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Os(VIII)-catalysed oxidation of sulfides by sodium salt of *N*-chlorobenzenesulfonamide

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Abstract

Catalytic activity of Os(VIII) in the oxidation of some twenty organic sulfides with sodium salt of *N*-chlorobenzenesulfonamide (CAB) has been investigated in alkaline (pH ~ 8.7) *t*-butanol–water (1:1 v/v) medium. Significant retarding influence of $[OH^-]$ on the reactivity is exhibited. The catalysed reaction is strongly accelerated in the presence of Hg(II). Imperfections are observed in the linear Hammett relationship in the case of $-NO_2$ substituents. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Sulfides; Os(VIII) catalysis; Chloramine-B

1. Introduction

The kinetics of redox reaction involving platinum group metals such as osmium(VIII), ruthenium(III) and iridium(III) as homogeneous catalysts, have been studied extensively. OsO_4 is known to be an efficient catalyst in the oxidation of several organic compounds by various oxidants in aqueous alkaline as well as in acid media [1–3]. It is known to react across olefinic double bonds, as it is a well-known agent for *cis*-hydroxylation. However, its ability to form complexes with compounds having no double bonds and thereby facilitating the oxidation in alkaline medium has been investigated [4].

We have reported the Os(VIII)-catalysed oxidation of methyl phenyl sulfide with bromamine-B in alkaline medium [5]. Herein we examine the effect of many mumber of substituents on the reactivity of sulfides with *N*-chlorobenzenesulfonamide (CAB) and the structure–reactivity relationships are ascertained.

2. Results and discussion

2.1. Os(VIII) catalysis in the oxidation of aryl methyl sulfides

First-order dependence on [CAB] was evidenced by the linear semilogarithmic plots of titre versus time. Linearity is observed up to 75% of the reaction was over (Fig. 1). The plot of k_{obs} as a function of methyl phenyl sulfide concentration at constant temperature is linear with a zero intercept $[r = 0.99,\ s = 6.87 \times 10^{-5}]$. Same behaviour is observed in all the

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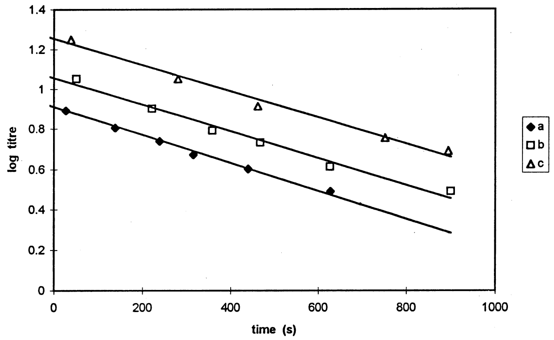


Fig. 1. Typical first-order plots for the oxidation of MPS with CAB at 303 K. $a = 10^3$[CAB] = 0.871 mol dm^{-3}; $b = 10^3$[CAB] = 1.31 mol dm^{-3}; $c = 10^3$[CAB] = 2.18 mol dm^{-3}.

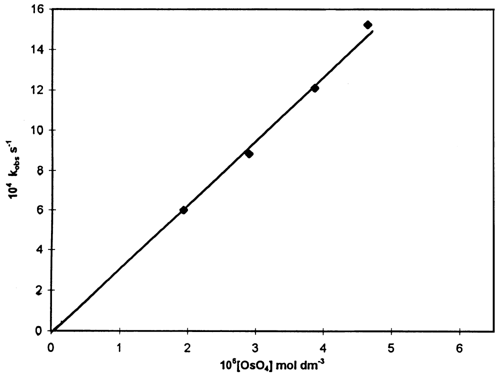


Fig. 2. Effect of [OsO$_4$] on the reaction rate.

substituted aryl methyl sulfides. Near constancy in k_2 values listed in Table 1 confirms the first-order dependence with respect to [sulfide]. CAB oxidises sulfides to sulfoxides in the presence of Os(VIII) as catalyst. The pseudo-first-order rate constants are proportional to the concentration of OsO$_4$. The catalyst increases the electrophilic activity of the oxidant and the reaction proceeds with selectivity (Fig. 2). Product analysis clearly confirms the selective oxidation of sulfides to sulfoxides. Negligible presence of sulfone is in agreement with the reactivity difference between sulfides and sulfoxides under identical experimental conditions.

