Electron Transfer Reaction of Oxo(salen)chromium(V) Ion with Anilines

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The kinetics of oxidation of 16 *meta*-, *ortho*-, and *para*-substituted anilines with nine oxo(salen)chromium(V) ions have been studied by spectrophotometric, ESIMS, and EPR techniques. During the course of the reaction, two new peaks with λ_{max} at 470 and 730 nm appear in the absorption spectrum, and these peaks are due to the formation of emeraldine forms of oligomers of aniline supported by the ESIMS peaks with m/z values 274 and 365 (for the trimer and tetramer of aniline). The rate of the reaction is highly sensitive to the change of substituents in the aryl moiety of aniline and in the salen ligand of chromium(V) complexes. Application of the Hammett equation to analyze kinetic data yields a ρ value of -3.8 for the substituent variation in aniline and $+2.2$ for the substituent variation in the salen ligand of the metal complex. On the basis of the spectral, kinetic, and product analysis studies, a mechanism involving an electron transfer from the nitrogen of aniline to the metal complex in the rate controlling step has been proposed. The Marcus equation has been successfully applied to this system, and the calculated values are compliant with the measured values.

Introduction

The metal–salen [*N*,*N*′-bis(salicylidene)-ethylenediamine] complexes are simpler analogues of metal–porphyrin complexes. Salen, a tetradentate ligand, consists of two nitrogen atoms and two oxygen atoms available for coordination with a metal rather than the four nitrogen donors involved in porphyrin. However, these salen ligands have been shown to form metal complexes that parallel the catalytic activity of metal–porphyrins.[1–3] For example, iron(III)–salen complexes are similar to iron(III)–porphyrins in that both tetradentate ligands take up a square planar geometry, often with a fifth ligand (e.g., H_2O) in an apical position and an open sixth coordination site.[4,5] Most importantly, salens are relatively easy to synthesize from readily available precur-

sors, through the condensation of derivatives of salicylaldehyde and ethylenediamine.[6–8] Further, it is easy to tune the redox properties of oxo(salen)metal complexes by introducing electron donating and withdrawing groups in the *para*-position of phenolic moiety.[9,10] Because of these advantages, we and others have extensively used oxo(salen)metal complexes for the oxygenation of organic substrates, particularly for the sulfoxidation and epoxidation reactions.[5–20] In recent years, Cr(III)–salen complexes have been widely used as

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catalysts for the oxidation of organic substrates.[2,6,8,10,14,15,20-28] Gilheany and co-workers[8,10,21,22] have used these complexes extensively for the epoxidation reactions with PhIO, particularly in the presence of ligand oxides, Adam et al.[26] used them for the chemoselective C—H oxidation, and we[20,27,28] for the selective oxidation of sulfides to sulfoxides.

Amines and their derivatives are more widely distributed in nature than any other functional group family. The enzymatic oxidation of aromatic amines plays a significant role in many biotransformation processes, such as chemical carcinogenesis and drug metabolism.[29] The oxidation of aromatic amines may produce a large number of products. The most important of them are phenylhydroxylamine, nitrosobenzene, nitrobenzene, azobenzene, azoxybenzene, and oligomers and polymers of aniline.[30-38] In the past two decades, relatively long-lived chromium(V) intermediates

have been detected in the reaction of Cr(VI) both in vivo and in vitro. Since Cr(V) intermediates are generally considered labile and reactive, this chromium species is considered to be the key species in the mechanism of Cr(VI) carcinogenesis. Of the Cr(V) complexes studied as biomimetics, some noteworthy ones are chromium complexes containing the ligands 2-ethyl-2-hydroxybutyric acid (ehba), salen, picolinic acid (PA), ethylenediamine (en), phenanthroline (phen), and glutathione (GSH). Of these ligand systems, salen type ligands, as a class, consist of flexible and kinetically nonlabile templates wherein both steric and electronic properties of the metal center can be tuned in a synthetically straightforward manner. Further, the Cr(V)—salen complexes chosen for the present study mimic Cr—peptide complexes that may form upon intracellular reduction of Cr(VI) by virtue of the mixed nitrogen and oxygen ligand chelation.

Realizing the role of Cr(III)—salen complexes as efficient catalysts for the oxidation of organic sulfides to sulfoxides and alkenes to epoxides, we wanted to use them for the selective oxidation of aromatic amines to *N*-oxides. With this aim, we have initiated a systematic study on the oxidation of primary, secondary, and tertiary aromatic amines using several Cr(III)—salen complexes as catalysts. Interestingly, the reaction of oxo(salen)chromium(V) ions, generated from Cr(III)—salens and PhIO, with amines is facile and relatively fast. This reaction leads not to *N*-oxides but to the formation of oligomers of anilines as products, when primary amines are taken as the substrates. The introduction of substituents either at the aryl moiety of anilines or at the phenolic moiety of salen ligands leads to substantial variation in the reactivity yielding appreciably high reaction constant values (ρ) and interesting spectral changes. The advantage of Cr(III)—salen complexes as catalysts when compared to Fe(III)—salen and Mn(III)—salen ions is that oxo(salen)chromium(V) ions are stable and isolated unlike the oxo(salen)iron and oxo(salen)-manganese species which have fleeting existences.[39-44] In this article, we present spectral, kinetic, and mechanistic details on the oxo(salen)chromium(V) ion oxidation of 16 *meta*-, *ortho*-, and *para*-substituted anilines. In order to account for the spectral and kinetic results, we have proposed an electron transfer mechanism for the reaction. As the redox potentials of Cr^V/Cr^{IV} and $ArNH_2^{\bullet+}/ArNH_2$ couples are now available, we have applied Marcus theory to calculate the

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rate constant for the electron transfer reaction, and the calculated values comply well with the experimental values. This seems to be the first report for oxo(salen)chromium(V) complexes participating in a redox reaction through electron transfer mechanism and the first application of Marcus theory to such a reaction.

Experimental Section

Various salenH$_2$ analogues as Schiff base adducts were prepared from ethylenediamine, cyclohexane 1,2-diamine, or *o*-phenylenediamine and the corresponding salicylaldehydes (Aldrich) by standard methods.[14,18−20] Cr(III) complexes of these ligands, **Ia−i**, were synthesized using established procedures.[15,20] The purity of the complexes was checked by recording IR, EPR, ESIMS, and UV−vis spectral data and comparing them with the reported values.[10,14,15] Iodosobenzenediacetate and iodosylbenzene were prepared as reported by the earlier procedure.[45] Oxo(salen)chromium(V) complexes **IIa−i** (*Caution! Cr(V) compounds are known carcinogens.*) are prepared from their Cr(III) analogues by the oxidation of Cr(III)−salen complexes with PhIO; the experimental details are given in our previous reports.[20,27] Cr(III) and Cr(V) complexes synthesized in the present study were characterized by IR spectra and ESIMS. ESIMS study confirms the octahedral coordination of Cr(III) complexes. The structures of Cr(III)−salen and oxo(salen)chromium(V) complexes used in the present study and the abbreviations are shown in the equation given here.
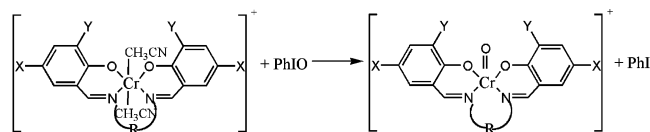
Ia, IIa: X = H, Y = H, R = -CH$_2$CH$_2$-

