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KINETICS AND MECHANISM OF OXIDATION OF SOME SUBSTITUTED PHENYL METHYL SULPHOXIDES BY N-CHLOROPHTHALIMIDE

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THOUGH many N-chloro compounds such as chloramine-T, N-chlorosuccinimide, N-chlorobenzamide etc., have been used as oxidants extensively in the kinetic studies, such a study using N-chlorophthalimide (NCP) is lacking. The oxidation kinetics of various sulphoxides have already been reported[1-8]. We report in this note our results on the kinetics of oxidation of some *o*-, *m*- and *p*-substituted phenyl methyl sulphoxides with NCP in aqueous acetic acid in the presence of perchloric acid.

All the sulphoxides were prepared and purified by standard methods. Acetic acid was purified by refluxing with chromium trioxide. NCP was prepared according to the literature method[9].

Kinetic studies were carried out in 50% (v/v) acetic acid containing 0.05 M perchloric acid under pseudo-first order conditions in vessels coated on the outside with black paint. The reaction was followed by estimating the unchanged NCP by iodometric procedure[10]. Reproducible results giving first order plots ($r \simeq 0.99$) were obtained for reactions run in duplicate in each substrate and at all the temperatures studied. The pseudo-first order rate constants (k_1) were calculated by the least-square method. The stoichiometry of the reaction is 1:1 and the product obtained is identified as methyl phenyl sulphone by its m.p and the mixed m.p with an authentic sample.

The oxidation of methyl phenyl sulphoxide has been studied in detail. An increase in [sulphoxide] increases the rate. The plot of log k_1 *vs* log [sulphoxide] is linear with unit slope. Also the second-order rate constants ($k_2 = k_1/$[sulphoxide] are constant confirming a unit dependence on sulphoxide (table 1). The reaction is also found to be first order with respect to NCP as evidenced by the constancy of the first order rate constants for various concentrations of NCP (table 1). Keeping the [sulphoxide] and [NCP] constant, an incraese in the [$HClO_4$] from 0 to 0.4 M does not produce any marked change in the rate constants. The reaction rate is not altered by the addition of sodium perchlorate.

The reaction rate decreases with increase in the acetic acid content of the solvent medium. The second-order rate constants for the oxidation of methyl phenyl sulphoxide were 2.58, 2.03, 1.78. 1.34 and 0.81×10^{-2} litre mol^{-1} sec^{-1} in 20, 40, 50, 60 and 80% acetic acid respectively.

To gain more information about the nature of the transition state and the mechanism, the rates of oxidation of several *o*-, *m*- and *p*-substituted phenyl methyl sulphoxides have been studied. The data in table 2 indicate that electron-releasing substituents in the benzene ring accelerate the rate while the electron-

TABLE 1

Effect of varying reactant's concentration on the reaction rate

[NCP] $\times 10^3$ M	[$C_6H_5SOCH_3$] $\times 10^4$ M	$k_1 \times 10^4$ sec^{-1}	$k_2 \times 10^2$ lit mol^{-1} sec^{-1}
0.5	2	3.56	1.78
1	2	3.57	1.79
1.5	2	3.37	1.69
2	2	3.48	1.74
1	1	1.76	1.76
1	3	5.22	1.74
1	4	6.71	1.68
1	5	9.18	1.84