The concentration of OH$^-$ has a significant retarding effect on the reactivity of sulfides. Two and half times increase in the concentration of OH$^-$ decreases the first-order rate constants from 20.3×10^{-4} to 4.08×10^{-4} (s^{-1}). This type of behaviour has been reported in the reaction of bromamine-B with *p*-nitrophenol [6]. Chloramine-T reactions with *p*-cresol [7], succinimide [8,9], 3-aminonaphthaldehyde [10], α-hydroxy acids [11], ketones [12], sulfides [13–15] and aminoacids [16] exhibit an inhibitory effect of [OH$^-$] on the oxidation. Dielectric changes have a marked effect and the reactivity of sulfides increases as the amount of water in the solvent is increased (Table 2). The rate coefficients analysed with Grunwald and Winstein equation [17] give a satisfactory fit ($r = 0.97$). An m value of 0.82 suggests a highly polar transition state. In the oxidation of sulfides with sodium periodate [18] m value of 0.722 is explained by a polar transition state.

The insensitivity of rates of added acrylonitrile rules out a mechanism involving free radi-

Table 1
Effect of reactants on the oxidation of methyl phenyl sulfide at 30°C

10^3 [S] (mol dm^{-3})	10^2 [CAB] (mol dm^{-3})	10^4 k_{obs} (s^{-1})	10^2 k_2^a (dm^3 mol^{-1} s^{-1})
1.50	1.30	9.9	6.6
1.90	1.30	10.9	5.7
2.00	1.30	11.1	5.6
2.52	1.30	15.2	6.0
3.15	1.30	18.2	5.8
4.40	1.30	26.0	5.9
2.52	0.87	15.4	–
2.52	1.09	15.1	–
2.52	1.30	15.2	–
2.52	2.20	15.0	–

[OsO$_4$] = 4.6×10^{-6} mol dm^{-3}; *t*-BuOH:water = 50:50 (v/v); [NaOH] = 2.1×10^{-4} mol dm^{-3}.

[a] $k_2 = k_{obs}$/[S].

Table 2
Effect of dielectric changes on the reactivity of methyl phenyl sulfide at 30°C

t-BuOH:water	D^a	10^4 k_{obs} (s^{-1})
40:60	52.12	60.7
45:55	48.82	21.9
50:50	45.52	15.2
55:45	42.22	13.1
65:35	35.61	1.9

[CAB] = 1.3×10^{-3} mol dm^{-3}; [NaOH] = 2.1×10^{-4} mol dm^{-3}; [OsO$_4$] = 4.6×10^{-6} mol dm^{-3}; [S] = 2.52×10^{-2} mol dm^{-3}.

[a] Dielectric constant values are calculated from the values of pure solvents.

Table 3
Effect of ionic strength, product and Hg(II) on the reactivity of methyl phenyl sulfide at 30°C

10^5 [Hg(II)] (mol dm^{-3})	10^4 [BSA] (mol dm^{-3})	10^4 [$NaClO_4$] (mol dm^{-3})	10^4 k_{obs} (s^{-1})
–	–	–	12.10
2.51	–	–	19.50
5.02	–	–	25.00
10.03	–	–	34.50
15.05	–	–	69.40
–	1.22	–	10.60
–	2.45	–	8.60
–	4.90	–	8.24
–	7.34	–	7.95
–	–	2.33	12.25
–	–	4.66	11.90
–	–	9.32	11.50
–	–	13.98	12.18

$[CAB] = 1.3 \times 10^{-3}$ mol dm^{-3}; $[NaOH] = 2.1 \times 10^{-4}$ mol dm^{-3}; $[OsO_4] = 3.9 \times 10^{-6}$ mol dm^{-3}; $[S] = 2.52 \times 10^{-2}$ mol dm^{-3}.

cals in the reaction sequence. There was no appreciable change in the rate with the change in ionic strength of the medium affected by $NaClO_4$. The product benzenesulfonamide depresses the reactivity as shown in Table 3.

