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KINETICS AND MECHANISM OF ZnCl_2 CATALYSED OXIDATION OF ORGANIC SULFOXIDES BY PERMANGANATE IN NON-AQUEOUS MEDIUM

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Abstract: The rates and mechanism of zinc chloride (Lewis acid) catalysed oxidation of several organic sulfoxides by permanganate have been studied in anhydrous acetone solutions. The kinetic rate law obtained indicates that a complex between permanganate and the Lewis acid (ZnCl_2) is formed before oxidation of the sulfoxides occurs. The function of the zinc chloride is to enhance the reactivity of permanganate. A Hammett ρ value of -2.18 ± 0.09 is obtained for the oxidation of sulfoxides at 23.0°C . A negative ρ value means that the sulfur is electron deficient in the transition state. Values for the HOMO energies of sulfoxides and the LUMO energies for permanganate ion and the permanganate-zinc chloride complex have been calculated. The results indicate that electron donating substituents on the ring increase the rate of the reaction and electron withdrawing groups slow down the reaction.

Keywords: Sulfoxides, permanganate, acid catalysed oxidation, LUMO, HOMO.

I. INTRODUCTION

Many sulfur-containing compounds are present in natural biological systems and play key roles in the activity of some enzymes [1-2]. An understanding of the deactivation of these enzymes by oxidation requires knowledge of the mechanisms by which sulfur compounds are oxidized [3]. The observation that Cytochrome P-450 can readily catalyze the oxidation of nitrogen and sulfur compounds [4] relates a study of the reactivity of transition metal-oxo compounds to some biological processes. For example, the transfer of oxygen from the lungs, via hemoglobin and myoglobin, to the cells where metabolism occurs involves the use of a transition metal; iron, as an oxygen transfer agent.

An improved understanding of transition metal based oxygen transfer reactions may also find application in organic synthesis [5]. Oxygen transfers are necessary steps in the manufacture of a number of commercially important organic compounds. In addition, similar reactions may be used for environmental clean-ups that involve destruction of odoriferous sulfur containing compounds [6]. A better understanding of these reactions, therefore, has implications for both commerce and health. In continuation of research works on Lewis acid catalysed oxidation of organic-sulfur compounds [7], here we report the Lewis acid (ZnCl_2) catalysed oxidation of sulfoxides by permanganate.

The objective of the research paper reported herein is to improve our understanding of kinetics and mechanism of the reaction between potassium permanganate and sulfur-containing organic compounds viz. sulfoxides, when ZnCl_2 , a Lewis acid is present as a catalyst in anhydrous acetone as non-aqueous medium.

I. MATERIALS & METHODS

Potassium permanganate was BDH Analar grade. Acetone, used as the solvent in all kinetic experiments, was Fisher HPLC grade. Anhydrous zinc chloride was obtained from Aldrich and stored in a desiccator. Solvents and reagents used in synthesis were all analytical grade and used without further purification. Silica gel used in column chromatography (200 meshes) was from BDH.

A. Synthesis of Sulfoxides

Methyl *p*-nitrophenyl sulfide (22.0g, 0.13 mol) was dissolved in 125 mL acetone. Then 30% H_2O_2 (20 g) was added. The mixture was thoroughly stirred at room temperature until TLC showed no sulfide. The reaction mixture was extracted with CHCl_3 (450 ml). The CHCl_3 extracts were combined and dried overnight with MgSO_4 . Removal of CHCl_3 from the solution by evaporation afforded a yellow solid. The crude product was a mixture of sulfoxide and sulfone which were separated by column chromatography (eluent: chloroform/ethyl acetate 1/1). Yield: 4.82 g, (20%). mp 148.5°C (lit. $148-149^\circ\text{C}$ [8]).

p-Methoxyphenyl methyl sulfoxide, methyl phenyl sulfoxide, *p*-fluorophenyl methyl sulfoxide, *p*-chlorophenyl methyl sulfoxide and *p*-nitrophenyl methyl sulfoxide were prepared in essentially the same manner except that

the reaction took place at a lower temperature (using an ice-water bath). The yields, the observed melting points and structural data are summarized in Tables-1 and -2 respectively.

