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RESEARCH ARTICLE

Kinetics and Mechanism of $ZnCl_2$ Catalyzed Oxidation of Organic Sulfides by Permanganate in Non-Aqueous Medium

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Abstract: The rates of zinc chloride (Lewis acid) catalysed oxidation of thioanisole and several *para*-substituted thioanisoles 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 sulfur-containing compounds occurs. The function of the zinc chloride is to enhance the reactivity of permanganate. A Hammett ρ value of -1.09 ± 0.05 is obtained for the oxidation of sulfides at 23.0 ^{0}C**.** A negative ρ value means that the sulfur is electron deficient in the transition state. Values for the HOMO energies of sulfides 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: Thioanisoles, Permanganate, Acid catalysedoxidation, LUMO, HOMO

Introduction

Many oxidants containing high-valent transition metals are capable of transferring oxygen to substrates such as alkenes, alkanes, amines, phosphines, sulfides and sulfoxides. Compounds containing transition metal oxos (M=O) have been extensively used for the oxidation of sulfur-organic cornpounds. Some of these oxidants are used instoichiometric quantities; others function as catalysts[1]. Oxygen transfer from metal-oxos to sulfur atoms in sulfides occurs without accompanying bond cleavage in the organic substrate. Other oxygen transfer reactions, such as alkene hydroxylations, epoddations or allylic oxidations, are more complicated because they require C-C or C-H bond cleavage as well as oxygen transfer. Because of the greater simplicity of the sulfide reactions, a great deal of the work in our laboratory in past several years has focused on the transfer of oxygen from the high-valent transition metal-oxo compounds to sulfur.

Potassium permanganate is an inexpensive and widely used oxidant. It is a vigorous oxidant and has been employed for the oxidation of a wide range of organic compounds including alkanes, alkenes, alcohols, ethers, aldehydes, ketones, amines, sulfides and sulfoxides.

The mechanisms of these reactions have been extensively studied and a great deal of knowledge concerning them is currently available[2–8]. From the literature survey, the reactions of sulfides with oxidants, it is apparent that there is currently no single, generally accepted mechanism for these processes. The overall objective of the present research article is to learn more about those reactions of potassium permanganate as the transition metal oxo compound withseveral organic sulfides as the oxygen-acceptors and determine if all oxygen transfers from oxidant containing Mn-oxos can be considered to occur by way of a single general mechanism and if not, to identify those features of a particular reaction that causes it to proceed via a unique pathway.

Experimental

The thioanisole, *para*-methoxythioanisole, *para*-methylthioanisole, *para*-fluorothioanisole and *para*-chlorothioanisole were received as liquids with 97% or above purity. These sulfides were carefully distilled under reduced pressure and the part of the distillates collected. GC or HPLC analysis indicated purities of middle 99.5% to 99.9% for the distillates.

The *para*-nitrothioanisole was obtained commercially as technical grade (90%). It was recrystallized from ethanol three times and then purified by column chromatography (silica gel, eluent: chloroform/ethyl acetate 1 / 1)[9].

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 mesh) was from BDH.

Kinetic methods

The kinetic study of the reduction of permanganate by thioanisole and various ring substituted thioanisoles 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 supernant 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 thioanisole 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. The initial concentration of permanganate was approximately 3 ± 10^{-4} M for all experiments, while the concentration of zinc chloride was varied from 5 ± 10^{-4} to 7 ± 10^{-3} M. For determination of the order with respect to zinc chloride, the concentration of zinc chloride was varied over a larger range. The thioanisole concentration was varied from 6 ± 10^{-3} to 0.12 M.

