Kinetics and Mechanism of Oxidation of D-Fructose and D-Glucose by Sodium Salts of *N*-(Chloro)-mono/ di-substituted Benzenesulfonamides in Aqueous Alkaline Medium

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ABSTRACT: In an effort to introduce *N*-chloroarylsulfonamides of different oxidizing strengths, nine sodium salts of mono- and di-substituted *N*-chloroarylsulfonamides are employed as oxidants for studying the kinetics of oxidation of D-fructose and D-glucose in aqueous alkaline medium. The results are analyzed along with those by the sodium salts of *N*-chlorobenzenesulfonamide and *N*-chloro-4-methylbenzenesulfonamide. The reactions show first-order kinetics each in [oxidant], [Fru/Glu], and [OH^-]. The rates slightly increase with increase in ionic strength of the medium. Further, the rate of oxidation of fructose is higher by 4 to 5 times than that of the glucose oxidation, by the same oxidant. Similarly, E_a values for glucose oxidations are higher by about 1.5 times the E_a values for fructose oxidations. The results have been explained by a plausible mechanism, and the related rate law deduced. The significant changes in the kinetics and thermodynamic data are observed with change of substituent in the benzene ring. It is because Cl^+ is the effective oxidizing species in the reactions of *N*-chloroarylsulfonamides. The oxidative strengths of the latter therefore depend on the ease with which Cl^+ is released from them. The ease with which Cl^+ is released from *N*-chloroarylsulfonamides depends on the electron density of the nitrogen atom of the

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sulfonamide group, which in turn depends on the nature of the substituent in the benzene ring. The following Hammett equations are valid for the oxidation of fructose and glucose, $\log k_{obs} = -3.13 + 0.54\,\sigma p$ and $\log k_{obs} = -3.81 + 0.28\,\sigma p$, respectively. The enthalpies and entropies of activations for oxidations by all the *N*-chloroarylsulfonamides correlate well with isokinetic temperatures of 301 K and 299 K, for fructose and glucose oxidations, respectively. The effect of substitution in the oxidants on the E_a and log A for the oxidations is also considered. © 2005 Wiley Periodicals, Inc. Int J Chem Kinet 37: 572–582, 2005

INTRODUCTION

N-Haloarylsulfonamides have received considerable attention due to their diverse properties [1–11]. They act as halonium cations, hypohalite species, and N-anions that behave both as bases and nucleophiles. Although the various aspects of two members of this class of reagents, the sodium salts of *N*-chlorobenzenesulfonamide (chloramine-B, NCBS) and *N*-chloro-4-methylbenzenesulfonamide (chloramine-T, NC4MBS) have been studied, there are no efforts in altering the electron environment around sulfonamide group to get Cl^+ released either at ease or with difficulty, by making appropriate substitution in the benzene ring to produce *N*-chloroarylsulfonamide of required oxidizing strength for a specific purpose. Hence in an effort to introduce *N*-chloroarylsulfonamides of varying oxidizing strengths, we have recently reported several sodium salts of *N*-chloro-mono/di-substituted benzenesulfonamides (NCSBS) as oxidants [10–15].

Carbohydrates comprise one of the largest classes of biologically important compounds and are characterized by the presence of an aldehydic or ketonic carbonyl group [16,17]. The monosaccharides such as glucose and fructose have wide synthetic applications. Glucose is a source of energy in plants and animals and also serves as the monomeric unit of cellulose, the structural framework in woody plants. Hence the reactions involving carbohydrates are of considerable interest. Although oxidation of carbohydrates by chloramine-B and chloramine-T has been studied [18,19], individually, there are no reports on the systematic oxidation of carbohydrates by substituted *N*-chloro-substituted benzenesulfonamides. We report herein the kinetics of oxidation of D-fructose and D-glucose by nine sodium salts of *N*-chloro-substituted benzenesulfonamides in aqueous alkaline medium and analyze the results with those by NCBS and NC4MBS. The sodium salts of mono- and di-substituted *N*-chlorobenzenesulfonamides (NCSBS) employed as oxidants are of the general formulae: i-X-$C_6H_4SO_2NaNCl \cdot xH_2O$, where i-X = 4-$C_2H_5$ (*N*-chloro-4-ethylbenzene-sulfonamide, NC4EBS); 4-F (*N*-chloro-4-fluorobenzenesulfonamide, NC4FBS); 4-Cl (*N*-chloro-4-chlorobenzenesulfonamide, NC4 CBS) or 4-Br (*N*-chloro-4-bromobenzenesulfonamide, NC4BBS) and i-X-j-Y-$C_6H_3SO_2$-$NaNCl \cdot xH_2O$, where i-X-j-Y = 2,3-$(CH_3)_2$ (*N*-choro-2,3-dimethylbenzenesulfonamide, NC23DMBS); 2,4-$(CH_3)_2$(*N*-choro-2,4-dimethylbenzenesulfonamide, NC24DMBS); 2-CH_3-4-Cl (*N*-chloro-2-methyl-4-chlorobenzenesulfonamide, NC2M4CBS); 2,4-Cl_2 (*N*-chloro-2,4-dichlorobenzenesulfonamide, NC24D CBS) and 3,4-Cl_2 (*N*-chloro-3,4-dichlorobenzenesulfonamide, NC34DCBS).

MATERIALS AND METHODS

Preparation of Arylsulfonamides and Sodium Salts of N-chloroarylsulfonamides. The nine sodium salts of *N*-chloroarylsulfonamides, NC4EBS, NC4FBS, NC4CBS, NC4BBS, NC23DMBS, NC24DMBS, NC2M4CBS, NC24DCBS, and NC34DCBS, were prepared in two steps [12,13]. In the first step, the substituted benzenes were chlorosulfonated with chlorosulfonic acid to the corresponding sulfonylchlorides and the latter were converted into the respective substituted benzenesulfonamides, by boiling them with concentrated ammonium hydroxide. The resulting arylsulfonamides were recrystallized to constant melting points from diluted ethanol and dried at 105°C [12,13]. The arylsulfonamides were then *N*-chlorinated by bubbling pure chlorine gas through clear aqueous solutions of them in 4 M NaOH at 70°C for about 1 h. The precipitated sodium salts of *N*-chloro-substituted benzenesulfonamides (NCSBS) were filtered, washed, dried, and recrystallized from water. The purity of all the reagents was checked by determining the melting points [12,13] and by estimating iodometrically, the amounts of active chlorine which they contained. All the arylsulfonamides and their *N*-chloro compounds were further characterized by recording their infrared spectra.

