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Effect of added donor ligands on the selective oxygenation of organic sulfides by oxo(salen)chromium(V) complexes

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Abstract—Oxo(salen)chromium(V) complexes, $[(salen)Cr^{V}{=}O]^{+}$, oxidize organic sulfides selectively to sulfoxides in high yield. This oxygenation reaction is catalyzed by ligand oxides (LO's), pyridine *N*-oxide, 4-picoline *N*-oxide, 4-phenyl pyridine *N*-oxide and triphenylphosphine oxide. The rate is accelerated by 10–20 times with an increase in yield of sulfoxide in less reaction time. This catalytic activity is highly sensitive to the nature of the substituent in the phenyl ring of ArSMe and in the 3- and 5-position of the salen ligand. The reaction constant (ρ) value obtained with the ligand oxide catalyzed reaction is low compared to the value in the absence of LO. The strong binding and catalytic activity of ligand oxides on the oxo(salen)chromium(V) ion oxygenation is explained in terms of binding constants and a mechanism involving the electrophilic attack of $[(salen)Cr^{V}{=}O]^{+}$–LO adduct on the sulfur centre of phenyl methyl sulfide.

1. Introduction

The use of metal–salen complexes as efficient catalysts in oxygenation reactions, particularly epoxidation and sulfoxidation, has been widespread in recent years.[1–10] Though the catalytic role of many metal–salen complexes is reported in the literature, most of the work is concerned with Fe(III)–salen, Mn(III)–salen and Cr(III)–salen complexes. Among these metal complexes, Cr(III)–salen has the advantage that the oxo(salen)chromium(V) ion, $[(salen)Cr^{V}{=}O]^{+}$, generated from Cr(III)–salen complex and PhIO, is stable and can be isolated unlike the oxo(salen)manganese and oxo(salen)Iron ion, which has a fleeting existence.[1,2,8,9,11] The $[(salen)Cr^{V}{=}O]^{+}$ ion has been characterized definitely by spectroscopic techniques and by single crystal X-ray structure determination. Consequently, there is no ambiguity concerning the identity of the active oxidizing agent. Thus the use of the isolated oxo(salen)chromium(V) complex allows reactions to be carried out stoichiometrically, in the absence of co-oxidants, facilitating kinetic studies and mechanistic evaluation. Recently Venkataramanan et al.[13] have studied the oxygenation reaction of organic sulfides and sulfoxides with 10 oxo(salen)chromium(V) complexes by varying the substituents on the salen ligand electronically and sterically. This redox reaction is highly sensitive to the change in structure of the ligand in the Cr(V)–salen complex and of the substrate. In recent years, Gilheany and co-workers[14–17] in a series of publications have shown that the stereoselectivity in the epoxidation of alkenes with oxo(salen)chromium(V) complexes is substantially changed on the addition of certain oxygen containing donor ligands such as phosphine oxide and amine *N*-oxides. In most cases the presence of ligand oxides (LO's) has a significant effect, increasing the ee by 30%. It is known that such additives are coordinated to the metal atom at the axial position through the oxygen atom of LO's, which weakens the Cr=O bond in $[(salen)Cr^{V}{=}O]^{+}$ ion and thereby increases the reactivity.[1,14–17] Though the effect of such additives on the reactivity of oxo(salen)metal complexes has been studied on the epoxidation reaction, no attempt has been made to look at such an effect on the sulfoxidation reaction. Moreover, the addition of ligand oxides was found to change the reaction mechanism.[18] To get a clear picture we have attempted a study, on the oxidation of sulfides with several oxo(salen)-chromium(V) in the presence of donor ligands, like triphenylphosphine oxide (TPPO), pyridine *N*-oxide (PyO), 4-picoline *N*-oxide (PicNO) and 4-phenyl pyridine *N*-oxide (PPNO). These were studied using spectrophotometric and EPR techniques and the observed results are presented in this article.

2. Results

2.1. Spectral studies

The selective oxidation of several substituted phenyl methyl sulfides with 10 oxo(salen)chromium(V) complexes was