Ib, IIb: X =CH$_3$, Y = H, R = -CH$_2$CH$_2$-

Ic, IIc: X = Cl, Y = H, R = -CH$_2$CH$_2$-

Id, IId: X = Br, Y = H, R = -CH$_2$CH$_2$-

Ie, IIe: X=OMe, Y = H, R = -CH$_2$CH$_2$-

If, IIf: X= t-Bu, Y= t-Bu, R= -CH$_2$CH$_2$-

Ig, IIg: X = H, Y = H, R = -C$_6$H$_4$-

Ih, IIh: X = H, Y = H, R = -C$_6$H$_{10}$-

Ii, IIi: X = t-Bu, Y = H, R = -C$_6$H$_{10}$-

Various substituted anilines, which are liquids and low melting solids at room temperature, (Aldrich and Fluka) were purified by distillation under reduced pressure. Others were recrystallized from solvents as already reported.[46] The solutions for reaction were prepared in CH$_3$CN, kept under a nitrogen atmosphere in volumetric flasks, and stored in the dark. HPLC grade CH$_3$CN (Merck) was distilled under a nitrogen atmosphere and stored in bottles fitted with Teflon stoppers.

Kinetic Measurements. An Analytik-Jena Specord S100 diode array spectrophotometer was used to record the absorption spectra of Cr(III)−salen and oxo(salen)chromium(V) complexes used in the present study and to follow the kinetics of the reaction. The kinetic studies were carried out in CH$_3$CN under pseudo-first-order conditions with [anilines] ≫ [oxidant]. The progress of the reaction was monitored by following the decay of absorbance of oxo(salen)chromium(V) ion at appropriate wavelengths (λ_{max}) given in Table

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Table 1. Absorption Spectral Data (λ_{max}) and Redox Potentials of Cr(III)−Salen and Oxo(salen)chromium(V) Complexes in CH$_3$CN at 298 K

ligand	λ_{max} (nm) for Cr^{III}−(salen) ion	λ_{max} (nm) for oxo(salen)-chromium(V) ion	E_{red}, V (SCE)
salen	361, 415	560	0.44
5-Me-salen	338, 429	557	0.41
5-Cl-salen	350, 426	584	0.60
5-Br-salen	346, 424	590	0.61
3,3′,5,5′-tetra-*tert*-butylsalen	358, 427	595	0.24
5-OMe-salen	337, 448	577	
salophen	376, 420	600	0.61
cyclosalen	356, 425	600	0.45
3,3′,5,5′-tetra-*tert*-butylcyclosalen	354, 430	610	0.22

1. The color of the reaction mixture changed from an initial greenish-brown (shade varies slightly with substituents at 5,5′-position of oxidant) to a final yellow to violet depending on the substrate utilized. The pseudo-first-order rate constant, k_1, has been estimated by the least-squares method from the log OD versus time plots. It is important to mention that because of the complexity of the reaction, the rate constant has been estimated from the initial rates (∼20%). The duplicate runs carried out under similar conditions show that the k_1 value is reproducible within ±5%. The second-order rate constant, k_2, has been evaluated from the relation $k_2 = k_1/[\text{aniline}]$.

The thermodynamic parameters, enthalpy of activation ($\Delta H^{\ddagger}$) and entropy of activation ($\Delta S^{\ddagger}$), were evaluated by the least-squares method, using the Eyring equation, from the linear plot of log [k_2/T] versus $1/T$; the details are given in our previous report.[20]

EPR Spectral Study. As both Cr(III) and Cr(V) complexes are EPR active, the EPR spectra of these complexes were recorded at liquid nitrogen and room temperatures, respectively, in CH$_3$CN, with a JEOL JES-TE100 X-band EPR spectrometer using a YOKOVA 3024 *X−Y* plotter. The spectra for Cr(III) were acquired at a frequency of ca. 9.04 GHz, 1.00 mW microwave power, 0−5500 G sweep width, and 320 G modulation amplitude. The spectra for Cr(V) were acquired at a frequency of ca. 9.39 GHz, 1.04 mW microwave power, 3300−3340 G sweep width, and 25 G modulation amplitude. The kinetics of the reaction was also followed by measuring the decrease in the intensity of EPR signal of the Cr(V) complex at different time intervals.

ESIMS Study. The electrospray ionization mass spectra (ESIMS) data were acquired using a Quattro LC mass spectrometer (Micromass, Manchester, U.K.) using the Masslynx data system. Samples were introduced into the source by a direct infusion pump (Harvard apparatus) at a rate of 5 μL/min. Capillary and cone voltages were, respectively, kept at 3.9 kV and 15 V. For CID experiments, argon was used as the collision gas keeping the gas pressure at 3.3 × 10^{-4} mBar and varying the collision energy from 40 to 60 eV. Under these conditions, the ES emitter has no influence on the observed aniline oligomers. The progress of the titled reaction has been followed at different time intervals to know the intermediates and the products of the reaction.

Stoichiometry. Aniline in various proportions was mixed with oxo(salen)chromium(V) ion (1 × 10^{-3} M) in CH$_3$CN at 298 K. After 1 h, the resultant mixtures were extracted with hexane to remove unreacted aniline, and the extract was subjected to gas chromatography. From the concentration of unreacted aniline and the initial concentration of reactants, the stoichiometry was estimated to be >5:1 for aniline and Cr(V), respectively.

Product Analysis. In a typical experiment, a solution of 0.185 g (0.10 M) of substrate in 20 mL of CH$_3$CN was added to a solution
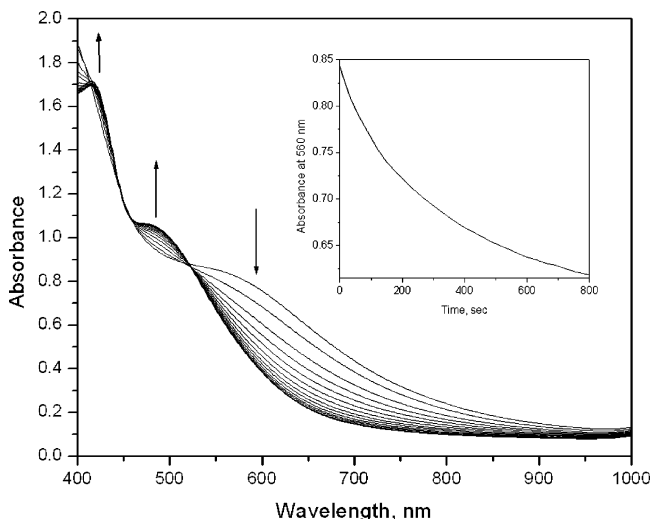
Figure 1. Change of absorbance of **IIa** with time in the presence of aniline. [**IIa**] = 4×10^{-4} M, [aniline] = 4×10^{-3} M. Inset: Change of absorbance with time at 560 nm.