Aqueous stock solutions (0.1 mol dm^{-3}) of *N*-chloroarylsulfonamides were prepared in doubly distilled water and stored in amber-colored bottles. The solutions were standardized by the iodometric method. Fresh solutions of D-fructose and D-glucose (E. Merck) in doubly distilled water (0.10 mol dm^{-3}) were prepared as and when required. Ionic strength

of the medium was maintained at 0.50 mol dm^{-3} using concentrated aqueous solution of sodium nitrate (E. Merck). All other reagents employed were of analytical grades of purity.

RESULTS AND DISCUSSION

Stoichiometry and Product Analysis

The reaction mixture containing the carbohydrate, NaOH, and excess of NCSBS was equilibrated for 48 h. Excess oxidant was then determined iodometrically. Varying stoichiometries were observed corresponding to the formation of a mixture of products as shown by the following stoichiometric equations. The major products of oxidation were arabinonic, ribonic, and erythronic acids. The minor products were glyceric and hexonic acids. The mechanism of formation of these products will be given later.

$$C_6H_{12}O_6 + ArSO_2NCl^- + H_2O + OH^- \rightarrow C_5H_{10}O_6 + CH_2(OH)_2 + ArSO_2NH^- + Cl^- \quad (1)$$
(Arabinonic or ribonic acids)

$$C_6H_{12}O_6 + 2ArSO_2NCl^- + 3OH^- \rightarrow C_4H_8O_5 + CH_2(OH)COO^- + 2ArSO_2NH^- + 2Cl^- + H_2O \quad (2)$$
(Erythronic acid)

$$C_6H_{12}O_6 + 3ArSO_2NCl^- + 5OH^- \rightarrow C_3H_6O_4 + CH_2(OH)COO^- + HCOO^- + 3ArSO_2NH^- + 3Cl^- + 2H_2O \quad (3)$$
Glyceric acid

$$C_6H_{12}O_6 + ArSO_2NCl^- + OH^- \rightarrow C_6H_{12}O_7 + ArSO_2NH^- + Cl^- \quad (4)$$
Hexonic acid

where Ar = C_6H_5, 4-$CH_3C_6H_4$, 4-$C_2H_5C_6H_4$, 4-FC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 2,3-$(CH_3)_2C_6H_3$, 2,4-$(CH_3)_2C_6H_3$, 2-CH_3-4-ClC_6H_3, 2,4-$Cl_2C_6H_3$, and 3,4-$Cl_2C_6H_3$.

The reduction products, arylsulfonamides ($ArSO_2NH_2$, SBSA), were identified by TLC [20] using petroleum ether–chloroform–butanol (2:2:1 v/v) as the solvent system and iodine as spray reagent.

Table I Pseudo-First-Order Rate Constants (k_{obs}) for the Oxidation of D-Fructose (Fru) by the Sodium Salts of N-chloro-para-substituted Benzenesulfonamides (NCSBS) in Aqueous Alkaline Medium at 303 K (I = 0.5 mol dm^{-3} Except During Its Variation)

10^3[NCSBS]$_0$ (mol dm^{-3})	10^2[Fru]$_0$ (mol dm^{-3})	10[NaOH] (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1}) i-X-$C_6H_4SO_2$(Na)NCl·$x H_2O$, X =					
			Parent	4-CH_3	4-C_2H_5	4-F	4-Cl	4-Br
Effect of varying [NCSBS]$_0$								
0.5	2.0	1.0	9.6	7.4	7.7	10.9	12.3	12.2
1.0	2.0	1.0	9.6	7.5	7.7	10.8	12.4	12.1
2.0	2.0	1.0	9.4	7.4	7.5	10.9	12.4	12.3
4.0	2.0	1.0	9.5	7.1	7.4	10.9	12.6	12.4
Effect of varying [Fru]$_0$								
1.0	0.5	1.0	2.5	1.2	1.5	1.9	1.0	2.4
1.0	1.0	1.0	3.6	3.2	3.1	4.7	5.4	5.8
1.0	2.0	1.0	9.6	7.5	7.7	10.8	12.4	12.1
1.0	3.0	1.0	12.5	10.3	10.9	14.5	18.6	21.0
1.0	5.0	1.0	20.3	17.2	16.7	23.4	34.6	32.8
Effect of varying [NaOH]								
1.0	2.0	0.3	3.0	1.4	1.2	1.8	2.2	2.2
1.0	2.0	0.5	4.0	2.9	2.6	4.3	4.8	5.2
1.0	2.0	1.0	9.6	7.5	7.7	10.8	12.4	12.1
1.0	2.0	2.0	22.0	14.9	18.1	24.8	28.1	25.3
1.0	2.0	3.0	30.2	24.0	27.9	30.6	35.0	41.8
Effect of varying ionic strength								
1.0[a]	2.0	1.0	8.4	6.7	5.9	8.7	10.9	10.0
1.0	2.0	1.0	9.6	7.5	7.7	10.8	12.4	12.1
1.0[b]	2.0	1.0	10.0	8.4	8.3	11.5	12.8	14.7

[a] I = 0.30 mol dm^{-3}.
[b] I = 0.70 mol dm^{-3}.

