Oxovanadium(IV)-Salen Ion Catalyzed H₂O₂ Oxidation of Tertiary Amines to N-Oxides – Critical Role of Acetate Ion as External Axial Ligand

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Received 7 October 2014; revised 2 March 2015; accepted 2 March 2015

DOI 10.1002/kin.20910 Published online 24 March 2015 in Wiley Online Library (wileyonlinelibrary.com).

> ABSTRACT: The oxovanadium(IV)-salen ion catalyzed H_2O_2 oxidation of N,N-dimethylaniline forms N-oxide as the product of the reaction. The reaction follows Michaelis–Menten kinetics and the rate of the reaction is accelerated by electron donating groups present in the substrate as well as in the salen ligand. This peculiar substituent effect is accounted for in terms of rate determining bond formation between peroxo bond of the oxidant and the N-atom of the substrate in the transition state. Trichloroacetic acid (TCA) shifts the λ_{max} value of the oxidant to the red region and catalyzes reaction enormously. The cleavage of N–O bond by vanadium complex leads to moderate yield of the product. But the percentage yield of the product becomes excellent in the presence of TCA. © 2015 Wiley Periodicals, Inc. Int J Chem Kinet 47: 315–326, 2015

INTRODUCTION

The catalytic role of vanadium in the +4 and +5 oxidation states has received an intense attention in the

past three decades after the discovery of vanadatedependent enzymes, vanadium haloperoxidases [1–3], from various sea algae and terrestrial fungi [4]. These enzymes serve as efficient catalysts for the oxidative halogenation and oxidation of organic substrates using H_2O_2 as the oxidant [5–7]. Several oxo- and dioxovanadium(V) complexes serve as functional models of haloperoxidases and catalyze oxyhalogenation of aromatic substrates [4,8,9]. Vanadium(V) complexes

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with O, N coordination are regarded as bioinorganic catalysts as prosthetic groups present in the enzymes vanadate-dependent peroxidases have similar coordination environment. Apart from their role as catalysts, V(IV)/V(V) complexes have also been tested as insulin-like agents but recent reports indicate their anticancer activity also [13].

In the past three decades, salen (N,N'bis(saliylidene)ethylenediaminato) and its derivatives have received attention of many researchers because of their extensive application in the fields of synthesis and catalysis [14-16]. Salen ligand binds metal ions through a tetradentate binding motif, reminiscent of the porphyrin framework in the heme-based oxidase enzymes [17-19] but salen derivatives can be more easily manipulated to create an asymmetric environment around the active metal site. Metal-salen complexes form a standard system in coordination chemistry having great potential as catalysts for oxo transfer reactions [20,21] and other processes [22]. One of the first vanadyl-catalyzed reactions is the V(IV)-salen-catalyzed oxidation of organic sulfides reported by Fujita et al. [23]. Sun et al. [24] also reported an efficient asymmetric oxidation of sulfides catalyzed by vanadium-salen systems. Further V(IV) and V(V) oxo/peroxo species are considered as important intermediates in the proposed reaction mechanisms [18,25].

The reaction of oxovanadium(IV)-Schiff base complexes with an organic peroxide leads to the final form of the active oxovanadium(V) species [25b]. Curci et al. [26] proposed that in the oxidation of dibutyl sulfide with *tert*-butyl hydroperoxide (TBHP) catalyzed by VO(acac)₂, the catalytically active species is a vanadium(V) and not a vanadium(IV) species. In the V(IV)-catalyzed reactions, the possible intermediate is a metal-oxo, metal-peroxo or bridging oxo complex of various types [25,27]. The terminal oxo complex can arise when a single catalytic metal ion abstracts an oxygen atom from an oxygen source making twoelectron-oxidized metal oxo species [28].

The oxidation of tertiary amines may lead to the formation of different products such as *N*-oxide, demethylated products, and polyanilines [29]. Demethylation is a biologically important process and oxidation of *N*-compounds to *N*-oxides is an important transformation from biological and synthetic point of view [30]. *N*-Oxides find novel applications in inorganic and organic chemistry as protecting groups, oxidants, catalysts, and ligands [31]. Though many oxidants have been utilized for the oxidation of *tertiary* amines to *N*-oxides, the selective oxidation is still a challenging process. In several cases, *N*-oxides are more active than their corresponding tertiary amines.

