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Kinetics of oxidation of acidic amino acids and their monoamides by *N*-chloroarylsulphonamides in aqueous acidic medium

B. Thimme Gowda* and Mahesha Shetty

Department of Post-Graduate Studies and Research in Chemistry, Mangalore University, Mangalagangothri 574 199, Mangalore, India

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ABSTRACT: Twelve sodium salts of *N*-chloroarylsulphonamides were employed as oxidants for studying the kinetics of oxidation of two acidic amino acids (aspartic and glutamic acid) and their monoamides (aspargine and glutamine) in aqueous acidic medium under various conditions, to see how the oxidative strength of these reagents vary with substitution. The sodium salts of *N*-chloroarylsulphonamides employed are of the general formulae *i*-X-$C_6H_4SO_2$-NaNCl·*x*H_2O (where *i*-X = 4-C_2H_5, 4-F, 4-Cl or 4-Br) and *i*-X-*j*-Y-$C_6H_3SO_2$NaNCl·*x*H_2O [where *i*-X-*j*-Y = 2,3-$(CH_3)_2$, 2,4-$(CH_3)_2$, 2,5-$(CH_3)_2$, 2-CH_3-4-Cl, 2,4-Cl_2 and 3,4-Cl_2]. The reactions show second-order kinetics in [oxidant], fractional order in [amino acid] and an inverse dependence on [H^+]. Addition of the reduced product of the oxidants or variation in ionic strength of the medium has no significant effect on the rates of oxidations. Mechanisms in conformity with the observed kinetics are discussed. The effective oxidizing species of the oxidants is Cl^+ in different forms. The oxidizing strengths of *N*-chloroarylsulphonamides depend on the ease with which Cl^+ is released from them. The study reveals that the introduction of electron-withdrawing groups such as halides to the benzene ring eases the release of Cl^+ from the reagent and hence increases the oxidizing strengths of the *N*-chloroarylsulphonamides. The effect of substituents on E_a of the reactions was analysed by optimising E_a with reference to log *A*, and log *A* with reference to E_a of the parent oxidant. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: *N*-chloroarylsulphonamides; amino acids; kinetics of oxidation; substituent effect

INTRODUCTION

Many arylsulphonamides and their *N*-halo compounds are of fundamental chemical interest owing to their diverse physical, chemical and biological properties.[1–9] They also exhibit fungicidal and herbicidal activities, due to their oxidizing action in aqueous, partially aqueous and non-aqueous media. *N*-Haloarylsulphonamides act as sources of halonium cations, hypohalite species and *N*-anions which behave both as bases and nucleophiles. Although the various aspects of the prominent members of this class of reagents, namely *N*-chlorobenzenesulphonamide (NCBS) and *N*-chloro-4-methylbenzene-sulphonamide (NC4MBS) have been studied, there have been no efforts to alter the electron environment around the sulphonamide group to obtain Cl^+ released either at ease or with difficulty, as the ease with which Cl^+ is released from the reagent decides the oxidizing strength of the oxidant. This in turn depends on the electron density on the nitrogen atom of the sulphonamide group, which may be altered by making appropriate substitutions in the benzene ring. Thus, *N*-chloroarylsulphonamides of required oxidizing capacity may be produced by altering the electron density on the nitrogen atom of the sulphonamide group to obtain Cl^+ released either at ease or with difficulty. Hence, in an effort to introduce *N*-chloroarylsulphonamides of different oxidizing strengths, we have recently prepared and characterized several mono- and disubstituted *N*-chlorobenzenesulphonamides (NCSBS)[10,11] of the general formulae *i*-X-$C_6H_4SO_2$NaNCl·*x*H_2O [where *i*-X = 4-H (NCBS), 4-CH_3 (NC4MBS), 4-C_2H_5 (NC4EBS), 4-F (NC4FBS), 4-Cl (NC4CBS) or 4-Br (NC4BBS)] and *i*-X-*j*-Y-$C_6H_3SO_2$NaNCl·*x*H_2O [where *i*-X-*j*-Y = 2,3-$(CH_3)_2$ (NC23DMBS), 2,4-$(CH_3)_2$ (NC24DMBS), 2,5-$(CH_3)_2$ (NC25DMBS), 2-CH_3-4-Cl (NC2M4CBS), 2,4-Cl_2(NC24DCBS) and 3,4-Cl_2 (NC34DCBS)]. Here we employed these 12 reagents as oxidants for studying the kinetics of oxidation of two acidic amino acids (AA), aspartic acid (Asp) and glutamic acid (Glu), and their monoamides, aspargine (Asn) and glutamine (Gln), in aqueous acidic medium. Although studies with two of the reagents have been partly reported, the kinetics of oxidation of all four amino acids by these oxidants were also carried out under identical conditions and are included in the paper for comparison and completeness of the work.

**Correspondence to:* B. T. Gowda, Department of Post-Graduate Studies and Research in Chemistry, Mangalore University, Mangalagangothri 574 199, Mangalore, India.
E-mail: gowdabt@yahoo.com

RESULTS AND DISCUSSION

Kinetic measurements

The kinetic studies were carried out in glass-stoppered Pyrex boiling tubes under pseudo-second-order conditions with [amino acid] ≫ [NCSBS] (by 5–50-fold). 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 amino acid (0.005–0.04 mol dm^{-3}), perchloric acid (0.01–0.10 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 iodimetric determination of unreacted oxidant at regular intervals of time. The pseudo-second-order rate constants (k_{obs}) were calculated by graphical methods and the values were reproducible to within ±3% error.