Table II Pseudo-First-Order Rate Constants (k_{obs}) for the Oxidation of D-Fructose (Fru) by the Sodium Salts of *N*-chloro-di-substituted Benzenesulfonamides (NCSBS) in Aqueous Alkaline Medium at 303 K ($I = 0.5$ mol dm^{-3} Except During Its Variation)

10^3[NCSBS]$_0$ (mol dm^{-3})	10^2[Fru]$_0$ (mol dm^{-3})	10[NaOH] (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1}) i-X, j-Y-$C_6H_3SO_2$(Na)NCl·xH$_2$O, i-X, j-Y =				
			2,3-$(CH_3)_2$	2,4-$(CH_3)_2$	2-CH_3,4-Cl	2,4-Cl_2	3,4-Cl_2
Effect of varying [NCSBS]$_0$							
0.5	2.0	1.0	5.8	7.2	9.9	20.2	16.7
1.0	2.0	1.0	5.8	7.7	9.8	20.0	16.1
2.0	2.0	1.0	5.8	7.8	9.8	20.1	16.2
4.0	2.0	1.0	5.9	8.5	10.0	20.1	16.1
Effect of varying [Fru]$_0$							
1.0	0.5	1.0	0.9	1.0	1.8	4.5	3.2
1.0	1.0	1.0	2.4	2.9	4.2	8.4	6.7
1.0	2.0	1.0	5.8	7.7	9.8	20.0	16.1
1.0	3.0	1.0	10.5	10.9	13.7	27.1	29.6
1.0	5.0	1.0	19.1	14.9	20.4	39.2	35.6
Effect of varying [NaOH]							
1.0	2.0	0.3	0.7	1.1	1.8	4.9	3.0
1.0	2.0	0.5	1.8	2.7	4.0	7.2	6.7
1.0	2.0	1.0	5.8	7.7	9.8	20.0	16.1
1.0	2.0	2.0	12.3	17.9	19.4	37.7	34.6
1.0	2.0	3.0	20.0	23.6	30.2	54.7	44.8
Effect of varying ionic strength							
1.0[a]	2.0	1.0	4.8	5.8	8.0	16.8	14.0
1.0	2.0	1.0	5.8	7.7	9.8	20.0	16.1
1.0[b]	2.0	1.0	6.8	7.8	11.9	22.9	16.8

[a] $I = 0.30$ mol dm^{-3}.
[b] $I = 0.70$ mol dm^{-3}.

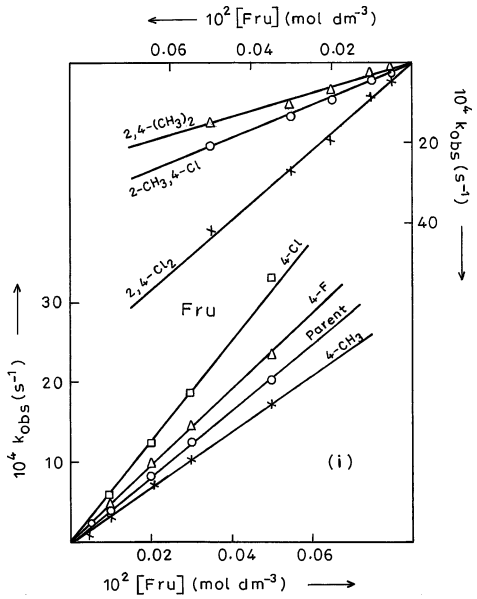


Figure 1 Plots of k_{obs} versus [Fru]$_0$; 10^3[NCSBS]$_0$ = 10[NaOH] = $2I$ = 1.0 mol dm^{-3}, temperature 303 K. NCSBS : i-X-$C_6H_4SO_2$NaNCl, where X = 4-H, 4-CH_3, 4-F, or 4-Cl and i-X-j-Y-$C_6H_3SO_2$NaNCl, where i-X-j-Y = 2,4-$(CH_3)_2$, 2-CH_3-4-Cl, or 2,4-Cl_2.

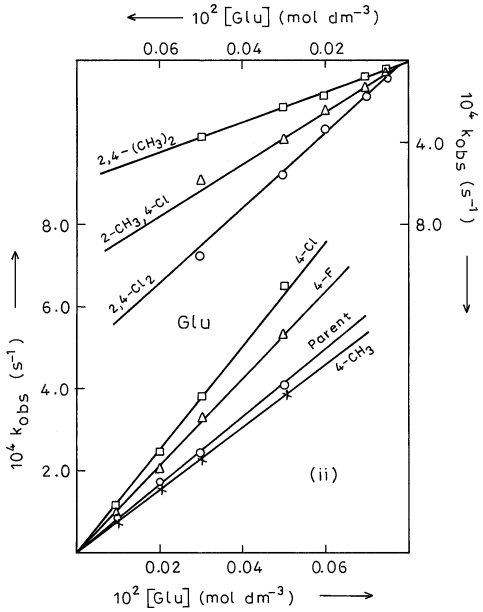


Figure 2 Plots of k_{obs} versus [Glu]$_0$; 10^3[NCSBS]$_0$ = 10[NaOH] = $2I$ = 1.0 mol dm^{-3}, temperature 303 K. NCSBS : i-X-$C_6H_4SO_2$NaNCl, where X = 4-H, 4-CH_3, 4-F or 4-Cl and i-X-j-Y-$C_6H_3SO_2$NaNCl, where i-X-j-Y = 2,4-$(CH_3)_2$, 2-CH_3-4-Cl or 2,4-Cl_2.

Table III Pseudo-First-Order Rate Constants (k_{obs}) for the Oxidation of D-Glucose (Glu) by the Sodium Salts of *N*-chloro-para-substituted Benzenesulfonamides (NCSBS) in Aqueous Alkaline Medium at 303 K ($I = 0.5$ mol dm^{-3} Except During Its Variation)