Results and Discussion

Order of reaction with respect to permanganate

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

$$\text{Rate} = k\,[MnO_4^-]^x\,[RSR']^y\,[LA]^z \quad (1)$$

The orders with respect to permanganate, sulfide and Lewis acid are designated as x, y and z respectively. Under pseudo order reaction conditions where sulfide is used in at least ten-fold excess over the concentration of permanganate and the concentration of the catalyst, $ZnCl_2$, is constant, the rate law can be restated in terms of equations (2) and (3).

$$\text{Rate} = k'\,[MnO_4^-]^x \quad (2)$$

$$k' = k[RSR']^y\,[LA]^z \quad (3)$$

Since the reaction was monitored by following the decrease in an absorbance band due to permanganate, the rate of reaction can be expressed as:

$$\text{Rate} = -d[MnO_4^-] / dt \quad (4)$$

According to the Beer-Lambert law, the concentration of permanganate can be expressed in terms of absorbance and the extinction coefficient as in equation (5):

$$[MnO_4^-] = A / (\varepsilon^* l) \quad (5)$$

Where is the length of light pathway (1.0 cm in all experiments). The equation (4) can then be rewritten in the form of equation (6):

$$-dA / (\varepsilon^* dt) = k'\,(A/\varepsilon)^x \quad (6)$$

If the reaction is first order in permanganate, that is x = 1, rearrangement and integration of equation (6) gives the integrated form of rate law, equation (7):

$$\ln(A-A_f) = -k't + \ln(A_0-A_f) \quad (7)$$

The approximate linearity of plots of ln $(A-A_f)$ *vs.* time indicates that the reaction is first order with respect to permanganate. However, the slight upward curvature of some of these plots indicates that the reaction is subject to autocatalysis, a well-known phenomenon when MnO_2 is one of the products[10-13]. To avoid possible errors caused by this curvature, initial reaction rates were used to determine the rate constants. The equation (6) can be restated in terms of the initial rate and the initial absorbance (A_i) as in equation (8) and (9).

$$-(dA/dt)_i = k''A_i^x \quad (8)$$

$$k'' = k'\,\varepsilon^{1-x} \quad (9)$$

To prevent the introduction of human bias, the initial rates were determined by fitting the absorbance / time data to a standard curve as defined in equation (10)[14].

$$A = a_0 + a_1t + a_2t^2 + a_3t^3 + a_4t^4 + a_5t^5 \quad (10)$$

Differentiation with respect to time of the equation obtained from computer modeling of the data and setting time equal to zero, gives the observed initial rate. $R_i = -(dA/dt)_i = -a_i$. Since permanganate is slowly reduced by acetone in the absence of other reductants, it is necessary to correct the observed initial rate for the "blank rate" which has been designated as R_b. This correction did not reduce the initial rate by more than 10% under any conditions. The corrected initial rate is therefore given by equation (11).

$$\text{Corrected initial rate} = R_i - R_b \tag{11}$$

A plot of R_i - R_b (the initial rate) *vs.* A (the initial absorbance) is linear (Figure 1), confirming that x = 1; *i.e.*, the reaction is first order with respect to permanganate.

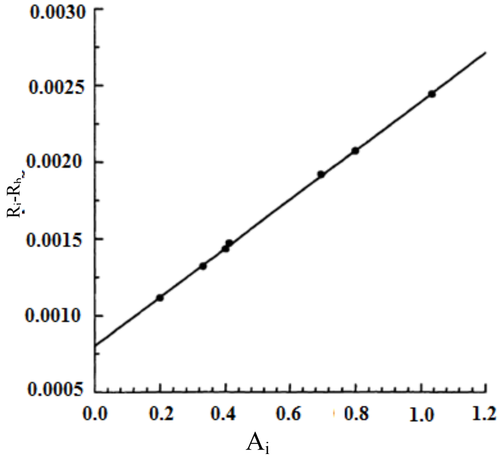


Figure 1. Plot indicating the order with respect to permanganate in anhydrous acetone solution; [PhSMe] = 6.81×10^{-3}M; [ZnCl$_2$] = 7.19×10^{-4}M; $r^2 = 1.00$; T = 23±0.1 ^{0}C; Slope = $(1.59\pm0.04)\times10^{-3}$

Order of reaction with respect to zinc chloride

When the initial concentration of thioanisole is held in a constant large excess while the concentration of zinc chloride is varied. Equation (1) can be rewritten as equation (12),

$$\text{Rate} = k' [MnO_4^-] [ZnCl_2]^z \tag{12}$$

Where $k' = k [RSR']^y$. When $[MnO_4^-]$ is expressed in terms of absorbance A, equation (13) is obtained.

$$-(dA / dt)_i = k' A_i [ZnCl_2]^z \tag{13}$$

Using the definition of initial rate (equation-1), equations (14) and (15) can be derived:

$$(R_i - R_b) = k' A_i [ZnCl_2]^z \tag{14}$$

$$\ln [(R_i - R_b) / A_i)] = z \ln [ZnCl_2] + \ln k' \tag{15}$$

The slope of the plot of ln $[(R_i - R_b) / A_i)]$ *vs.* ln [ZnCl$_2$], will be the reaction order with respect to zinc chloride, z. The experimental result shows that z = 1.1±0.1 (Figure 2), which indicates that the order with respect to Lewis acid (ZnCl$_2$) is unity.

