Journal of Molecular Catalysis A: Chemical 390 (2014) 159–168

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Proximal effect of the nitrogen bases in the oxidative decarboxylation of phenylsulfinylacetic acids by oxo(salen)chromium(V) complexes

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ARTICLE INFO

Article history:
Received 22 November 2013
Received in revised form 19 March 2014
Accepted 21 March 2014
Available online 31 March 2014

Keywords:
Oxo(salen)chromium(V)
Phenylsulfinylacetic acid
Oxidative decarboxylation
Oxygen transfer reaction
Effect of nitrogen bases

ABSTRACT

Oxidative decarboxylation of phenylsulfinylacetic acid (PSAA) and several substituted PSAAs with three oxo(salen)chromium(V) complexes in the presence of nitrogen bases are investigated in 100% acetonitrile medium using spectrophotometric technique. The nitrogenous bases such as imidazole, 1-methyl imidazole and pyridine catalyse the reaction and Michaelis–Menten kinetics is observed with respect to these bases. Among the various bases employed, imidazole with strong π donating ability shows the least accelerating effect and the maximum catalytic activity is observed with pyridine. Both the electron donating and electron withdrawing substituents in PSAA accelerate the reaction rate. The Hammett plots for the three oxo(salen)chromium(V) complexes with three nitrogen bases display a nonlinear upward curvature. The Hammett parameter ρ, changes from large negative to small positive values as the substituents are changed from electron donating to electron withdrawing groups. A mechanism involving direct oxygen transfer from oxo(salen)chromium(V)-nitrogen base adduct to PSAA with simultaneous decarboxylation to yield sulfone is proposed. The nonlinear Hammett plot has been ascribed to a shift in the rate determining step caused by the formation and decomposition of the sulfonium ion intermediate which is susceptible to substituent effect.

1. Introduction

Decarboxylation process plays an important role in the different areas of organic synthesis, biochemical reactions and in biological systems. Several works on decarboxylation by thermal [1,2], photochemical [3,4] and catalytic methods [5,6] have been reported. Drug metabolism taking place in presence of substances like indomethacin and ibuprofen are reported to act through a cytochrome p-450 induced decarboxylation process leading to the release of carbon dioxide that mitigates pain effects [7,8]. Many drugs, herbicides and pesticides containing a carboxyl group produce radical intermediates via decarboxylation [9].

Sulfoxides as synthetic intermediates find wider application in the construction of chemically and biologically important molecules [10–13]. Hence oxidation of sulfoxides to sulfones has been the subject of extensive studies. Phenylsulfinylacetic acid (PSAA) is an ambidentate ligand and with its three donor atoms acts as a good chelating agent. It is used in the preparation of many cephalosporin derivatives, the famous broad spectrum antibiotic. Like cytochrome p-450 and metalloporphyrin complexes many metal(salen) complexes (salen = N,N′-bis(salicylidene)ethylenediaminato) act as efficient catalysts in the epoxidation [14–17] and sulfoxidation [18–21] reactions of organic substrates with hydrogen peroxide, periodates, hypochlorites and iodosylarenes. Among the various salen complexes, the oxo(salen)chromium(V) species ($[(salen)Cr^{V}=O]^{+}$) generated from $[Cr^{III}(salen)]^{+}PF_6^{-}$ complex and PhIO is more stable in non-aqueous solvents and thus facilitates kinetic studies. Oxo(salen)chromium(V) ion mimics Cr(V) peptide complexes which are formed during the intracellular reduction of Cr(VI) by virtue of mixed N and O ligand chelation.

The reactivity of metal(salen) complexes is tuned [22–24] by adding donor ligands in the reaction mixture. Addition of imidazole, 1-methyl imidazole, pyridine or pyridine-N-oxide to metal(salen) complexes significantly lowers the oxidation potential by coordination with the metal and results in altering their electrochemical properties and reactivity [25–29]. The added nitrogen

Abbreviations: PSAA, phenylsulfinylacetic acid; salen, N,N′-bis(salicylidene)-ethylenediaminato; Im, imidazole; MeIm, 1-methyl imidazole; Py, pyridine; GC–MS, gas chromatography–mass spectrometry; LC–MS, liquid chromatography–mass spectrometry; OD, optical density; *r*, correlation coefficient.

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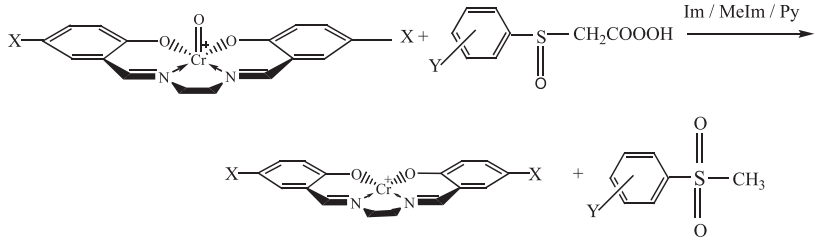
http://dx.doi.org/10.1016/j.molcata.2014.03.021
1381-1169/

bases alter the selectivity of products in many oxygenation reactions. Realizing the importance of Cr(V) species in biological studies it is considered worthwhile to study the influence of nitrogen bases on the electronic structure of oxo(salen)chromium(V) complexes and also their influence on the reaction rate towards oxidative decarboxylation. Further, no systematic kinetic study is reported so far in the literature on PSAA except our recent works on co-oxidative decarboxylation of PSAA-oxalic acid mixture by Cr(VI) [30] and oxidative decarboxylation of PSAA with Cr(VI) [31]. This paper attempts to unravel the effect of substituents in the salen moiety of oxo(salen)chromium(V) and phenyl ring of PSAA and that of nitrogen bases like imidazole (Im), 1-methylimidazole (MeIm) and pyridine (Py) on the oxidative decarboxylation of PSAA. The overall reaction scheme is represented as



