

## Effect of substituents on the oxidation of some alkyl-aryl sulphoxides by chloramine-T

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**Abstract.** The oxidation rates of some substituted phenyl methyl sulphoxides with chloramine-T have been studied in alkaline and neutral media.  $\text{OsO}_4$  is used as catalyst in alkaline medium where the meta and para substituents show no effect on the reaction rate. This is explained on the basis of isokinetic relationship. In both the media, the orthosubstituents show steric effect.

**Keywords.** Chloramine-T; isokinetic; kinetics; steric effect; sulphoxides.

### 1. Introduction

The kinetics of oxidation of some substituted phenyl methyl sulphoxides by CAT in alkaline medium (Ganapathy and Jayagandhi 1982a) and in buffered ethanol-water (Ganapathy and Jayagandhi 1982b) have been studied. In this paper, the substituent effects are analysed in terms of steric factor and isokinetic relationship.

### 2. Experimental

Chloramine-T and the sulphoxides were prepared and purified using standard methods. Alkaline medium was maintained using NaOH. *t*-Butanol-water mixture (1 : 1 v/v) was used as solvent. For the buffered medium, phosphate buffer (pH 7) was used and ethanol-water mixture (1 : 1 v/v) was used as solvent. Both the kinetics were followed iodometrically.

### 3. Results and discussion

#### 3.1 Alkaline medium

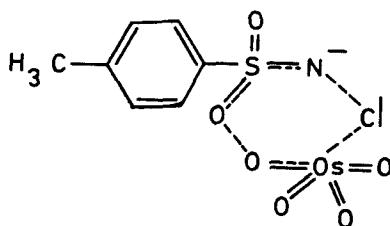
The observed rate-law for the Os(VIII)-catalysed oxidation of substituted phenyl methyl sulphoxides by CAT (Ganapathy *et al* 1982a) is

$$-d[\text{CAT}]/dt = k_{1.5}[\text{CAT}][\text{SO}]^{1/2}.$$

The mechanism is proposed by assuming the formation of the following cyclic complex between CAT and  $\text{OsO}_4$ .

The cyclic structure indicates that the electron density around nitrogen is decreased

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in complexation, weakening the N-Cl bond. Therefore, the interaction with the sulphoxides is increased resulting in the formation of chlorosulphonium ion intermediates. This, on hydrolysis, gives the sulphone.

The calculated rate constants and the activation parameters for the meta and para substituted phenyl methyl sulphoxides are given in tables 1 and 2 respectively.

A perusal of the rate data indicate that there is no substituent effect on the reaction rate. This may be due to two factors (i) a zero-order dependence on the substrate and (ii) the experimental temperature being too close to the isokinetic temperature (Leffler 1955; Leffler and Grumwald 1963; Peterson *et al* 1961). The first probability is ruled out as the present reaction showed a clear dependence (0.5) on the substrate. Hence, the only probability is that the experimental temperature should be in the neighbourhood of isokinetic temperature.

A plot of  $\Delta H^\ddagger$  vs  $\Delta S^\ddagger$  gives an excellent straight line with a correlation coefficient ( $r$ ) of 1. The isokinetic temperature obtained from the slope is 305°K. It is probable that at the experimental temperatures employed (298, 303 and 308°K) there will be equilization of the rates.

The free energy of activation  $\Delta G^\ddagger$  is equal to  $(\Delta H^\ddagger - T\Delta S^\ddagger)$  and it follows that if there is an exact linear relationship between  $T\Delta S^\ddagger$  and  $\Delta H^\ddagger$ , with unit slope, there will be no variation in  $\Delta G^\ddagger$  i.e. all the rate constants are equal. The present reaction series showed an excellent relationship between  $T\Delta S^\ddagger$  and  $\Delta H^\ddagger$  with a correlation coefficient of 0.998. The slope of the line was 0.984 (nearly unity) which clearly explains that there

**Table 1.** Rate constants for Os(VIII)-catalysed oxidation of meta and para substituted phenyl methyl sulphoxides by chloramine-T.  
[NaOH] = 0.002 M; [OsO<sub>4</sub>] = 0.0002 M