Keywords: Cr(III)–salen; Sulfide; Sulfoxide oxygenation; Ligand oxides; Rate enhancement.
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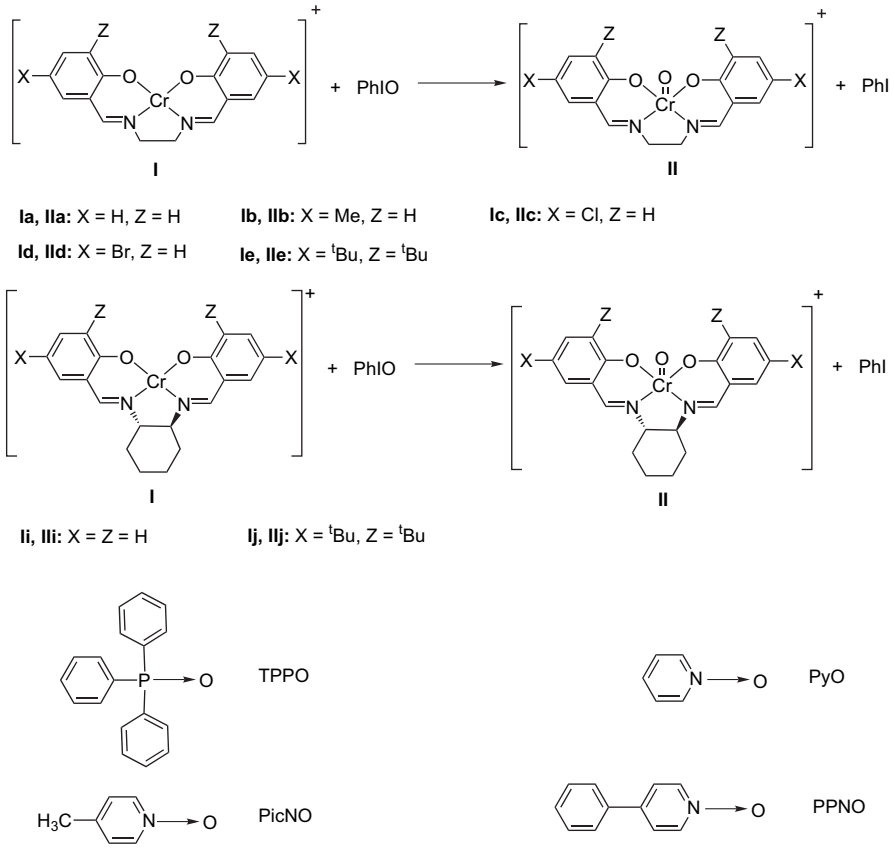


Scheme 1. Structure of complexes **IIa**–**IIg** and the ligand oxides (LO's).

well studied.[10b,13] A mechanism involving an electrophilic attack of the oxygen of the oxidant at the electron-rich sulfur centre of the substrate has been proposed. Realizing the importance of donor ligands on the oxygenation reaction with oxo-metal complexes[10b,14–19] we have investigated the effect of LO's on the sulfoxidation reaction with oxo (salen)chromium(V) complexes and the structures of Cr(III) and Cr(V) complexes and the donor ligands used in the present study are shown in Scheme 1.

The parent oxo(salen)chromium(V) ion has an absorption maximum (λ_{max}) at 560 nm in CH_3CN. When the ligand oxide, LO, is added to the Cr(V) ion a substantial red shift is noticed in the absorption maximum. This shift in the λ_{max} depends on the nature of the LO and is in the range of 15–100 nm. The λ_{max} values of all substituted oxo (salen)chromium(V) complexes in the absence and presence of additives are given in Table 1. Further, an increase in the concentration of additive increases the absorbance of Cr(V)–LO adduct. A sample spectrum to show the increase of absorption with [LO] is given in Figure 1.

Table 1. Absorption maxima, λ_{max}, of $[(salen)Cr^{V}{=}O]^{+}$ complexes in the presence and absence of LO

Serial number	Complex	λ_{max} (nm) in the absence of LO	λ_{max} (nm) in the presence of LO			
			TTPO	PyO	PicNO	PPNO
1.	**IIa**	560	627	612	608	615
2.	**IIb**	557	640	620	642	655
3.	**IIc**	584	645	630	630	630
4.	**IId**	590	645	632	630	625
5.	**IIe**	595	610	671	650	654
6.	**IIf**	600	620	615	610	615
7.	**IIg**	610	630	685	664	665