II. KINETIC METHODS

The kinetic study of the reduction of permanganate by phenyl sulfoxide and various ring substituted sulfoxides was completed using anhydrous acetone solutions containing different concentrations of ZnCl_2 as the Lewis acid. All kinetic studies were carried out under pseudo first order conditions with the substrate concentration at least ten times that of permanganate. All substrates were carefully purified before being used in kinetic studies by recrystallization, distillation or preparative chromatography. The reaction rates were determined by monitoring UV/Vis spectral changes as the reaction progressed. The decrease in absorbance at 550 nm was followed on the spectrophotometer.

In the experiment, a solution of zinc chloride in anhydrous acetone was sealed in a 50 mL Erlenmeyer flask and immersed in a constant temperature bath for one hour. While the zinc chloride solution was being thermostated, a permanganate solution was prepared by placing a few milligrams of KMnO_4 in a 50 mL Erlenmeyer flask and adding 40 mL of anhydrous acetone. After swirling for about 30 seconds, the supernatant was transferred, using a disposable pipette, to another flask suspended in the constant temperature bath. The flask was stoppered and sealed to prevent contact with moisture in the air. An aliquot of the zinc chloride solution (2.0 mL) was then transferred to a 10 mm cuvette and a stock solution of sulfoxide in anhydrous acetone (0.10 mL) was added using a microliter syringe. The cuvette was placed in the thermostated cell compartment of the spectrophotometer, the background of the instrument was recorded, and after a few minutes, the reaction was initiated by adding permanganate solution (0.50 mL) using a microliter syringe. The cuvette was quickly inverted several times to ensure good mixing and spectra were collected every five seconds until the reaction was complete. For determination of the order with respect to zinc chloride, the concentration of zinc chloride was varied over a larger range. The concentration of sulfoxides was varied from 6.0×10^{-3} to 1.3×10^{-1} M.

Table-1: Yields, melting points of para-substituted phenyl methyl sulfoxides

Substrates	Yield	MP ($^{\circ}\text{C}$)
<i>p</i> -MeO PhSOCH_3	30	42-43
<i>p</i> -Me PhSOCH_3	24	41-43
PhSOCH_3	20	146-148
<i>p</i> -F PhSOCH_3	68	125-127
<i>p</i> -Cl PhSOCH_3	35	46-47
<i>p</i> -NO $_2$ PhSOCH_3	20	147-148

Table-2: NMR and IR Data for para-substituted phenyl methyl sulfoxides

Substrates	^1H NMR (δ , ppm)	IR (ν , cm^{-1})
<i>p</i> -MeO PhSOCH_3	2.67(s,3H), 3.95(s,3H), 7.0(d,2H), 7.8(d,2H)	1048(s), 1255(s), 1497(s), 1595(s), 2837-3200(s)
<i>p</i> -Me PhSOCH_3	2.38(s,3H), 2.65(s,3H), 7.28(d,2H), 7.68(d,2H)	1056(s), 1448(m) 3000(s)
PhSOCH_3	2.70(s,3H), 7.50(m,3H), 7.65(d,2H)	1048(s), 1481(s), 1582(s), 2900(s), 3010(s)
<i>p</i> -F PhSOCH_3	2.65(s,3H), 7.15(d,2H), 7.60(d,2H)	1049(s), 1087(s), 1493(s), 1590(m), 2900- 3100(w)
<i>p</i> -Cl PhSOCH_3	2.70(s,3H), 7.50(d,2H), 7.60(d,2H)	1051(s), 1476(s), 1576(m), 2359(m), 3274(m)
<i>p</i> -NO $_2$ PhSOCH_3	2.70(s,3H), 7.60(d,2H), 8.35(d,2H)	852(s), 1048(s), 1340(s), 1529(s), 1460(s)(nujol)

III. RESULTS & DISCUSSION

The general rate law for the reaction between permanganate and sulfoxide can be expressed as in equation-1 (LA is an acronym for Lewis acid):

$$\text{Rate} = k [\text{MnO}_4^-]^x [\text{RSOR}']^y [\text{LA}]^z \quad (1)$$

The orders with respect to permanganate, sulfoxide and Lewis acid are designated as x, y and z respectively.