Figure 2. Change of absorbance of **IIa** with time in the presence of *m*-toluidine. [**IIa**] = 4×10^{-4} M, [*m*-toluidine] = 4×10^{-3} M. Inset: Change of absorbance with time at 560 and 730 nm.

of 0.091 g (0.01 M) of oxo(salen)chromium(V) complex in 20 mL of CH₃CN. The solution was stirred at 298 K for 2 h, and the product mixture was rotary evaporated and subjected to column chromatography using neutral alumina. The column was eluted first with hexane, which removed unreacted aniline, and then with a 50/50 (v/v) petroleum ether−dichloromethane mixture. The first fraction gave the aniline oligomers as identified by their UV−vis, IR, and ESIMS data. UV−vis spectra of the first fraction with λ_{max} at 470 nm ($\epsilon = 13\,500$ M^{-1} cm^{-1}) and 730 nm ($\epsilon = 16\,850$ M^{-1} cm^{-1}) correspond to soluble oligomers of emeraldine forms of aniline and *m*-toluidine, respectively.[47−49] The second fraction corresponds to the Cr(III)−salen complex. The complete solubility of the rotary evaporated product mixture in acetonitrile indicates low molecular weight species as the products.[48]

IR Spectra. The IR spectral analysis of the product shows an NH band at 3400 cm^{-1}, which is very weak, indicating polymerization; bands at 690 and 750 cm^{-1} are present indicating coupling through the *para*-position with a low degree of polymerization. A peak at 1502 cm^{-1} corresponds to the C=N stretch of emeraldine present in the first fraction.[49]

Results

Nine chromium(III)−salen (**Ia−i**) and oxo(salen)chromium(V) complexes (**IIa−i**) have been synthesized in this work, and the structures of Cr(III) and Cr(V) complexes used in the present study are shown in the Experimental Section.

UV−Vis Spectral Study. The absorption maxima (λ_{max}) of all Cr(III) and Cr(V) complexes in CH₃CN are collected in Table 1. Figure 1 shows the change in the absorbance of **IIa** (the parent oxo(salen)chromium(V) ion) with time in the presence of aniline. The decay of absorption at 560 nm with time corresponds to the decrease in the concentration of the Cr(V) ion. The decrease in the absorbance of the Cr(V) at
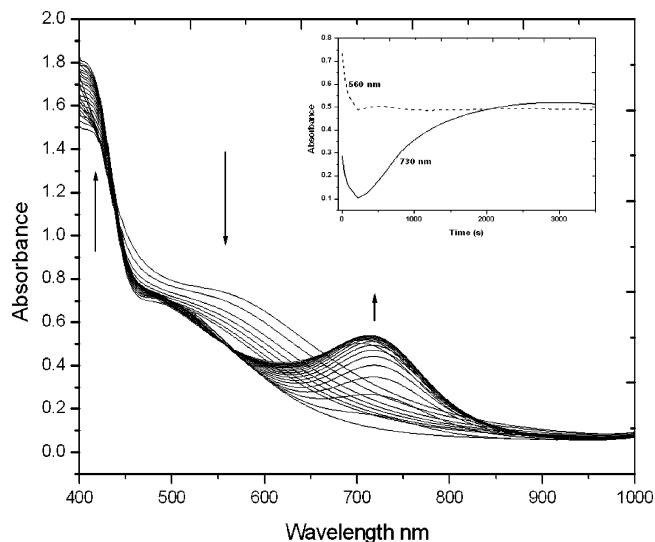
560 nm accompanies the growth of peaks at 420 and 470 nm with an isobestic point at 518 nm. It is known that Cr(III)−salen ion has a λ_{max} value at 420 nm. The absorption maximum at 470 nm (orange-red in color) corresponds to the oligomer of aniline (vide infra). When *m*-toluidine is used as the substrate, apart from the peak at 470 nm, a new peak is developed at 730 nm, and the absorbance at 730 nm (greenish blue in color) increases with time (Figure 2). The new peaks at 470 and 730 nm indicate the formation of oligomers of aniline and 3-methyl aniline as the major products of the reaction (vide infra).[47]

Kinetics. When the time dependent absorption spectrum of **IIa** is monitored at 560 nm (λ_{max} of **IIa**) under pseudo-first-order conditions ([aniline] ≫ [Cr^V]), the plot of log OD versus *t* was found to be linear for the initial part (∼20%). The plot of the pseudo-first-order rate constant as a function of aniline concentration is linear, and the slope is equal to the second-order rate constant of the reaction (Figure 3A,B). These data taken together show that the rate determining step is first-order with respect to both aniline and the oxo(salen)-chromium(V) ion. The rates of oxidation of 16 *meta*-, *ortho*-, and *para*-substituted anilines with nine oxo(salen)chromium(V) complexes (**IIa−i**) were measured under identical conditions, and the second-order rate constant data are summarized in Table 2. The oxo(salen)chromium(V) ion carrying the methoxy group in the 5,5′-positions of the salen ligand is less stable. The kinetic data obtained for the oxidation of anilines with this complex are not reproducible and thus not included in the table.[10,15] The data provided in Table 2 show that the redox reaction is highly sensitive to the change of substituents in the phenyl ring of aniline and in the 5,5′-positions of salen ligand.

To quantify these substituent effects, log k_2 values of anilines are plotted against Hammett σ constants,[50,51] and

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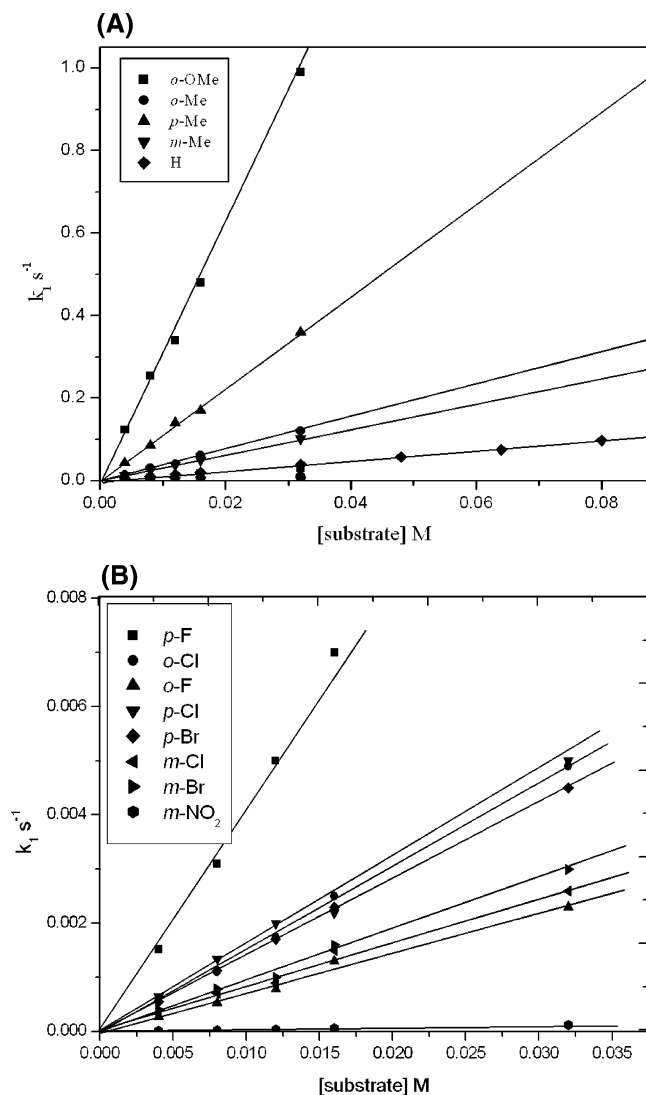(51) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979−4987.