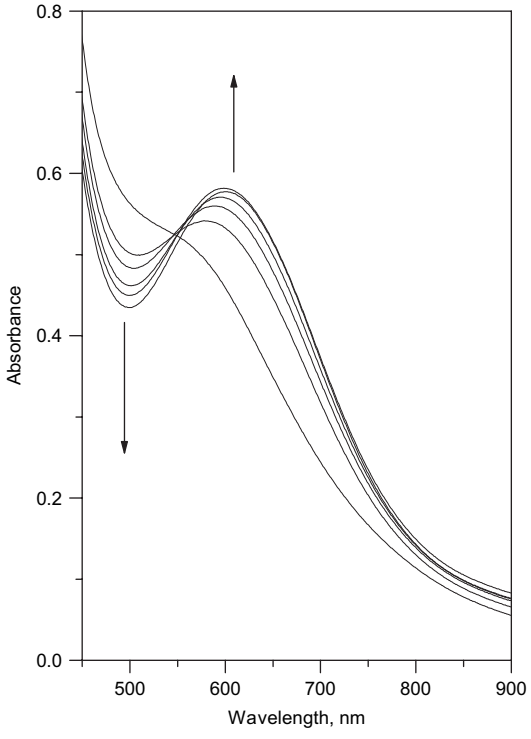


Figure 1. Absorption spectra of **IIa** in the absence of PyO and at 0.025 M, 0.05 M, 0.075 M, 0.1 M and 0.125 M PyO. [**IIa**]=3×10^{-4} M.

Table 2. Binding constants for the complex formed between **IIa–IIg** and ligand oxides

Serial number	Complex	Ligand oxides (LO's)			
		TPPO	PyO	PicNO	PPNO
1.	**IIa**	44±11	125±21	165±32	183±41
2.	**IIb**	32±11	140±14	146±42.0	150±31.5
3.	**IIc**	71±19	123±24.2	241±34.1	192±21.4
4.	**IId**	84±31	184±44	321±48	230±36
5.	**IIe**	24±9	73±14.4	112±21.4	156±15
6.	**IIf**	41±10	101±12.2	185±16.4	646±51
7.	**IIg**	27±11	69±18.8	142±34.8	150±29

From these spectral changes we have estimated the binding constants by using the Benesi–Hildebrand equation and the values of binding constants are given in Table 2.

The binding constant depends on the nature of the LO's as well as the substituents in the salen ligand. Furthermore, the metal ion containing electron donating groups in the 5-position of the salen ligands has a low binding constant value compared to those carrying electron withdrawing groups. This is expected as the electrophilicity of metal centre is decided by the nature of the substituents in the salen ligand. The low binding constant values for the complexes **IIe** and **IIg** can be accounted for on the basis of the presence of the bulky *tert*-butyl group at the 3-position, which may hinder the binding of the LO's to the metal centre.

Kochi and co-workers[1] have isolated the oxo(salen)chromium(V) ion and its adduct with PyO and determined their structure by X-ray analysis. The authors have shown that the Cr(V) ion and the Cr(V)–LO adduct have roughly the square pyramidal and octahedral geometries in which the Cr atom is displaced 0.53 and 0.26 Å units above the mean-salen plane, respectively. Thus the LO binds strongly with metal centre and affects the strength of Cr–O bond. In the present study the enormous shift observed in the λ_{max} value of [(salen) Cr^{V}═O]$^{+}$ on the addition of LO and large binding constants support the strong binding of LO to the metal resulting in the formation of O═Cr–O–L.

2.2. Kinetics

The progress of the title reaction is followed by measuring the change in OD of the Cr(V)–LO adduct at the wavelength given in Table 1. A sample run to show the decrease in OD of Cr(V)–LO adduct with time is shown in Figure 2.

The reaction is of first order for both the oxidant and the substrate. The first order dependence in the oxidant is evident from the linear log OD versus time plot (figure not shown) and in the substrate is confirmed from the linear k_1 versus [substrate] plot (Fig. 3).

To know the effect of LO's on reaction rates, experiments were carried out with different [LO]. At low concentration, the k_1 values vary linearly and at high [LO] the rate reaches the maximum. Further increase in [LO] has no profound influence on the rate of the reaction. Thus the reaction follows saturation kinetics with respect to the added LO's.

The rate constants for the oxygenation of several *para*-substituted phenyl methyl sulfides with oxo(salen) chromium(V) complexes (**IIa–IIg**) in the absence and presence of donor ligands are presented in Tables 3–7. These kinetic data show that the reaction is highly sensitive to the change of substituents in the phenyl ring of ArSMe, and in the 5,5′-positions of the salen ligand. The kinetic data in Tables 3–7 have been analyzed using the Hammett equation, and the reaction constant (ρ) values obtained for the substituent variation in ArSMe are given at the bottom of the tables and for the substituent variation in the salen ligand of oxo(salen)chromium(V) complexes in the 7th column of the tables. Though the ρ value is highly sensitive to the structure of the salen ligand and nature of the LO it is not very sensitive to the change of the substituent in the aryl moiety of ArSMe. The important point to be noted regarding ρ value is that the ρ value is always small in the presence of LO's compared to the ρ value in the absence of LO.