The experimentally determined rate law (first order in oxidant, first order in Lewis acid and of variable order between unity and zero in reductant) is of the form (equation-2) expected if zinc chloride acts as a catalyst by combining with permanganate prior to the redox step. Thus, the Lewis acid forms complex with the permanganate in first step of the reaction and the sulfoxides are subsequently oxidized by this complex in a second step. The corresponding rate law is given by equation -2:

$$-d[\text{MnO}_4^-] / dt = k_1 k_2 [\text{MnO}_4^-] [\text{ZnCl}_2] [\text{RSOR}'] / k_1 + k_2 [\text{RSOR}'] \quad (2)$$

The rate constants for the oxidation of methyl phenyl sulfoxide at various temperatures, obtained using the method described for sulfides, are summarized in table-3. The oxidations of *p*-chlorophenyl methyl sulfoxide

and methyl *p*-nitrophenyl sulfoxide are very slow. Although the plots $(R_i - R_b)/A_i$ vs. the concentration of sulfoxide fit equation-3. The data, therefore, were found to fit equation -3 better. Under such conditions the reaction would appear to be first order with respect to sulfoxide, as indicated in equation-3:

$$(R_i - R_b) / A_i = k_1 k_2 [\text{ZnCl}_2] [\text{RSOR}'] / k_1 \quad (3)$$

Use of the same definitions as in previous sections, for K and k_{obs}

($K = k_1/k_2$ and $k_{\text{obs}} = Kk_1$) gives equations 4-6 as:

$$(R_i - R_b) / A_i = k_{\text{obs}} [\text{ZnCl}_2] [\text{RSOR}'] \quad (4)$$

$$(R_i - R_b) / A_i = k [\text{RSOR}'] \quad (5)$$

$$K' = k_{\text{obs}} [\text{ZnCl}_2] \quad (6)$$

The values for K were obtained from the slope of plots of $(R_i - R_b) / A_i$ vs the concentration of sulfoxide and values of k_{obs} were calculated from the relationship show in equation-7:

$$k_{\text{obs}} = K' / [\text{ZnCl}_2] \quad (7)$$

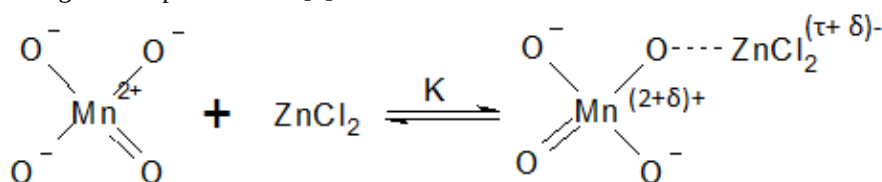
The values for K' and k_{obs} , at 23.0°C obtained in this way for investigaed sulfoxides are presented in table-3.

Table-3: Rate constants for the oxidation of sulfoxides when ZnCl_2 , is used as Lewis acid catalyst at 23°C and $[\text{ZnCl}_2] = 1.16 \times 10^{-3} \text{ M}$

Substrates	σ	σ^+	$k_i (\text{M}^{-1} \text{s}^{-1})$	$K_{\text{obs}} (\text{M}^{-2} \text{s}^{-1})$
<i>p</i> -MeO PhSOCH_3	-0.268	-0.778	28	337
<i>p</i> -Me PhSOCH_3	-0.170	-0.311	26	148
PhSOCH_3	0.000	0.000	27	98
<i>p</i> -F PhSOCH_3	0.062	0.073	27	52
<i>p</i> -Cl PhSOCH_3	0.227	0.114	25	22
<i>p</i> -NO $_2\text{PhSOCH}_3$	0.778	0.790	02	1.5

A. Role of Lewis Acid in the Reaction

Lewis acids have a significant catalytic effect on the rates of oxidation of sulfoxides by permanganate. There is almost no reaction between permanganate and sulfoxide in the absence of a Lewis acid. The reaction between a Lewis acid and permanganate is consistent with the possibility that it makes permanganate a more reactive oxidant. Reaction of the Lewis acid with permanganate would cause the metal center (manganese) to become more positive, as in scheme-1. The Lewis acid acts in much the same way as a Bronsted acid does in the reactions of permanganate in protic media [9].