10^3[NCSBS]$_0$ (mol dm^{-3})	10^2[Glu]$_0$ (mol dm^{-3})	10[NaOH] (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1}) i-X-$C_6H_4SO_2$(Na)NCl·xH$_2$O, X =					
			Parent	4-CH_3	4-C_2 H_5	4-F	4-Cl	4-Br
Effect of varying [NCSBS]$_0$								
0.5	2.0	1.0	1.8	1.6	2.4	2.1	2.4	2.2
1.0	2.0	1.0	1.8	1.7	2.4	2.1	2.4	2.2
2.0	2.0	1.0	1.7	1.6	2.1	2.2	2.4	2.1
4.0	2.0	1.0	1.7	1.6	2.1	2.1	2.4	2.1
Effect of varying [Glu]$_0$								
1.0	0.5	1.0	0.5	0.5	0.5	0.5	0.6	0.7
1.0	1.0	1.0	1.0	0.9	0.8	1.1	1.1	1.3
1.0	2.0	1.0	1.8	1.7	2.4	2.1	2.4	2.2
1.0	3.0	1.0	2.2	2.5	3.4	3.3	3.8	5.7
1.0	5.0	1.0	4.1	4.1	6.4	5.3	6.5	8.2
Effect of varying [NaOH]								
1.0	2.0	0.3	0.3	0.4	0.3	0.4	0.5	0.3
1.0	2.0	0.5	0.7	0.7	1.0	0.8	0.9	1.0
1.0	2.0	1.0	1.8	1.7	2.4	2.1	2.4	2.2
1.0	2.0	2.0	3.3	4.7	3.9	5.0	6.5	7.7
1.0	2.0	3.0	6.3	6.1	5.6	8.9	11.3	10.2
Effect of varying ionic strength								
1.0[a]	2.0	1.0	1.4	1.3	1.8	1.7	2.1	1.8
1.0	2.0	1.0	1.8	1.7	2.4	2.1	2.4	2.2
1.0[b]	2.0	1.0	2.1	2.0	2.7	2.6	2.8	2.9

[a] $I = 0.30$ mol dm^{-3}.
[b] $I = 0.70$ mol dm^{-3}.

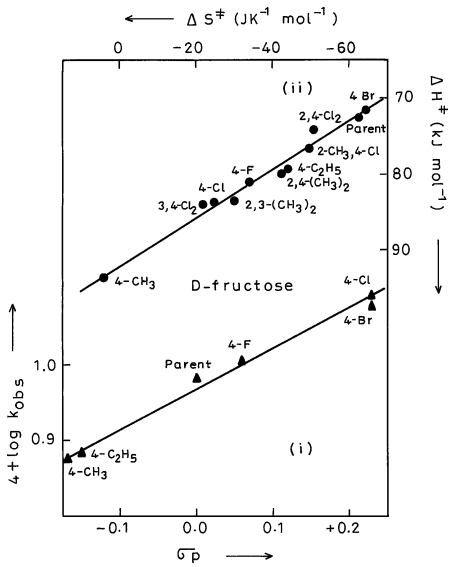


Figure 3 (i) Plot of log k_{obs} versus σp (for Fru oxidation); 10^3[NCSBS]$_0$ = 50[Fru]$_0$ = 10[NaOH] = $2I$ = 1.0 mol dm^{-3}, temperature 303 K. NCSBS : i-X-$C_6H_4SO_2$NaNCl, where X = 4-H, 4-CH_3, 4-C_2H_5, 4-F, 4-Cl, or 4-Br. (ii) Plot of $\Delta H^{\neq}$ versus $\Delta S^{\neq}$(for Fru oxidation) i-X-$C_6H_4SO_2$NaNCl, where i-X = 4-H, 4-CH_3, 4-C_2H_5, 4-F, 4-Cl, or 4-Br and i-X-j-Y-$C_6H_3SO_2$NaNCl, where i-X-j-Y = 2,3-$(CH_3)_2$, 2,4-$(CH_3)_2$, 2-CH_3-4-Cl, 2,4-Cl_2, or 3,4-Cl_2.

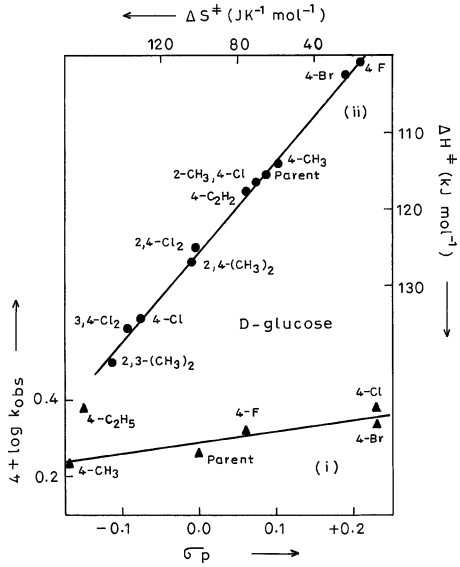


Figure 4 (i) Plot of log k_{obs} versus σp (for Glu oxidation); 10^3[NCSBS]$_0$ = 50 [Glu]$_0$ = 10[NaOH] = $2I$ = 1.0 mol dm^{-3}, temperature 303 K. NCSBS : i-X-$C_6H_4SO_2$NaNCl, where X = 4-H, 4-CH_3, 4-C_2H_5, 4-F, 4-Cl, or 4-Br. (ii) Plot of $\Delta H^{\neq}$ versus $\Delta S^{\neq}$(for Glu oxidation) i-X-$C_6H_4SO_2$NaNCl, where i-X = 4-H, 4-CH_3, 4-C_2H_5, 4-F, 4-Cl, or 4-Br and i-X-j-Y-$C_6H_3SO_2$NaNCl, where i-X-j-Y = 2,3-$(CH_3)_2$, 2,4-$(CH_3)_2$, 2-CH_3-4-Cl, 2,4-Cl_2, or 3,4-Cl_2.

