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ORIGINAL ARTICLE

Correlation analysis of reactivity in the oxidation of some organic diols by tripropylammonium fluorochromate in non-aqueous media

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Abstract The kinetics of oxidation of some organic diols by tripropylammonium fluorochromate (TriPAFC) have been studied in dimethylsulfoxide (DMSO). The main product of oxidation is the corresponding hydroxy aldehydes. The reaction is first order with respect to TriPAFC and exhibited Michaelis-Menten type kinetics with respect to organic diols. The reaction is catalyzed by hydrogen ions. The hydrogen ion dependence has the form: $k_{\text{obs}} = a + b[\text{H}^+]$. Various thermodynamic parameters for the oxidation have been reported and discussed along with the validity of isokinetic relationship. Oxidation of diols was studied in 18 different organic solvents. The rate data are showing satisfactory correlation with Kamlet–Taft solvatochromic parameters (α , β and π^*). A suitable mechanism of oxidation has been proposed.

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1. Introduction

Specific and selective oxidation of organic compounds under non-aqueous conditions is an important reaction in synthetic organic chemistry. Chromium(VI) reagents are widely used in organic chemistry for oxidation of primary and secondary alcohols to carbonyl compounds. Cr(VI) as chromate or dichromate is highly soluble in water, and is reported to be highly toxic (Losi et al., 1994; Viamajala et al., 2004), there is continued interest in the development of new chromium(VI) reagents for the effective and selective oxidation of organic substrates, in particular alcohols, under mild conditions. Therefore, the search for new oxidizing agents is of interest to synthetic organic chemists.

In recent years, some new chromium(VI) based reagents like tetraethyl ammonium bromochromate (Mansoor and Shafi, 2011), tetraethylammonium chlorochromate (Swami et al., 2010), tetrabutylammonium bromochromate (Ghammamy

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et al., 2007), tetraheptylammonium bromochromate (Ghammamy et al., 2009a), tetrahexylammonium fluorochromate (Koohestani et al., 2008), tetramethylammonium fluorochromate (Sadeghy and Ghammami, 2005), benzyltrimethylammonium fluorochromate (Kassae et al., 2004) and tributylammonium chlorochromate (Mansoor and Shafi, 2010) were proposed.

Tripropylammonium fluorochromate (Ghammamy and Hashemzadeh, 2004) is also one such oxidant developed recently. It is a more efficient and stronger oxidizing agent. 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 times and high yields.

The kinetics of oxidation of organic diols has been studied by many reagents, such as 2,2'-bipyridiniumchlorochromate (Loonker et al., 1997), bromine in acid solution (Sharma et al., 1998), pyridinium bromochromate (Rao et al., 1998), hexamethylenetetramine-bromine (Gangwani et al., 1999), quinolinium fluorochromate (Choudhary et al., 1999), benzyltrimethyl ammonium dichloroiodate (Mehla et al., 2000), benzyltrimethyl ammonium tribromide (Goswami et al., 2001), and trialkyl fluorochromate (Ghammamy et al., 2009b). We have been interested in the kinetic and mechanistic studies of Cr(VI) species. Literature survey reveals that no report is available on the kinetics of the oxidation of organic diols by TriPAFC. It was considered important to investigate the oxidation by TriPAFC. Hence, we report herein the kinetics of the oxidation of some organic diols by TriPAFC in 18 different organic solvents.

2. Experimental

2.1. Materials

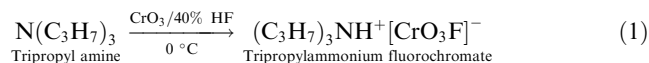
Tripropylamine and chromium trioxide were obtained from Fluka (Buchs, Switzerland). The organic diols used were ethane 1,2-diol, propane 1,2-diol, propane 1,3-diol, butane 1,2-diol, butane 1,4-diol, butane 2,3-diol, pentane 1,2-diol, pentane 1,3-diol and pentane 1,5-diol. The procedure used for the purification of alcohols has been described earlier (Banerji et al., 1993). [1,1,2,2-²H₄] ethanediol (DED) was prepared by reducing diethyl oxalate with lithium aluminium deuteride (Kemp and Waters, 1963). Its isotopic purity, as ascertained by its NMR spectra, was 90 ± 4%.

