2] to be a linear polymer of chromium and oxygen atoms with two additional oxygen atoms linked to each chromium trioxide dissolves in water with accompanied depolymerisation.

$$(CrO_3)\ n + nH_2O \rightarrow nH_2CrO_4$$

The so formed chromic acid is fairly strong acid[3].

It has also been suggested that chromium (VI) dissolved in acetic acid solutions may exist in the form of an acetyl chromate ion.

$$HCrO^-_4 + HOCOCH_3 \rightarrow OCrO_2OCOCH_3 + H_2OOCrO_2OOCCH_3$$

Complex formation between chromic acid and an anion results in a change in the dissociation constant; the more electron withdrawing anion, the large dissociation constant appear to be, thus the order of increasing effect on the constant for the above reported species is

$$H_3PO_4 < HCl < H_2SO_4{}^4$$

Several salts $M(CrO_3\ X)$ have been described (X-halogen, M-alkaline metal (or) ammonium). For

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example potassium chlorochromate can be prepared as orange crystals simply by dissolving potassium dichromate in hot 6M hydrochloric acid[1g-1i]. By adding an organic heterocyclic base to the aqueous solution of chlorochromic acid the corresponding salts may be obtained as coloured crystalline solids:

$HCrO_3Cl + B: \rightarrow BH^+CrO_3Cl^-$

B: - heterocyclic base.

Pyridinium chlorochromate (PCC) and Bipyridinium chlorochromate (BPCC) which represent useful oxidising reagents are examples of this kind of compounds[2].


(PCC) (BPCC)

Figure 1.

Another type of chromium (VI) compound arises from the Lewis acid properties displayed by chromium trioxide. Chromium trioxide indeed forms many adducts with organic heterocyclic bases of general formula CrO_3. Base, in which the base may be, eg pyridine(1),dimethyl pyrazole(2) or picoline or quinoline(3)

$CrO_{3\,+}$ 2 Base $CrO_{3.}$2 Base

Base =

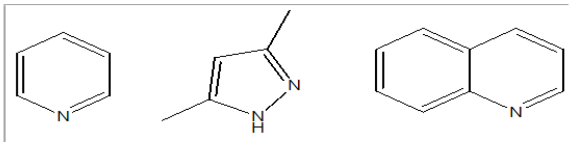
(1) (2) (3)

Figure 2.

etc

Some of these adducts for example the chromium trioxide – (Pyridine)2 adduct which is easily obtained by simple mixing the components at room temperature, represent useful reagent for the oxidation of the organic compounds under mild conditions[3].

2. Bipyridinium chloromate (BPCC) as Oxidant in Organic Chemistry

The oxidation of glycolic, lactic, malic and a few substituted mandelic acids by BPCC in dimethyl sulphoxide lead to the formation of corresponding oxoacid. The reaction is first order each in BPCC and the hydroxyl acid. The reaction is catalysed by hydrogen ions. The hydrogen ion dependence has the form $K_{obs} = a+b\,[H^+]$. The oxidation of deuteriomandelic acid exhibited a substantial primary kinetic isotope effect ($K_H/K_d = 5.29$ at 303 K). The oxidation of p-methylmandelic acid was studied in 19 different organic solvents. The solvent has been analysed by using Kamlet's and Swain's multiparametric equation. A mechanism involving a hydride ion transfer via a chromate ester proposed[19,4-6].

3. CrVI - Phenanathroline Complex as Oxidant

Catalytic activity of 1, 10 – phenanthroline (phen) in the HCrO4 oxidation of substituted trans cinnamic acids to the corresponding benzaldehydes, has been investigated in acidic medium. The CrVI – phen complex is believed to be the probable electrophile in the catalyzed oxidation. The catalytic activity is quite likely to be due to the shift in redox potential of the oxidant. Pyridine has no effect in this conversion. The catalytic efficiencies of pyridine bases are compared. Nonadherence to LFER studies; resulting in a continuously changing Hammett curve, gives an insight into the nature of the transition state.

4. Scope of the Present Work

The reagent 2, 2'-bipyridinium chromate (BPCC) was introduced by G. Cardillo as an oxidising agent in oxidation of several compounds. The reagent quinolinium chlorochromate (QCC) is also one of the novel oxidising agents in organic chemistry. Several works were carried out on the oxidation of cinnamic acid using Cr VI. In order to find out the order with respect to oxidant, substrate and acid and to suggest the mechanism of oxidation of cinnamic acid, the reaction is studied using BPCC and QCC. The effect of solvent is also studied to find out the nature of reaction .Thermodynamic parameters are also evaluated by studying the reaction at three different temperatures[7].

5. Experimental Work

5.1 Purification of Materials

5.1.1 Acetic acid

Acetic acid (AR grade) was refluxed with potassium dichromate and a small quantity of acetic dride. The solid that separate out were filtered off and the acid was distilled from an all glass apparatus. Large head and tail fractions were rejected and the fraction distilling at 118 °C (d_4 = 1.038, nD^{30} = 1.368) was collected and used.

