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Suitable combination of promoter and micellar catalyst for kilo fold rate acceleration on propanol to propionaldehyde conversion in aqueous media

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ABSTRACT

Oxidation of propanol by chromic acid produces propionaldehyde under kinetic condition $[\text{propanol}]_T \gg [\text{Cr(VI)}]_T$. This oxidation reaction is performed also in presence of micellar catalysts (anionic, cationic and neutral) and hetero-aromatic nitrogen bases promoters (picolinic acid, 2,2′-bipyridine, 1,10-phenanthroline) in aqueous media. The product is confirmed by 2,4-DNP test and ^{1}H NMR spectroscopy. Anionic surfactant sodium dodecyl sulphate (SDS), neutral surfactant triton X-100 (TX-100) accelerated the reaction both in presence and absence of promoters whereas cationic surfactant N-cetyl pyridinium chloride (CPC) inhibited the reaction. Combination of SDS and bipy is found to be the most efficient for this oxidation.

1. Introduction

Hexavalent chromium compounds are very powerful and important oxidizing agents suitable for organic synthesis [1]. Their most common application is oxidation of primary and secondary alcohols to produce aldehydes, ketones, or carboxylic acids, depending on reagent and conditions. Pyridinium chloro chromate (PCC), pyridinium di chromate (PDC), pyridinium fluoro chromate (PFC), imidazolium dichromates (IDC) are few examples of hexavalent chromium containing compounds important for several selective oxidations [2]. All these reagents require organic solvents like dichloromethane, acetone, or dimethylformamide, which are hazardous in cases of skin contact, eye contact, ingestion, or inhalation.

Use of environmentally acceptable, abundant and low cost water instead of hazardous solvents has gained importance as an essential component of the development of sustainable chemistry [3]. To minimize the harmful effects of organic solvents, $K_2Cr_2O_7$ is used as an oxidizing agent for the oxidation of propanol to propionaldehyde in aqueous acid medium. Chromic acid oxidation of alcohols is a reaction, which has been investigated by numerous investigators over a period of many years. It was previously reported that the rate of the chromic acid oxidation of isopropyl alcohol increases with the first power of the concentration of the alcohol, and the first power of the concentration of the acid chromate ion (as contrasted to the dichromate ion). Under the experimental and kinetic conditions, the apparent first-order rate constant varies, with the concentration of chromic acid for the chromic acid oxidation of isopropyl alcohol. The rate constant increases and the reaction is most nearly first order for the most dilute solutions [4]. We have carried out the propanol oxidation reaction in environmental friendly aqueous solvent rather than any other hazardous carcinogenic organic solvent (like acetic acid, DMSO, $CHCl_3$, THF, toluene etc) [5].

Many enzyme can catalyze the oxidation reaction of alcohols to corresponding aldehydes.

Again it can also oxidize aldehydes to acids by a dismutation. Such as liver alcohol dehydrogenase (LADH) catalyzes the rate of reaction of NAD^+ and benzyl alcohol to form NADH in which benzaldehyde is the predominant product. But one of the drawbacks of this enzyme catalysis oxidation is that the enzyme–alcohol complexes form at high concentrations of benzyl alcohol, and this leads to dismutation [6] of benzaldehyde to benzoic acid ($2RCHO \rightarrow RCH_2OH + RCOOH$). Moreover no experimental support was found to detect the active precursor of the enzyme in the enzymatic oxidation of alcohol.

Separation of the product aldehyde from the reaction mixture is often becomes a major problem in organic transformations, which has been solved in this work. The present work has been carried out in a very simple way. No drastic conditions were used. Replacement of these organic solvents by aqueous micellar media has been drawn a special attention on the reaction kinetics. Reaction rate is

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accelerated in a dramatic way. The used micellar catalysts can be recycled for further purpose

The overall mechanism of the promoted path has been proposed by varying the concentration of substrate, proton and promoter and from earlier literature.

Although the oxidation with aqueous chromic acid has long been a standard method, there are so many modified procedures have been developed to simplify the isolation process, to achieve definite selectivity, and to develop the yield as well as the purity of the product [7]. Oxidation is made selective to propionaldehyde by stopping the over-oxidation to propionic acid by maintaining pseudo first order condition. The remaining propanol can be re oxidized to deserved product with addition of chromic acid maintaining the reaction condition same. No traces of carboxylic acids or other by-products were detected in this work. The only products isolated were the expected carbonyl compounds (propionaldehyde) and, in the cases where the reaction had not gone to completion [8] the starting material was recovered. The products were identified either by simple conventional spot test, 2,4-DNP test or by spectroscopic, proton NMR spectral analysis.

Primary alcohols are oxidized to carboxylic acids with intermediate formation of aldehydes. In aqueous solutions the latter are very reactive, so the reaction proceeds to the acid. However, most unsaturated aliphatic alcohols are oxidized to the corresponding aldehydes with high selectivity, because either the hydroxyl group is located next to an unsaturated site or the reactions were performed in non-aqueous media [9]. Extensive kinetic and mechanistic studies on the oxidation of alcohols with chromic acid have revealed that such reactions ordinarily involve a three-electron change, whereby the oxidant, Cr(VI) species, is reduced to Cr(III) [7].