From an environmental and economical stand point, catalytic oxidation processes are valuable and those employing atom-efficient oxidants such as H_2O_2 are less expensive. This process involving H2O2 as the oxidant generating water as the only by-product is particularly attractive from green chemistry point of view. A recyclable silica-supported [VO(acac)₂]-catalyzed oxidation of tertiary amines to the corresponding N-oxides with 30% H_2O_2 is reported [32]. The recent reports from the laboratory of Crucianelli and co-workers [33] highlight the importance of catalytic role of V(IV) complexes on the H₂O₂ oxidation of simple and conjugated olefins and styrene derivatives. Recently, we have reported a new and highly efficient methodology for the oxidation of tertiary amines to N-oxides with aqueous H₂O₂ in the presence of catalytic amounts of the catalyst, nanoruthenium (Ru(PVP)/ γ -Al₂O₃ [34].

In this report, we present our results on the catalytic activities of a series of [V(IV)-salen] complexes on the H₂O₂ oxidation of *N*,*N'*-dimethylanilines. This reaction is interesting in the sense that the rate of the reaction is accelerated by the electron-donating groups present in the substrate as well as in the oxidant and negative reaction constant (ρ) value is obtained from the study of substituent effect on the oxidant as well as on the substrate. This is a very rare reaction where the formation of the transition state is facilitated by the introduction of electron-releasing substituent in the oxidant as well as on the substrate. Further, the title reaction is catalyzed and the product yield improved enormously by trichloroacetic acid (TCA).

EXPERIMENTAL

Materials

Salicylaldehyde and substituted salicylaldehydes (5methyl, 5-methoxy, 5-chloro, 5-bromo, 5-nitro, 3,5dichloro, 3,5-di-*tert*-butyl), N,N'-dimethylaniline, and four substituted N,N'-dimethylanilines (methyl, cyano, bromo, and carboxylic) were purchased from Aldrich and used as such. HPLC-grade dichloromethane as the solvent and 30% H₂O₂ as the oxidant were used as received.

Instrumentation

The UV-vis absorption spectral measurements have been carried out in a quartz cuvette of 1 cm using JASCO 530 UV-vis spectrophotometer and Analytik Jena Specord S 100 diode spectrophotometer with a constant accumulation of 10 and a constant integration time of 40 ms over a wavelength range of 200–1000 nm. The infrared spectra of the complexes have been recorded in a JASCO FTIR-410 spectrophotometer, in solid phase, as KBr pellets. ¹H NMR spectra were recorded on a Bruker 300 MHz NMR spectrometer with CDCl₃ as the solvent. Cyclic voltammograms (CVs) were obtained using Sinsil CH work station electrochemical system with a three-electrode system and a personal computer for data storage and processing. An Ag/AgCl (saturated KCl)/3M KCl reference electrode, a Pt wire (counter electrode), and glassy carbon working electrode were employed for electrochemical studies. EPR spectra were recorded using Bruker EMX Micro premium X spectrometer at liquid N₂ and at room temperature at X band (9.4 GHz).

Synthesis of Salen Ligands and [Oxovanadium(IV)(Salen)] Complexes (I-VIII)

The salen ligands, $5,5'-(CH_3)_2$ -salen, $5,5'-(OCH_3)_2$ salen, $5,5'-(Cl)_2$ -salen, $5,5'-(Br)_2$ -salen, $5,5'-(NO_2)_2$ salen, $3,3',5,5'-(Cl)_4$ -salen, and $3,3',5,5'-(tert-Bu)_4$ salen were prepared by condensing the corresponding substituted salicylaldehyde with ethylene diamine in ethanol [35] and recrystallized from cold methanol. The ¹H and ¹³C NMR data are given in supporting information (Tables S-I and S-II) and the data are in close agreement with the previous reports [36].

[Oxovanadium(IV)(salen)] complexes (I–VIII) were prepared by the literature procedures by the reaction of stoichiometric amounts of the respective ligand with vanadyl sulfate in alcoholic medium [37–40]. All the eight [oxovanadium(IV)(salen)] complexes were characterized by UV-vis, ESI–MS, FTIR, EPR spectral studies, and cyclic voltammetric measurements and the data are given in Table I. The spectra of some complexes are given in supporting information (Figs. S1–S21) and the relevant spectral and electrochemical data in the Tables S-III to S-V.