[$HClO_4$] = 0.05 M; solvent = 50% HOAC–H_2O (v/v); temperature = 35° C

TABLE 2

Data of substituted phenyl methyl sulphoxides at different temperatures

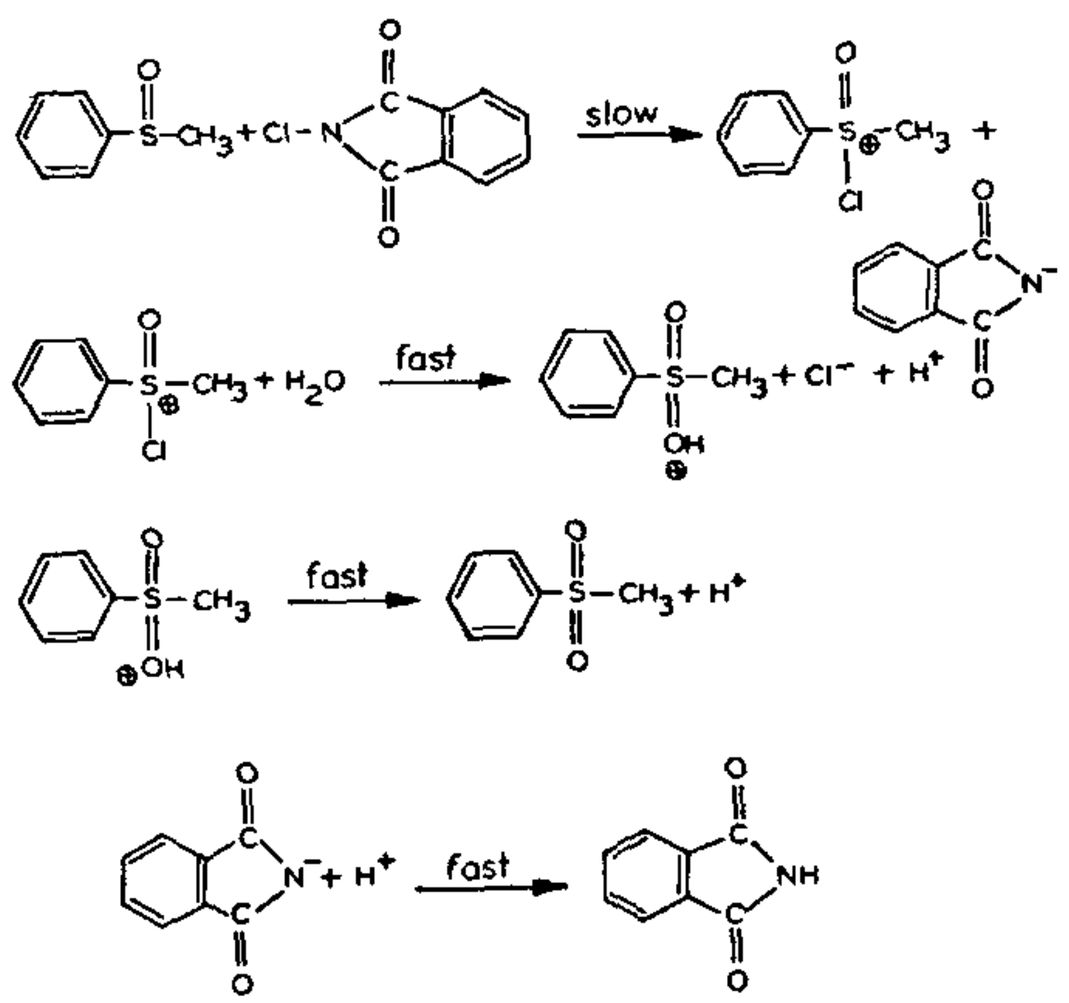
	$k_2 \times 10^4$ at 350° C	lit. 40° C	mol^{-1} sec^{-1} 45° C	$\Delta H^{\pm}$ 40° *k* cals	$-\Delta S^{\pm}$ 40° C e.u.
H	178.4	250.6	350.1	12.2	27.0
p-CH_3	332.5	490.7	667.8	12.2	25.7
p-OCH_3	483.7	731.7	1072.2	14.0	19.0
p-Cl	42.9	64.3	98.5	14.9	20.9
p-NO_2	6.2	9.1	12.9	13.6	29.1
m-CH_3	246.2	345.7	479.7	11.0	30.1
m-OCH_3	92.0	136.5	207.7	12.7	26.6
m-Cl	14.9	21.0	30.2	12.7	30.4
m-NO_2	6.6	10.4	15.1	14.3	26.7
o-CH_3	30.6	48.3	68.1	16.2	17.4
o-OCH_3	202.9	293.3	424.2	14.2	20.4
o-Cl	5.5	8.1	11.3	13.8	28.6
o-NO_2	2.6	3.5	5.7	16.0	23.3

$[HClO_4] = 0.05$ M; solvent 50% HOAC–H_2O (v/v)

withdrawing substituent retards the rate. It is of interest to find out if any Hammett type correlation exists for the oxidation of aryl methyl sulphoxides by NCP. A satisfactory correlation exists between log k_2 and σ constants ($\rho = -1.93$; $r = -0.985$ at 40° C) indicating that the same mechanism operates in all the compounds. The negative ρ value indicates that the nucleophilic sulphur atom of the sulphoxide is more positively charged in the transition state than it is in the reactant.

Due to the steric effect of the ortho substituents, the rate constants of *o*-substituted phenyl methyl sulphoxides (table 2) are very much lower than those obtained for the corresponding *m*-and *p*-substituted sulphoxides. Among the *o*-substituted phenyl methyl sulphoxides the highest rate was observed for *o*-methoxyphenyl methyl sulphoxide. Moreover, the rate constant for this sulphoxide is higher than that of methyl phenyl sulphoxide. The presence of an *o*-substituent restricts the free rotation of the methoxy group and increases its probability of attaining planarity with the benzene ring. Thus there can be enhanced resonance interaction of the methoxy group with the reaction centre. This may explain the high rate observed for *o*-methoxyphenyl methyl sulphoxide.