Substituent	$k_{1.5} \times 10^3 \text{ l}^{1/2} \text{ mol}^{-1/2} \text{ sec}^{-1}$		
	25°	30°	35°
None	4.612	5.850	7.086
<i>p</i> -OCH <sub>3</sub>	4.990	5.975	7.372
<i>p</i> -Cl	4.557	5.727	6.551
<i>p</i> -Br	4.756	5.982	7.224
<i>p</i> -CH <sub>3</sub>	4.662	5.968	7.503
<i>p</i> -NO <sub>2</sub>	4.907	6.085	7.835
<i>m</i> -OCH <sub>3</sub>	4.618	5.967	7.232
<i>m</i> -Cl	4.637	5.778	7.290
<i>m</i> -CH <sub>3</sub>	4.189	5.583	7.420
<i>m</i> -NO <sub>2</sub>	4.607	6.126	7.116

**Table 2.** Activation parameters for Os(VIII)-catalysed oxidation of meta and para substituted phenyl methyl sulphoxides by chloramine-T.

Substituent	E (kJ mol <sup>-1</sup> )	$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> at 30°)	$\Delta S^\ddagger$ (kJ <sup>-1</sup> mol <sup>-1</sup> at 30°)	$\Delta G^\ddagger$ (kJ mol <sup>-1</sup> at 30°)
None	33.77	31.25	-185.2	87.36
<i>p</i> -OCH <sub>3</sub>	29.16	26.64	-200.2	87.31
<i>p</i> -Cl	28.71	26.19	-201.5	87.25
<i>p</i> -Br	32.48	29.96	-189.3	87.31
<i>p</i> -CH <sub>3</sub>	35.78	33.26	-178.4	87.31
<i>p</i> -NO <sub>2</sub>	36.54	34.02	-175.7	87.26
<i>m</i> -OCH <sub>3</sub>	32.81	30.20	-188.2	87.31
<i>m</i> -Cl	33.77	31.25	-185.3	87.40
<i>m</i> -CH <sub>3</sub>	42.83	40.31	-155.7	87.48
<i>m</i> -NO <sub>2</sub>	28.71	26.19	-201.5	87.25

**Table 3.** Rate constants for Os(VIII)-catalysed oxidation of ortho-substituted phenyl methyl sulphoxides with chloramine-T.[NaOH] = 0.002 M; [OsO<sub>4</sub>] = 0.0002 M

Substituent	$k_{1.5} \times 10^3 \text{ l}^{1/2} \text{ mol}^{-1/2} \text{ sec}^{-1}$		
	25°	30°	35°
None	4.612	5.850	7.086
Cl	1.697	2.041	2.516
Br	1.676	2.093	2.771
OCH <sub>3</sub>	2.146	2.652	3.359
CH <sub>3</sub>	1.915	2.334	3.140
NO <sub>2</sub>	2.441	3.079	3.845
2,6-(CH <sub>3</sub> ) <sub>2</sub>	0.796	1.134	1.642

is exact compensation between  $T\Delta S^\ddagger$  and  $\Delta H^\ddagger$ .

The rate constants and the thermodynamic parameters for the orthosubstituted phenyl methyl sulphoxides are given in tables 3 and 4 respectively. Leffler (1955) pointed out that moderate changes in the degree of steric hindrance often do not remove a reaction from its isokinetic line but merely move it to a new location on the same line. With a considerable increase in steric hindrance in the transition state, a combined increase in the enthalpy of activation and decrease in entropy of activation are to be expected. Such points lie above the isokinetic line for the other reactions. In this study the points corresponding to the orthosubstituted sulphoxides lie above the isokinetic line showing steric effect (figure 1).

## 2.2 Neutral medium

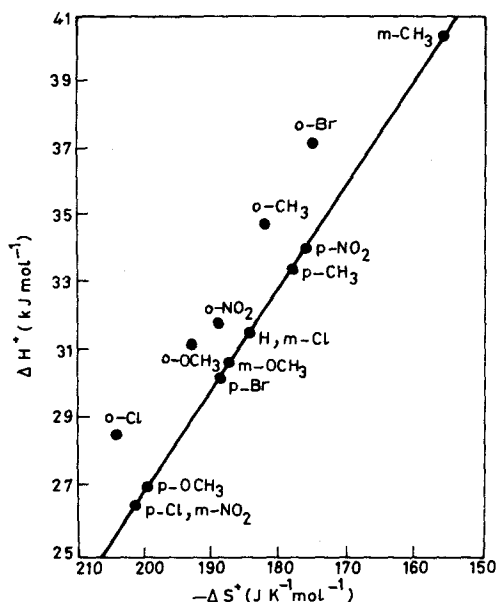
The rate-law used to calculate the rate constants  $k_1$  and  $k'_2$  is