Order of reaction with respect to thioanisoles

When the initial concentration of zinc chloride is held constant and the concentration of thioanisoles varied, equation (16) is obtained.

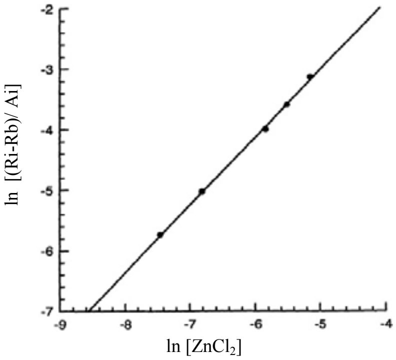


Figure 2. Plotindicating the order with respect to zinc chloride; [PhSMe] = 6.81×10^{-3}M; $r^2 = 0.999$; T = 23.0±0.1 ^{0}C; Slope = 1.10±0.10

$$\ln \{(R_i - R_b) / A_i)\} = y \ln [RSR'] + \ln k''' \quad (16)$$

Plots of $\ln \{(R_i - R_b) / A_i)\}$ *vs*. ln [RSR'], appear to be linear, but with a slope much less than unity (Figure 3). A plot of initial rate *vs*. reductant concentration indicates that the order with respect to thioanisoles changes from approximately unity at low concentrations to approximately zero at high concentrations.

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-17) 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 sulfidesare subsequently oxidized by this complex in a second step. The corresponding rate law is given by equation (17):

$$-d[MnO_4^-] / dt = k_1k_2[MnO_4^-][ZnCl_2][RSR'] / k_1 + k_2[RSR'] \quad (17)$$

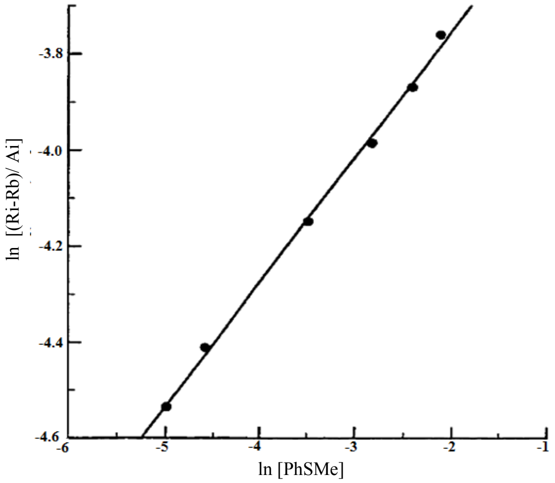


Figure 3. Plot indicating the apparent order with respect to Thioanisole; [ZnCl$_2$] = 7.19×10^{-4} M; $r^2 = 0.998$; T = 25±0.1 ^{0}C; Slope = 0.26±0.01

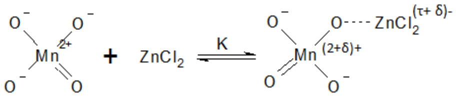
The experimentally determined values for the rate constants k_1 and k_{obs} for the oxidation of thioanisole and substituted thioanisoles at various concentration of ZnCl$_2$ at 25.0±0.1 ^{0}C temperature are presented in Table 1.