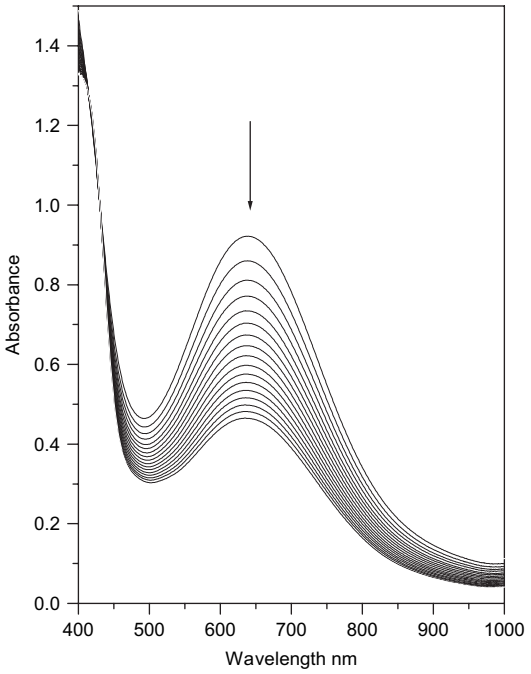


Figure 2. Sample run showing the change in OD of **IIc**–TPPO adduct with time in the presence of PhSMe. [**IIc**]=5×10^{-4} M, [MPS]=0.01 M and [TPPO]=0.01 M.

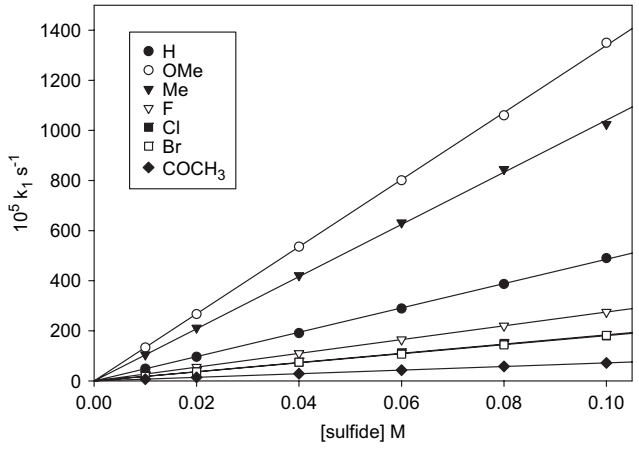


Figure 3. Plot of k_1 versus [sulfide] for the oxidation of sulfides by **IIa** in the presence of TPPO at 298 K. [TPPO]=0.01 M and [**IIa**]=5×10^{-4} M.

Table 3. Second-order rate constant (k_2) and reaction constant (ρ) values for the **IIa–IIg** oxygenation of X–C_6H_4SMe in the absence of LO

X–$C_6H_4SCH_3$ (*p*-X=)	$k_2\times10^3$ M^{-1} s^{-1}							
	IIa	**IIb**	**IIc**	**IId**	**IIe**	ρ	**IIf**	**IIg**
H	1.31±0.03	1.15±0.04	36.4±0.9	45.8±1.4	0.11±0.00	2.2(0.980)	1.20±0.03	0.19±0.01
OMe	25.9±0.60	4.60±0.13	320±9.6	526±14	0.36±0.01	2.6(0.995)	5.10±0.15	0.37±0.01
Me	11.4±0.23	2.60±0.52	114±2.4	140±4.2	0.17±0.00	2.4(0.988)	2.20±0.06	0.28±0.00
F	1.58±0.08	0.59±0.10	26.9±0.4	61.0±1.3	0.06±0.00	2.4(0.995)	1.10±0.04	0.15±0.00
Cl	0.93±0.01	0.32±0.01	21.6±0.4	43.8±1.0	0.06±0.00	2.4(0.995)	0.65±0.02	0.13±0.00
Br	0.93±0.01	0.28±0.06	18.8±0.8	24.2±0.4	0.04±0.00	2.4(0.998)	0.42±0.01	0.09±0.00
$COCH_3$	0.16±0.01	0.23±0.01	7.40±0.22	8.80±0.2	0.02±0.00	2.3(0.965)	0.22±0.00	0.06±0.00
ρ	−2.8	−1.9	−2.0	−2.2	−1.8		−1.8	−1.1
r	0.965	0.980	0.972	0.953	0.970		0.988	0.990

Table 4. Second-order rate constant (k_2) and reaction constant (ρ) values for the **IIa–IIg** oxygenation of X–C_6H_4SMe in the presence of TPPO