(A)

(B)

Figure 3. (A) Plot of k_1 vs [X−C$_6$H$_4$NH$_2$]. (B) Plot of k_1 vs [X−C$_6$H$_4$NH$_2$].

the sample plot is shown in Figure 4. The correlation of log k_2 versus σ is good, and the reaction constant (ρ) values for eight complexes are collected at the bottom of Table 2. It is important to note that *ortho*-substituted anilines have slightly low k_2 values compared to those for the corresponding *para*-substituted anilines (Figure 4). Here, for the *ortho*-substituted anilines, the polar constants for *ortho*-substituents derived from Taft's σ_o* values have been used. As these substituent constants quantify only a polar effect, the deviation of rate constant data from these σ values may point out the operation of another effect, presumably a steric effect. Figure 4 shows that the points corresponding to *ortho*-substituted anilines deviate slightly from the linear plot. This observation indicates the smaller importance of the steric effect in this reaction. Though the k_2 values obtained for the *ortho*-substituted anilines are included in the Hammett plot, they are not used in obtaining the best line, and the ρ value is calculated using *meta*- and *para*-substituted anilines. The reaction constant value is negative, and its magnitude depends on the nature of substituent in the salen ligand. The ρ value is in the range −1.4 to −4.4 (for details, cf. Table

2). The negative ρ values indicate that a positive charge is developed on the nitrogen center of the substrate at the transition state of the reaction. The magnitudes of ρ values indicate the extent of positive charge development on the nitrogen. The Hammett equation has also been applied to the analysis of the substituent effects when substituents are introduced in the salen ligand. A sample plot is shown in the Supporting Information (Figure S1). Here also, log k_2 versus σ is linear giving a positive ρ value ($\rho = 2.2$). The ρ value obtained for each aniline substrate is given in the 8th column of Table 2. The positive ρ value points out that negative charge is developed at the metal center in the transition state. The kinetic data collected in columns 4 and 7 show the k_2 values obtained for Cr(V) complexes carrying 5-Me, **IIb**, and 3,5-*tert* butyl groups, **IIf**, in the salen ligand. The k_2 values observed for the latter complex are low when compared to the values of the former.

Kinetics in the Presence of Acrylonitrile. The redox reaction of 3-methyl aniline with the parent oxo(salen)-chromium(V) ion is carried out in the presence of a vinyl monomer, acrylonitrile. The second-order rate constant of this redox reaction is not affected appreciably by the presence of vinyl monomer acrylonitrile. The formation of oligomer at $\lambda_{max} = 730$ nm has also been followed, and the second-order rate constant is found to be 2.38 M^{-1} s^{-1} in the absence of acrylonitrile and 0.55 M^{-1} s^{-1} in the presence of acrylonitrile. Thus, the rate of oligomer formation is enormously inhibited by radical scavenger, acrylonitrile, indicating the formation of radical in the rate controlling step.

Electrochemistry of Oxo(salen)chromium(V) Complexes. Though oxo(salen)chromium(V) complexes have been extensively used as oxidants for the oxidation of a variety of organic substrates, less attention has been paid to the study of electrochemistry except the preliminary report by Kochi and co-workers.[14] The cyclic voltammograms of eight oxo(salen)chromium(V) complexes were recorded, and the reduction potential values measured in CH$_3$CN are collected in Table 1. The first scan of the cyclic voltammogram of complex **IIc** is shown in Figure 5. The starting potential of the cyclic voltammogram is +1.2 V, and the cyclic voltammogram was run in the reductive scan. During consecutive scans, the shape of the cyclic voltammogram changed, and the peak disappeared. From the peak separation, we are unable to conclude on the reversibility of the redox cycle. We are unable to calculate the ratio of the peak current due to the change in the cyclic voltammogram from the second scan onward. We presume that the first reduction observed around 0.60 V is for the reduction of Cr^V to Cr^{IV}. The reduced complex may undergo chemical transformation to give an oxidation peak around 0.9 V. The reduction potentials of the various chromium(V)−salen complexes **IIa−i** are reported in Table 1(corrected to ±5 mV). From the data collected in Table 1, we understand that the reduction potential value (E_{red}, V) is susceptible to the nature of the substituent in the salen ligand.

It is interesting to compare the reduction potentials of these oxo(salen)chromium(V) complexes with that of

Table 2. Second-Order Rate Constant (k_2) Values for Oxo(salen)chromium(V) Complexes Oxidation of $XC_6H_4NH_2$ in CH_3CN at 298 K

no.	X	a	$10^2 k_2, M^{-1} s^{-1}$
			IIa[b]	**IIb**[b]	**IIc**[b]	**IId**[b]	**IIf**[b]	ρ	r	**IIg**[b]	**IIh**[b]	**IIi**[b]
1	2-OMe	0.76	3090	501			6.97	2.0	0.990		110	3.15
2	2-Me	0.85	374	103	4510		5.24	2.3	0.999	3450	23.1	2.94
3	4-Me	0.78	1090	135	5680		12.1	2.1	0.992	3030	58.2	4.90
4	3-Me	0.84	328	103	4430		6.51	2.2	0.998	1010	32.9	2.80
5	H	0.87	121	56.9	1610	3200	3.50	2.2	0.990	365	21.8	3.12
6	3-OMe	0.89	92.1	36.5	1220	1770	3.51	2.0	0.998	662	10.9	2.15
7	4-F	0.92	38.0	23.0	1120	711	2.65	1.9	0.982	159	7.10	1.43
8	2-Cl	0.96	14.0	18.4	178	325	2.30	1.5	0.979	62.2	2.31	0.78
9	2-F	0.96	6.90	8.90	95.1	178	2.04	1.6	0.969	20.7	2.13	0.79
10	4-Cl	0.95	16.2	9.30	207	271	2.19	1.6	0.976	40.4	4.09	1.27
11	4-Br	0.96	13.7	8.60	340	338	2.09	1.7	0.981	30.3	1.58	0.81
12	3-Cl	0.98	8.70	2.60	23.0	24.0	0.81	1.4	0.972	15.7	1.22	1.03
13	3-Br	0.97	9.98	3.80	21.0	21.4	0.81	1.5	0.948	16.1	1.09	0.92
14	$3-NO_2$		0.35	0.56	4.00	5.80	0.20			0.50	0.15	0.25
15	$2-NO_2$		0.14	0.22	0.61	0.38	0.09			0.16	0.05	0.11
16	$4-NO_2$		0.20	0.33	1.21	1.20	0.10			0.20	0.13	0.10
	ρ		−3.8	−2.8	−4.1	−4.4	−2.2			−4.4	−3.1	−1.4
	r		0.993	0.986	0.956	0.965	0.954			0.985	0.987	0.976