5.1.2 Perchloric acid (AR)

This was pure and standardized after appropriate dilution by titrating against standard sodium carbonate using methyl orange as the indicator[8-10].

5.1.3 Sulphuric acid (AR)

This was pure and standardized after appropriate dilution by titration against standard sodium carbonate using methyl orange as the indicator[26].

5.1.4 Chromium (IV) oxide (E. Merck)

Chromium (VI) oxide was twice recrystallized from conductivity water.

5.1.5 Potassium dichromate (BDH ANALAR)

This was heated to 130 °C for an hour in an air oven, was cooled and preserved in desicator.

5.1.6 Bipyridine

CDH sample was used as such.

5.1.7 Cinnamic acid

LOBA CHEMIE sample was used as such.

6. Preparation of 2.2'-Bipyridinium Chloro Chromate

The reagent was prepared by the procedure of G. Cainelli and G. Cardillo. To 18 cc of 6M HCl (0.11 M) was added 10 g of CrO_3 (0.1 mole) rapidly with stirring. After 5 min, the homogeneous solution was cooled to 0˚C and 9.2 g of bipyridine (0.1 M) was carefully added over 10 min. Recooling to 0˚C gave a yellow crystalline solid which was cooled on a sintered glass funnel and dried for 1 hour in vacuo. The solid is non hygroscopic and air stable and still effective after 3 months of storage[21].

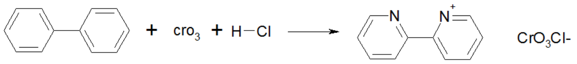

Figure 3.

$(C_5H_4N)_2$
Guziec F. S., Jr. LUZZIO, F. A syn 1980, 691.

7. Kinetic Method

All the standard flask and reaction bottles were of pyrex glass and the stoppers were all ground[25]. The loss of solvent was found to be negligible. The pipettes used were duly standardised. An electrically operated thermostat was used. It was provided with sufficient thermal lagging, suitable heaters and Stirrers with proper cooling arrangements for continuous work[11]. Jacksoin thermometers (A Gallen kemp, England) working in conjunction with sunvic electronic relay maintained the temperature accurately with fluctuations not more than 0 K temperature were recorded by a sensitive thermometer reading to tenths of a degree[24]. The bath liquid was water which was covered with a thin layer of paraffin oil to maintain heat loss due to evaporation at the minimum. The standard stock solutions of chromium (VI) were prepared by dissolving a known weight of pure oxidants (PCC and QCC) in acetic acid and were standardized iodometrically.

7.1 Velocity Measurements

The rate of oxidation of cinnamic acid by hexavalent chromium (VI) reagents employed in the presence study was followed titrimetrically. In a typical kinetic run, the substrate and the chromium (VI) solution of appropriate concentrate were prepared in suitable composition of solvent medium (50 % HOAC – 50 % H_20). These solutions were thermostated. After allowing sufficient time, for thermal equilibrium to be obtained, the reaction was initiated by adding a requisite amount of chromium (VI) solution.

The solution was shaken for proper mixing. The instant of half delivery of the oxidant solution was taken as zero time. The reaction was followed by pipetting out 5 cc of the reaction mixture at various intervals of time. Here also the half delivery correction was applied. The aliquots were mixed with potassium iodide in the presence of sulphuric acid and the iodine liberated was titrated against sodium thiosulphate solution. The pseudo first order rate constants were calculated from the slopes of the plots of log (a – x) versus time. The integral rate equation.

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Where the letters have their usual significance consistently it was found that the rate constants were reproducible[20-23]. All the first order rate constants are expressed in sec^{-1}. In all the cases where rate determination were done at three different temperature activation energies were obtained using least square equation[12].

7.2 The Thermodynamic Function of Activation

According to the theory of absolute reaction rate given by Glasstone, Laidler and Eyring the rate constants K_r of the reaction can be expressed as

$$K_r = \frac{K_B Tk}{h} = \frac{K_B T}{h} e^{-\Delta G \neq \int RT}$$

Where

K_B is Boltzmann constant,

h is Plank's constant,

K≠ is the equilibrium constant of the reaction between the reactants and activate complex $\Delta G^{\neq}$, the standard free energy of activation[19]. The value of $\Delta G^{\neq}$ can be got from the relation, $\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$ where $\Delta H^{\neq}$ is the enthalpy of and $\Delta S^{\neq}$ is the entropy of activation. These are known as the parameters of thermodynamics.