Scheme-1: The reaction between permanganate and zinc chloride

B. Substituent Effects

The rate constants for the reaction between permanganate and different aryl methyl sulfoxides at 23.0 °C are summarized in table-3. The substituted results indicate that sulfoxides with electron donating groups react faster than those with electron withdrawing groups. The Hammett plot using a substituent constants, reproduced in figure-1, gives ρ value of -2.18 ± 0.09 at 23.0 °C. As indicated by figure-2, the correlation when σ^+ values are used is less exact. The reactions of permanganate with sulfoxides are, therefore, much more sensitive to substituent effects than the corresponding reactions of sulfides where the ρ value was observed to be only -1.09 ± 0.05 at the same temperature.

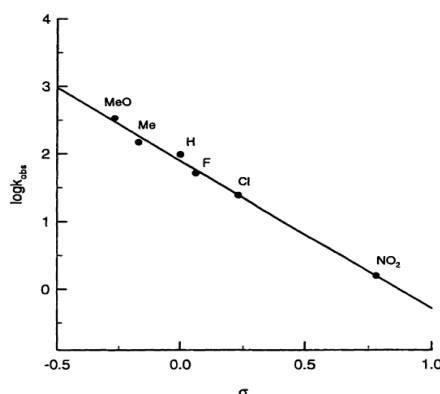


Figure-1: Hammett plot for the oxidation of methyl *p*-substituted phenyl sulfoxides by permanganate at 23.0°C; $[\text{ZnCl}_2] = 1.16 \times 10^{-3} \text{ M}$; Slope = -2.18 ± 0.09 ; Intercept = 1.89 ± 0.03 ; $r^2 = 0.993$

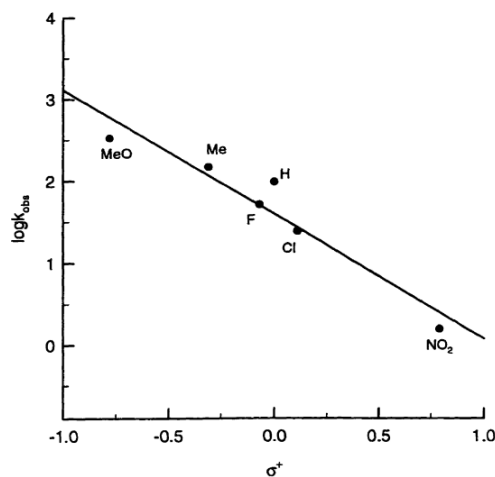


Figure-2: Hammett plot using σ^+ values for the oxidation of methyl *p*-substituted phenyl sulfoxides by permanganate at 23.0°C; $\{[ZnCl_2] = 1.16 \times 10^{-3} \text{ M}; \text{Slope} = -1.52 \pm 0.23; \text{Intercept} = 1.59 \pm 0.11; r^2 = 0.919\}$

C. Activation Parameters

The enthalpies and entropies of activation were determined for each substituted phenyl methyl sulfoxide using $ZnCl_2$ as the Lewis acid catalyst. The Gibbs free energies of activation for these reactions were calculated using equation-8. The data are summarized in tables-4 and -5.

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (8)$$

The activation energies, ΔG^* , for these reactions were also correlated well with the calculated HOMO energies for the sulfoxides (figure-3).