Product Analysis

A solution containing 4-X-N,N'-dimethylanilines (X = $-CH_3$, -H, -Br, -COOH, -CN) was reacted with excess H_2O_2 in the presence of [oxovanadium(IV)(salen)] complex in CH_2Cl_2 and the reaction mixture was stirred for 3–10 h depending on the nature of substrate. The organic product was extracted several times in chloroform and analyzed in GC. The solvent was evaporated and the product was analyzed using ¹H NMR, ESI–MS, FTIR, and GC techniques. The product investigations through the spectral studies reveal the formation of *N*-oxides as the product of the reaction. The details of the product analyses are elaborated in the discussion section.

RESULTS AND DISCUSSION

The structures of five *tert*-amines and eight synthesized [oxovanadium(IV)(salen)] complexes used in the present study are shown in Chart 1. All eight [oxovanadium(IV)(salen)] complexes (**I–VIII**) synthesized in the present study are known compounds and the spectral and electrochemical data collected in Table I are in good agreement with reported results [37–42].

Absorption Spectral Studies

The [oxovanadium(IV)(salen)] complexes I-V and VIII are soluble in CH_2Cl_2 whereas the complexes VI and VII are soluble in DMSO. These V(IV)-salen complexes are poorly soluble in CH₃CN and alcohols. The absorption of parent [oxovanadium(IV)(salen)] complex (I) at 243 and 263 nm in CH₂Cl₂ (Fig. S1) corresponds to the ligand centered (LC) transition and the absorption at 368 nm corresponds to ligand to metal charge transfer (LMCT) transition [39a]. This LMCT absorption maximum is sensitive to the

			ESI MS	\mathbf{H} data (am ⁻¹) us as	E _{1/2} (V)	vs. SCE	EDD Data
Complexes	λ (nm)	$(\mathrm{M}^{-1}\mathrm{cm}^{-1})$	Data	$\nu_{C-O} \nu_{V=O}$	DCM	DMSO	(g_{\perp})
I	243, 263, 368	9860	334	1622, 1302, 986	0.641	0.372	2.02
II	244, 265, 381	7752	362	1622, 1298, 962	0.544	0.302	1.89
III	247, 266, 403	5219	394	1630, 1281, 974	0.567	0.340	2.00
IV	244, 261, 379	5845	441	1616, 1294, 966	0.663	0.483	1.89
V	244, 262, 380	4510	_	1616, 1294, 966	0.683	0.486	1.89
VI	238, 260, 336	9262	_	1601, 1309, 876	_	0.635	_
VII	272, 383	9262	_	1637, 1300, 867	_	0.452	_
VIII	243, 267, 338, 619	3812	567	1622, 1333, 974	0.402	0.216	1.90

Table I UV-Vis, ESI-MS, FTIR, CV and EPR Data of [Oxovanadium(IV)(Salen)] Complexes



Chart 1 Structure of [oxovanadium(IV)(salen)] complexes and tert-amines.



Figure 1 (A) UV-vis absorption spectral changes observed on the addition of H_2O_2 (10 mM) to I (0.1 mM) in CH_2Cl_2 at 298 K. (B) Changes observed in the d-d band absorption of I (0.5 mM) on the addition of H_2O_2 (50 mM).

nature of substituent present in the salen ligand (Table I). Introduction of 5-OMe group at the benzene ring (**III**) shifts the λ_{max} value from 368 nm to 403 nm (red shift) in DCM whereas 5-Cl and 5-Br (**IV** and **V**) groups cause a comparatively less shift from 368 nm to 379 nm. The shift in the λ_{max} to red region is due to the stabilization of excited state by electron-donating groups [43,44]. A substantial change in the absorption intensity of [V(IV)-salen] complex **I** is observed on the addition of H₂O₂ not only at the LMCT band at 370 nm but also at the d–d band at 570 nm. The details of spectral changes of complex **I** at 370 and 570 nm at low and high [H₂O₂] are shown in Fig. 1.

