

A KINETIC STUDY OF OXIDATION OF ORGANIC SUBSTRATE BENZYL ALCOHOL BY QUINOXALINIUM DICHROMATE

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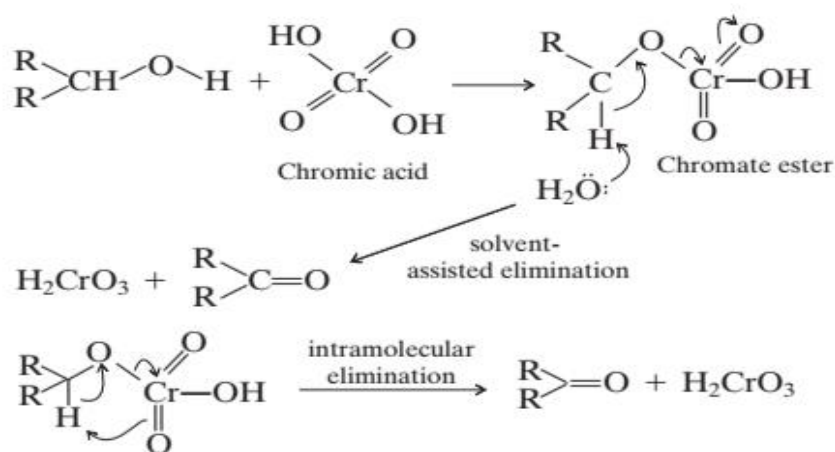
ABSTRACT

The kinetics of oxidation of benzyl alcohol and its derivatives by Quinoxalinium dichromate has been studied in the solvent of dimethyl sulfoxide and in the presence of acid. The products of oxidation are the corresponding benzaldehydes. The rate of the reaction is dependent on the concentration of the substrate, Quinoxalinium dichromate and acid. Electron - releasing substituents increase the rate, while electron - withdrawing substituents decrease it and thus, the rate data obeys Hammett's relationship. A suitable mechanism has been proposed.

Keywords : Oxidation, Quinoxalinium dichromate, and Kinetics.

INTRODUCTION

A number of Cr(VI) reagents have been developed to oxidize 1° and 2° alcohols, more generally the 2° alcohols, to respective carbonyl compounds. For example, Jones reagent, that is CrO₃ in 8NH₂SO₄ using acetone as the solvent. In this case, acetone serves the following two purposes. (i) It acts as an excellent solvent for the substrate. (ii) It prevents overoxidation of the primary product formed. The oxidation involves the formation of an inorganic ester, the chromate ester of the alcohol as an intermediate, which may decompose either in a solvent-assisted or an intramolecular elimination of chromous acid to give the ketone.



The strongly acidic condition of Jones reagent is unsuitable for oxidizing acid sensitive substrates. So, a number of Cr(VI) reagents have been developed in which heterocyclic bases are

used, which ligate with the Cr(VI) and stabilize it. These het-erocycles maintain a basic environment for the oxidation.

The selective oxidation of primary and secondary alcohols to aldehydes and ketones is one of the most important reactions in organic chemistry. Quinoxalinium dichromate is a mild and selective oxidising agent in synthetic organic chemistry. Primary and secondary alcohols may be converted to the corresponding Aldehydes and carbonyl compounds .

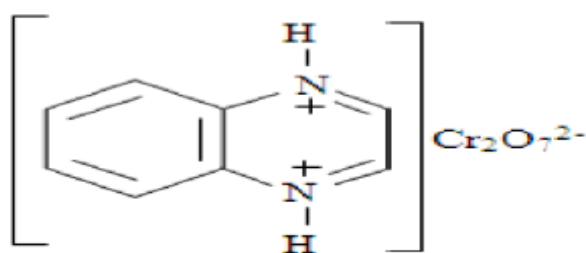
Some of the chromium(VI) reagents developed so far include quinoxalinium fluorochromate (1) pyridinium chlorochromate (2) pyridinium dichromate (3) pyridinium fluorochromate (4) pyridinium bromo chromate (5) quinoxalinium chlorochromate (6) quinoxalinium dichromate

(7) imidazolium dichromate (8). A new Cr (VI) reagents together with special reaction conditions have been developed. Anhydrous conditions are more conducive to complexation of substrates with chromium (VI) compounds to mild oxidation. The chromium (VI) reagents developed so far all suffer from at least one of the following drawbacks : high acidity , photo sensitivity , instability, or requirement of large excess of reagent. Therefore, the search for a new reagent persisted to the synthesis of Quinoxalinium dichromate.



A new chromium (VI) reagent Quinoxalinium dichromate, was prepared by reacting quinoxaline with CrO_3 in water.

