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Importance of ground state stabilization in the oxovanadium(IV)-salophen mediated reactions of phenylsulfinylacetic acids by hydrogen peroxide – Non-linear Hammett correlation

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ABSTRACT

A systematic study on the oxidative decarboxylation of a series of phenylsulfinylacetic acids (PSAA) by hydrogen peroxide with four oxovanadium(IV)-salophen catalysts in 100% acetonitrile medium is presented. The hydroperoxovanadium(V)-salophen generated from the reaction mixture is identified as the bonafide active oxidizing species. Introduction of electron donating groups (EDG) in the oxovanadium(IV)-salophen catalyst and electron withdrawing groups (EWG) in PSAA enhances the reactivity, whereas EWG in the catalyst and EDG in PSAA have a retarding effect on the reaction. A Hammett correlation displays a non-linear downward curvature, which consists of two intersecting straight lines and the ρ value shifts from small positive to moderately high as the substituents change from EWG to EDG. The importance of the ground state stabilization of PSAA is inferred from a linear Yukawa–Tsuno plot. Based on the observed substituent effects and the spectral changes, a mechanism involving electrophilic attack of PSAA on the nucleophilic peroxo oxygen atom of the vanadium complex in the rate determining step followed by oxygen atom transfer is proposed.

1. Introduction

The coordination chemistry of vanadium is of current interest because of its existence in abiotic as well as biotic systems. The presence of vanadium in biological systems, its insulin enhancing action [1] and anticancer activity [2] has driven a considerable amount of research. Several Schiff base vanadium complexes have been used as insulin enhancing agents, oral insulin substitutes for the treatment of diabetes and for the treatment of obesity and hypertension [3]. Schiff base complexes formed between oxovanadium(IV)/dioxovanadium(V) and chelating ligands with hetero atoms are found to be involved in a variety of biochemical and medicinal processes, such as haloperoxidation [4], phosphorylation [5], nitrogen fixation [6], tumor growth inhibition and prophylaxis against carcinogenesis [7]. Metal complexes of salen and salophen ligands have been used in medicinal studies as models for superoxide dismutase [8,9]. While manganese-salophen/salen derivatives display cyto-protective features in fibroblast cultures via hydrogen peroxide scavenging [10], oxovanadium(IV)-salophen complexes inhibit the growth of AGS gastric cell lines [11]. Certain metal-salophen complexes have been designed for their application as functional materials [12].

Recent advances have shown vanadium complexes to be effective catalysts for the activation of peroxides by virtue of vanadium in terms of stereoselectivity, reactivity and specificity [13,14]. The capability of these complexes to form metalloperoxo species, which in turn effectively transfer an oxygen atom to reductants with a high degree of selectivity, made them synthetically useful for obtaining valuable molecules. Oxovanadium-Schiff base complexes have been reported as effective catalysts in the oxidation of sulfides [15,16], alcohols [13], phenols [17], tertiary amines to N-oxides [18], epoxidation of olefins [19] and hydroxylation of phenols [20,21]. Salophen, a tetradentate Schiff base derived from 1,2-phenylenediamine and salicylaldehyde, and its derivatives are able to stabilize different metal ions in various oxidation states and control a variety of catalytic transformations [22].

Oxidative decarboxylation plays an important role in biological systems, organic synthesis and drug metabolism. In humans,

Abbreviations: PSAA, phenylsulfinylacetic acid; EWG, electron withdrawing group; EDG, electron donating group; GS, ground state; OD, optical density; *r*, correlation coefficient.

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oxidative decarboxylation continually produces carbon dioxide in all live tissues during metabolism. Oxidative decarboxylation, in conjunction with electron transport and oxidative phosphorylation, takes place in the mitochondrial membrane and provides the basis of human cell respiration [23]. Anti-inflammatory drugs such as indomethacin and ibuprofen are decarboxylated during drug metabolism by cytochrome p-450 in vivo and the carbon dioxide released was found to reduce pain [24,25]. Enantiopure sulfoxides constitute a class of versatile chiral controllers and useful synthons in asymmetric synthesis and the pharmaceutical industry [26]. Further, sulfur substituted amino acids, vitamins, drugs and other xenobiotics are often involved in metabolism/-catabolism [27]. The chemistry of sulfones has been explored due to their therapeutic activities like antimicrobial [28], anticancer [29], anti-HIV [30], antimalarial [31] and anti-inflammatory [32]. Additionally, several drug molecules used for the treatment of leprosy, dermatitis herpetiformis [33] and tuberculosis [34] are found to contain the sulfone moiety. Hence the oxidation of organic sulfur compounds has been the subject of extensive studies in recent years. Phenylsulfinylacetic acid (PSAA), a sulfoxide containing acid group, is an ambidentate ligand and with its three donor atoms acts as a good chelating agent.