Kinetic Studies

The kinetic studies for the [V(IV)-salen] complex catalyzed H_2O_2 oxidation of 4-X-substituted *N*,*N'*-dimethylanilines (X = H, $-CH_{3,-}CN, -Br, -COOH)$ were carried out in CH_2Cl_2 medium under pseudo-first order conditions using excess of substrate over the oxidant. *N*,*N'*-dimethylaniline has absorption bands

at 243, 266, and 302 nm. The rate of decay of active species generated in the reaction mixture was followed spectrophotometrically from the decrease in absorbance at appropriate wavelength (Table I).

The absorption intensity of the mixture of **I** and H_2O_2 at 367 and 280 nm decreases whereas the absorbance at 324 and 425 nm increases with isosbestic points at 300, 345, and 400 nm (Fig. 1). At higher concentration of **I** and $[H_2O_2]$ the intensity of d–d absorption band decreases with time at 572 nm. These spectral changes can be taken as evidence for the formation of active species which may be formulated as vanadium(V)-peroxo complex or vanadium- H_2O_2 adduct (vide infra) [45]. Similar results were also observed for the solution of $[V^{IV}O$ (sal-his) (acac)] in methanol on the addition of H_2O_2 due to the formation oxoperoxo species [45e]. The formation of active species is evident from the color change from green to red [46].

The spectral changes shown in Fig. 2 also reveal the formation of N-oxide as the product of the reaction which is evident from the increase of absorbance at



Figure 2 Change of absorbance of **III** with time in the presence of H_2O_2 and *N*,*N'*-dimethylaniline (DMA). [**III**] = 1×10^{-4} M, [H₂O₂] = 1×10^{-2} M, [DMA] = 1×10^{-3} M.

440 nm and *N*-oxide binds to the vanadium(IV) center. Similar spectral changes have been reported in the oxidation of *N*,*N'*-dimethylanilines using iron-salen + H_2O_2 system to form the corresponding *N*-oxide [43c]. The plot of log Abs vs. time given in the Supporting information (Fig. S22) shows that there is a decrease in the absorption intensity (at 381 nm) up to 400 s but the intensity starts to increase after 400 s for the oxidation of 1 catalyzed by II + H_2O_2 system. It indicates that the oxidation reaction is a reversible process. From the decrease in absorbance at 381 nm with the time for the complex II, the rate constant of the reaction is calculated and the rate constant data for the substituted *N*,*N*-dimethylanilines are collected in the Supporting information (Table S-VI).

Michaelis-Menten Kinetics

The plot of k_1 vs. [substrate] given in Fig. 3 shows that the rate constant of the reaction increases with increasing the substrate concentration, reaches maximum, and then attains saturation. At high [substrate], saturation behavior is observed and the reaction proceeds through Michaelis–Menten kinetics (Fig. 3).

The rate constant k for the formation of the product is obtained by using the Michaelis–Menten kinetics, Eqs. (1) and (2).

$$Oxidant + Substrate \rightleftharpoons Complex \qquad (1)$$

$$Complex \to Product \qquad (2)$$



Figure 3 Plot of k_1 vs [S] for the oxidation of 4-X-*N*,*N*-dimethylanilines with II-H₂O₂ system at 298 K. (1. X = H, 2. X = CH₃, 3. X = CN, 4. X = Br, 5. X = COOH).

Based on the Michaelis–Menten formulation the observed rate constant (k_1) is given by Eq. (3).

$$k_1 = k_{\rm obs} = k({\rm substrate})/K_{\rm M} + ({\rm substrate})$$
 (3)

The rearrangement of Eq. (3) leads to Eq. (4)

$$1/k_1 = 1/k + K_{\rm M}/k[{\rm substrate}]$$
(4)

where $K_{\rm M}$ is the Michaelis–Menten constant, k is the rate constant for the oxidation of substrate. From the plot of $1/k_1$ vs. 1/[S] (Fig. S23) using Eq. (4), the values of $K_{\rm M}$ and k are calculated and given in Tables II and III, respectively.

