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Oxidation of aliphatic alcohols by triethylammonium chlorochromate in non-aqueous medium – A kinetic and mechanistic study

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Abstract The oxidation of some aliphatic alcohols by triethylammonium chlorochromate (Tri-EACC) in dimethyl sulfoxide leads to the formation of the corresponding carbonyl compounds. The reaction is first order with respect to TriEACC. The reaction exhibited Michaelis–Menten type kinetics with respect to alcohol. The reaction is catalyzed by hydrogen ions. The hydrogen-ion dependence has the form: $k_{obs} = a + b[H^+]$. The oxidation of $[1,1\text{-}^2H_2]$ ethanol ($MeCD_2OH$) exhibits a substantial primary kinetic isotope effect. Oxidation of aliphatic alcohol was studied in 19 different organic solvents. The solvent effect has been analysed using Kamlet's and Swain's multi-parametric equation. A suitable mechanism has been proposed.

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1. Introduction

Chromium(VI) is established as a versatile oxidant for many types of substrates varying from metal ions to naturally occurring organic compounds, and has a wide range of applications spanning the synthesis of sulfur nanoparticles (Lan et al., 2005) and the determination of biological oxygen demand in organic polluted water. 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.

Many such reagents have been developed in recent years with some success, some of the important entries in the list of reagents are tetramethylammonium fluorochromate (Ghammami and Sadeghy, 2005), caffeinilium chlorochromate (Shirini et al., 2003), quinolinium chlorochromate (Elango et al., 2002), benzimidazolium fluorochromate (Mansoor, 2010), tributylammonium chlorochromate (TriBACC) (Mansoor and Shafi, 2010a,b), prolinium chlorochromate (Mamaghani et al., 2002) and tripropylammonium fluorochromate (Mansoor and Shafi, 2010a,b).

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Triethylammonium chlorochromate (Ghammamy and Dastpeyman, 2008) is also one such oxidant that developed recently. It is more efficient and a 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. In this paper, we describe the kinetics and mechanism of the oxidation of eight primary and three secondary aliphatic alcohols by TriEACC in dimethyl sulfoxide (DMSO) as the solvent.

Kinetics of oxidation of aliphatic alcohols by various oxidizing agents has been well studied (Sharma and Baghmar, 2001; Banerji et al.,1999, 2005, 2008; Jamel,1999). Large number of aliphatic alcohols are either commercially available or can be easily prepared. There seems to be no report on the oxidation of aliphatic alcohols by TriEACC. Therefore, we studied the kinetics of oxidation of aliphatic alcohols by TriEACC in DMSO. In aqueous solutions primary alcohols are usually oxidized to carboxylic acids (Lee and Spitzer, 1970; Robertson, 1941), while in the absence of water the oxidation will stop at the aldehyde. The major objective of this investigation is to study the solvent effect for the substrates undergoing oxidation and to propose a suitable mechanism for the oxidation.

2. Materials and methods

2.1. Reagents

Triethylamine and chromium trioxide were obtained from Fluka (Buchs, Switzerland). The aliphatic alcohols used were methanol, ethanol, propanol-1, butanol-1, pentanol-1, hexanol-1, heptanol-1, octanol-1, propanol-2, butanol-2 and pentanol-2. The procedure used for the purification of alcohols has been described earlier (Banerji et al., 1993). $[1,1-^2H_2]$ ethanol ($MeCD_2OH$) was prepared by Kalpan's method (Kalpan, 1958). Its isotopic purity, as ascertained by its NMR spectra, was $91 \pm 4\%$. Due to the non-aqueous nature of the medium, p-toluenesulphonic 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 ionised. Solvents were purified by the usual method (Perrin et al., 1966).

2.2. Preparation of triethylammonium chlorochromate $(C_2H_5)_3NH^+[CrO_3Cl^-]$

Chromium(VI) oxide (1.0 g, 0.01 mol) was dissolved in water and 6 M hydrochloric acid (0.25 ml, 0.015 mol) was added with stirring at 0 °C. To the resulting orange solution, triethylamine (0.101 ml, 0.01 mol) was added drop-wise with stirring over a period of 30 min and the stirring was continued for 30 min at −4 °C. The precipitated orange solid was isolated by filtration, washed with petroleum ether (3 × 60 ml) and dried under vacuum for 2 h at room temperature (Ghammamy and Dastpeyman, 2008). Yield: (54%); m.p. 120 °C;

$$N(C_2H_5)_3 \underset{0\,°C}{\overset{CrO_3/6\,M\,HCl}{\rightarrow}} (C_2H_5)_3NH^+[CrO_3Cl]^- \qquad (1)$$
Triethyl amine   Triethylammonium chlorochromate
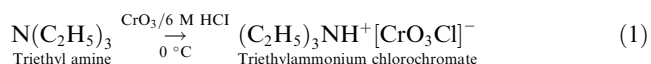
2.3. Product analysis

The product analysis was carried out under kinetic conditions. In a typical experiment, ethanol (2.30 g, 0.05 mol) and TriEACC (2.37 g, 0.01 mol) were made up to 50 cm³ in DMSO and kept in the dark for about 15 h to ensure the completion of the reaction. The solution was then treated with an excess (200 cm³) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm⁻³ HCl and kept overnight in a refrigerator. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol and weighed again. The yield of DNP before and after recrystallization was 2.0 g (90%) and 1.8 g (80%), respectively. The DNP was found identical (m.p. and mixed m.p.) with the DNP of acetaldehyde. Similar experiments with other alcohols led to the formation of DNP of the corresponding carbonyl compounds in yields ranging from 71% to 83%, after recrystallization. Iodometric determinations of the oxidation state of chromium in completely reduced reaction mixtures indicated that the oxidation state of the reduced chromium species was 3.94 ± 0.16.

3. Experimental procedures

3.1. Kinetic measurements

The reactions were followed under pseudo-first-order conditions by keeping a large excess (×15 or greater) of the alcohol over TriEACC. The temperature was kept constant to ± 0.1 K. The solvent was DMSO, unless specified otherwise. The reactions were followed by monitoring the decrease in the concentration of TriEACC spectrophotometrically at 364 nm for 80% of the reaction. The pseudo-first-order rate constants, k_{obs}, were evaluated from the linear ($r = 0.990$–0.999) plots of log[TriEACC] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within $\pm 3\%$. Multivariate and simple linear regression analyses were carried out by the least-squares method.

4. Results and discussion

The rate and other experimental data were obtained for all the aliphatic alcohols. Since the results are similar, only representative data are reproduced here.

4.1. Stoichiometric studies

The oxidation of alcohols results in the formation of the corresponding carbonyl compounds. The overall reaction may be represented as Eq. (1):

$$RCH_2OH + CrO_2ClO^-NH^+Et_3$$
$$\rightarrow RCHO + H_2O + CrOClO^-NH^+Et_3 \qquad (1)$$

Thus TriEACC undergoes a two-electron change. This accords with the earlier observations with PFC (Banerji, 1988a,b) and QFC (Murugesan and Pandurangan, 1995).

4.2. Rate law

The reaction is first order with respect to TriEACC. Michaelis–Menten type kinetics was observed with respect to alcohols (Table 1). A plot of log k_{obs} vs log[EtOH] is linear with slope va-