Used oxidizing agent $K_2Cr_2O_7$ is a well known human carcinogen and under pseudo first order condition it is totally reduced to non toxic trivalent form [10,11].

Rate of chromic acid oxidation of propanol is accelerated using non-functional surfactants as micellar catalyst and hetero-aromatic nitrogen bases as promoter [12–18]. Above critical micellar concentration, surfactants aggregates to form micelles in the solvent region. These micelles acts as nano-reactors and efficiently increases the effective concentration of the reactants into small core inside it [19–22]. This study appears to be the first report of the effect of PA, bipy, phen on chromic acid oxidation of propanol in aqueous micellar media.

Upon oxidation surfactants remains unreacted in the reaction mixture and can be recycled. The promoters do not get oxidized by Cr(VI) and remains in the solution as Cr(III)–promoter complex.

The chromic acid oxidation of propanol is represented as follows

$$3CH_3CH_2CH_2OH + HCrO_4^- + 8H^+ \rightarrow Cr(III) + CH_3CH_2CHO + H_2O$$

2. Experimental

2.1. Materials and reagents

Propanol (AR, SRL) was purified by refluxing with an excess of freshly burnt quicklime followed by distillation and purity was checked by density measurement. Picolinic acid (AR, BDH), 1,10-phenanthroline (AR, Merck), 2,2′-bipyridine (AR, Qualigens), SDS (AR, SRL), CPC (AR, SRL), TX-100 (AR, SRL), Iodine (AR, Merck) and all other necessary chemicals used were of highest purity available commercially. Solutions were prepared by using doubly distilled water.

2.2. Procedure and kinetic measurements

All kinetic runs should be achieved under pseudo-first order conditions by keeping the concentration of substrate (propanol) in large excess (≥15 fold) relative to the oxidant (potassiuim dichromate, $K_2Cr_2O_7$) concentration for each of the reaction. The oxidation reaction was initiated by adding requisite quantities of the oxidant solution placed separately into the mixture containing the substrate, H_2SO_4 in presence and absence of surfactant (SDS, CPC, TX-100) and promoter (PA, bipy, phen).

Solutions of the oxidant and a reaction mixture containing known quantities of substrate (i.e. propanol) and promoter are prepared under the kinetic condition $[\text{propanol}]_T \gg [\text{Cr(VI)}]_T$. The acid and other necessary chemicals were separately thermostated (±0.10 °C). The reaction was initiated by mixing the requisite amount of the oxidant with the reaction mixture. Progress of the reaction was monitored by following decay of the oxidant, Cr(VI), with time by use of UV–visible spectrophotometer [UV-VIS-NIR-3600 (SHIMADZU)] at 450 nm wavelength. Quartz cuvettes of path length 1 cm were used. Pseudo first-order rate constants (k_{obs}) were calculated from the slopes of plots of $\ln(A_{450})$ versus time (t) which were linear. No other reactant or product had any significant absorption at this wavelength. The scanned spectra, spectrum after completion of reaction and other spectra were recorded with UV-VIS-1800 (SHIMADZU).

3. Results

3.1. Dependence on Cr(VI)

Under the kinetic and experimental conditions $[\text{propanol}]_T \gg [\text{Cr(VI)}]_T$ both in presence and absence of promoter, the rate of disappearance of Cr(VI) showed a first order dependence on $[\text{Cr(VI)}]_T$. The first order dependence on Cr(VI) was also maintained in the presence of surfactants [23]. The pseudo-first order rate constants k_{obs} was directly evaluated from the slope of the linear plot of $\log[\text{Cr(VI)}]_T$ versus time (t).

3.2. Dependence on substrate

From the previous work it was observed that the rate of the reaction was first order with respect to substrate [23] and is also true for in presence of surfactants.

3.3. Dependence on H^+

The reaction is second order with respect to H^+ ion concentration, which was previously observed [23,24].

3.4. Determination of critical micelle concentration (CMC) of used surfactants

Surfactants aggregate and behave as nanoreactor above CMC. The CMC values of CPC and SDS were measured by using conductometric method with the help of a water analyzer kit (Eutech instrument, Cyber Scan 6000 Series Meters). The conductivity of different solutions were measured at 30 °C with a conductivity cell (CON 6000, cell constant 1 cm^{-1}) provided with a built-in temperature sensor immersed in the beaker containing the surfactant solution. Conductance values were plotted against concentration of CPC and SDS and CMC values obtained from the plots are given in supplementary data. These CMC values are 8.2 mM and 1.1 mM for SDS and CPC, respectively, which resembles with the literature values [25,26].

CMC of TX-100 was analyzed by interaction of saturated aqueous solution of iodine with varying concentration of TX-100 solution and the value is determined spectrophotometrically at