X–$C_6H_4SCH_3$ (*p*-X=)	$k_2\times10^3$ M^{-1} s^{-1}							
	IIa	**IIb**	**IIc**	**IId**	**IIe**	ρ	**IIf**	**IIg**
H	48.8±1.5	10.4±0.4	184±5.4	207±7.4	0.20±0.01	2.3(0.934)	8.98±0.3	0.23±0.01
OMe	133±4.1	24.2±0.8	561±17	744±27	0.60±0.02	2.2(0.979)	21.9±0.7	0.60±0.02
Me	105±3.3	16.4±0.5	499±14	702±23	0.35±0.01	2.4(0.981)	18.9±0.6	0.37±0.01
F	27.4±0.8	5.75±0.1	190±4.2	145±4.5	0.13±0.00	2.2(0.980)	6.91±0.2	0.18±0.01
Cl	18.5±0.4	3.92±0.0	142±2.4	147±3.4	0.11±0.00	2.3(0.987)	5.30±0.1	0.13±0.00
Br	18.1±0.3	3.22±0.0	137±1.5	122±2.1	0.08±0.00	2.3(0.985)	4.63±0.08	0.10±0.00
$COCH_3$	7.21±0.1	2.76±0.0	72.8±0.7	69.4±1.0	0.05±0.00	2.2(0.983)	3.68±0.00	0.07±0.00
ρ	−1.8	−1.4	−1.2	−1.5	−1.5		−1.2	−1.3
r	0.994	0.989	0.965	0.967	0.996		0.984	0.991

Table 5. Second-order rate constant (k_2) and reaction constant (ρ) values for the **IIa–IIg** oxygenation of X–C_6H_4SMe in the presence of PyO

X–$C_6H_4SCH_3$ (*p*-X=)	$k_2\times10^3$ M^{-1} s^{-1}							
	IIa	**IIb**	**IIc**	**IId**	**IIe**	ρ	**IIf**	**IIg**
H	37.3±1.2	5.6±0.21	64.9±2.5	140±5.5	0.48±0.02	1.9(0.950)	18.9±0.72	0.30±0.02
OMe	90.9±2.7	35.5±1.4	334±11	677±23	0.88±0.02	2.2(0.942)	31.6±1.23	0.55±0.02
Me	38.5±1.5	21.2±0.72	230±9	527±15	0.65±0.01	2.2(0.958)	26.7±0.65	0.37±0.02
F	17.2±0.35	4.3±0.13	39.6±1.6	120±2.7	0.42±0.01	1.8(0.965)	12.2±0.26	0.19±0.01
Cl	10.4±0.17	3.3±0.08	30.2±0.91	93.5±1.8	0.29±0.00	1.9(0.967)	8.5±0.12	0.14±0.00
Br	9.77±0.14	3.1±0.05	27.4±0.55	86.1±1.2	0.25±0.00	1.9(0.966)	8.2±0.09	0.12±0.00
$COCH_3$	4.69±0.06	1.6±0.02	13.1±0.14	38.0±0.40	0.20±0.00	1.7(0.974)	3.2±0.01	0.07±0.00
ρ	−1.7	−1.8	−2.0	−1.7	−0.90		−1.3	−1.2
r	0.989	0.975	0.988	0.972	0.990		0.980	0.994

Table 6. Second-order rate constant (k_2) and reaction constant (ρ) values for the **IIa–IIg** oxygenation of X–C_6H_4SMe in the presence of PicNO

X–$C_6H_4SCH_3$ (*p*-X=)	$k_2\times10^3$ M^{-1} s^{-1}							
	IIa	**IIb**	**IIc**	**IId**	**IIe**	ρ	**IIf**	**IIg**
H	16.6±0.7	10.4±0.3	99.72±3.1	146±5.5	0.63±0.02	1.8(0.966)	3.91±0.12	0.25±0.01
OMe	45.2±1.5	20.5±0.5	338.6±11	518±20	0.86±0.03	2.1(0.971)	14.5±0.28	0.48±0.02
Me	27.2±0.5	15.9±0.4	192.3±7	304±9.2	0.75±0.03	2.0(0.967)	9.44±0.29	0.37±0.01
F	15.3±0.3	6.72±0.1	64.3±1.8	103.6±3.0	0.44±0.01	1.8(0.966)	3.68±0.10	0.23±0.00
Cl	14.3±0.3	3.45±0.07	38.5±1.1	72.8±1.8	0.33±0.01	1.8(0.968)	3.22±0.07	0.19±0.00
Br	13.8±0.2	2.76±0.03	37.5±0.53	69.8±1.3	0.32±0.01	1.8(0.973)	2.99±0.06	0.19±0.00
$COCH_3$	7.27±0.08	1.61±0.02	21.2±0.30	40.5±0.45	0.22±0.00	1.8(0.979)	2.19±0.03	0.17±0.00
ρ	−0.95	−1.6	−1.7	−1.5	−0.89		−1.1	−0.65
r	0.963	0.984	0.997	0.994	0.992		0.960	0.977