The data collected in Table II shows that the rate constant for the formation of product is sensitive to the nature of substituents present in the of aryl moiety of N,N'-dimethylanilines. The electron-donating groups

Table II Rate Constant ($k \times 10^3 \text{ s}^{-1}$) Values for the Formation of Product from the Oxidation of 4-X-N,N'-Dimethylanilines of by [Vanadium(IV)(Salen)] + H₂O₂ System and the Reaction Constant (ρ) Values

$\begin{array}{l} \text{Complex} \rightarrow \\ \text{Substrate} \downarrow \end{array}$	·I	п	III	IV	V	ρ	r
Н	5.0	6.4	6.6	1.9	2.0	-0.9	0.95
-CH ₃	6.2	8.5	7.1	3.0	2.4	-0.5	0.97
-CN	0.9	0.7	5.6	0.24	0.38	-1.2	0.99
–Br	4.0	1.8	6.3	0.95	1.4	-0.5	0.96
-COOH	1.8	3.0	2.7	0.4	0.84	-0.6	0.97
ρ	-0.7	-1.5	-1.2	-1.0	-0.6	_	_
r	0.99	0.98	0.97	0.99	0.98	_	_

values					
$\frac{\text{Complex} \rightarrow}{\text{Substrate}} \downarrow$	Ι	II	III	IV	V
-H 1	3.1	5.0	3.4	5.8	4.3
-CH ₃ 2	8.6	8.3	6.1	5.9	7.0
-CN 3	1.3	1.7	2.4	0.9	1.3
-Br 4	1.7	2.3	2.0	1.5	2.2
-COOH 5	5.8	4.3	6.2	4.2	1.0

Table III Michaelis–Menten Constant, $K_M \times 10^3$, Values

Table IVMichaelis–Menten Constant (K_M) and RateConstant (k) Data for the **VI** and **VII** Catalyzed H_2O_2 Oxidation of 4-X-N,N'-Dimethylanilines in DMSO at298 K

	Complex	VI	Complex VII		
Substrate ↓	$\overline{K_{\rm M} \times 10^3 ({\rm M})}$	$k \times 10^3$	$\overline{K_{\rm M} \times 10^3 \rm M}$	$k \times 10^3$	
CH ₃	5.6	5.1	9.0	6.7	
Н	2.1	2.1	6.4	3.5	
CN	0.7	0.3	1.0	0.7	
Br	0.9	0.7	1.5	3.2	
СООН	1.7	0.6	9.3	2.3	
ρ	_	-0.6	_	-0.6	
r	_	0.96	-	0.93	

present in the *para*-position accelerates the rate of reaction and the electron withdrawing groups decelerate the rate of reaction. Similar substituent effect is observed when the substituents are introduced in the salen ligand (vide infra).

The complexes **VI** and **VII** have better solubility in DMSO and so the reactions of these complexes with N,N'-dimethylanilines have been studied in DMSO. The pseudo first-order rate constant (k_1) values for the oxidation of N'N-dimethylanilines (1–5) with **VII**–H₂O₂ system are collected in the supporting information (Table S-VII). The Michaelis–Menten constant (K_M) and the rate constant (k) values for the H₂O₂ oxidation reaction using the complexes **VI** and **VII** in DMSO are given in Table IV.

Substituent Effects

Application of Hammett equation to the rate constant data (Fig. 4) gives good correlation and the values of reaction constant (ρ) in the range of -0.6 to -1.5 are given in Table II.

$$\log k/k_0 = \rho\sigma \tag{5}$$



Figure 4 Hammett plot for the oxidation of *para-X-N,N'*-dimethylaniline using **II** and H_2O_2 .

Here, k_0 is the rate constant for the parent compound; k is the rate constant for the para-substituted compound; σ the substituent constant, depends only on the specific substituent; and the reaction constants ρ depend only on the type of reaction. This negative ρ value indicates that the substrate carries positive charge in the transition state of reaction. It is important to compare these results with the results observed for the oxidation of N, N'-dimethylanilines with other oxidants to get a clue on the mechanism of the reaction. Nam and coworkers [47] observed a ρ value in the range -2.2to -3.3 for demethylation reaction with oxoiron(IV) complexes. But the ρ value is -1.0 for the dioxirane oxidation of N,N'-dimethylanilines to the corresponding N-oxides [48]. The ρ value for the oxidation of N,N'-dimethylanilines by [Cr(III)-salen]-H₂O₂ system is in the range of -1.5 to -3.8 [44b] and in the range of -1.4 to -2.6 for Fe(III)–H₂O₂ system [43c].

We have also analyzed the kinetic data observed for the different [V(IV)-salen] complexes carrying electron-donating and -withdrawing groups in the salen ligand. The electron-donating groups present in 5, 5'position of the salen ligand also accelerate the reaction, and the observed ρ values are negative in the range -0.5 to -1.2. Interestingly, the behavior of the substituents present in the 5, 5'-position in the salen ligand of vanadium(IV) complexes is found to be different from the substituent effects observed with other metal-salen complexes [Fe(III), Cr(III), Mn(III) and Co(II)] [43,44,49,50].