Under homogeneous conditions, Os(VIII)-catalysed oxidation rates of sulfides appeared to be rather accelerated in the presence of Hg(II) (Table 3). In recent years, the transition metal ions, such as osmium, ruthenium, iridinium either alone or as binary mixtures as catalysts [19,20] in the oxidation of several redox processes have been reported.

2.2. Effect of substituents

Substituent effects are used to probe the reaction mechanism. Structure–reactivity relationships are ascertained by employing some 14 *meta*-, *para*- and *ortho*-substituted aryl methyl sulfides at three different temperatures and the kinetic observations reveal that electron-releasing groups enhance the reactivity while electron-withdrawing ones inhibit the rate. The rate coefficients and activation parameters evaluated from the plots of ln k_2/T vs. $1/T$ are listed in Table 4. The rate data are well correlated with the Hammett $\rho\sigma$ and Brown–Okamoto $\rho\sigma^+$ relationships (barring –NO_2 substituents) at all the three temperatures ($r > 0.97$) (Fig. 3). The ρ values are -2.45, -2.53 and -2.34 at 20°, 30° and 40° respectively. Negative ρ values are in favour of a mechanism in which sulfide suffers the electrophilic attack. Small reaction constant values are generally associated with reactions involving free radicals [21,22]. Largely negative ρ values in this system favour very

Table 4
Rate constants and activation parameters for the oxidation of aryl methyl sulfides with CAB

Sample No.	Substrate	10^2 k_2 (dm^3 mol^{-1} s^{-1})			$\Delta H^{\#}$ (kJ mol^{-1})	$-\Delta S^{\#}$ (J K^{-1} mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
		293 K	303 K	313 K			
1	H	2.28	3.52	5.70	32.40	165.9	82.7
2	*p*-OCH_3	24.54	34.38	39.24	15.47	203.5	77.1
3	*p*-CH_3	5.34	11.24	17.85	43.60	120.1	80.0
4	*p*-Cl	0.47	0.92	1.70	46.91	129.4	86.1
5	*p*-Br	0.54	0.90	1.46	35.59	166.9	86.2
6	*p*-NO_2	0.42	0.62	0.86	24.70	206.0	87.1
7	*m*-Cl	0.40	0.64	1.09	35.40	170.0	86.9
8	*m*-CH_3	3.41	5.38	10.40	39.87	137.3	81.5
9	*m*-NO_2	0.28	0.42	0.99	45.80	138.2	87.7
10	*o*-OCH_3	6.41	11.14	14.01	27.40	173.8	80.1
11	*o*-CH_3	1.36	3.51	4.52	43.70	130.7	83.3
12	*o*-Cl	0.43	0.53	0.95	27.10	198.2	87.2
13	*o*-Br	0.28	0.46	0.75	34.90	174.8	87.8
14	*o*-NO_2	0.23	0.28	1.00	53.00	116.0	88.2

$[CAB] = 1.3 \times 10^{-3}$ mol dm^{-3}; $[NaOH] = 2.1 \times 10^{-4}$ mol dm^{-3}; $[OsO_4] = 2.9 \times 10^{-6}$ mol dm^{-3}.

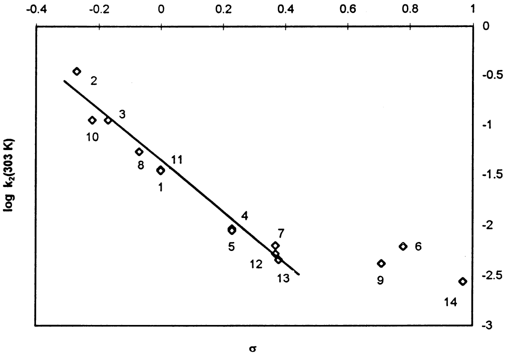


Fig. 3. Hammett plot (numbered as in Table 4).

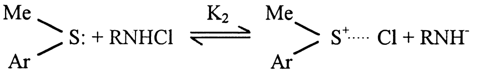
much a transition state with a fully developed positive charge on sulfur.