Because oxygen has a higher electronegativity than sulfur, the double bond between sulfur and oxygen in sulfoxides is polarized, placing positive charge on sulfur. Our theoretical calculations indicate that a charge of +1.0 resides on sulfur and - 0.8 charges on oxygen. This results in a lower electron density on sulfur in the sulfoxide than in the corresponding sulfide and decreases the ease of electron loss from sulfur.

According to our theoretical calculations, the lone pair of electrons on the sulfur of a sulfoxide resides on the HOMO orbital. The HOMO orbital is primarily an oxygen *p* orbital. The reaction of a sulfoxide with permanganate would therefore involve an interaction between the O and Mn atoms.

The HOMO energy of a sulfoxide is lower than that of the corresponding sulfide. Therefore the energy gap between the HOMO of the sulfoxide and the LUMO of the $MnO_4 \cdot ZnCl_2^-$ complex is larger than that between the HOMO of the corresponding sulfide and the LUMO of the $MnO_4 \cdot ZnCl_2^-$ complex [7]. This difference in energy is consistent with the difference between reaction rates of sulfoxides and sulfides and is consistent with the proposed mechanism which involves nucleophilic attack by the reductant on the oxidant. The activation energies, ΔG^* , for these reactions also correlate well with the calculated HOMO energies for the sulfoxides (Figure -3).

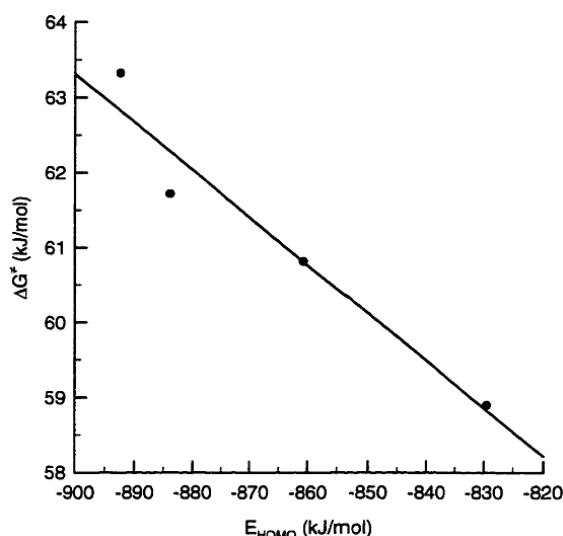


Figure-3: Plot of HOMO energy vs. free energy of activation for $ZnCl_2$ catalysed oxidation of sulfoxides by permanganate in non-aqueous medium

Table-4: Activation parameters for the formation of the $\text{MnO}_4^- \text{ZnCl}_2$ complex (k_i) when sulfoxides are used as reductants; $\{[\text{ZnCl}_2] = 1.16 \times 10^{-3} \text{ M}]\}$

Substrates	$\Delta H_1^* (\text{kJmol}^{-1})$	$\Delta S_1^* (\text{Jmol}^{-1}\text{K}^{-1})$	$\Delta G_1^* (\text{kJmol}^{-1})$
<i>p</i> -MeOPhSOCH ₃	59.5	-17.9	64.8
<i>p</i> -MePhSOCH ₃	59.2	-19.6	65.0
PhSOCH ₃	60.0	-16.4	64.9
<i>p</i> -FPhSOCH ₃	59.8	-17.4	65.0

Table-5: Activation parameters for the reaction of the $\text{MnO}_4^- \text{ZnCl}_2$ complex (k_{obs}) with sulfoxides $\{\Delta G^*$ is calculated at 23.0°C and $[\text{ZnCl}_2] = 1.16 \times 10^{-3} \text{ M}]\}$

Substrates	$\Delta H_1^* (\text{kJmol}^{-1})$	$\Delta S_1^* (\text{Jmol}^{-1}\text{K}^{-1})$	$\Delta G_1^* (\text{kJmol}^{-1})$
<i>p</i> -MeOPhSOCH ₃	19.8	-132	58.9
<i>p</i> -MePhSOCH ₃	22.9	-128	60.8
PhSOCH ₃	24.4	-126	61.7
<i>p</i> -FPhSOCH ₃	26.3	-125	63.3