It is appropriate to quote the similar results reported recently in the literature. The catalytic potential of



 $\label{eq:Scheme 1} \begin{array}{ll} \mbox{Mechanism of oxidation of } V^{IV} \mbox{ complex by } H_2O_2 \mbox{ to form the protonated } V^V \mbox{ complex.} \end{array}$

vanadyl complexes has been tested using cyclo-octene and styrene as the substrates and TBHP as the oxidant. The presence of electron-donating substituents on the aromatic ring as well as imine bond of salen effectively improves the catalytic activity [45h]. The presence of two methoxy substituents at the ortho-position of phenyl groups of vanadium(IV) complexes enhances the electron density on the ligating atoms of the ligand through π -donation of the phenyl groups. The metal center of vanadyl complex is expected to be more electron-rich and the redox potential of V(V)/V(IV)shifts in the cathodic direction and the complex becomes easier to be oxidized. Thus depending on the transition state of the reaction the electron-donating groups present in the ligand of the metal complex may facilitate the reaction by increasing the electron density on the metal center. As the substituent effect observed with the present study is similar to the results observed by Rayati et al. [45h] we propose a similar transition state.

Overall the results observed in the present study seem to be peculiar because the change of the substituents in the oxidant as well as substrate leads to similar results and negative (ρ) values are obtained in both cases. Thus, the formation of transition state is facilitated by the electron-donating groups present in the oxidant as well as in the substrate. In order to account for these interesting and novel results we have proposed a mechanism involving a transition state, the formation of which is facilitated by the electron-donating groups present in the substrate as well as in the oxidant.

Active Oxidant Species

The parent [oxovanadium(IV)(salen)] complex has LMCT absorption maximum at 368 nm [PhO⁻ \rightarrow VO(IV) transition]. Addition of H₂O₂ to the vanadium(IV) complex leads to a substantial change in the absorption spectrum (Fig. 1). These spectral changes can be taken as evidence for the formation of active oxidant species which may be formulated as peroxovanadium(V) complex or vanadium(IV)-H₂O₂ adduct (vide infra) [45,46]. The formation of the active species is also evident from the color change from green to red [46]. The vanadium(IV) complex in the presence of H₂O₂ forms stable dioxoV(V) complex or in the absence of base, the corresponding protonated oxocompound [51,52]. This dioxoV(V) complex further reacts with the oxidant, H_2O_2 to form peroxo complex, which is the active species. Scheme 1 shows that the vanadium(IV) complex is oxidized to vanadium(V) peroxo complex and further converted into hydroperoxovanadium(V) [53,54].

Proposed Mechanism for the Oxidation of N,N-Dimethylanilines

On the basis of the observed UV-vis absorption spectral changes, we presume that the active species formed is hydroperoxovanadium(V) (c) as shown in Schemes 1 and 2. In the first step, oxovanadium(IV) complex (a) is oxidized to oxovanadium(V) (b) by H_2O_2 and further reaction of H_2O_2 with (b) forms oxoperoxovanadium(V) complex (c) [45]. This complex (c) forms oxidant-substrate complex in which the oxygen atom is transferred from the active oxidant species to the *tert*-amine to produce the corresponding Noxide as the product. It has been established that in the other H₂O₂ oxidation reactions catalyzed by oxovanadium(IV) complex the active species is the species similar to complex (c). The negative ρ value observed from the study of substituent effect with the change of structure of tert-amine indicates that the substrate carries positive charge in the transition state of the reaction. The substituents present in the 5, 5'-position in the salen ligand of vanadium(IV) complex have behavior similar to that of the substrate. The bond formation between O-O of the oxidant and N atom of the substrate is facilitated by more electron density on the nitrogen center and thus the rate acceleration by electron-releasing groups in the substrate. Further, the vanadium-peroxo complex will be more stable with the increase of electron density on the vanadium center, which is possible with the introduction of electronreleasing group in the salen ligand and thus the negative ρ value observed with the change of substituent in the salen ligand also supports the proposed mechanism.