Structure of Quinoxalinium dichromate [QxDC]

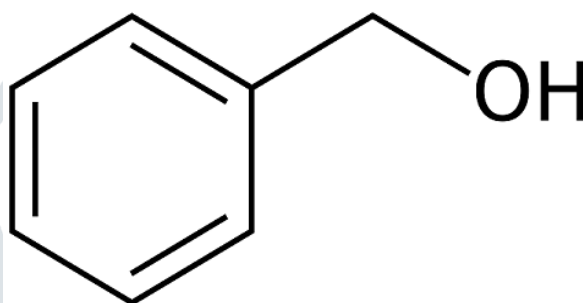


Quinoxalinium dichromate

Benzyl alcohol

Benzyl alcohol is an aromatic alcohol with the formula $C_6H_5CH_2OH$. At room temperature, benzyl alcohol exists as a colourless liquid that has a mildly aromatic odour. This compound is not very soluble in water (49/100ml). However, it forms miscible mixtures with diethyl ether and other alcohols. This compound is soluble in several organic solvents such as benzene, methanol, acetone and ether.

Structure of Benzyl alcohol



Benzyl alcohol reacts with acrylonitrile to give N-benzyl acrylamide. This is an example of a Ritter reaction [6].



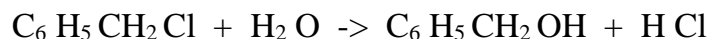
EXPERIMENTAL METHODS

Preparation of Quinoxalinium dichromate [QxDC]

A solution of 26.4g quinoxaline (0.2mol) in 60ml water was slowly added to 21.09g of chromium trioxide (0.2mol) in 20 ml water. Reaction mixture was diluted after 30 min, with 40ml acetone and cooled to -15°C . A light orange colour, non-hygroscopic and stable solid compound was obtained. It was filtered, washed with acetone and then dried in vacuum. The compound was melted at (116°C) (literature value of m.p. $115-116^\circ\text{C}$). The yield was 79% and it was taken for further analysis.

Preparation of Benzyl alcohol

Benzyl alcohol is prepared industrially from toluene by hydrolysis.



The use of sodium hydroxide in the hydrolysis of benzyl chloride yields benzyl alcohol and sodium chloride as the products :

$$\text{NaOH} + \text{C}_6\text{H}_5\text{CH}_2\text{Cl} \rightarrow \text{NaCl} + \text{C}_6\text{H}_5\text{CH}_2\text{OH} .$$

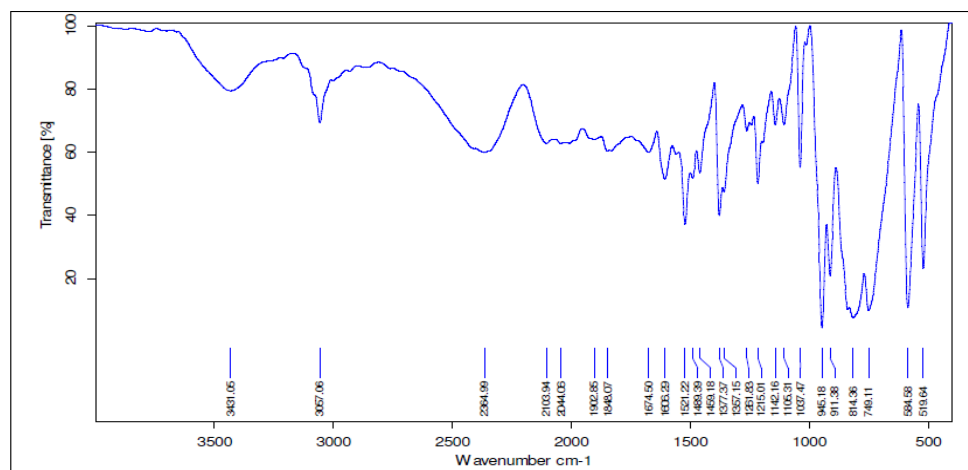
Kinetics

The rate of the reaction is dependent on the concentration of substrate, Quinoxalium dichromate and acid. The data obey Hammett's relationship.[5] The reaction constant P was -1.09 ± 0.01 at 303k. Oxidation of α - α -dideuteriobenzyl alcohol exhibited a substantial primary kinetics isotope effect ($K_H/K_D=6.78$ at 303k). The oxidation of benzyl alcohol by QxDC, failed to induce the polymerization of acrylonitrile.

Results

Quinoxalium dichromate was prepared in high yield say about, (79%) by addition of Quinoxaline to a solution of chromium trioxide in water in a molar ratio of 1:1 QxDC is a yellow, non-hygroscopic and stable solid compound which can be stored in the darkness for months without losing its activity.