2.3. Mechanism and rate law

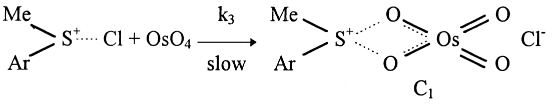
Octahedral complexes of *trans*-$[OsO_4(OH)_2]^{2-}$ and $[OsO_4(OH)(H_2O)]^-$ have been reported by Griffith [23]. In alkaline medium possibly it exists in the form $[OsO_4(OH)_2]^{2-}$ [24].

CAB like CAT behaves like a strong electrolyte in aqueous solution. In alkaline solution the possible oxidising species are RNHCl, HOCl, OCl^- and $RNCl^-$ [25]. The effective electrophile depends on pH and experimental conditions maintained. Chloronium ion transfer between *N*-chlorocompounds and sulfides to give $R^1R^2SCl^+$ and $ArSO_2NH^-$ ions has been reported [14,26–29]. Retarding influence of OH^- strongly favours the equilibrium

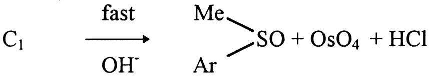
$$RNClNa + H_2O \overset{K_1}{\rightleftharpoons} RNHCl + NaOH \tag{1}$$



$$\mathrm{Me(Ar)S{:}} + RNHCl \overset{K_2}{\rightleftharpoons} \mathrm{Me(Ar)S^{+}\cdots Cl} + RNH^- \tag{2}$$



(3)



$$C_1 \xrightarrow[OH^-]{fast} \mathrm{Me(Ar)SO} + OsO_4 + HCl \tag{4}$$

The observed kinetic results can be accounted by the rate law where,

$$\frac{-d[CAB]}{dt} = k_3\,[OsO_4]\,[>S^{+}\cdots Cl] \tag{5}$$

Applying equilibrium treatment,

$$k_{obs} = \frac{-d[CAB]}{dt} = \frac{k_3K_2K_1'[S][OsO_4]}{[RNH^-][OH^-]} \tag{6}$$

where $K_1' = K_1[H_2O]$. The deduced rate equation is quite consistent with the experimental observations.

The rate acceleration in the presence of Hg(II) is quite likely due to the enhanced electrophilic activity of OsO_4 in the presence of Hg(II). Complex formation involving Os(VIII) in the presence and absence of Hg(II) could not be evidenced by spectral studies. Largely negative entropy of activation values suggest a cyclic complex in the transition state in agreement with the proposed mechanism. The $\Delta S^{\#}$ values are similar to corresponding data measured for typical reactions involving oxygen transfer [30]. Near constancy in $\Delta G^{\#}$ values implies that a common mechanism is operating in all the sulfides. The linear plot of log k_2 (303 K) vs. log

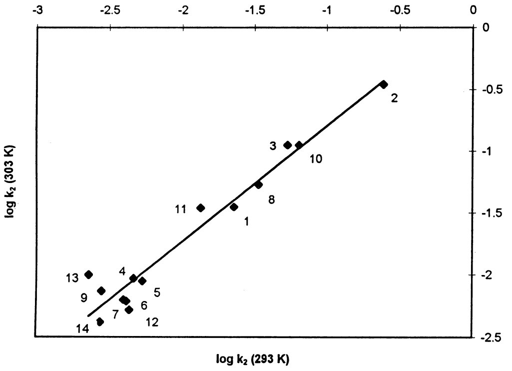


Fig. 4. The Exner plot (numbered as in Table 4).

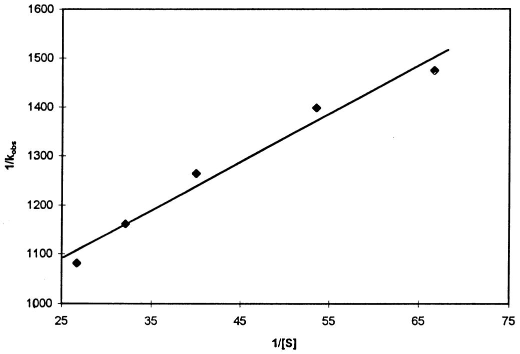


Fig. 5. Michaelis–Menton plot for the oxidation of $(\text{ethyl})_2S$ at 303 K.