The solvents acetonitrile (MeCN), chloroform (CF), 1,2-dichloroethane (DCE), dichloromethane (DCM), dimethyl sulfoxide (DMSO), acetone (Me₂CO), dimethylformamide (DMF), butanone (Bu), nitrobenzene (NB), benzene (Bz), cyclohexane (CH), toluene (TE), acetophenone (Ph₂CO), tetrahydrofuran (THF), *tert*-butanol (*t*-BuOH), 1,4-dioxane (DO), 1,2-dimethoxyethane (DME) and ethyl acetate (EA), are of analytical grade and purified by conventional methods (Perrin et al., 1966). Due to non-aqueous nature of the solvent, *p*-toluene sulfonic acid (TsOH) was used as a source of hydrogen ions. TsOH is a strong acid and in a polar medium like DMSO; it is likely to be completely ionized.

2.2. Preparation of tripropylammonium fluorochromate

Tripropylammonium fluorochromate is easily prepared as follows: chromium(VI) oxide (15.0 g, 0.150 mol) was dissolved in

water in a polyethylene beaker and 40% hydrofluoric acid (11.3 ml, 0.225 mol) was added with stirring at 0 °C. To the resultant orange solution, tripropylamine (28.3 ml, 0.150 mol) was added drop wise with stirring to this solution over a period of 0.5 h and stirring was continued for 0.5 h at 0 °C. The precipitated orange solid was isolated by filtration, washed with petroleum ether (3 × 60 ml) and dried in vacuum for 2 h at room temperature (Ghammamy and Hashemzadeh, 2004). Yield 37.5 g (95%); mp 142 °C:



The bright orange crystalline reagent can be stored in polyethylene containers for long periods without decomposition. The chromium(VI) content may be easily determined iodometrically.

2.3. Product analysis

Product analysis was carried out under kinetic conditions. In a typical experiment, diol (0.1 mol) and TriPAFC (0.01 mol) were made up to 100 ml in DMSO and kept in the dark for 24 h to ensure completion of the reaction. The solution was then treated with an excess (200 cm³) of a saturated solution of 2,4-dinitrophenyl hydrazine in 2 mol dm⁻³ HCl and kept over night in a refrigerator. The solvent was removed and the precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried and recrystallized from ethanol. In the oxidation of ethanediol the identity of the product was confirmed by determining the mp with authentic samples of hydroxyethanal. Similar experiments were performed with other diols also.

3. Experimental procedure

3.1. Kinetic measurements

The pseudo-first-order conditions were attained by maintaining a large excess (×15 or more) of diol over TriPAFC. The solvent was DMSO, unless specified otherwise. The reactions were followed, at constant temperatures (±0.01 K), by monitoring the decrease in [TriPAFC] spectrophotometrically at 361 nm. No other reactant or product has any significant absorption at this wavelength. The pseudo-first-order rate constant, *k*_{obs} was evaluated from the linear (*r* = 0.990–0.999) plots of log[TriPAFC] against time for up to 80% reaction. Duplicate kinetic runs showed that the rate constants were reproducible to within ±3%. The second order rate constant *k*₂ was obtained from the relation *k*₂ = *k*_{obs}/[Diol]. All experiments, other than those for studying the effect of hydrogen ions, were carried out in the absence of TsOH.

3.2. Data analysis

Correlation analyses were carried out using Microcal origin (version 6) computer software. The goodness of the fit was discussed using the correlation coefficient (*r* in the case of simple linear regression and *R* in the case of multiple linear regressions) and standard deviation (SD).

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