Table 7. Second-order rate constant (k_2) and reaction constant (ρ) values for the **IIa–IIg** oxygenation of X–C_6H_4SMe in the presence of PPNO

X–$C_6H_4SCH_3$ (*p*-X=)	$k_2\times10^3$ M^{-1} s^{-1}							
	IIa	**IIb**	**IIc**	**IId**	**IIe**	ρ	**IIf**	**IIg**
H	12.9±0.4	12.6±0.5	152±5.3	186±7.4	0.65±0.01	1.9(0.964)	29.4±1.0	0.51±0.02
OMe	35.2±1.3	26.1±0.8	522±18	488±17	0.99±0.03	2.2(0.962)	111±3.9	0.99±0.04
Me	24.0±0.9	23.6±0.5	310±12	304±11	0.71±0.02	2.1(0.952)	56.1±2.3	0.78±0.02
F	9.93±0.3	9.2±0.3	94.9±2.9	129±4.8	0.58±0.01	1.9(0.966)	31.6±1.0	0.45±0.01
Cl	7.60±0.16	8.7±0.2	68.4±2.0	88.2±2.7	0.46±0.01	1.8(0.953)	20.6±0.7	0.39±0.00
Br	6.68±0.08	8.4±0.2	65.8±1.4	63.8±1.3	0.45±0.01	1.7(0.945)	20.5±0.6	0.35±0.00
$COCH_3$	4.38±0.05	3.7±0.01	29.9±0.5	28.5±1.0	0.35±0.00	1.6(0.964)	12.0±0.2	0.23±0.00
ρ	−1.3	−1.1	−1.7	−1.6	−0.59		−1.2	−0.85
r	0.995	0.972	0.997	0.989	−0.986		0.976	0.989

This trend is expected based on the reactivity–selectivity principle (RSP).[10,11,21–23,25] As the reactivity in the presence of LO is more than that in the absence of LO, we expect that the ρ value, an empirical term representing the selectivity of the reaction, should be less than what is actually observed.

2.3. EPR studies

The added advantage of Cr(V) complexes is that they are EPR active and hence EPR spectra were recorded at room temperature for the complexes and they show a strong signal at ca. $\langle g\rangle$=1.987 and possess nitrogen and ^{53}Cr hyperfine splitting. Upon addition of LO to the oxo(salen) chromium(V) ion, the g value shifts from 1.987 to 1.975 with the disappearance of the hyperfine splitting, indicating the binding of the LO to the metal centre.[1] The kinetics of the reaction can also be followed by this EPR technique. The change in the intensity of the EPR signal of [O═Cr(V) salen]$^+$ ion with time is used to follow the kinetics of the reaction. A sample run to show the change in the EPR signal intensity with time obtained during the reaction of **IIc** with MPS in the presence of TPPO as the additive is shown in Figure 4. The rate constant obtained by EPR technique is found to be in close agreement with the values obtained by the spectrophotometric method.

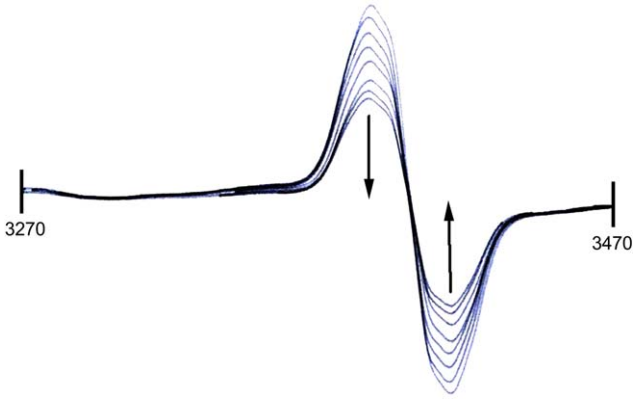


Figure 4. EPR spectra showing the change in the intensity with time for the oxidation of MPS by **IIc** in the presence of TPPO as ligand oxide.

2.4. Effect of donor ligand on product yield

Table 8 shows the effect of added donor ligands on the yield of sulfoxide formed in the stoichiometric oxidation of organic sulfides. From the data given in Table 8 we can understand that the added LO's have a small effect on the product yield. All the LO's increase the percentage of product formed with less reaction time. Thus the data indicate that in the presence of ligand oxides, product yield is improved along with the increase in the rate of the reaction. When we compare the analogous epoxidation reactions with similar complexes, Gilheany and co-workers found that yields did not exceed 50%. Furthermore the rates of oxidation in the presence LO's for sulfides are in the range of 10^{-3} M^{-1} s^{-1} and that of epoxidation are in 10^{-2} M^{-1} s^{-1}.[1b] Thus both the kinetic data and percentage of sulfoxide formed support the catalytic role of all LO's used in the reaction.