Table 1. Rate constants for the oxidation of thioanisole and substituted thioanisoles at various concentration of $ZnCl_2$ at 25.0±0.1 ^{0}C temperature

	$k_1(M^{-1}s^{-1})$		
Substrates	$[ZnCl_2]$ = 0.00116 (M)	$[ZnCl_2]$ = 0.000719 (M)	$[ZnCl_2]$ = 0.000669 (M)
$PhSCH_2OCH_3$		29.4±2.8	26.6±0.4
$PhSCH_3$	31.9±1.7	29.1±2.4	30.0±2.4
p-$MePhSCH_3$	31.0±1.4	29.1±0.1	
		$k_{obs} * 10^{-3}$ $(M^{-2}s^{-1})$	
Substrates	$[ZnCl_2]$ = 0.00116 (M)	$[ZnCl_2]$ = 0.000719 (M)	$[ZnCl_2]$ = 0.000669 (M)
$PhSCH_2OCH_3$		2.1±0.02	2.10±0.19
$PhSCH_3$	1.71±0.07	1.73±0.12	1.79±0.14
p-$MePhSCH_3$	2.72±0.50	2.66±0.08	

Role of Lewis acid in the reaction

Lewis acids have a significant catalytic effect on the rates of oxidation of sulfides by permanganate. There is almost no reaction between permanganate and sulfide 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[15].



Scheme 1. The reaction between permanganate and zinc chloride

The oxidation of thioanisole was studied at three different concentrations of zinc chloride and the reaction of methyl *p*-tolyl sulfide and methoxymethylphenyl sulfide at two different concentrations each.The results summarized in Table 1 indicate that changes in the concentration of zinc chloride have no effect on the rate constants, k_1 and k_{obs}, within experimental error.

Substituent effects

The experimental results show that under identical conditions (of temperature, solvent and Lewis acid concentration) substituents at the *para* position of phenyl methyl sulfides have significant effects on the second step of the reaction sequence; electron-donating groups increase the magnitude of k_{obs} and electron-withdrawing groups decrease the magnitude of k_{obs}. The observation that the magnitude of k_l is independent of the structure of the sulfide is consistent with the suggestion that the first step is a reaction between $MnO_4^-$and $ZnCl_2$ as in Scheme 1.

Quantitative values for each substituent were obtained by a comparison of the dissociation constants of substituted benzoic acids $(k_{obs})_x$ with that of the parent compound (k_H) as expressed in equation (18) (Hammett equation):

$$\log(k_{obs})_x = \sigma\rho + \log(k_{obs})_H \tag{18}$$

Where; $(k_{obs})_H$ = rate constant for the unsubstituted compound, $(k_{obs})_x$ = rate constant for compounds with substituents, σ = substituent constant and ρ = reaction constant. According to the equation a plot of log k_{obs} *vs.* σ should be linear and the slope of the plot, ρ, would represent the extent of the effect of substituents on k_{obs}. Thioanisole and five para-substituted thioanisoles were employed in the Hammett study. All were found to conform to the same rate law. The results indicate that electron donating substituents on the ring increase the rate of the reaction and electron withdrawing groups slow down the reaction. The rate constants at 23.0 ^{0}C, which were derived from interpolation of plots of ln k_{obs}/T *vs*. 1/T, are summarized in Table 2.

Table 2. Rate constants for the oxidation of thioanisole and substitutedthioanisoles at 23.0 ^{0}C when [$ZnCl_2$] = 1.16x10^{-4} M

Substrates	σ	σ^+	$k_1(M^{-1}s^{-1})$	$k_{obs}^* 10^{-3}$ $(M^{-2}s^{-1})$
p-$MeOPhSCH_3$	-0.28	-0.78	25.9±0.1	3.63±0.05
p-$MePhSCH_3$	-0.17	-0.31	26.1±0.1	2.48±0.11
$PhSCH_3$	0	0	26.9±0.4	1.58±0.02
p-$FPhSCH_3$	0.06	-0.07	24.8±0.4	1.43±0.02
p-$ClPhSCH_3$	0.23	0.11	26.6±0.1	0.951±0.006
p-NO_2PhSCH_3	0.78	0.79	26.5±0.2	0.228±0.005

The ρ value for the oxidation of sulfide by permanganate with zinc chloride at 23.0±0.1 ^{0}C is -1.09±0.07. A negative ρ value means that the sulfur is electron deficient in the transition state.

Effect of ring substituents on k_l

From Table 2, it can be seen that within the limits of experimental uncertainty, substituents on the ring have no effect on the magnitude of k_1. This confirms that the sulfidesare not involved in the first step of the reaction.