$$\text{rate}/[\text{C}][\text{SO}] = k_1 + k'_2[\text{C}]/[\text{SA}]$$

$$k'_2 = K_d k_2; \quad K_d = k_d/k_{-d}$$

**Table 4.** Activation parameters for the oxidation of ortho-substituted phenyl methyl sulphoxides with chloramine-T.

Substituent	E (kJ mol <sup>-1</sup> )	$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> at 30°)	$\Delta S^\ddagger$ (kJ <sup>-1</sup> mol <sup>-1</sup> at 30°)	$\Delta G^\ddagger$ (kJ mol <sup>-1</sup> at 30°)
None	33.77	31.25	-185.2	87.36
Cl	30.83	28.31	-203.7	90.02
Br	39.55	37.03	-174.7	89.95
OCH <sub>3</sub>	33.49	30.97	-192.7	89.36
CH <sub>3</sub>	37.21	34.69	-181.5	89.68
NO <sub>2</sub>	34.17	31.65	-189.2	88.98
2,6-(CH <sub>3</sub> ) <sub>2</sub>	57.41	54.89	-120.8	91.50

**Figure 1.** Plot of  $\Delta H^\ddagger$  vs  $\Delta S^\ddagger$  for the reaction of chloramine-T with substituted phenyl methyl sulphoxides in alkaline medium.

where  $[SA]$  is the concentration of *p*-toluenesulphonamide formed during the reaction.  $k_1$  and  $k_2$  are the rate constants for the reaction of  $RNHCl$  and  $RNCl_2$  with the sulphoxides, respectively. The rate constants  $k_1$  and  $k_2'$  are given in tables 5 and 6 respectively.

The rate constants of ortho-substituted phenyl methyl sulphoxides clearly reveal that the rates are very much lower than those obtained for the corresponding meta and para substituted sulphoxides. The steric effect of an ortho-substituent can be estimated by calculating the ratio of the rate constants of the ortho and para substituted sulphoxides (Capon 1964). The very small relative rate values for methyl and chloro substituents

**Table 5.** Rate constants for the reaction of RNHCl with ortho-substituted phenyl methyl sulphoxides.

Substituent	$k_1 \times 10^4 \text{ l mol}^{-1} \text{ sec}^{-1}$		
	35°	40°	45°
None	46.67	67.68	104.20
OCH <sub>3</sub>	48.32 (0.463)	53.45 (0.371)	61.70 (0.322)
CH <sub>3</sub>	9.26 (0.075)	10.50 (0.066)	11.78 (0.068)
Cl	1.13 (0.069)	1.59 (0.077)	3.43 (0.131)
Br } NO <sub>2</sub> }	The reactions are too slow for measurement		

The  $k_1(o)/k_1(p)$  values are given within brackets.

**Table 6.** Rate constants for the reaction of RNCl<sub>2</sub> with ortho-substituted phenyl methyl sulphoxides.

Substituent	$k'_2 \times 10^5 \text{ l mol}^{-1} \text{ sec}^{-1}$		
	35°	40°	45°
None	1678	2069	2265
OCH <sub>3</sub>	1001 (0.394)	1095 (0.349)	1246 (0.323)
CH <sub>3</sub>	310.8 (0.128)	412.0 (0.120)	486.3 (0.122)
Cl	4.82 (0.012)	6.02 (0.013)	8.95 (0.015)
Br } NO <sub>2</sub> }	The reactions are too slow for measurement		

The  $k'_2(o)/k'_2(p)$  values are given within brackets.

show the steric effect. The reactions of CAT with nitro and bromo substituted sulphoxides are too slow for measurement. This may be due to the lower stability of the transition state because there is greater crowding in the transition state.

Among the ortho-substituted phenyl methyl sulphoxides, the highest rate was observed for *o*-methoxyphenyl methyl sulphoxide, whose rate constant ( $k_1$ ) is higher than that for methyl phenyl sulphoxide. Such a high rate deserves special attention in view of the neighbouring group effect on the *o*-OCH<sub>3</sub> group. The presence of an ortho-substituent (in this case the reaction centre itself) restricts the free rotation of the methoxy group and increases its probability of attaining planarity with the benzene ring. Thus there can be enhanced conjugation of the methoxy group with the reaction centre. This may explain the higher rate observed for *o*-methoxyphenyl methyl sulphoxide. Similar observations have been made by earlier workers (Satyanarayana 1977; Ruff *et al* 1978).

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