k_2 (293 K) with an excellent correlation coefficient (Fig. 4) ($r = 0.991$, $s = 0.09$) further supports a similar mechanism in all the sulfides. The isokinetic temperature, β was calculated from the relation,

$$\beta = \frac{T_1T_2(1-f)}{(T_1 - T_2 f)}$$

where f is the slope of the Exner plot. The value of β is found to be 146.5 K, which is lower than the experimental temperature. Since $\beta - T$ is negative, the reaction is believed to be entropy controlled. The marked deviation observed in the reactivities of $-NO_2$ substituents may be attributed to the negatively polarized nitro-oxygen atom.

2.4. Os(VIII) catalysis in the oxidation of dialkyl sulfides

Linearity is observed in the log titre–time profile for a typical diethyl sulfide oxidation kinetic run. Michaelis–Menten dependence on [sulfide] is confirmed by the linear plot of k_{obs}^{-1} vs. $[S]^{-1}$ ($r = 0.99$, $s = 30.5$) with a nonzero intercept on Y-axis (Fig. 5). Os(VIII) catalyses the reaction and the order dependence is fractional throughout the entire range of catalyst concentrations studied. The retarding effect of the concentration of OH^- on the reactivity is quite significant. The kinetic results are summarised in Table 5.

Dielectric changes have a marked effect on the reactivity. A ninefold increase in the first-order rate constant is observed by changing the solvent composition from 35% of water (v/v) to 60% (v/v). Number of dialkyl sulfides are

Table 5
Effect of reactants on the oxidation of diethyl sulfide at 303 K

10^2 [DES] (mol dm^{-3})	10^3 [CAB] (mol dm^{-3})	10^6 [OsO_4] (mol dm^{-3})	10^3 [NaOH] (mol dm^{-3})	10^4 k_{obs} (s^{-1})
1.5	1.3	1.93	3.5	5.44
1.5	1.3	2.89	3.5	6.78
1.5	1.3	3.86	3.5	8.90
1.5	1.3	4.82	3.5	10.58
1.5	1.3	2.89	3.5	6.78
1.9	1.3	2.89	3.5	7.15
2.5	1.3	2.89	3.5	7.91
3.1	1.3	2.89	3.5	8.61
3.7	1.3	2.89	3.5	9.25
1.5	0.9	2.89	3.5	6.50
1.5	1.1	2.89	3.5	6.37
1.5	1.3	2.89	3.5	6.78
1.5	1.5	2.89	3.5	6.06
1.5	1.3	2.89	2.4	11.85
1.5	1.3	2.89	2.9	7.07
1.5	1.3	2.89	3.5	6.78
1.5	1.3	2.89	3.9	5.17
1.5	1.3	2.89	4.4	2.62

t-BuOH:water = 50:50 (v/v).

Table 6
Order of reactivity of dialkyl sulfides

Sample No.	Substrate	10^4 k'[a]
1	$(\text{methyl})_2$S	21.47
2	$(\text{ethyl})_2$S	28.88
3	$(i\text{-propyl})_2$S	13.08
4	$(n\text{-butyl})_2$S	10.14
5	$(t\text{-butyl})_2$S	8.01

$[\text{CAB}] = 1.3\times10^{-3}$ mol dm^{-3}; $[\text{NaOH}] = 3.5\times10^{-3}$ mol dm^{-3}; $[\text{OsO}_4] = 2.89\times10^{-6}$ mol dm^{-3}.