One of the prerequisites for a reaction to obey the Hammett equation is that a linear relationship exists between the activation enthalpy and activation entropy[16-17]. The entropies of activation in the present series of reactions, ΔS^*, are linearly related to the enthalpies of activation, ΔH^*, by equation (19)[18-19].

$$\Delta H^* = \Delta H_o + \beta \Delta S^* \tag{19}$$

The Figure 4 shows excellent linearity between ΔH^* and ΔS^* for thioanisole and *para*-substituted thioanisoles. The data for this plot are found in Table 3. The existence of such a linear relationship between ΔH^* and ΔS^* indicates that a single mechanism is operating throughout the series[20-22]. The negative entropies of activation are consistent with a well-organized transition state.

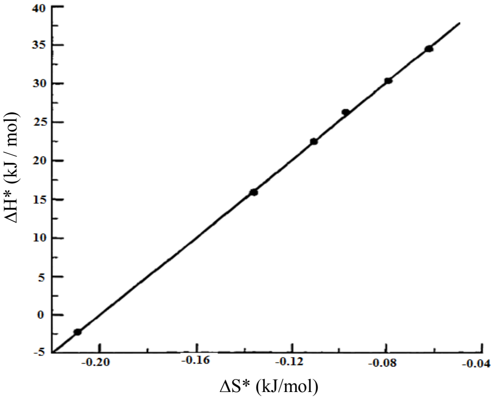
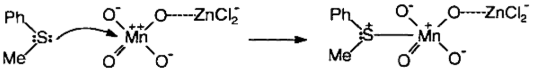


Figure 4. Plot of enthalpy of activation *vs*. entropy of activation for the oxidation of sulfides [$ZnCl_2$] = 1.16x10^{-3} M, Slope = 251, Intercept = 50.1, r^2= 0.9998

Table 3. Activation parameters for the oxidation of sulfides (k_{obs}) when $[ZnCl_2] = 1.16 \times 10^{-3}$ M

Substrates	ΔH^*, kJ mol^{-1}	ΔS^*, J mol^{-1} K^{-1}
p-MeOPhSCH$_3$	34.4±0.6	-62±1.9
p-MePhSCH$_3$	30.3±1.5	-79±5.2
PhSCH$_3$	26.2±0.3	-96.9±1.2
p-FPhSCH$_3$	22.4±0.3	-111±1
p-ClPhSCH$_3$	15.8±0.1	-136±1
p-NO$_2$PhSCH$_3$	-2.29±0.27	-209±1

The negative ρ value for the Hammett plot indicates the development of electron-deficient sulfur in the transition state. A positively charged sulfur in the transition state (as compared to the ground state) is consistent with a mechanism in which the sulfur atom shares a lone pair of electrons with the complex formed by permanganate and the Lewis acid as shown in Scheme 2. The electrons would becontributed from the highest occupied molecular orbital (HOMO) of the sulfide and accepted by the lowest unoccupied molecular orbital (LUMO) of the oxidant.



Scheme 2. Reaction between thioanisole and the $MnO_4^-ZnCl_2$ complex

The poor Hammett correlations observed when σ* values are used suggest that the mechanism of the reaction does not involve a single electron transfer as in equation (20):

$$ArSMe + MnO_4.ZnCl_2^- \rightarrow ArS^+Me + MnO_4.ZnCl_2^{2-} \tag{20}$$

Theoretical calculations show that the HOMO of thioanisole and its *para*-substituted derivatives is formed by a nonbonding combination of the sulfur 3*p* and the appropriate ring and substituent π orbitals with dominant contribution from thesulfur lone pair. The LUMO of the $MnO_4^-ZnCl_2$complexis contributed mainly from vacant manganese d orbitals.

It is therefore approximately correct to depict the interaction between the HOMO and the LUMO as an interaction between the lone pair on sulfur and a vacant *d* orbital on manganese as in Scheme 2.

Because it is not possible for the positive charge on sulfur to be delocalized over the aromatic ring, substituents in the *para*-position correlate better with σ values than with σ* values.