D. Linear Free Energy Relationships

The activation energy of a redox reaction involving oxygen transfer reactions should be proportional to the difference between the energies of the reductants' HOMOs and the oxidants' LUMOs; i.e., the primary process involves a transfer of electrons from the reductant to the oxidant. The ΔG^* values are related to the rate constants through the Eyring equation (equation-9)

$$\ln k_{\text{obs}} = X (E_{\text{HOMO}} / RT) + \text{constant} \quad (9)$$

The relationship expressed in equation-9 indicates that, under constant conditions, the natural logarithms of the rate constants should be linearly related to the energies of the highest occupied molecular orbitals of the reductants for oxidation by a particular oxidant. HOMO energies for a number of sulfoxides are presented in table-6. HOMO and LUMO energies and the internal energies (ΔE) for MnO_4^- ; the Lewis acids and their complexes were calculated using Gaussian 94 with the LANL2DZ basis set [10].

Table-6: Highest Occupied Molecular Orbital Energies calculated using Gaussian 94 at the RHF/6-31G(d) level at 296.15K

Compound	E_{HOMO} (Hartree)	E_{HOMO} (kJ/mol)	E_{HOMO} / RT
<i>p</i> -MeOPhSOCH ₃	-0.31601	-829.5	-336.9
<i>p</i> -MePhSOCH ₃	-0.32790	-860.7	-349.6
PhSOCH ₃	-0.33671	-883.9	-359.0
<i>p</i> -FPhSOCH ₃	-0.33996	-892.4	-362.4
<i>p</i> -ClPhSOCH ₃	-0.34103	-895.2	-363.6
<i>p</i> -NO ₂ PhSOCH ₃	-0.36114	-948.0	-385.0

The plot of $\ln k_{\text{obs}}$ vs. E_{HOMO} / RT reproduced in figure-4 has an acceptable correlation coefficient of 0.936. The two points that cause the most deviation, *p*-chlorophenyl methyl sulfoxide and *p*-nitrophenyl methyl sulfoxide, are for the two rate constants that contain the greatest experimental uncertainty. If these two points are deleted from the plot, the correlation coefficient is excellent.

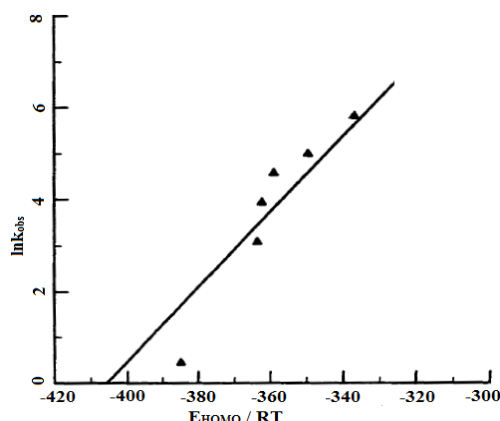


Figure-4: Plot of $\ln k_{\text{obs}}$ vs. E_{HOMO} / RT for para-substituted sulfoxides at 296.5K

$[\text{ZnCl}_2] = 1.16 \times 10^{-3} \text{ M}$, Slope = -0.0818, Intercept = 33.2, $r^2 = 0.936$

The empirical observation expressed in figure-3 is consistent with Frontier Molecular Orbital Theory which suggests that activation energies should be proportional to the difference between the HOMO energy of the electron pair donor and the LUMO energy of the electron pair acceptor [11].

Frontier Molecular Orbital Theory may also be used to account for the catalytic effect of Lewis acids. The calculations indicate that complexation of permanganate with zinc chloride lowers the LUMO energy by 0.06107 Hartrees (160.3 kJ/mol). Further, with reference to figure-5 it can be seen that a reduction in the energy of the oxidant's LUMO would reduce the LUMO-HOMO energy difference. If, as is predicted by this theory, the activation energy for a reaction is proportional to the LUMO-HOMO energy difference, a decrease in the energy of the LUMO or an increase in the energy of the HOMO would result in a decrease in activation energy and an increase in rate. It can be seen, therefore, that Frontier Molecular Orbital Theory accounts qualitatively for both the effect of substituents on the rate of the reaction and on the catalytic effect of Lewis acids (figure-5).