[a] $k' = k_{\text{obs}}/[\text{S}]^n$ where n is the order with respect to sulfide.

employed and in all the cases the same kinetic behaviour is observed. The rate coefficients are listed in Table 6 and the order of reactivity is,

$$(\text{ethyl})_2\text{S} > (\text{methyl})_2\text{S} > (i\text{-propyl})_2\text{S} > (n\text{-butyl})_2\text{S} > (t\text{-butyl})_2\text{S}.$$

The very low reactivity in the case of $(t\text{-butyl})_2$S suggests the predominance of steric effect.

$$\text{OsO}_4 + \text{RNHCl} \overset{K_1}{\rightleftharpoons} \text{C}_1 \qquad (7)$$

$$\text{C}_1 + [\text{S}] \overset{K_2}{\rightleftharpoons} \text{C}_2 \qquad (8)$$

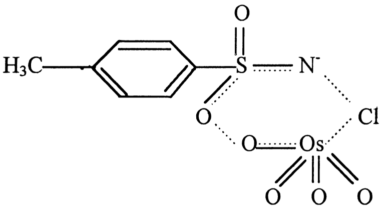
$$\text{C}_2 \xrightarrow[\text{OH}^-]{k_3} \text{products} \qquad (9)$$

$$\frac{-\text{d}[\text{CAB}]}{\text{d}t} = \frac{k_3 K_1 K_2 [\text{S}][\text{OsO}_4][\text{CAB}]_t}{1 + K_1[\text{OsO}_4] + K_1 K_2 [\text{S}][\text{OsO}_4]} \qquad (10)$$

where $[\text{CAB}]_t$ represents the initial concentration of CAB.

$$k_{\text{obs}} = \frac{k_3 K_1 K_2 [\text{S}][\text{OsO}_4]}{1 + K_1[\text{OsO}_4] + K_1 K_2 [\text{S}][\text{OsO}_4]} \qquad (11)$$

Mushran et al. [11] have proposed a cyclic structure between OsO_4 and RNCl^-wherein electron density around nitrogen atom in RNCl^- is decreased thereby weakening the N–Cl bond.



2.5. Os(VIII) catalysis in the oxidation of diphenyl sulfide

Conversion of diphenyl sulfide to sulfoxide by CAB [31] in the presence of Os(VIII) follows the rate law,

$$k_{\text{obs}} = \frac{k[\text{OsO}_4][\text{S}]}{[\text{OH}^-]\{1 + K[\text{S}]\}}$$

where K is the equilibrium constant for the reaction between RNHCl and diphenyl sulfide.

3. Conclusion

Contrasting kinetic behaviours are observed in the Os(VIII)-catalysed oxidation of alkyl aryl, dialkyl and diaryl sulfides with sodium salt of N-chlorobenzenesulfonamides in alkaline medium. RNHCl seems to be the effective electrophile. The pH-dependent reaction proceeds quantitatively, selectively and irreversibly to yield the product sulfoxide. All the substituted aryl methyl sulfides follow a common mechanism. The deduced rate equations are in consistence with the experimental observations. Strong rate acceleration in the presence of binary mixtures of transition metals as catalysts is to be probed further.

4. Experimental section

Pure chlorine gas was bubbled through a solution of benzenesulfonamide in 4 M sodium hydroxide over a period of 1 h at 70°. Chloramine-B obtained was dried and recrystallized from water. Osmium tetroxide (Johnson–Matthey) was used as such. t-Butyl alcohol was refluxed with quick lime for 6 h and distilled. The distilled alcohol was fractionated through a Dufton column.

All the aryl methyl sulfides were prepared by literature methods [32–34]. The purity was ascertained by TLC and spectroscopic methods. Diphenyl and dialkyl sulfides (Aldrich) were used as such. Experiments were performed under pseudo-first-order conditions by keeping the substrate always in excess. The reaction mixture was homogeneous throughout the course of the reaction. The reactions were followed iodometrically. Computation of the rate constants were made from the plot of log titre vs. time. All the rate constants are averages of two or more determinations.

4.1. Stoichiometry and product analysis

The amount of sulfoxide formed corresponds to the amount of CAB consumed which gives a stoichiometry of 1:1 of sulfide and CAB.

$$>S + C_6H_5SO_2N^-ClNa^+ + H_2O \longrightarrow >SO + C_6H_5SO_2NH_2 + NaCl$$

The reaction mixture was analysed by Co-TLC. The two spots corresponded to the R_f values of the authentic samples of sulfide and sulfoxide. IR spectrum of the product was identical with sulfoxide. Negligible presence of sulfone indicates that the reaction under the experimental conditions takes place only up to sulfoxide stage.

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