Activation parameters

According to transition state theory[23], the activation parameters for a reaction can be calculated from the Eyring Equation[24] as expressed in equation (21):

$$\ln(k/T) = -\Delta H^*/RT + \ln(\kappa / h) + \Delta S^*/R \tag{21}$$

Where, k = reaction rate constant; **κ** = Boltzmann constant (1.686×10^{-23} JK^{-1}); h = Planck constant (6.626×10^{-34} Js); R = Molar gas constant (8.315 Jmol^{-1} K^{-1}); T = Absolute temperature (K); ΔH^* = Enthalpy of activation (kJ mol^{-1}); ΔS^* = Entropy of activation (J mol^{-1} K^{-1}).

The plots of ln (k/T) *vs*. 1/T should therefore be linear with slopes equal to $--\Delta H^*/R$ and intercepts equal to (ln (**κ** / h) + $\Delta S^*/R$). Activation parameters were determined for both k_1 and k_{obs} using this approach. The Gibbs free energies of activation (ΔG^*) can be calculated from the relationship in equation (22):

$$\Delta G^* = \Delta H^* - T\Delta S^* \tag{22}$$

The activation parameters obtained for thioanisole and several para-substituted thioanisoles when the concentration of zinc chloride is 1.16x10^{-3}M are summarized in Tables 4 and Table 5.

Table 4. Activation parameters for the formation of the $MnO_4^-ZnC1_2$ complex (k_1) when sulfides are used as reductants {ΔG^* is calculated at 23.0 ^{0}C and [$ZnCl_2$] = 1.16×10^{-3} M}

Substrates	ΔH_1^* kJ mol^{-1}	ΔS_1^* J mol^{-1} K^{-1}	ΔG_1^* kJ mol^{-1}
p-MeOPhSCH$_3$	60.6±0.2	-18.5±1.0	66.1±0.3
p-MePhSCH$_3$	60.2±0.2	-16.2±0.6	65.0±0.3
PhSCH$_3$	60.1±0.7	-16.2±2.4	64.9±1.0
p-FPhSCH$_3$	59.8±0.7	-17.1±2.4	64.9±1.0
p-ClPhSCH$_3$	59.4±0.2	-18.5±0.6	64.9±03
p-NO$_2$PhSCH$_3$	60.7±0.5	-18.5±1.7	66.2±0.7

Table 5. Activation parameters for the reaction of the $MnO_4^-ZnCl_2$ complex (k_{obs}) with suifides {ΔG^* is calculated at 23.0 ^{0}C and [$ZnCl_2$] = 1.16x10^{-3} M}

Substrates	ΔH_1^* kJ mol^{-1}	ΔS_1^* J mol^{-1} K^{-1}	ΔG_1^* kJ mol^{-1}
p-MeOPhSCH$_3$	34.4±0.6	-62.2±1.9	52.8±0.8
p-MePhSCH$_3$	30.3±1.5	-79.0±5.2	53.7±2.1
PhSCH$_3$	26.2±0.3	-96.9±1.2	54.9±0.5
p-FPhSCH$_3$	22.4±0.3	-111±1	55.3±0.5
p-ClPhSCH$_3$	15.8±0.1	-136±1	56.1±0.3
p-NO$_2$PhSCH$_3$	-2.29±0.27	-209±1	59.6±0.4

Activation parameters and the correlation of activation energies with frontier molecular orbital calculations

The experimentally determined Gibbs activation energy, ΔG^*, increases as the substituents at *para* position change from methoxy, to methyl, to hydrogen, to fluoro, to chloro and to nitro (Table 6). This is the same order in which the HOMO energies of the sulfides decrease. Figure 5 shows that a good linear correlation exists between the activation energies and the HOMO energies of the sulfides. (Because the LUMO energy of the oxidant is the same for all reactions, the plot of activation energy *vs*. the LUMO-HOMO energy gap is identical to a plot of ΔG^* *vs*. HOMO energy except with respect to the value of the intercept.)