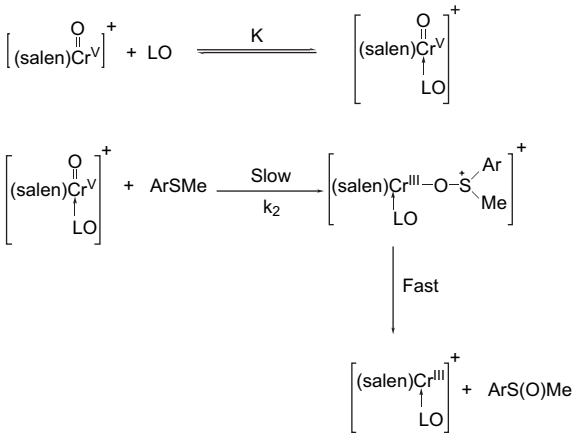
3. Discussion

The spectral and kinetic data given in Figures 1–4 and Tables 1–8 show the catalytic role of the added ligand oxide, LO. The addition of LO shifts the λ_{max} of **IIa–IIg** enormously and accelerates the reaction rate by 10–20 times. The coordination of the LO occurs at the axial position to complete the octahedral coordination of chromium. The infrared spectrum of the LO bound chromium(V) complex indicates that significant bond weakening occurs upon axial coordination.[1a,2b] Among the five LO's used, triphenylphosphine oxide was known to have a better binding ability, but 4-phenyl pyridine *N*-oxide was found to have highest binding constant and the maximum rate. This unusual behaviour may be attributed to the steric hinderance created by TPPO during the binding with the metal centre.[12a]

The spectral, kinetic and product yield data presented above confirm the formation of oxidant–ligand oxide adduct as the first step, which in turn acts as a more powerful oxidant than the oxo(salen)chromium(V) ion. At least two different modes of oxidation may be envisaged to account for the type of reactivity observed: (i) a bimolecular electrophilic oxygen transfer from [O═Cr^V(salen)]$^+$ to the substrate and (ii) a bimolecular electrophilic oxidation performed by [O═Cr^V(salen)–LO]$^+$. As the binding constant of LO with Cr(V) ion is high and the rate of oxidation in the presence of LO is 10–20 times more than that in the absence of LO; the bimolecular electrophilic oxidation of the complex alone is less important compared to bimolecular electrophilic oxidation of the adduct complex under the present experimental conditions. Hence a mechanism involving electrophilic attack of [(salen)Cr^V═O]$^+$–LO adduct on the sulfur centre of ArSMe (Scheme 2) can be proposed.

Table 8. Percentage of sulfoxide formed from the selective oxidation of *p*-X–$C_6H_4SCH_3$ with **IIa** in CH_3CN in the presence and absence of ligand oxides at 298 K

X–$C_6H_4SCH_3$ X=	Without LO			TTPO	PyO	PicNO
	Reaction time (min)	% of sulfoxide	Reaction time (min)	% of sulfoxide	% of sulfoxide	% of sulfoxide
H	240	96	90	97	96	94
OMe	60	95	60	99	98	97
Me	75	93	60	94	98	98
F	200	78	90	81	72	76
Cl	240	60	90	76	68	72
Br	240	61	90	56	65	64
$COCH_3$	240	40	90	55	48	49



Scheme 2.

The ligand oxide binds strongly with the oxo(salen)chromium(V) ion via oxygen atom of the ligand oxide(LO) to chromium. The binding of the oxygen of the LO to the metal weakens the Cr=O bond in the oxo(salen)chromium(V) complex and facilitates the removal of oxygen atom from the oxo complex to form sulfoxide as the product. When the Cr(III) complex is formed as the product, the ligand oxide occupies two coordination sites making the product octahedral. It is pertinent to recall that Kochi and co-workers[1] have isolated the Cr(III) complex, $[Cr^{III}(salen)(OPEt_3)_2]^+$, which indicates that the one molecule of ligand oxide entered the coordination sphere of oxo(salen)chromium(V) ion prior to oxygen transfer to the substrate since the rate of incorporation of ligand oxide into the substitutionally inert Cr(III)–salen is slow.[1]