[a] Oxidation potential of anilines (V). [b] (a) Salen. (b) 5,5′-Methylsalen. (c) 5,5′-Chlorosalen. (d) 5,5′-Bromosalen. (f) 3,3′5,5′-Tetra-*tert*-butylsalen. (g) Salophen. (h) Cyclosalen. (i) 3,3′,5,5′-Tetra-*tert*-butylcyclosalen.
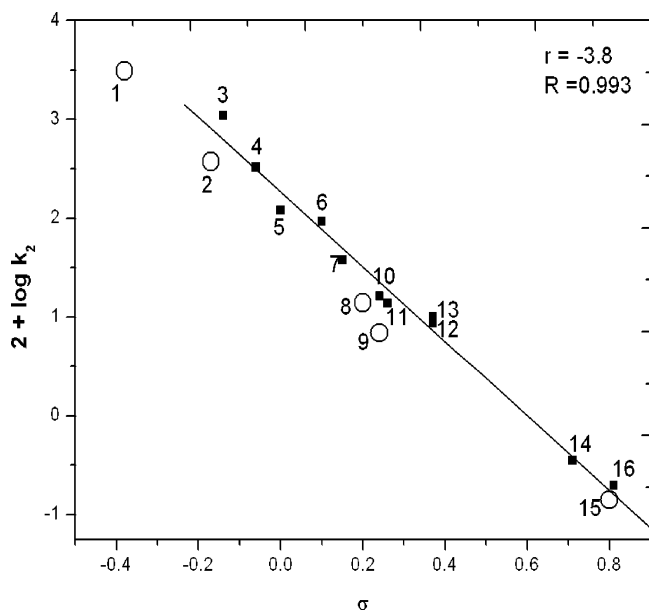

Figure 4. Hammett plot for the oxidation of *meta*- and *para*-substituted anilines with **IIa**. (Though the k_2 values obtained for the *ortho*-substituted anilines are included in the Hammett plot, they are not used in obtaining the best line and the ρ value.) Labeling is per Table 2. (σ values for 1 = −0.38, 2 = −0.17, 3 = −0.14, 4 = −0.06, 5 = 0.0, 6 = 0.10, 7 = 0.15, 8 = 0.2, 9 = 0.24, 10 = 0.24, 11 = 0.26, 12 = 0.37, 13 = 0.37, 14 = 0.71, 15 = 0.8, 16 = 0.81.)

Figure 5. Cyclic voltammogram of **IIc** in deaerated acetonitrile solution containing 0.1 M TBAP.

$[Cr^V(O)(ehba)_2]^-$ (ehba = 2-ethyl-2-hydroxybutyric acid).[52] The Cr(V) ion, $[Cr^V(O)(ehba)_2]^-$, has been extensively used as an oxidant and a reactive intermediate to check the carc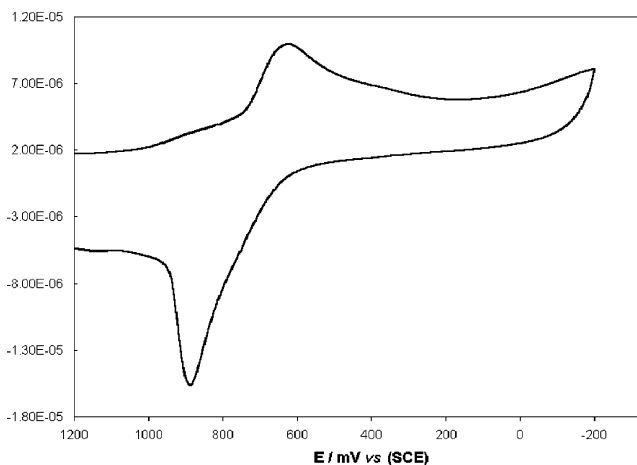inogenicity of Cr(VI).[53−55] The formal reduction potential of $[Cr^V(O)(ehba)_2]^-$ is similar (0.44 V) to that of the parent Cr^V−salen complex. Since a quasireversible one-electron redox process corresponding to $[O=Cr^V(salen)]^+ + e \rightleftharpoons [O=Cr^{IV}(salen)]$ is observed, it is inferred that the conversion of Cr^V to Cr^{III} is difficult, and this is probably due to an extremely sluggish electrokinetic process for the reduction of the Cr(IV) intermediate. Marked structural dissimilarities between Cr(IV) and Cr(III) complexes are likely to contribute to the electroreduction process studied here as observed in the case of $[Cr^V(O)(ehba)_2]^-$ ion.[52]

ESIMS Data. To get more details on the intermediates and products of the reaction, we have followed the progress of the reaction using electrospray ionization mass spectra. The ESIMS data of the reaction mixture, prepared using **IIa** as the oxidant and aniline or 3-methyl aniline as substrate, were recorded by direct infusion of the reaction mixture at definite intervals of time (1, 10, 30, 60 min). This study shows that the intensity of the peak with m/z value 334 (corresponding to the Cr(V)−salen complex) decreases with time with concomitant increase in the intensity of peaks with m/z values 318, 359, and 400 (Supporting Information Figure

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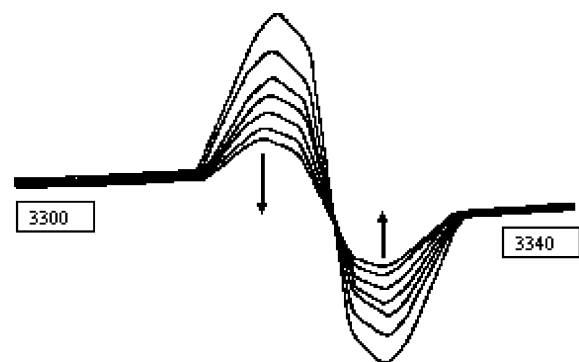(55) Gould, E. S. *Acc. Chem. Res.* **1986**, *19*, 66−72.

Figure 6. EPR spectra showing change in the intensity of **IIa** during the oxidation of aniline.

S2). The peaks with m/z values 318, 359, and 400 correspond to [Cr(III)(salen)]$^+$, [Cr(III)(salen)(CH$_3$CN)]$^+$, and [Cr(III)-(salen) (CH$_3$CN)$_2$]$^+$ ions, respectively.

Apart from the spectral changes shown here, new peaks at 183, 274, and 365 develop step by step indicating the oligomerization process (Supporting Information Figure S3). These ions were further subjected to collision induced dissociation (CID), and the resulting spectra established the approximate identity of the compounds. The peak at 183 fragmented to give ions at m/z 182, 167, 108, and 77, the peak at 274 fragmented to give ions at m/z 196, 181, 108, and 77, and the peak at m/z 365 fragmented to give ions at m/z 349, 274, 258, 196, 181, 108, and 77. From these spectral studies, we infer that the species with m/z values 183, 274, and 365 correspond to the protonated forms of dimer, trimer, and tetramer of aniline, respectively.