Table 6. HOMO Energies and free energies of activation for different substituted suifides when [$ZnCl_2$] = 1.16x10^{-3} M and ΔG^* is calculated at 23.0 ^{0}C

Sulphide	HOMO(Hartree)	HOMO, kJ/mol	ΔG^*, kJ/mol
p-MeOPhSCH$_3$	-0.28001	-735.0	52.8
p-MePhSCH$_3$	-0.28800	-756.0	53.7
PhSCH$_3$	-0.29486	-774.0	54.9
p-FPhSCH$_3$	-0.29849	-783.5	55.3
p-ClPhSCH$_3$	-0.30194	-792.6	56.1
p-NO$_2$PhSCH$_3$	-0.32683	-857.9	59.6

The empirical observation expressed in Figure 5 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[25].

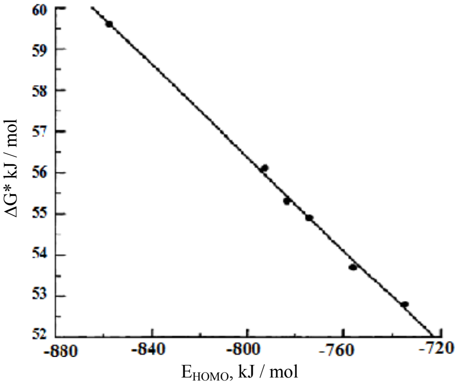


Figure 5. Plot of HOMO energy *vs*. free energy of activation for sulfides when $ZnCl_2$ is used as the Lewis acid; $[ZnCl_2] = 1.16x10^{-3}$ M, Slope = -0.0563, Intercept = 11.3, r^2= 0.997

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 6 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 adecrease 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 substituentson the rate of the reaction and on the catalytic effect of Lewis acids.

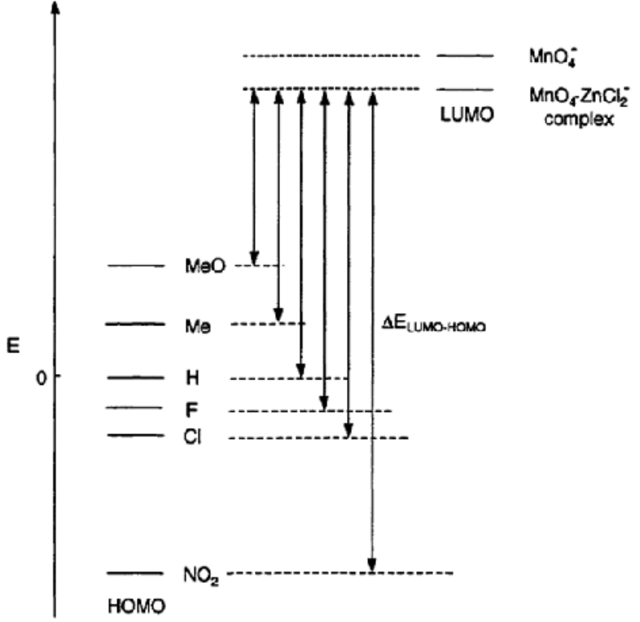


Figure 6. The energy difference between the HOMO of para-substituted sulfides and the LUMO of the$MnO_4^-ZnCl_2$ complex

Structures

$ZnCl_2$, solvated by two acetone molecules, has a tetrahedral geometry as shown in structure (Figure 7). This structure was modeled theoretically. The bond lengths and angles of the theoretically optimized structure are:

Bond length (in Å)
Zn-Cl = 2.307
Zn-O = 2.043

Bond angle (in ^{0})
Cl-Zn-Cl = 126.6^0
O-Zn-O = 104.6^0
Cl-Zn-O = 105.1^0

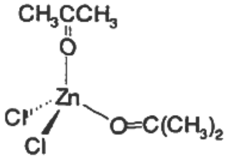


Figure 7. Optirnized structure of $ZnCl_2$ in acetone

The structure for the permanganate-zinc chloride complex modeled is shown as structure in Figure 8.The calculated bond lengths and angles in this structure are:

Bond length (in Å)
Mn-O(2) = 1.592
Zn-O(2) = 2.054
Zn-O(4) = 2.110
Zn-Cl(5) = 2.231
Zn-Cl(6) = 2.231
(4)-C(7) = 1.229

Bond angle (in ^{0})
Mn-O(2)-Zn = 152.9^0
O(2)-Zn–O(4) = 88.3^0
Cl(5)-Zn-Cl(6) = 124.9^0
O(4)-Zn-Cl(5) = O(4)-Zn-Cl(6) = 106.2^0
Zn-O(4)-C = 140.7
O(2)-Zn-Cl(5) = O(2)-Zn-Cl(6) = 112.2^0

and the rest of Mn-O bond lengths in permanganate ion are 1.556 A^0 and Mn is in tetrahedral geometry.