When we compare the rate constant and product yield data carefully, we realize that the rate constant in the presence of ligand oxides is 10–20 times more than that in the absence of ligand oxides. An increase in the product yield in the presence of LO is also observed. This was because the rates of oxidation of sulfides are much higher compared to that of epoxides. Therefore the formation of an unreactive μ-oxo dimer by the reaction between $[O{=}Cr^{V}(salen)]^+$ and $[Cr^{III}(salen)]^+$ in sulfoxidation has less effect compared to the epoxidation reaction.[16,17] On the other hand, in the case of oxo(salen)manganese complexes the μ-oxo dimer, Mn(IV)–O–Mn(IV) formed is an alternative source of $[(salen)Mn^{V}{=}O]^+$ for the epoxidation and sulfoxidation reactions.[11,26–28]

4. Experimental

4.1. Materials

Chromium(III)–salen [salen=*N*,*N*-bis(salicylidine) ethylenediaminato] complex was synthesized[1,2] using the established procedure. Iodosylbenzene was prepared by alkaline hydrolysis of iodosobenzene diacetate according to the reported method.[20] The purity of ligands was checked by ^{1}H NMR spectroscopy and that of Cr(III) complexes was checked by IR and ESI-MS spectroscopy. The oxo(salen)-chromium(V) complexes **IIa–IIg** were obtained from chromium(III) complexes **Ia–Ig** by the general procedure described below. A slight excess of iodosylbenzene is added to Cr^{III}–salen complex dissolved in ~25 mL of CH_3CN. The colour of the reaction mixture has turned from orange to dark green. This slurry is stirred for 20 min and then filtered to remove the unreacted iodosylbenzene. Ether is slowly added to the dark filtrate in order to precipitate crystals of oxo(salen)chromium(V) salts. The ligand oxides used as donor ligands are commercial samples from Aldrich and they were used as such without further purification. Various substituted phenyl methyl sulfides were prepared[29,30] and their purity checked by established methods. The solvents used in the study were of HPLC grade.

4.2. Estimation of binding constants

The complexation/adduct formation of LO with the oxo (salen)chromium(V) cation was monitored by UV–vis spectroscopy. A 5×10^{-4} M solution of oxo(salen)chromium(V) ion in acetonitrile, taken in a quartz cuvette with 1 cm path length, was treated with successive aliquots of concentrated solution of LO in the same solvent. The absorption spectrum of the oxo(salen)chromium(V) ion exhibited a red shift upon the addition of LO. The formation of complex/adduct was evident from the colour change (dark green to emerald green) and the shift in the λ_{max}. By measuring the OD at different concentration of a particular LO at the appropriate λ_{max}, the binding constant has been calculated by using the modified Benesi–Hildebrand (double reciprocal plot) equation.[24]

$$\frac{[\text{oxid}][\text{LO}]}{\Delta\text{OD}} = \frac{[\text{oxid}]+[\text{LO}]}{\Delta\varepsilon} + \frac{1}{K_f\Delta\varepsilon}$$

In the above equation ΔOD is the difference in the absorption intensities of $[(salen)Cr^{V}{=}O]^+$ in the presence and absence of LO and K_f is the equilibrium constant for the formation of adduct or complex. The plot of [oxid][LO]/ΔOD versus [oxid]+[LO] is linear and from the values of slope and intercept, K_f values for the complex formation with LO have been calculated.

4.3. Kinetic measurements

An analytik-jena Specrod-diode array photometer (Specord S100) was employed to record the absorption spectra of Cr(III) and oxo(salen)chromium(V) complexes used in the present study and to follow the kinetics.

The kinetic studies of oxidation of *para*-substituted phenyl methyl sulfides with oxo(salen)chromium(V) complexes were carried out in acetonitrile under pseudo first order conditions using excess of substrate over the oxidant (10:1). The rate of oxygenation of organic sulfides in the presence of donor ligands was followed by measuring the change in the absorbance of Cr^{V}–ligand oxide adduct at the wavelength given in Table 1. The concentration of the ligand oxides was chosen in such a way that the OD of the oxo(salen)chromium(V) complexes was unaffected by the further addition of the donor ligand.

4.4. Product analysis

In a typical experiment involving the selective oxidation of sulfides to sulfoxides, 2 mM oxo(salen)chromium(V)

complex, and the same equivalent of ligand oxides, LO (triphenylphosphine oxide, pyridine oxide, 4-picoline *N*-oxide and 4-phenyl pyridine *N*-oxide) are taken in 5 mL of solvent. To this is added the 2 mM *p*-substituted phenyl methyl sulfide. The solution was stirred at 298 K for 60–240 min depending on the nature of the sulfide. After the removal of the solvent under reduced pressure, the organic product was extracted with dry ether, dried and the solvent removed. The resulting residue was analyzed by GC. Product yields were determined by comparison with authentic samples and sulfoxide was the only product under the present experimental conditions.

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