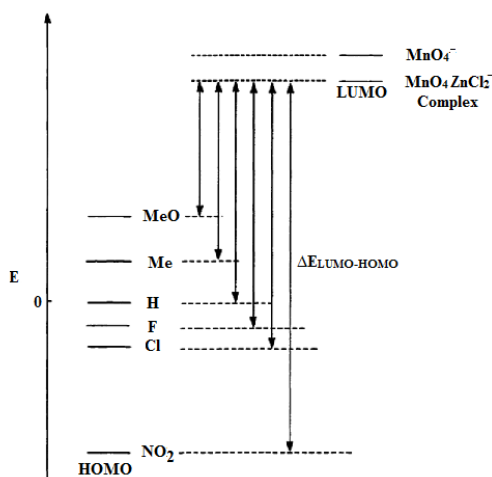


Figure-5: The energy difference between the HOMO of para-substituted sulfides and the LUMO of the $\text{MnO}_4.\text{ZnCl}_2^-$ complex

E. Structures

ZnCl_2 , solvated by two acetone molecules, has a tetrahedral geometry as shown in structure (figure-6). This structure was modeled theoretically. The bond lengths and angles of the theoretically optimized structure are:

Bond length (in Å)

$\text{Zn-Cl} = 2.307$

$\text{Zn-O} = 2.043$

Bond angle (in $^\circ$)

$\text{Cl-Zn-Cl} = 126.6^\circ$

$\text{O-Zn-O} = 104.6^\circ$

$\text{Cl-Zn-O} = 105.1^\circ$

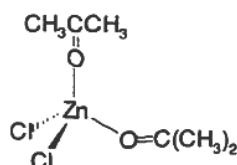


Figure-6: Optimized structure of ZnCl_2 in acetone

The structure for the permanganate-zinc chloride complex modeled is shown as structure in figure-7. The calculated bond lengths and angles in this structure are:

Bond length (in Å)

$\text{Mn-O(2)} = 1.592$

$\text{Zn-O(2)} = 2.054$

$\text{Zn-O(4)} = 2.110$

$\text{Zn-Cl(5)} = 2.231$

$\text{Zn-Cl(6)} = 2.231$

$(4)\text{-C(7)} = 1.229$

Bond angle (in $^\circ$)

$\text{Mn-O(2)-Zn} = 152.9^\circ$

$\text{O(2)-Zn-O(4)} = 88.3^\circ$

$\text{Cl(5)-Zn-Cl(6)} = 124.9^\circ$

$\text{O(4)-Zn-Cl(5)} = \text{O(4)-Zn-Cl(6)} = 106.2^\circ$

$\text{Zn-O(4)-C} = 140.7^\circ$

$\text{O(2)-Zn-Cl(5)} = \text{O(2)-Zn-Cl(6)} = 112.2^\circ$

and the rest of Mn-O bond lengths in permanganate ion are 1.556 Å , and Mn is in tetrahedral geometry.

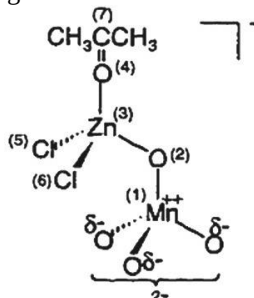
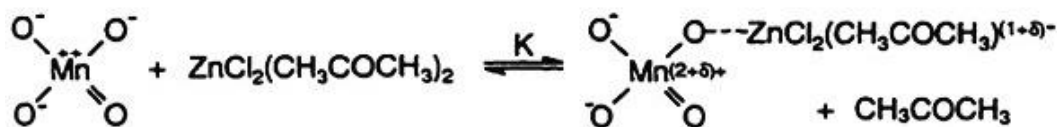