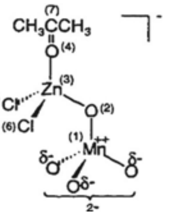
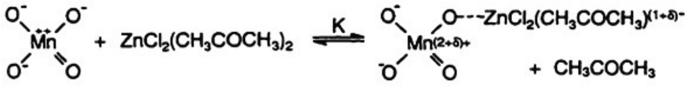


Figure 8. Optimized structure of the $MnO_4^-ZnCl_2$ complex

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 3):

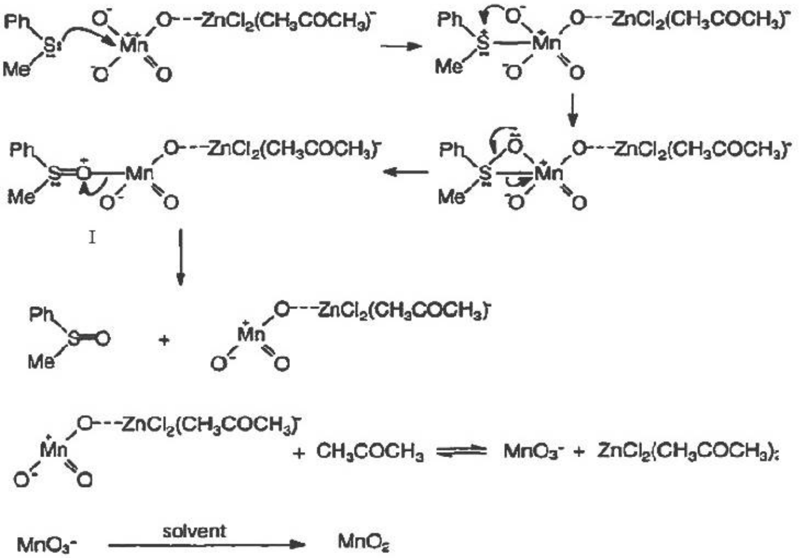


Scheme 3. The equilibrium for the formation of the $MnO_4.ZnCl_2^-$ complex

A mechanism for sulfide oxidation that is consistent with our experimental results and theoretical calculations is proposed in Scheme 4. The sulfide is first bonded to manganese as a ligand with sulfur as the chelating atom.

The formation of a three-membered ring composed of sulfur, manganese and oxygen is followed by cleavage of the S-Mn bond to give a structure in which the sulfoxide is a ligand, **I**. Although indicated as two distinct steps in Scheme 4, this may be a concerted process.

Permanganate is reduced to manganate(V) in this process. Because Mn(V) is stable only under very alkaline conditions, it would quickly be reduced to manganese (IV), MnO_2, by the solvent[26].



Scheme 4. Mechanism of the oxidation of thioanisole by the $MnO_4.ZnCl_2^-$ complex

Conclusion

The rates of oxidation of thioanisole and several*para*-substituted thioanisoles by permanganate have been studied in anhydrous acetone solutions. These reactions are catalyzed by zinc chloride. The kinetic rate law obtained indicates that a complex between permanganate andthe Lewis acid ($ZnCl_2$) is formed before oxidation of the sulfur-containing compounds occurs. The function of the zinc chloride is to enhance the reactivity of permanganate. A Hammett ρvalue of -1.09 ± 0.05 is obtained for the oxidation of sulfides at 23.0 ^{0}C**.** A negative ρ value means that the sulfur is electron deficient in the transition state.Values for the HOMO energies of sulfides and the LUMO energies for permanganate ion and the permanganate-zinc chloride complex havebeen calculated. A new linear free energy relationship, based on frontier molecular orbitaltheory, has been derived from first principles. This equation was used tosimultaneously correlate the rate constants for the oxidation of sulfides 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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