EPR Study. The advantage with Cr(III) and Cr(V) complexes is that they are EPR active. The EPR spectra of the parent Cr(III)−salen and oxo(salen)chromium(V) complexes are shown in the Supporting Information (Figure S4). The kinetics of the reaction of the oxo(salen)chromium(V) ion with aniline have been followed by an EPR technique also, and the change in the intensity of the EPR signal with time is shown in Figure 6. The rate constant obtained from this study is similar to the value observed from the spectro-photometric study.

Thermodynamic Parameters. The kinetics of the reaction of anilines with oxo(salen)chromium(V) complexes have been studied at four different temperatures, and the thermo-dynamic parameters, enthalpy of activation ($\Delta H^{\ddagger}$) and entropy of activation ($\Delta S^{\ddagger}$), were calculated. The kinetic data at four different temperatures and thermodynamic parameters evaluated from them are collected in Table 3. From the thermodynamic data, we realize that though both $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ values vary with the structure of aniline, the change in $\Delta H^{\ddagger}$ value is substantial with the change of substituent in the aniline, and thus, the reaction is enthalpy controlled. To check the applicability of an isokinetic relationship here, we have plotted $\Delta H^{\ddagger}$ against $\Delta S^{\ddagger}$, and the plot is shown in the Supporting Information (Figure S5). From the slope of the plot, we get the value of the isokinetic temperature (β) as 519 K. Though much importance cannot be attached to the plot, we presume that the linear isokinetic plot points out the operation of the similar mechanism for the oxidation of

Table 3. Second-Order Rate Constant, k_2, Values at Four Different Temperatures and Values of Enthalpy ($\Delta H^{\ddagger}$) and Entropy ($\Delta S^{\ddagger}$) of Activation for [O=Cr^V(salen)]$^+$PF$_6^-$ Oxidation of X−C$_6$H$_4$NH$_2$ in CH$_3$CN

| | $10^2\ k_2\,M^{-1}s^{-1}$ | | | | $\Delta H^{\ddagger}$, kcal mol^{-1} | $-\Delta S^{\ddagger}$, cal K^{-1} mol^{-1} |
X	288 K	298 K	303 K	313 K		
2-OMe	2310	3090	3600	4680	4.47	36.7
2-Me	250	374	440	530	4.83	36.8
4-Me	790	1090	1310	1830	5.44	35.5
3-Me	210	328	388	534	6.03	36.0
H	77.8	121	150	202	6.27	37.2
3-OMe	59.2	92.1	120	162	6.73	36.1
4-F	25.9	38.0	51.1	76.2	7.19	36.2
2-Cl	7.84	14.0	19.8	24.7	7.95	35.8
2-F	4.12	6.90	9.83	13.1	7.92	35.4
4-Cl	11.2	16.2	21.4	40.1	8.66	32.9
4-Br	9.79	13.7	20.1	34.1	8.46	33.9
3-Cl	5.60	8.70	12.2	24.9	9.97	29.7
3-Br	6.60	9.98	15.3	26.5	9.54	30.8
3-NO$_2$	0.21	0.35	0.71	1.89	15.5	17.3
2-NO$_2$	0.06	0.14	0.31	0.70	17.8	11.4
4-NO$_2$	0.09	0.20	0.48	1.00	17.5	11.8

all the anilines. As the experimental temperature is far from the isokinetic temperature, the applicability of the Hammett equation to the analysis of kinetic data of this reaction is valid.

Discussion

The spectral and kinetic data presented here indicate that the oxidation of anilines with oxo(salen)chromium(V) com-plexes follows clean second-order kinetics, first-order with respect to the oxidant and first-order in the substrate. The redox reaction has been carried out in the presence of radical scavenger, acrylonitrile. Though the rate of disappearance of oxo(salen)chromium(V) ion is not affected appreciably, the rate of oligomerization of aniline is inhibited enormously, confirming the formation of anilinium radical ion in the rate determining step. The product analysis study shows dimer, trimer, and tetramers of aniline as the major products of the reaction. UV−vis spectral and ESI-MS studies also indicate that, in the present study, the oligomers of aniline are the major products of the reaction. This conclusion was arrived at from the following spectral observations.

Figure 1 shows the complete disappearance of the peak at 560 nm for Cr(V) and the appearance of a peak at 420 nm for Cr(III) with an isobestic point at 518 nm. Thus, the final inorganic product is the Cr(III)−salen complex. Inter-estingly, apart from the spectral features indicated above, an additional peak appears at 470 nm (orange-red in color), and the intensity of peak increases with time. Further, when anilines containing electron releasing groups such as Me and OMe are used as substrates, in addition to the peak at 470 nm, one more peak emerges at 730 nm (green-blue in color) whose absorbance increases steadily with time (Figure 2). To account for these two new bands, we searched through the literature of the organic compounds derived from aniline having absorptions at 470−500 and 730 nm. There are reports available which show that the trimer and tetramer of aniline absorb at 470−500 and 730 nm.[47,56−58] The clean

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Scheme 1. Sequence of Steps Leading to the Formation of Oligomers in the Oxo(salen)chromium(V) Ion Oxidation of Anilines in CH_3CN
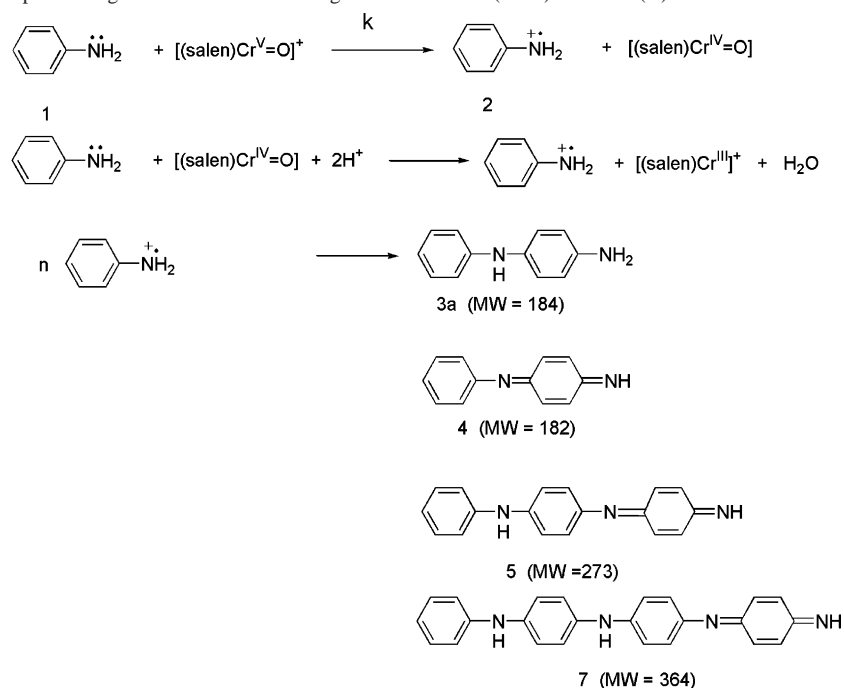
conversion of Cr(V) to Cr(III) and formation of oligomers of aniline as the organic products are also evident from the mass spectral study. The peak with a m/z value 334 for the ion $[(salen)Cr^V{=}O]^+$ disappears, and new peaks with m/z values 318, 359, and 400 emerge (details are given in the Results section). To account for these spectral and kinetic observations, the following steps (Scheme 1) may be proposed which are similar to those envisaged for the electrochemical oxidation of anilines. There is a possibility for the formation of N−N coupling and C−C coupling products from aniline radicals in addition to C−N coupling products. The possibility of N−N coupling and C−C coupling products here was excluded on the basis of the MS-MS fragmentation pattern of the peaks observed for oligomers of anilines.