Figure-7: Optimized structure of the $\text{MnO}_4.\text{ZnCl}_2^-$ complex

F. The Reaction Mechanism

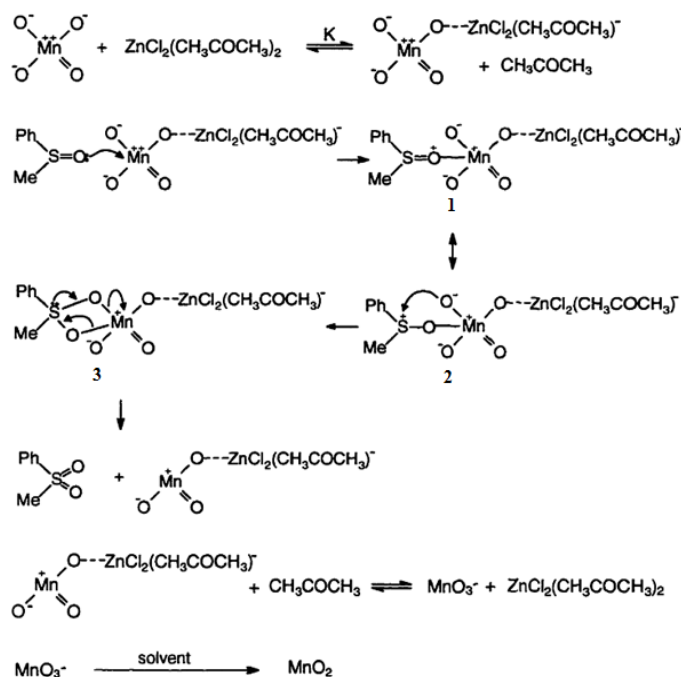
The experimental data indicate that the equilibrium for the formation of the permanganate-zinc chloride complex is established before oxidation of the sulfide occurs (scheme-2):



Scheme-2: The equilibrium for the formation of the $\text{MnO}_4 \cdot \text{ZnCl}_2$ complex

A mechanism for sulfoxide oxidation that is consistent with our experimental results and theoretical calculations is proposed in scheme-3. The formation of permanganate - zinc chloride complex is followed by a reaction in which the sulfoxide becomes a ligand on manganese. Since the highest occupied molecular orbital in the sulfoxide is oxygen $2p$ orbital containing a lone pair of electrons, bonding to the metal would be through oxygen rather than sulfur. The resulting positive charge would be delocalized over oxygen and sulfur as indicated by the resonance structures 1 and 2. The reaction of the electron deficient sulfur with 3, an adjacent oxide ligand would give an intermediate, containing a four membered ring, similar to a proposal previously made by Block [12]. The decomposition of 3 by transfer of electrons as indicated would give the product, a sulfone, along with manganese (V) compound which would be rapidly reduced to MnO_2 under these conditions. The transition state is more organized than the ground state as suggested by the negative entropies of activation.

Scheme-3: Proposed mechanism for the zinc chloride catalysed oxidation of sulfoxide by permanganate in acetone medium



IV. CONCLUSIONS

The rates of ZnCl_2 catalysed oxidation of several *para*-substituted sulfoxides by permanganate have been studied in anhydrous acetone solutions. The kinetic rate law obtained indicates that a complex between permanganate and the Lewis acid (ZnCl_2) is formed before oxidation of the sulfoxides occurs. The function of the zinc chloride is to enhance the reactivity of permanganate. A Hammett ρ value of -2.18 ± 0.09 is obtained for the oxidation of sulfoxides at 23.0°C . Values for the HOMO energies of sulfoxides and the LUMO energies for permanganate ion and the permanganate-zinc chloride complex have been calculated. A new linear free energy relationship, based on frontier molecular orbital theory, has been derived from first principles. This equation was used to simultaneously correlate the rate constants for the oxidation of sulfoxides with the energies of their highest occupied molecular orbital. The results indicate that electron donating substituents on the ring increase the rate of the reaction and electron withdrawing groups slow down the reaction.

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