Effect of Trichloroacetic Acid

Figure S6 shows the spectral changes during the addition of TCA to the complex **II**. In the UV-vis



Scheme 2 The proposed mechanism for the H_2O_2 oxidation of 4-X-*N*,*N*'-dimethylanilines catalyzed by [oxovana-dium(IV)(salen)] complex.

absorption spectrum, the new broadband appears at around 615 nm but no peak at the same wavelength in the absence of TCA. The addition of TCA to the V(IV) complex also leads to color change from green to dark blue. Similar spectral changes have also been observed for the addition of TCA to [oxo(salen)chromium(V)] ion which is attributed to the binding of carboxylate ion to the metal center [49d]. The critical role of external axial ligands in the chirality amplification of metalsalen complex has recently been highlighted by Fujii and co-workers [55].

The changes in the absorption spectral data on the addition of TCA to the [oxovanadium(IV)(salen)] complexes (I–V) in CH_2Cl_2 (LMCT and d–d band) are collected in Table V. It is interesting to compare these

Table VAbsorption Spectral Data of Complexes (I–V)[0.2 mM]in the Absence and Presence of TCA [0.05 M]

Complex	λ (nm), ε (M ⁻¹ cm ⁻¹) Absence of TCA	λ (nm), ε (M ⁻¹ cm ⁻¹) Presence of TCA
I	369, 584(400)	376, 594(6720)
п	381, 594(700)	400, 615(5400)
III	403, 583(750)	413, 695(4650)
IV	379, 600(660)	389, 615(6560)
V	380, 601(620)	392, 617(8430)



Figure 5 UV-vis absorption spectral changes observed on the addition of H_2O_2 to I + TCA mixture.

spectral changes observed in the presence of TCA with those obtained during the reaction of H_2O_2 with **I** in the absence of TCA (Figs. 2 and 5). The UV-vis absorption spectral changes for the oxidation of N,N'-dimethylaniline by $\mathbf{I}+H_2O_2$ system in the presence of TCA show that there is a decrease in absorbance at 595 nm as shown in Fig. 5. The increase in absorbance change at 500 nm shown in Fig. 5 indicates

the formation of corresponding N-oxide. As the axial position of V(IV)-salen complex is now occupied by trichloroacetate ion, N-oxide is not able to bind with the V(IV)-salen complex [49d].

As indicated above the green-colored complexes I-V are changed into dark blue by the addition of TCA but on the addition of oxidant and the substrate the color changed from blue to pale yellow. The pseudo first-order rate constant (k_1) values are calculated by measuring the OD at the appropriate wavelength, $\lambda = 615$ nm, for the complex **II**, with respect to time. The rate for the oxidation of N, N'-dimethylanilines using V(IV)– H_2O_2 system in the presence of TCA is almost 10 times higher than in the absence of TCA. The plot of k_1 vs. [substrate] (supporting information) shows that the II-catalyzed H₂O₂ oxidation of N,N'-dimethylanilines in the presence of TCA is also fractional order with respect to substrate and the reaction proceeds through the Michaelis-Menten kinetics. The double reciprocal plot of $1/k_1$ vs. 1/[sub] for **II**catalyzed oxidation of N,N'-dimethylaniline by H₂O₂ in the presence of TCA is shown in the supporting information (Fig. S24).

From the double reciprocal plot the Michaelis-Menten constant $(K_{\rm M})$ and the rate constant (k) values for the formation of product are calculated and collected in Table VI. Figure S25 shows the Hammett plot for the oxidation of *para*-X-*N*,*N*'-dimethylanilines using II and H_2O_2 system in the presence of TCA. The interesting aspect is that the ρ value (-0.4) is less negative compared to the ρ value (-1.5) observed in the absence of TCA. The ρ value is always associated with the selectivity of the reaction. Thus in the presence of TCA, the reactivity of [V(IV)-salen]catalyzed H_2O_2 oxidation of N,N'-dimethylanilines is more but selectivity is less. Thus, these reactions are in accordance with the reactivity-selectivity principle (RSP). The operation of RSP has been observed in several other oxidation reactions of organic substrates catalyzed by [metal-salen] complexes [49c,56].