Thus, electron transfer from anilines to Cr^V, to form anilinium radical ions and Cr^{IV} as the intermediates, initiates the reaction. The Cr^{IV} that is formed reacts with aniline to form Cr^{III} as the final inorganic product. Anilinium ions then combine with aniline to form a dimer of aniline and finally to form stable oligomers of aniline as the products. This is also confirmed by the absorption spectra of the products with λ_{max} at 470 and 730 nm corresponding to tetramers, higher oligomers, and their emeraldine forms. A similar mechanism has been proposed for the electrochemical oxidation of aniline to oligomers and polymers of aniline. The interesting aspect here is that we are able to produce oligomers of aniline from a simple chemical reaction between anilines and a Cr(V) ion, an oxidation state proposed to be responsible for the carcinogenicity of chromium. To get support for the postulation of electron transfer in the rate determining step

we have plotted log k_2 values against the oxidation potentials of anilines and reduction potentials of oxo(salen)chromium(V) complexes; the plots are shown in Figure 7. These plots are reasonably linear and support the postulation of an electron transfer mechanism. Fukuzumi et al.[59,60] have taken the linearity in the plot of log k_2 versus oxidation potentials of anilines as supporting evidence for the operation of an electron transfer mechanism. The proposal that the oxidation of anilines by oxo(salen)chromium(V) complexes proceeds through an electron transfer mechanism is noteworthy in the context of carcinogenicity of chromium. The oxidation of proteins and lipids by one-electron transfer processes has been associated with the onset of several diseases and aging.[61] This observation is consistent with the belief that the carcinogenic properties of oxochromium compounds may be attributed to their tendency to engage in free radical oxidations.[62] Recently, Sugden et al.[63] have observed that cationic Cr(V)−salen complexes show specificity of oxidation toward the nucleic acid base guanine in contrast with the anionic Cr(V) complexes $[Cr^V(ehba)_2]^-$ that specifically oxidize the deoxyribose sugar moieties of DNA.[64]

Application of Marcus Theory of Electron Transfer. The kinetic data given in Table 2 show that the reactivity changes by 4−5 orders of magnitude with the change of structure of aniline and salen ligand. In order to account for

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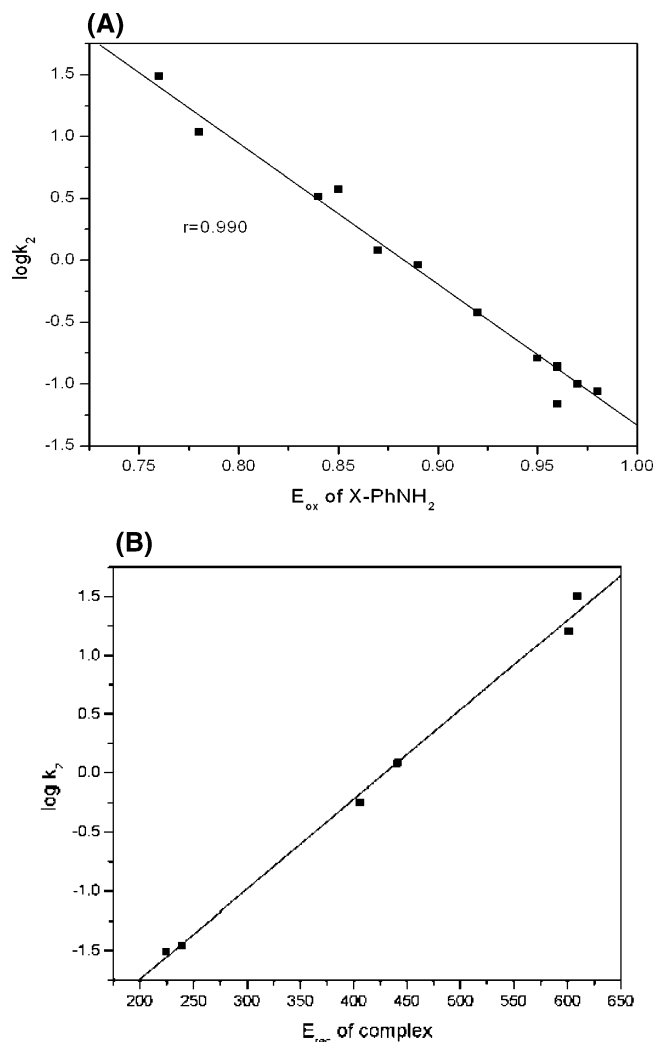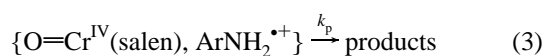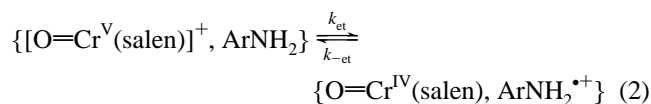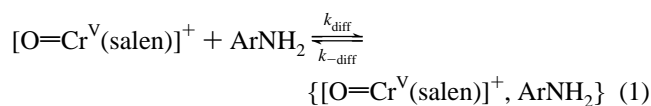
Figure 7. (a) Plot of log k_2 vs oxidation potential of anilines. (b) Plot of log k_2 vs reduction potential of oxo(salen)chromium(V) complexes.

the spectral and kinetic results, an electron transfer from the substrate to the oxidant in the rate controlling reaction step has been proposed. Over the past decades, a guiding principle for work on electron transfer (ET) processes has been the classical theory of ET as developed by Marcus, Hush, Sutin, and others.[65−70] The mechanistic scheme used for the analysis of the electron transfer is shown in eqs 1−3.

$$[O\!\!=\!\!Cr^V(salen)]^+ + ArNH_2 \underset{k_{-diff}}{\overset{k_{diff}}{\rightleftharpoons}}$$
$$\{[O\!\!=\!\!Cr^V(salen)]^+, ArNH_2\} \quad (1)$$

$$\{[O\!\!=\!\!Cr^V(salen)]^+, ArNH_2\} \underset{k_{-et}}{\overset{k_{et}}{\rightleftharpoons}}$$
$$\{O\!\!=\!\!Cr^{IV}(salen), ArNH_2^{\bullet+}\} \quad (2)$$

$$\{O\!\!=\!\!Cr^{IV}(salen), ArNH_2^{\bullet+}\} \overset{k_p}{\rightarrow} products \quad (3)$$

The diffusion rate constant (k_{diff}) represents the formation of a precursor complex, k_{-diff} the back diffusion rate constant, k_{et} the rate constant for electron transfer, k_{-et} the back electron-transfer rate constant, and k_p the irreversible product forming rate constant. The assumption that k_p is irreversible

is consistent with the data. The value of k_{et} (in eq 2) can be calculated from the theoretical expression, eq 4, which can be derived from the transition state and Marcus theories.