For reactions in solution, the heat ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) of activation can be calculated from the experimentally determined value of parameters of Arrhenius equation. The activation energy (E_a) is evaluated from the method of least squares. The other parameters were calculated from the following expressions:

$$\Delta H^{\neq} = E_a - RT$$

$$\frac{\Delta S^{\neq}}{4.576} = \log K_r - 10.753 - 2.496 + \frac{E_a}{4.576\text{xT}}$$

$$\Delta G^{\neq} = \Delta H^{\neq} - Tx\Delta S^{\neq}$$

8. Results of Oxidation of Cinnamic acid by BPCC

8.1 Oxidation of Cinnamic acid by BPCC

The results of oxidation of cinnamic acid by BPCC are presented below:

8.1.1 Order with Respect to BPCC

The first order dependence of rate on concentration of BPCC is clearly shown by the plot of log (a-x) Vs time (figure 1) which is found to be linear[13,15-18]. Further the constancy in the value of k, over a range of BPCC concentration confirm the fact that order with respect to BPCC is unity (Table 1)

[Cinnamic acid] = 4.73 $x10^{-2}$ M

50% HOAC -50% H_2O (v/v)

$[H_2SO_4]$ = 1.07 $x10^{-1}$ M

Temperature = 313 ± 0.1K

Table 1.

10^3(BPCC)M	10^4 $K_1(s^{-1})$
5.12	0.817
7.68	0.869

Order with Respect to BPCC

[CA] = 4.73 X 10^{-2} M

Solvent = 50 % Aq. HOAc

Temp. = 313± 0.1K

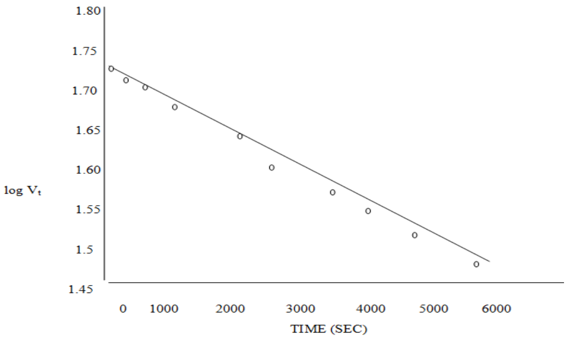

Figure 4.

8.1.2 Effect of Variation of Cinnamic acid

The dependence of rate on concentration of cinnamic acid is found to be unity by linearity of plot of log k1 Vs log [cinnamic acid] with slope equal to unity (figure – 2 Table – 2)

[BPCC] = 5.12 x 10^{-3} M
50 % HOAC – 50 % H_2O
[H_2SO_4] = 1.07 X 10^{-1} M
Temp = 313 ± 0.1 K

Table 2.

10^2(cinnamic acid) M	$10_4 k_1 (S^{-1})$
4.73	0.82
5.90	0.94
7.10	1.1

8.1.3 Dependence of Rate on Acidity

Dependence of rate on varying perchloric acid concentration on the oxidation of cinnamic acid by BPCC is given in Table 3

The reaction is found to be acid catalysed and the plot of log k_1 Vs log [acid] is linear (figure 3).

[Cinnamic acid] = 4.73 x10^{-2} M
50% HOAC -50% H_2O (v/v)
[BPCC] = 5.12 x10^{-3} M
Temperature =313 ± 0.1K

Table 3.

(10^1) perchloric acid M	10^4 $k_1(s^{-1})$
2.03	2.44
3.05	3.60
4.07	4.13

Effect of Variation of [CA]
[BPCC] = 5.12 X x10^{-3} M Solvent = 50 % Aq. HOAc
Temp. = 313± 0.1K

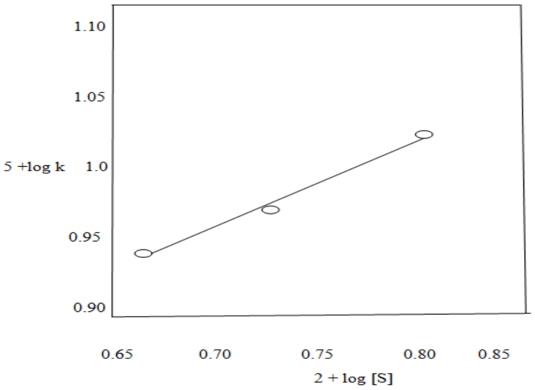

Figure 5.

9. Summary

The kinetics of oxidation of cinnamic acid by BPCC in aqueous acetic acid (50%-50% v/v) in the presence of sulphuric acid has been studied. In order to arrive at a correlation between the synthetic efficacy and structure of reagent, the kinetics of oxidation of cinnamic acid with BPCC have been carried out in aqueous acetic acid. The reaction exhibit first order dependence on both the oxidant and substrate concentrations[14-17]. The order with respect to sulphuric acid is unity. The rate of reaction is enhanced by increasing the acetic acid content of the medium. The experimental observations indicate that BPCC is an effective oxidising agent, in the oxidation of cinnamic acid. Based on the experimental investigation s, a possible mechanism is proposed for the oxidation of cinnamic acid using BPCC.

It was found that the rate of oxidation of cinnamic acid using BPCC is increased with increase of concentration of cinnamic acid.

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