Table IV Pseudo-First-Order Rate Constants (k_{obs}) for the Oxidation of D-Glucose (Glu) by the Sodium Salts of *N*-chloro-di-substituted Benzenesulfonamides (NCSBS) in Aqueous Alkaline Medium at 303 K ($I = 0.5$ mol dm^{-3} Except During Its Variation)

10^3[NCSBS]$_0$ (mol dm^{-3})	10^2[Glu]$_0$ (mol dm^{-3})	10[NaOH] (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1}) i-X, j-Y-$C_6H_3SO_2$(Na)NCl·xH$_2$O, i-X, j-Y =				
			2,3-$(CH_3)_2$	2,4-$(CH_3)_2$	2-CH_3,4-Cl	2,4-Cl_2	3,4-Cl_2
Effect of varying [NCSBS]$_0$							
0.5	2.0	1.0	1.7	1.8	2.4	4.2	3.5
1.0	2.0	1.0	1.7	1.8	2.4	4.1	3.5
2.0	2.0	1.0	1.7	1.8	2.4	4.0	3.4
4.0	2.0	1.0	1.8	1.7	2.0	3.7	3.4
Effect of varying [Glu]$_0$							
1.0	0.5	1.0	0.4	0.4	0.7	0.9	0.6
1.0	1.0	1.0	0.8	0.8	1.4	1.7	1.2
1.0	2.0	1.0	1.7	1.8	2.4	4.1	3.4
1.0	3.0	1.0	2.2	2.3	3.8	5.5	5.6
1.0	5.0	1.0	3.0	3.8	4.7	9.7	7.4
Effect of varying [NaOH]							
1.0	2.0	0.3	0.2	0.2	0.2	0.5	0.9
1.0	2.0	0.5	0.6	0.7	0.5	1.7	1.5
1.0	2.0	1.0	1.7	1.8	2.4	4.1	3.4
1.0	2.0	2.0	5.3	3.4	8.2	11.2	6.3
1.0	2.0	3.0	8.7	5.2	11.2	17.2	10.4
Effect of varying ionic strength							
1.0[a]	2.0	1.0	1.3	1.3	2.1	3.8	2.9
1.0	2.0	1.0	1.7	1.8	2.4	4.1	3.4
1.0[b]	2.0	1.0	2.2	2.4	2.9	4.4	4.1

[a] $I = 0.30$ mol dm^{-3}.
[b] $I = 0.70$ mol dm^{-3}.

The R_f values of the reduced arylsulfonamides compared with the values of the corresponding pure arylsulfonamides are C_6H_5: 0.89 (0.88), 4-$CH_3C_6H_4$: 0.92 (0.91), 4-$C_2H_5C_6H_4$: 0.93 (0.94), 4-FC_6H_4: 0.90 (0.92), 4-ClC_6H_4: 0.91(0.93), 4-BrC_6H_4: 0.88 (0.89), 2,3-$(CH_3)_2C_6H_3$: 0.91 (0.92), 2,4-$(CH_3)_2C_6H_3$: 0.96 (0.96), 2-CH_3-4-ClC_6H_3: 0.95 (0.96), 2,4-$Cl_2C_6H_3$: 0.93 (0.92), and 3,4-$Cl_2C_6H_3$: 0.93 (0.94) sulfonamides, respectively (values in parenthesis are for the pure arylsulfonamides).

Kinetic Measurements

The kinetic studies were made in glass-stoppered pyrex boiling tubes under pseudo-first-order conditions with [Fru or Glu] ≫ [NCSBS] (by 5–50 times). The reactions were initiated by the rapid addition of known amounts of oxidant solution (0.0005–0.004 mol dm^{-3}), pre-equilibrated at a desired temperature, to mixtures containing the required amounts of substrates (0.005–0.05 mol dm^{-3}), sodium hydroxide (0.03–0.30 mol dm^{-3}), sodium nitrate and water in the boiling tube, thermostated at the same temperature. The progress of the reactions was monitored for at least two half-lives by the iodometric determination of unreacted oxidant at regular intervals of time. The pseudo-first-order rate constants (k_{obs}) were computed by the graphical methods, and the values were reproducible within ±4% error.

The kinetic data on the oxidation of D-fructose and D-glucose by NC4EBS, NC4FBS, NC4CBS, NC4BBS, NC23DMBS, NC24DMBS, NC2M4CBS, NC24DCBS, and NC34DCBS in aqueous alkaline medium under varying conditions of [NCSBS], [Fru or Glu], [NaOH], and ionic strength of the medium are shown in Tables I–IV and Figs. 1–4. At constant [Fru or Glu]$_0$ (5–50-fold excess over [NCSBS]$_0$) and [NaOH], the plots of log[NCSBS] versus time were linear up to at least 75% completion of the reactions. The pseudo-first-order rate constants computed from the plots remained unaffected by the changes in [NCSBS] (Tables I–IV), establishing first-order dependence of the rate on [NCSBS] for the oxidation of both the substrates by all the reagents. At constant [NCSBS]$_0$ and [NaOH], the rates increased with increase in [Fru or Glu]$_0$ with first-order dependences in all the cases (Tables I–IV). The plots of k_{obs} versus [Fru or Glu]$_0$ gave straight lines passing through the origin (Figs. 1

and 2). At constant $[NCSBS]_0$ and [Fru or Glu]$_0$, the rates increased with increase in $[OH^-]$ with first-order dependences on [NaOH] (Tables I–IV) for all the oxidations. At constant $[NCSBS]_0$, [Fru or Glu]$_0$, and [NaOH], the rates increased with increase in the ionic strength of the medium (Tables I–IV), indicating the interaction of similar ions in the rate-determining steps. The rates were measured at different temperatures for the oxidation of both the substrates by all the oxidants, and the activation parameters have been computed from the Arrhenius and Eyring plots (Tables V and VI).

The sodium salts of *N*-chloroarylsulfonamides (NCSBS) are fairly strong electrolytes in aqueous solution [1,3]. They furnish different reactive species depending on pH of the medium. The possible oxidizing species in alkaline solutions of NCSBS are $ArSO_2NCl^-$, $ArSO_2NHCl$, OCl^-, and $ArSO_2NCl_2$, depending on $[OH^-]$ (where Ar = C_6H_5; 4-$CH_3C_6H_4$, 4-$C_2H_5C_6H_4$, 4-FC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 2,3-$(CH_3)_2C_6H_3$, 2,4-$(CH_3)_2C_6H_3$, 2-CH_3,4-ClC_6H_3, 2,4-$Cl_2C_6H_3$, and 3,4-$Cl_2C_6H_3$).

$$ArSO_2NCl^- + H_2O \rightleftharpoons ArSO_2NH_2 + OCl^- \quad (5)$$

$$ArSO_2NCl^- + H_2O \rightleftharpoons ArSO_2NHCl + HO^- \quad (6)$$

$$ArSO_2NHCl + HO^- \rightleftharpoons ArSO_2NH_2 + OCl^- \quad (7)$$

Equations (5) and (7) predict retardation of rates by the reaction products, arylsulfonamides, while Eq. (6) expects retardation of rates by OH^- ions. Since the rate increases with increase in OH^- and is not affected by the addition of sulfonamides, it is likely that the anion $ArSO_2NCl^-$ is the active oxidant species.