$$k_{et} = \kappa Z \exp(-\lambda/4(1 + \Delta G°/\lambda)^2/RT) \quad (4)$$

Here, κ is the transmission coefficient, and Z is the value of collision frequency. For a bimolecular reaction, the value of κZ is taken as 10^{11} M^{-1} s^{-1}. The term $\Delta G°$ is the free energy change associated with eq 2, and λ represents the reorganization energy for the electron transfer. The value of $\Delta G°$ can be calculated from the reduction potential of the Cr(V) ion, $E°(Cr^V/Cr^{IV})$, and the oxidation potential of aniline, $E°(ArNH_2^{\bullet+}/ArNH_2)$ (eq 5).

$$\Delta G° = E°(ArNH_2^{\bullet+}/ArNH_2) - E°(Cr^V/Cr^{IV}) + W_p - W_r \quad (5)$$

Here, W_p and W_r are the terms representing the work required to bring together the reactants and products, respectively. Here, W_r is assumed to be zero since one of the reactants, aromatic amine, is neutral. W_p is calculated using eq 6

$$W_p = Z_D Z_A e^2 \{1/(1 + \beta d\mu^{1/2})\} \quad (6a)$$

where

$$\beta = \{(8\pi Ne^2)/(1000D_s k_B T)\} \quad (6b)$$

Here, Z_D and Z_A are the charges on the donor and acceptor, D_S is the static dielectric constant of the solvent, d is the sum of the radii of the reactants, and μ is the ionic strength of the medium. The value of W_p is calculated to be 0.05 eV for this reaction. The E_{ox} values for some of the anilines have been taken from the pre-existing literature,[71] and for other anilines, the values are estimated using the cyclic voltammometric technique (Table 4). The E_{red} values of Cr(V)−salen complexes determined in the present study are reported in Table 1. The value of λ is the sum of two terms, outer-sphere (λ_0) and inner-sphere (λ_{in}) reorganization energies (eq 7)

$$\lambda = \lambda_0 + \lambda_{in} \quad (7)$$

where λ_{in} is the contribution arising due to the intramolecular

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bond length and bond angle changes in the donor and acceptor during ET and λ_0 is the contribution arising due to the solvent reorganization.

In the present study, the value of λ_{in} is taken as 0.2 eV. It has been reported recently that when anilinium cation radical is formed from aniline, the change in C−N bond length is similar to the change in the C−O bond length when phenoxyl radical is formed from phenolate ion.[72] In our recent reports, we have taken the value of λ_{in} as 0.2 eV for the formation of phenoxyl radical from phenolate ion.[67,73] The small λ_{in} value chosen in the present study is reasonable because major structural changes occur in Cr(V) complexes only when Cr(IV) is converted into Cr(III) and not for Cr(V) to Cr(IV).[52] From the consideration of the nonequilibrium polarization of the medium and employing the dielectric continuum model for the solvent, the value of λ_0 can be estimated from eq 8

$$\lambda_0 = (\Delta e)^2/4\pi\epsilon_0(1/2r_D + 1/2r_A - 1/r_{DA})(1/D_{op} - 1/D_s) \quad (8)$$

where Δe, D_{op}, and D_s are the number of electrons transferred, the optical dielectric constant, and the static dielectric constant, respectively. The values of D_{op} and D_s for acetonitrile are 1.80 and 36.7, respectively.[68] The terms r_D, r_A, and r_{DA} are the radii of the electron donor (aniline) and the electron acceptor (Cr(V) ion), and sum of radii of the donor and the acceptor, respectively. We used the average values of r_D, r_A, and r_{DA} for the calculation of λ_0, because small differences in the radii of the donors and acceptors do not lead to any significant variation in the estimated λ_0 values. The radii of various anilines were taken as 3.0−3.8 Å and oxo(salen)chromium(V) ions in the range 7−9 Å as reported in the literature.[14,71] Similar radii value obtained using Edward's volume addition model have been used earlier by Tazuke, Balzani, and Pal for the application of the Marcus theory to the ET reaction of anilines.[71] The λ_0 value for the present system is estimated to be ∼0.9 eV using eq 8. In recent reports, the reorganization energy for the removal of electron from aromatic amines has been computed.[74]

Applying these equations, we have calculated the rate constants for electron transfer from aniline to Cr(V) complexes, and the values are given in Table 4. The compliance of the experimental values with calculated values supports the choice of the parameters for aromatic amines and Cr(V)−salen complexes.[71] Thus, the successful application of the Marcus theory of electron transfer to this redox reaction is additional support for the postulation of an electron transfer mechanism to this reaction. The data given in Table 4b show that a large difference exists between the experimental and calculated values in the case of Cr(V) complex **IIh**. We

Table 4. Second-Order Rate Constants ($k_{observed}$) for the Reaction of Substituted Anilines with **IIa** and Calculated Using the Marcus Equation ($k_{calculated}$) and Second-Order Rate Constants ($k_{observed}$) for the Reaction of Parent Aniline with **IIa−i** and Calculated Using the Marcus Equation ($k_{calculated}$)

(a) Substituted Anilines with **IIa**

X, in X−PhNH$_2$	E_{ox}	$k_{calculated}$	$k_{observed}$
2-OMe	0.76	19	30.9
4-Me	0.78	12	10.9
3-Me	0.84	2.8	3.28
2-Me	0.85	2.2	3.74
H	0.87	1.3	1.21
3-OMe	0.89	0.8	0.92
4-F	0.92	0.4	0.38
4-Cl	0.95	0.2	0.16
2-Cl	0.96	0.1	0.14
4-Br	0.96	0.1	0.14
2-F	0.96	0.1	0.06
3-Br	0.97	0.1	0.10
3-Cl	0.98	0.1	0.09

(b) Parent Aniline with **IIa−i**

complex	E_{red}	$k_{calculated}$	$k_{observed}$
IIa	0.44	1.3	1.21
IIb	0.41	0.6	0.57
IIc	0.60	59	16.1
IId	0.61	70	32.0
IIf	0.24	0.01	0.04
IIg	0.45	1.5	3.65
IIi	0.22	0.01	0.03
IIh	0.61	74	0.22

tentatively attribute this difference to the less reliable E_{red} value of **IIh**.

Conclusion

The spectral, kinetic, and product analysis studies show that the reaction of oxo(salen)chromium(V) complexes with anilines leads to the formation of chromium(III)−salen ion and oligomers of anilines as major products of the reaction. These experimental results and successful application of the Marcus theory to this reaction support a mechanism involving electron transfer from aniline to Cr(V) ion in the rate controlling step.

Supporting Information Available: Hammett plot for the oxidation of PhNH$_2$ with substituted oxo(salen)chromium(V) ions, time-resolved ESI-MS spectra for the reaction of PhNH$_2$ with **IIa**, ESI-MS spectra of the final products formed from the reaction of PhNH$_2$ with **IIa**, EPR spectra of parent Cr(III)−salen and oxo(salen)chromium(V) ion, and a plot of $\Delta H^\ddagger$ versus $\Delta S^\ddagger$. This material is available free of charge via the Internet at http://pubs.acs.org.

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