I : X = H; **II** : X = CH_3; **III** : X = Cl

Y = H, p-OMe, p-OEt, p-Me, m-Me, p-F, m-F, p-Cl, m-Cl, p-NO_2

2. Experimental

2.1. Preparation of oxo(salen)chromium(V) complexes

Oxo(salen)chromium(V) (**I**), oxo(5,5′-dimethylsalen)chromium (V) (**II**) and oxo(5,5′-dichlorosalen)chromium(V) (**III**) complexes were prepared by the oxidation of corresponding $[Cr^{III}(salen)]^+PF_6^-$ complexes with slight excess of iodosobenzene in acetonitrile. The dark green coloured oxo(salen)chromium(V) complexes formed were filtered and used for the kinetic study after appropriate dilution. $[Cr^{III}(salen)]^+PF_6^-$ complexes were synthesised by the reaction between chromium(III) chloride and the corresponding salen ligands using established procedure [32,33]. The purity of the $[Cr^{III}(salen)]^+PF_6^-$ and oxo(salen)chromium(V) complexes were checked by comparing their absorption spectra with the previous reports [34].

2.2. Preparation of phenylsulfinylacetic acids

Phenylsulfinylacetic acid and its meta- and para-substituted acids were prepared from the corresponding phenylmercaptoacetic acids by the controlled oxidation with equimolar hydrogen peroxide [35]. They were purified by recrystallisation from suitable solvents several times and their purities were checked by melting point [35,36] and LC–MS. The recrystallised PSAAs were kept inside a vacuum desiccator in order to avoid contact with moisture. Phenylmercaptoacetic acids were prepared by the condensation of the corresponding thiophenols with chloroacetic acid in alkaline medium [36]. p-Nitrophenylmercaptoacetic acid was prepared from p-chloronitrobenzene and thioglycollic acid [37].

Salicylaldehyde, 5-methyl and 5-chloro salicylaldehydes (Alfa Aeser), $CrCl_3{\cdot}6H_2O$ (Sigma–Aldrich), imidazole (GR, Merck), 1-methyl imidazole (Sigma–Aldrich), pyridine (SD fine), thiophenol (SD fine) and substituted thiophenols (Sigma–Aldrich) were purchased and used as such. H_2O_2 (GR, Merck) and acetonitrile (HPLC grade, Merck) were used as received.

2.3. Kinetic studies

The kinetic study of PSAA and substituted PSAAs with the oxo(salen)chromium(V) ion $[O=Cr^V(salen)]^+$, in the presence of nitrogen bases were carried out in acetonitrile medium under pseudo first order condition with excess of PSAA concentration over the $[O=Cr^V(salen)]^+$. The progress of the reaction was followed by monitoring the decrease in absorbance of oxo(salen)Cr(V)–PSAA–nitrogen base adduct at the appropriate wavelength. The absorption spectral change for the reaction between PSAA and complex **I** in the presence of pyridine is shown in Fig. 1 as a representative plot. The Fig. 1 clearly shows the existence of isobestic point at the λ_{max} of 421 nm. A double beam BL 222 Elico UV–vis bio spectrophotometer with an inbuilt thermostat was employed to record the absorption spectra to measure the absorbance of the adduct and also to follow the kinetics of decarboxylation reaction.

The pseudo first order rate constants were calculated from the slope of linear plots of log OD vs. time. The second order rate constants were calculated by dividing the pseudo first order rate constants with the concentration of the substrate. The error in the rate constants were given according to 95% of the student's *t*-test. Thermodynamic parameters – enthalpy of activation ($\Delta^{\ddagger}H$) and entropy of activation ($\Delta^{\ddagger}S$) were evaluated from the linear Eyring's plots of log (k_2/T) vs. $1/T$ by the least square method.

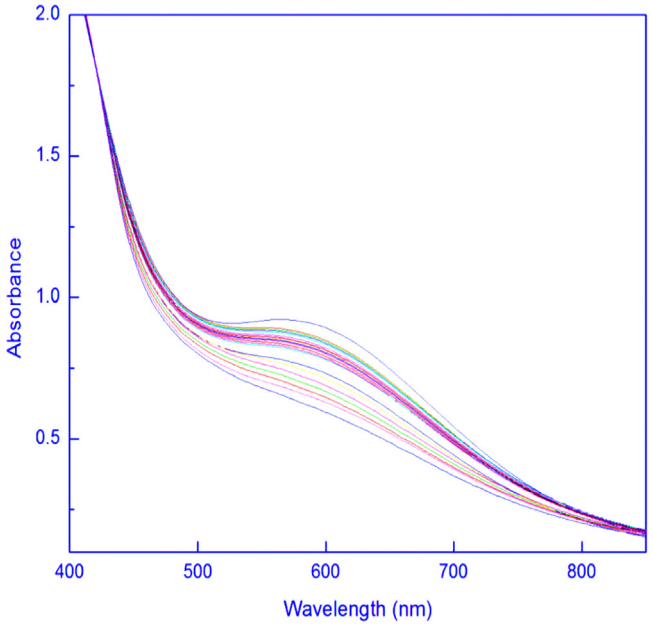


Fig. 1. The absorption spectral change for the reaction between PSAA and complex **I** in the presence of pyridine. [PSAA] = 5×10^{-2} M; [**I**] = 5×10^{-4} M; [Py] = 3×10^{-4} M; temp. = 303 K; solvent = 100% CH_3CN.