Table VIThe Value of Michaelis–Menten Constant (K_M) and the Rate Constant (k) for the Oxidation ofPara-Substituted N,N'-Dimethylanilines by II + H₂O₂ +TCA

Substrate	$10^3 \times K_{\rm M} ({\rm M}^{-1})$	$10^2 \times k$
CH ₃	10.2	2.6
Н	8.9	2.3
CN	4.3	1.2
Br	9.1	1.9
СООН	8.7	1.5

Table VII Product Yield of N-Oxides Formed from the Oxovanadium(IV)–Salen-Catalyzed H₂O₂ Oxidation of 4-X-N,N'-Dimethylanilines in the Presence of TCA

x	% Yield	% Yield in the presence of TCA
Me	27	92
Н	14	87
CN	13	81
Br	12	78
СООН	10	76

Product Yield

Table VII shows the % of product, the corresponding N-oxide, and yield obtained in the absence and presence of TCA. Though the reaction is efficient in the absence of TCA, the yield is low in all cases. This result is surprising but requires explanation. Recent report shows that the vanadium complexes have the excellent ability to cleave the N–O bond of N-oxides [57]. Thus, the major reason for the low yield of N-oxide formation is the cleavage of N–O bond by the V(IV) complex. This postulation is also supported by the reversibility of N-oxidation of tert-amines by H₂O₂ in the presence of V(IV)-salen complex and increase in the absorbance at 440 nm due to the formation of V(IV)-*N*-oxide adduct. Interestingly, the product yield is good to excellent in the presence of TCA. The yield is more for amine-carrying electron-donating substituents but less for electron-withdrawing substituents compared to the parent compound. This critical role of TCA makes this V(IV)-salen-H₂O₂ redox system as an excellent reagent for the selective oxidation of amines to N-oxides. Trichloroacetate ion binds on the axial position of V(IV)-salen complex thereby preventing the product N-oxide to bind with the catalyst and thus avoiding the decomposition of N-oxide and improving the product yield. Thus TCA plays a critical role in this reaction serving as an axial ligand of V(IV)-salen complex. Fujii et al. recently reported the critical role of N_3 and OCH₂CF₃ as axial ligands in the Mn(IV)-salen complex in chirality amplification [55].

The ESI–MS data of reaction mixture prepared using *N*,*N'*-dimethylaniline, [vanadium(IV)(salen)] complex **I**, and H₂O₂ show a peak with *m/z* value 138 confirming the formation of *N*-oxide as the product of the reaction. A sample spectrum is shown in the supporting information (Fig. S26). ESI–MS study also reveals the formation of dimerized product (*m/z* value 275). The IR spectrum of *N*,*N'*-dimethylaniline *N*-oxide is shown in the supporting information (Fig. S27) and the IR data are in close agreement with previous reports [34,58]. The peak at 944 cm⁻¹ corresponds to N–O stretching mode and the peak at 1347 cm⁻¹ corresponds to *tert*-amine. The product was also characterized by NMR spectral technique. The ¹H NMR spectrum of *N*-oxide of *N*,*N'*-dimethylaniline is shown in Fig. S28 and CDCl₃ is used as the solvent. There are distinct peaks δ at 3.53, 7.18–7.35 and 7.41–7.53 ppm and these values are in close agreement with our previous report [34]. This product analysis study demonstrates that *N*-oxide is the only product formed under the present reaction conditions.

CONCLUSION

This work presents a simple method for the efficient synthesis of N-oxides. The novelty of the present study is that the [vanadium(IV)(salen)]-catalyzed H₂O₂ oxidation of N,N'-dimethylanilines is facilitated by electron-donating groups present in the substrate as well as in the oxidant and the negative ρ value is observed from the study of substituent effect by the change of substituents in the substrate as well as in the oxidant. The N-oxide is the major product of the reaction in the presence of TCA confirmed by UVvisible, IR, Mass, and NMR spectral studies. In the rate-controlling step, the active oxidant oxoperoxovanadium(V) ion transfers oxygen to the substrate through direct oxygen transfer. TCA catalyzes the reaction through coordination to the V(V) center as the axial ligand.

Professor SR thanks UGC, New Delhi for sanctioning UGC-BSR Faculty Fellowship. AM thanks the UGC, New Delhi and the Management, V. O. C. College, Tuticorin for sanctioning permission to avail the benefits of Faculty Development Programme (FDP). AR is the recipient of UGC Meritorious fellowship under the Basic Scientific Research (BSR) Scheme.

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