In alkaline solutions, sugars undergo isomerization to an equilibrium mixture of aldoses and ketoses which exist as enediol anions (E^-) [21]. In the presence of oxidants, enolic anions react with $ArSO_2NCl^-$ to form intermediates, which subsequently undergo cleavages

Table V Activation Parameters for the Oxidation of D-Fructose by Sodium Salts of *N*-chloro-para- and di-substituted Benzenesulfonamides (NCSBS) in Aqueous Alkaline Medium

	i-X-$C_6H_4SO_2$(Na)NCl·xH_2O, X =					
Parameters	Parent	4-CH_3	4-C_2H_5	4-F	4-Cl	4-Br
E_a (kJ mol^{-1})	73.9	90.6	73.4	81.9	79.2	72.2
log A	9.7	12.5	9.5	11.2	10.8	9.5
$\Delta H^{\neq}$ (kJ mol^{-1})	72.6	93.6	78.9	81.1	83.6	71.6
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	−63.2	+4.0	−44.4	−34.3	−25.0	−64.5
$\Delta G^{\neq}$ (kJ mol^{-1})	91.8	92.4	92.4	91.5	91.2	91.2
	Optimized values with reference to log A value of the parent oxidant					
E_a (kJ mol^{-1})	73.8	74.4	74.3	73.5	73.1	73.2
$\Delta H^{\neq}$ (kJ mol^{-1})	71.3	71.9	71.8	71.0	70.6	70.7
	Optimized values with reference to E_a value of the parent oxidant					
log A	9.7	9.6	9.6	9.8	9.8	9.8
$\Delta S^{\neq}$ (J K^{-1}mol^{-1})	−67.7	−69.6	−69.6	−65.8	−65.8	−65.8
	i-X-j-Y-$C_6H_3SO_2$(Na)NCl·xH_2O, i-X-j-Y =					
	Parent	2,3-$(CH_3)_2$	2,4-$(CH_3)_2$	2-CH_3-4-Cl	2,4-Cl_2	3,4-Cl_2
E_a (kJ mol^{-1})	73.9	83.6	75.8	75.4	80.9	72.1
log A	9.7	11.2	10.0	10.0	11.2	9.7
$\Delta H^{\neq}$ (kJ mol^{-1})	72.6	83.9	79.2	76.6	84.0	74.3
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	−63.2	−30.1	−43.2	−49.9	−21.3	−51.4
$\Delta G^{\neq}$ (kJ mol^{-1})	91.8	93.0	92.3	91.7	90.5	90.0
	Optimized values with reference to log A value of the parent oxidant					
E_a (kJ mol^{-1})	73.8	75.1	74.3	73.7	71.9	72.5
$\Delta H^{\neq}$(kJ mol^{-1})	71.3	72.6	71.8	71.2	69.4	70.0
	Optimized values with reference to E_a value of the parent oxidant					
log A	9.7	9.5	9.6	9.7	10.0	9.9
$\Delta S^{\neq}$ (J K^{-}1mol^{-1})	−67.7	−71.5	−69.6	−67.7	−61.9	−63.9

Table VI Activation Parameters for the Oxidation of D-Glucose by Sodium Salts of *N*-chloro-para- and di-substituted Benzenesulfonamides in Aqueous Alkaline Medium

	i-X-$C_6H_4SO_2$(Na)NCl · xH_2O, X =					
Parameters	Parent	4-CH_3	4-C_2H_5	4-F	4-Cl	4-Br
E_a (kJ mol^{-1})	113.7	113.7	117.1	95.7	134.3	102.5
log A	15.9	15.8	16.6	12.8	19.5	14.0
$\Delta H^{\neq}$ (kJ mol^{-1})	115.6	114.2	117.8	100.2	134.7	102.4
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	+64.5	+59.6	+74.5	+15.0	+130.1	+22.7
$\Delta G^{\neq}$ (kJ mol^{-1})	96.1	96.1	95.2	95.6	95.3	95.5
	Optimized values with reference to log A value of the parent oxidant					
E_a (kJ mol^{-1})	113.9	114.1	113.2	113.6	113.2	113.5
$\Delta H^{\neq}$ (kJ mol^{-1})	111.4	111.6	110.7	111.1	110.7	111.0
	Optimized values with reference to E_a value of the parent oxidant					
log A	15.9	15.8	16.0	15.9	16.0	15.9
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	+51.0	+49.1	+53.0	+51.0	+53.0	+51.0
	i-X-j-Y-$C_6H_3SO_2$(Na)NCl · xH_2O, i-X-j-Y =					
	Parent	2,3-$(CH_3)_2$	2,4-$(CH_3)_2$	2-CH_3-4-Cl	2,4-Cl_2	3,4-Cl_2
E_a (kJ mol^{-1})	113.7	138.7	128.3	114.8	133.6	122.0
log A	15.9	20.1	18.4	16.2	19.6	17.6
$\Delta H^{\neq}$ (kJ mol^{-1})	115.6	140.1	127.2	116.4	135.6	125.3
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	+64.5	+145.4	+103.2	+69.8	+137.5	+102.1
$\Delta G^{\neq}$ (kJ mol^{-1})	96.1	96.0	95.9	95.3	94.0	94.4
	Optimized values with reference to log A value of the parent oxidant					
E_a (kJ mol^{-1})	113.9	114.1	113.9	113.2	112.4	111.9
$\Delta H^{\neq}$(kJ mol^{-1})	111.4	111.6	111.4	110.7	109.9	109.4
	Optimized values with reference to E_a value of the parent oxidant					
log A	15.9	15.8	15.9	16.0	16.1	16.2
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	+51.0	+49.1	+51.0	+53.0	+54.9	+56.8

to give the products. The hexoses react with the oxidants through keto-enolic anion intermediates, and they react very slowly in the aldo-enolic forms. The observed negative and positive entropies of activations for D-fructose and D-glucose indicate that fructose has more orderly structure than glucose. It is thus sterically favored for oxidation by the oxidants. Hence it is probable that in the case of glucose, the fructose isomer formed by the alkali-catalyzed isomerization reacts with the oxidants. This observation is supported by the fact that the rates with fructose are higher by 4–5 times than those with glucose for the same oxidant. Similarly E_a values are higher by about 1.5 times with glucose compared to E_a values for fructose. In other words, higher rates and lower E_a with fructose and lower rates and higher E_a with glucose support these observations.