The structure of the product is confirmed by its IR spectrum. The infrared absorption frequencies for the dichromate group at 950, 900 and 787 cm^{-1} in QxDC are attributable to $\nu_{\text{aSym}}(\text{CrO}_3)$, $\nu_{\text{Sym}}(\text{CrO}_3)$ and $\nu_{\text{Sym}}(\text{Cr-O-Cr})$; these assignments are in accordance with those found for $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ [13].



IR Spectrum of QxDC

Discussion

Quinoxalium dichromate is soluble in dimethyl formamide and dimethyl sulfoxide, sparingly soluble in dichloromethane, acetonitrile and insoluble in ether, nitro benzene and ethyl acetate. These reaction shows the ionic nature of QxDC. The reagents melts sharply at 115-116°C. The compound is diamagnetic. It is a 2:1 electrolyte ($\Lambda_m = 210 \text{ mho.cm}^2.\text{mol}^{-1}$ acetonitrile). Showing a PH of 2.30 in a 0.01 M aqueous solution.

Rate laws

Under pseudo-first-order conditions, the pseudo-first order plots of $\log(QxDC)$ Vs time at different initial concentrations of QxDC (0.001 to $0.009 \text{ mol dm}^{-3}$) are all linear with nearly the same slope. The rate of the reaction is dependent on the concentration of QxDC. The reaction exhibited first-order dependence with respect to QxDC concentration (Table.1). Further, under pseudo-first-order conditions, by keeping the substrate as constant, the rate constants was found to be independent of the initial concentration of QxDC. Now, by taking QxDC as constant, the k_{obs} values was measured at various concentrations of benzyl alcohol, in the range 0.04 to $0.50 \text{ mol. dm}^{-3}$ (Table.1). The result showed that increasing the concentration of substrate, increased the oxidation rate (Table 1). Thus, the reaction is first order with respect to the alcohol as well.

Table.1

Rate constants for the oxidation of BA by QxDC in the presence of acid at 303k

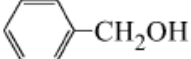
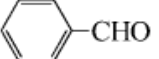
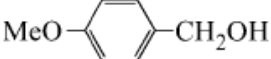

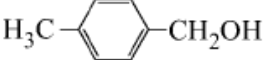
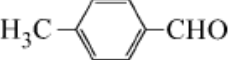
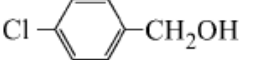
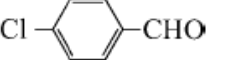
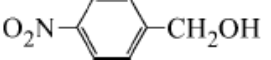

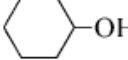
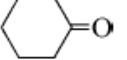
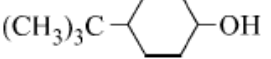
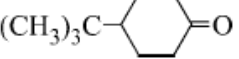
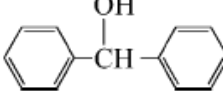
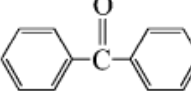
[BA]/M	10^3 [QxDC]/M	$10^4 k_1/s^{-1}$	$10^3 k_2/s^{-1} M^{-1}$
0.04	3.0	7.49	18.73
0.06	3.0	11.25	18.75
0.08	3.0	15.12	18.90
0.10	3.0	19.08	19.08
0.12	3.0	23.09	19.24
0.15	3.0	29.02	19.35
0.20	3.0	38.48	19.24
0.50	3.0	95.59	19.11
0.06	1.0	11.48	
0.06	2.0	11.24	
0.06 *	3.0	11.51	
0.06	4.0	11.41	
0.06	5.0	11.45	
0.06	6.0	11.03	
0.06	7.0	11.37	
0.06	8.0	11.58	
0.06	9.0	11.45	

* containing 10^{-3} m acrylonitrile

In order to show the efficacy of the reagent as an oxidant, it was tested on a wide array of substrates in dichloromethane at room temperature. QxDC readily oxidizes primary (Table.2 entries 1-6) and secondary alcohols (Table.2 entries 7-10) to their corresponding aldehydes and ketones (Scheme 1)

Table - 2

Oxidation of organic substrates with QxDC

Entry	Substrate	Product ^b	Uncatalyzed		Catalyzed ^d	
			t/h	Yield/% ^c	t/h	Yield/% ^c
1	$\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{OH}$	$\text{CH}_3(\text{CH}_2)_6\text{CHO}$	4	69	2	71
2			4	69	2	71
3			4	92	2	92
4			4	84	2	87
5			4	69	2	71
6			4	64	2	65
7			4	62	2	64
8			4	68	2	70
9			4	79	2	81

Conclusion :

The kinetics of oxidation of benzyl alcohol and its derivatives by quinoxalinium dichromate has been investigated and QxDC takes part in the oxidation reaction. The product of oxidation was their corresponding aldehydes and ketones. The result was found to be first order with respect benzyl alcohol and chromium (VI). Thus a suitable kinetics was proposed.