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ORIGINAL ARTICLE

Oxidation of aniline and some *para*-substituted anilines by benzimidazolium fluorochromate in aqueous acetic acid medium – A kinetic and mechanistic study

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Abstract The oxidation kinetics of some *para*-substituted anilines by benzimidazolium fluorochromate (BIFC) have been studied in aqueous acetic acid media in the presence of perchloric acid. The reaction is first order with respect to both aniline and BIFC and is catalysed by a hydrogen ion. The rate data obey Hammett relationship. The products of oxidation are the corresponding azo benzenes. Based on the kinetic results and product analysis, a suitable mechanism has been proposed for the reaction of BIFC with anilines.

1. Introduction

Chromium compounds have been used in aqueous and non-aqueous medium for the oxidation of a variety of organic compounds. Chromium compounds especially Cr(VI) reagents have been versatile reagents and are capable of oxidizing almost all the oxidisible organic functional groups (Wiberg, 1965). The development of newer chromium(VI) reagents for the oxidation of organic substrates continues to be of interest.

A number of new chromium(VI) containing compounds like pyrazinium chlorochromate (Sekar and Prabaharan, 2008), benzyltrimethyl ammonium chlorochromate (Mansoor and Shafi, 2009), triethylammonium chlorochromate (Sharma et al., 2010), morpholinium chlorochromate (Sharma et al., 2009a,b), 4-(dimethylamino) pyridinium chlorochromate (Rajarajan et al., 2008), quinolinium fluorochromate (Banerji et al., 2002), quinolinium bromochromate (Hiran et al., 2002), quinolinium dichromate (Medien, 2003), tributyl ammonium chlorochromate (Mansoor and Shafi, 2010a), tripropyl ammonium fluorochromate (Mansoor and Shafi, 2010b) and isoquinolinium bromochromate (Vibhute et al., 2009) have been used to study the kinetics and mechanism of various organic compounds.

The oxidation of aromatic amines by different oxidants have been the subject of study by various workers due to the complex behavior of their mode of oxidation due to the formation of polymeric products, many of which find application in

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drug and dyestuff industries. Kinetics and mechanism of oxidation of *p*-substituted anilines by peroxy sulphate ion in acetic acid–water medium have been reported (Gupta, 1985).

The present study focuses on the study of kinetics and mechanism of oxidation of *para* substituted anilines by BIFC in aqueous acetic acid media. Anilines (aromatic amines) are the most widespread and principal contaminants of industrial waste waters. These comprise of an important class of environmental contaminants and they are the building blocks for many textile dyes, agrochemicals and other class of synthetic chemicals. The reaction pathways of aromatic amines in natural systems are dominated by redox reactions with soil and sediment constituents. Better understanding of the mechanism of oxidation of such compounds/contaminants to harmless products is the important goal for basic research and industrial applications, hence, the present study.

One of the important tools in deciding the mechanism of reaction is the study of substituent effects and thermodynamic parameters. The isokinetic relationship is also an important tool for deciding the nature of a mechanism. Keeping this in view, a systematic study has been made to establish the reactivity and to decide the nature of the mechanism followed in the oxidation of several *para*-substituted anilines by BIFC.

Kinetics of oxidation of anilines by various oxidizing reagents have been well studied (Elango and Bhuvaseshwari, 2006a,b,c,d, 2007a,b; Patwari et al., 2009). However the kinetics of oxidation of substituted anilines by BIFC, a Cr(VI) reagent has not yet been studied. Hence, we have considered it worthwhile to study the kinetics and mechanism of oxidation of anilines by BIFC.

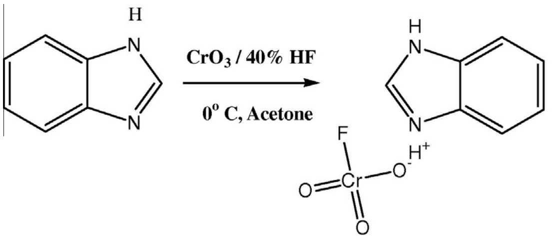
2. Experimental

2.1. Materials and reagents

All the chemicals and solvents used were of analytical grade. The anilines used were with substituents H, *p*-OCH_3, *p*-CH_3, *p*-Cl and *p*-NO_2. The solid anilines were used as such and the liquid anilines were used after vacuum distillation. Acetic acid was purified by the standard method and the fraction distilling at 118 °C was collected. Double distilled water was used for all purposes.

2.2. Preparation of benzimidazolium fluorochromate

Benzimidazolium fluorochromate has been prepared from benzimidazole, 40% hydrofluoric acid and chromium trioxide in the molar ratio 1:1.3:1 at 0 °C. BIFC is obtained as yellow orange crystals. It is non-hygroscopic, light insensitive on storage (Murugesan et al., 2005). The purity of BIFC was checked by the iodometric method.



Benzimidazole Benzimidazoliumfluorochromate

(1)

2.3. Kinetic measurements

The reactions were carried out under pseudo-first-order conditions by keeping an excess of substrate over BIFC. The temperature was kept constant to ±0.1 K. The progress of the reaction was followed by estimating the unreacted oxidant iodometrically at 298, 303, 308 and 313 K for up to 80% of the reaction. The pseudo-first-order rate constants, k_{obs}, were evaluated from the linear plots of log [BIFC] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within ± 4%.

2.4. Data analysis

Correlation analysis was carried out using Microcal Origin (Version 6.1) computer software. The goodness of the fit is discussed using the correlation coefficients and standard deviations.

2.5. Stoichiometry and product analysis

The stoichiometry of the reaction was determined by carrying out several sets of experiments with varying amounts of BIFC largely in excess over aniline. The estimation of unreacted BIFC showed that 1 mol of BIFC reacts with 1 mol of aniline. The oxidative products were analysed using preparative TLC on silica gel, which yields azobenzene m.p 66 °C (Lit 68 °C) and UV Abs. (EtOH) at λ_{max} 320 nm.

3. Results and discussion

The kinetics of oxidation of aniline by BIFC was studied in 50% acetic acid −50% water medium at 303 K, under the pseudo-first-order conditions. The observed pseudo-first-order rate constants (k_{obs}) are given in Table 1.

3.1. Order of reaction

The rate of oxidation was found to be first order each in [BIFC] and [Substrate]. Linear plots of log k_1 versus log [Substrate] (Fig. 1) with unit slope (H: slope = 1.03 ± 0.04, $r = 0.997$; *p*-OCH_3: slope = 1.02 ± 0.03, $r = 0.998$; *p*-CH_3: slope = 1.01 ± 0.03, $r = 0.999$; *p*-Cl: slope = 1.04 ± 0.04, $r = 0.997$; and *p*-NO_2: slope = 1.01 ± 0.03, $r = 0.998$) demonstrate the first-order dependence of the rate on [Substrate]. The k_1 values at different [Substrate] are given in Table 1. The k_1 values obtained at different concentration of BIFC reveal that the rates are almost independent of the initial concentration of BIFC. This ensures that the order of the reaction with respect to BIFC is one.

The dependence of the reaction rate on the hydrogen ion concentration has been investigated at different initial concentrations and keeping the concentrations of the other reactants constant (Table 1). It may be seen that the rate of reaction increases linearly with an increase in the hydrogen ion concentration. This establishes that the reaction rate is first order with respect to the hydrogen ion concentration. A plot of log k_1 versus log $[H^+]$ is linear (Fig. 2), showing that the reaction proceeds completely through an acid catalysed pathway (Banerji et al., 1986a,b).