Recently, systematic attempts have been made with PSAA in this laboratory to study the mechanism and substituent effects during co-oxidation with oxalic acid by Cr(VI) [35], oxidative decarboxylation by Cr(VI) [36] and its reaction in the presence of cetyltrimethylammonium bromide [37] and picolinic acid [38], electron transfer reactions with iron(III)-polypyridyl complexes [39] and the catalytic effect of nitrogen bases [40] and ligand oxides [41] in the reactions with oxo(salen)chromium(V) complexes. Although vanadium(IV)-salen systems have been used as efficient catalysts in the asymmetric oxidation of organic sulfides by Fujita et al. [42] and Sun et al. [43], no detailed kinetic study has been reported so far in the literature on organic sulfur compounds by oxovanadium(IV)-salophen complexes. Nevertheless, Coletti et al. [44] used several salophen oxovanadium complexes as catalysts during the selective oxidation of sulfides to sulfoxides. Recently Sankareswari et al. [11] have synthesized eight salophen ligands and their oxovanadium(IV) complexes having different substituents and characterized these complexes by UV–Vis, FT-IR, EPR, ESI-MS, ^{1}H and ^{13}C spectral methods. They also reported their interaction with bovine serum albumin and cytotoxicity against cancer. The synthesis and X-ray structural characterization of such complexes were reported even earlier by Weberski Jr. et al. [45]. All these facts paved the way to explore the catalytic activity of oxovanadium(IV)-salophen complexes in the reactions of PSAAs with H_2O_2 and the results obtained on the mechanistic and substituent effects are discussed in this paper. The overall scheme of the reaction is as shown below.

2. Experimental

2.1. Synthesis of the oxovanadium(IV)-salophen complexes

The synthesis of the oxovanadium(IV)-salophen complexes was accomplished by a procedure slightly different from that reported in the literature [46]. To a hot methanolic solution (50 cc) of vanadyl sulfate ($VOSO_4{\cdot}5H_2O$; 0.25 g, 1 mM), the appropriate salophen ligand (1 mM) was added with stirring. The mixture was refluxed for one hour and cooled to room temperature. The green crystals separated were filtered, washed with diethyl ether and dried. Recrystallization was carried out from pure hot methanol. The absorption spectral data for the complexes (**I** to **IV**) are consistent with the literature data [11,44]. Their absorption maxima are 396 (**I**), 440 (**II**), 416 (**III**) and 410 nm (**IV**). The salophen ligands were prepared by a procedure similar to that reported in the literature [44]. Two equivalents of salicylaldehyde were dissolved in a minimum volume of boiling methanol (20 ml) and it was added dropwise to one equivalent of 1,2-benzenediamine in 5 ml methanol. The solution was refluxed for one hour and then cooled to room temperature. The yellow solid thus obtained was filtered, washed with methanol, diethyl ether and dried. All the compounds gave UV–Vis spectra consistent with their structures and literature data [47].

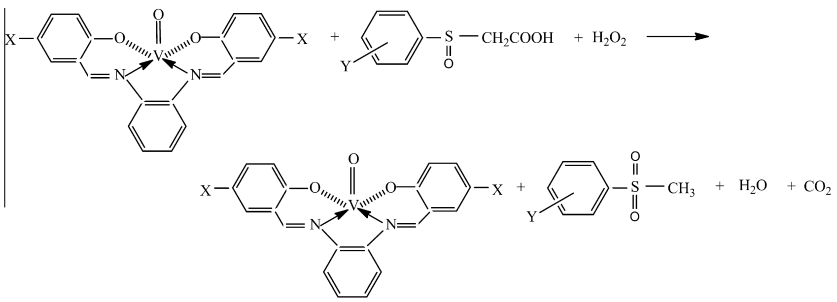
2.2. Preparation of phenylsulfinylacetic acids

Phenylsulfinylacetic acid and its meta- and para-substituted acids were prepared from the corresponding phenylmercaptoacetic acids by controlled oxidation with an equimolar amount of hydrogen peroxide [35]. PSAA and the *p*-chloro, *m*-chloro, *p*-bromo, *p*-fluro, *p*-methoxy and *p*-ethoxy PSAAs were purified by recrystallization from 1:1 benzene and ethyl acetate solvent mixture, whereas *p*-methyl PSAA was recrystallized with chloroform and PET ether. The purity of the PSAAs was checked by melting point [35] and LC–MS. The recrystallized PSAAs were kept inside a vacuum desiccator in order to prevent their decomposition with moisture in the atmosphere. The phenylmercaptoacetic acids were prepared by the condensation of the corresponding thiophenols with chloroacetic acid in alkaline medium [35].

Salicylaldehyde, 5-methyl, 5-methoxy and 5-chloro salicylaldehydes (Alfa Aeser), $VOSO_4{\cdot}5H_2O$ (Sigma–Aldrich), thiophenol (SD fine) and the 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

A double beam BL 222 Elico UV–Vis bio spectrophotometer with an inbuilt thermostat was employed to record the absorption



(**I**) X = H; (**II**) X = OCH_3; (**III**) X = CH_3; (**IV**) X = Cl

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