Under the acidic experimental condition employed, as in other N-halo oxidants[11, 12], here also there may be a possibility of three oxidising species *viz* NCP itself or protonated NCP as $>$ NHCl or its hydrolysis product HOCl. Since the reaction is not sensitive to hydrogen ion concentration the reactive species cannot be



Scheme – 1

$>$ NHCl or its hydrolysis product HOCl. So the reactive species can be NCP only. The likely mechanism is depicted in scheme 1.

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POLYSACCHARIDES OF *RICINUS COMMUNIS* SEED ENDOSPERM

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AQUEOUS extracts of the seed endosperm of *Ricinus communis* are reported to precipitate various blood group specific substances and type-XIV pneumococcal polysaccharide[1]. Though limited information is available on the toxic principles and proteins present in the seed endosperm, the nature of the polysaccharides, reported to be present upto 27.2%, is not known except for the reported presence of starch[2]. The present study is aimed at the isolation and characterisation of polysaccharides and glycoproteins present in the seed endosperm.

The endosperm of the seeds was defatted with chloroform-methanol (2:1, v/v). The resulting flour (100 g; protein content 70%) was repeatedly extracted with 1% sodium chloride solution at pH 9. The insoluble residue (70 g; protein, 57%) was used for the isolation of hemicelluloses. To the sodium chloride extract addition of 50% acetic acid to pH 4.5 precipitated the protein fraction (25 g) which was removed by centrifugation. To the supernatant addition of ethanol (5 vol.) gave a pale yellow precipitate (3 g; protein, 80%; carbohydrate, 20%). This fraction with 1% trifluoroacetic acid did not give any protein precipitate and remained unchanged on passing through Amberlite IR-120(H^+) and Amberlite IRA-400(CO_3^-) columns. Paper electrophoresis in 0.005 M *tris* buffer at pH 8.9 indicated one major and trace amounts of two fractions. Complete acid hydrolysis (4N HCl, 100° C, 36 hr) and paper chromatography (solvent: n-butanol: acetic acid: water—4:1:5, v/v; upper layer) revealed leucine, valine, alanine, threonine, glycine, glutamic acid, aspartic acid and other three unidentified aminoacids. Similar hydrolysis (1N H_2SO_4, 100° C, 6 hr) and paper chromatography (solvent: n-butanol: benzene: pyridine: water—5:1:3:3, v/v; upper layer) revealed L-arabinose and D-galactose in the ratio 5:1 with trace amounts of xylose, rhamnose and fucose. IR (Nujol) indicated broad absorption in the regions 3300, 1660 and 1540 cm^{-1}. Hence this soluble portion appears to be mainly a glycoprotein.

Extraction of the sodium chloride insoluble residue (35 g) with 10% sodium hydroxide solution under nitrogen gave an alkali insoluble residue (8 g) which was a cellulose-type glucan, and an alkaline extract which upon neutralisation with 50% acetic acid gave a polysaccharide fraction (2 g; hemicellulose A; protein 55%), removed by centrifugation. Addition of ethanol (3 vol.) to the supernatant precipitated another polysaccharide fraction (1.75 g, hemicellulose B, protein, nil). Complete hydrolysis of hemicelluloses A and B and identification of the sugars indicated the presence of D-glucose and mannose (1:1) in hemicellulose A; and D-xylose, L-arabinose, D-glucose, D-galactose, glucuronic acid, 4-0-methylglucuronic acid in the ratio 2:1:0.5:0.5:1:0.5, together with traces of mannose, rhamnose and fucose in hemicellulose B.

Hemicellulose B (100 mg) on barium hydroxide fractionation[3] gave a soluble fraction (20 mg) composed of mainly D-xylose along with D-glucose, D-galactose and 4-0-methylglucuronic acid with traces of mannose or arabinose. This on further fractionation with Fehling solution[4] precipitated an acidic polysaccharide and the mother liquor contained small amount of a polysaccharide composed of only neutral sugars. This acidic polysaccharide was found to be homogeneous by free-boundary electrophoresis (0.1% borate buffer, pH 9), and had $(\alpha)_D = +15°$ C (C, 0.1%). The barium hydroxide insoluble fraction (70 mg) contained all the glucuronic acid along with L-arabinose, D-xylose, D-glucose and D-galactose, in the ratio 1:5:2:1:0.5. Thus barium hydroxide fractionation separated hemicellulose B into glucuronic acid and 4-0-methylglucuronic acid containing polysaccharides.

Hemicellulose B (100 mg) on DEAE-cellulose (borate form) fractionation[5] afforded two acidic frac-