Based on these facts, the kinetics of first order each in [NCSBS], [S], and [OH^-], positive ionic strength and negligible product effects observed in the oxidation of the substrates by *N*-chloroarylsulfonamides are explained by the reaction sequences shown in Scheme 1.

The rate law in accordance with Scheme 1 is given by

$$\text{Rate} = -\text{d[NCSBS]}/\text{d}t = K_1k_2[\text{S}][\text{OH}^-][\text{NCSBS}]/[\text{H}_2\text{O}] \quad (8)$$

$$\text{S} + \text{OH}^- \underset{}{\overset{K_1}{\rightleftharpoons}} \text{E}^- + \text{H}_2\text{O}$$

$$\text{E}^- + \text{ArSO}_2\text{NCl}^- \xrightarrow[\text{rate limiting}]{k_2} \text{X} + \text{RN}^{2-}$$

$$\text{X} + \text{H}_2\text{O} / \text{OH}^- \xrightarrow[\text{fast}]{} \text{Products}$$

$$\text{RN}^{2-} + \text{H}_2\text{O} \xrightarrow[\text{fast}]{} \text{RNH}^- + \text{OH}^-$$

Scheme 1

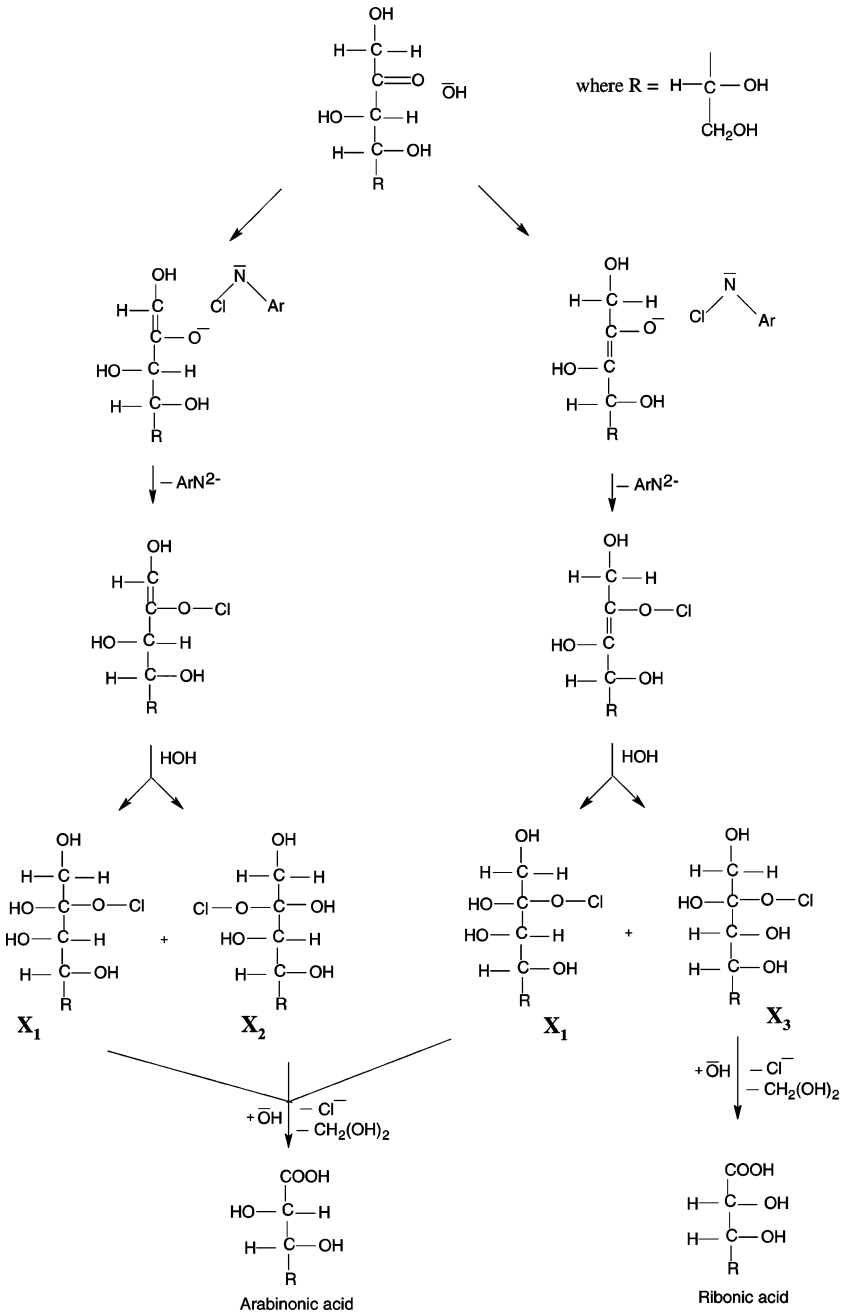
or

$$k_{obs} = K_1 k_2[S][OH^-]/[H_2O]$$
$$= K_1^1 k_2[S][OH^-],\ K_1^1 = K_1/[H_2O] \quad (9)$$

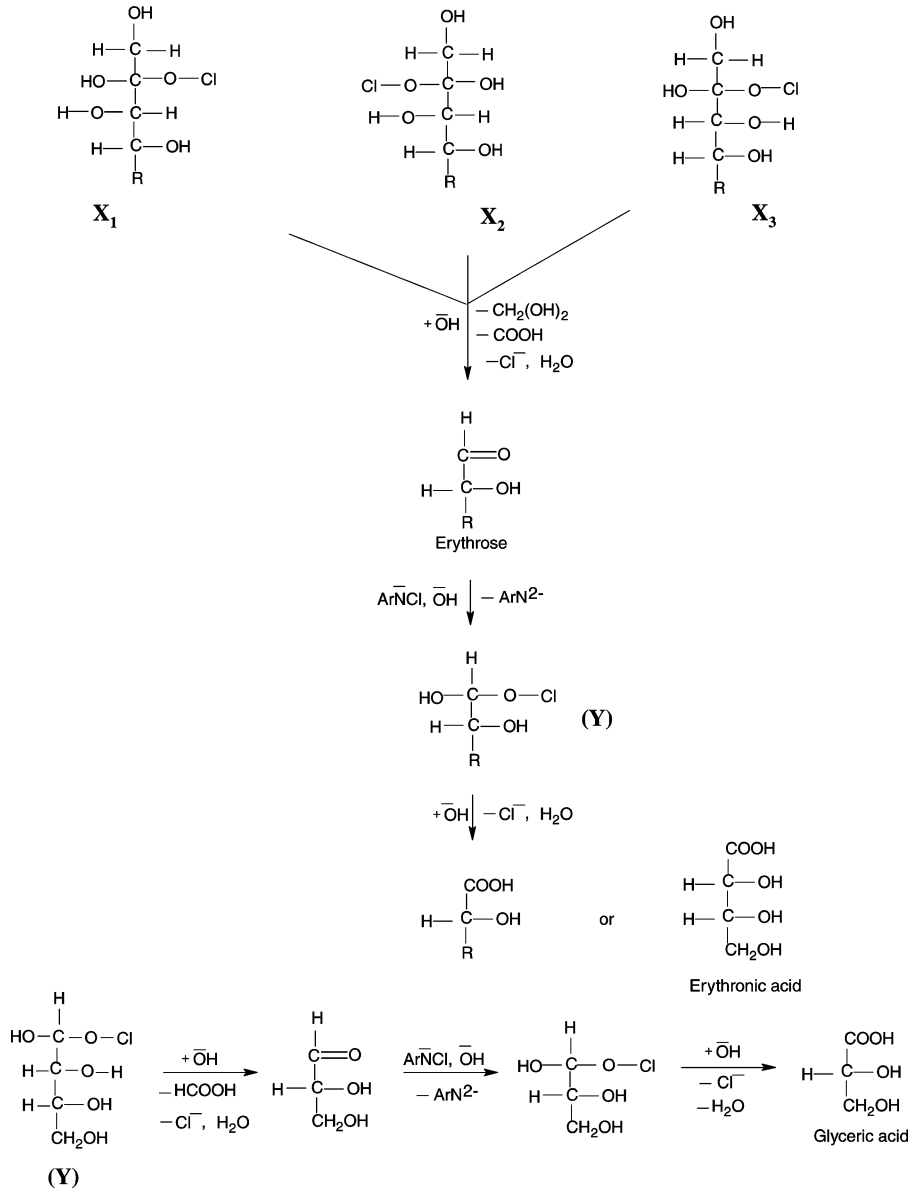
Applicability of Hammett equation [22] has also been tested for the oxidation of both fructose and glucose by all the oxidants. The plots of log k_{obs} versus σp were reasonably linear (Figs. 3 and 4), and the following relations were found to be valid:

$$\log k_{obs} = -3.13 + 0.54\,\sigma p$$
$$\log k_{obs} = -3.81 + 0.28\,\sigma p$$

The enthalpies and the free energies of activations for the oxidations of D-fructose and D-glucose by all the *N*-chloroarylsulfonamides have been correlated. The plots of $\Delta H^{\neq}$ versus $\Delta S^{\neq}$ (Figs. 3 and 4) were



Scheme 2



Scheme 2 Continued

reasonably linear with isokinetic temperatures of 301 K and 299 K for fructose and glucose oxidations, respectively. Further, to see the effect of substitution in the oxidants on the energy of activation, E_a values of *N*-chloroarylsulfonamides were optimized with reference to log *A* of the parent oxidant, *N*-chlorobenzenesulfonamide through the equation, $E_a = 2.303\ RT\ (\log A - \log k_{obs})$. The energies of activation for the oxidation of either D-fructose or D-glucose by the oxidants with electron-releasing groups in the benzene ring are slightly higher than that of the parent oxidant, while the values are little lower for the oxidants with electron withdrawing groups in the benzene ring (Tables V and VI). Enthalpies of activations have the same trend. Similarly, log *A* values for the oxidations of both fructose and glucose by the substituted oxidants were optimized with reference to E_a of the parent oxidant through the equation, $\log A = \log k_{obs} + E_a/2.303\ RT$ (Tables V and VI). Log *A* values are slightly higher for the oxidants with electron-withdrawing groups in the benzene ring, while the effect of electron-releasing groups on log *A* is negligible. The free energies of activation remain almost the same indicating operation of similar mechanisms in all the cases.

Effective oxidizing species of the oxidants employed in the present oxidations is Cl^+ in different forms, released from the oxidant. The introduction of different substituents into the benzene ring

of the oxidant affects the ability of it to release Cl^+ and hence its capacity to oxidize the substrate. It is evident from the rate data that the electron-releasing groups such as CH_3, C_2H_5 etc. inhibit the ease with which Cl^+ is released from the oxidant, while electron-withdrawing groups such as Cl, Br etc. enhance this ability and hence influence the rates of oxidations. The kinetic data for the oxidations of D-fructose and D-glucose by *N*-chloroarylsulfonamides have been intercorrelated in terms of the observed rate constants and thermodynamic parameters (figures not shown). These correlations were reasonably good.

A typical detailed mechanism of oxidation of fructose isomer by an oxidant is schematically shown in Scheme 2.

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