The kinetic data on the oxidations of Asp, Glu, Asn and Gln by NCBS, NC4MBS, NC4EBS, NC4FBS, NC4CBS, NC4BBS, NC23DMBS, NC24DMBS, NC25DMBS, NC2M4CBS, NC24DCBS and NC34DCBS in aqueous perchloric acid medium under various conditions of [NCSBS], [AA], [$HClO_4$] and solution composition of the medium are shown in Tables 1–9 and Figs 1and 2.

Effect of varying [oxidant]$_0$

At constant [AA]$_0$ (5–50-fold excess over [oxidant]$_0$) and [H^+], the second-order plots of 1/[oxidant] versus time were linear up to 70% completion of the reactions. The pseudo-second-order rate constants calculated from the plots remained unaffected by the changes in [oxidant]$_0$ (Tables 1–8), establishing a second-order dependence of the rate on [NCSBS]$_0$.

Effect of varying [AA]$_0$

At constant [NCSBS]$_0$ and [H^+], the rates increased with increase in [AA] with fractional order dependences in [AA] for all the oxidations (Tables 1–9). The plots of k_{obs} versus [AA] were linear with finite intercepts on the ordinates (Figs 1 and 2), indicating the operation of a two-pathway mechanism for the oxidations.

Effect of varying [H^+]

The rates decreased with increase in [H^+], at fixed [NCSBS]$_0$ and [AA]$_0$, with varying inverse order dependences in [H^+] (Tables 1–9).

Effect of varying ionic strength and other parameters of the medium

Variation in either the ionic strength of the medium or addition of the substituted benzenesulphonamides (SBSA), the reduced products of the oxidants, to the reaction mixtures had no significant effect on the rates of

Table 1. Pseudo-second-order rate constants (k_{obs}) for the oxidation of aspartic acid (Asp) by the sodium salts of *p*-substituted *N*-chlorobenzenesulphonamides (NCSBS) in aqueous perchloric acid at 303 K(I = 0.30 mol dm^{-3})

10^3[NCSBS]$_0$ (mol dm^{-3})	10^2[Asp]$_0$ (mol dm^{-3})	10^2[$HClO_4$] (mol dm^{-3})	$10\,k_{obs}$ (dm^3 mol^{-1} s^{-1}) for 4-X-$C_6H_4SO_2NaNCl$, where X =					
			H	CH_3	C_2H_5	F	Cl	Br
Effect of varying [NCSBS]$_0$								
0.5	2.0	3.0	2.9	2.8	2.9	4.8	6.8	8.5
1.0	2.0	3.0	2.7	2.7	2.9	4.6	6.7	8.4
2.0	2.0	3.0	2.7	2.6	2.7	4.6	6.7	8.4
4.0	2.0	3.0	2.6	2.5	2.7	4.5	6.6	8.3
1.0[a]	2.0	3.0	2.6	2.6	2.8	4.5	6.5	8.3
1.0[b]	2.0	3.0	2.8	2.8	3.2	4.8	6.8	8.6
Effect of varying [Asp]$_0$								
1.0	0.5	3.0	1.8	1.8	1.8	3.3	4.1	5.2
1.0	1.0	3.0	2.2	2.0	2.2	4.0	5.4	7.8
1.0	2.0	3.0	2.7	2.7	2.9	4.6	6.7	9.7
1.0	3.0	3.0	3.3	3.4	3.7	6.7	7.6	14.2
Effect of varying [$HClO_4$]								
1.0	2.0	1.0	7.0	9.2	9.7	19.2	28.9	20.8
1.0	2.0	2.0	4.0	4.3	5.0	8.4	13.4	16.6
1.0	2.0	3.0	2.7	2.7	2.9	4.7	6.6	9.0
1.0	2.0	5.0	1.4	1.5	1.7	3.0	4.1	7.6
1.0	2.0	10.0	0.6	0.9	0.8	1.6	2.0	3.4

[a] I = 0.10 mol dm^{-3}.
[b] I = 0.50 mol dm^{-3}.

Table 2. Pseudo-second-order rate constants (k_{obs}) for the oxidation of aspartic acid (Asp) by the sodium salts of disubstituted *N*-chlorobenzenesulphonamides (NCSBS) in aqueous perchloric acid at 303 K ($I = 0.30\ mol\ dm^{-3}$)

$10^3[NCSBS]_0$ ($mol\ dm^{-3}$)	$10^2[Asp]_0$ ($mol\ dm^{-3}$)	$10^2[HClO_4]$ ($mol\ dm^{-3}$)	$10\,k_{obs}$ ($dm^3\ mol^{-1}\ s^{-1}$) for *i*-X-*j*-Y-$C_6H_3SO_2NaNCl$, where *i*-X-*j*-Y =					
			2,3-$(CH_3)_2$	2,4-$(CH_3)_2$	2,5-$(CH_3)_2$	2-CH_3-4-Cl	2,4-Cl_2	3,4-Cl_2
Effect of varying $[NCSBS]_0$								
0.5	2.0	3.0	4.0	4.4	6.4	14.0	20.6	19.8
1.0	2.0	3.0	2.7	3.7	6.0	13.7	20.1	19.3
2.0	2.0	3.0	2.4	3.5	5.7	13.4	19.6	19.2
4.0	2.0	3.0	2.2	3.3	5.6	13.3	19.5	19.0
1.0[a]	2.0	3.0	2.6	3.3	5.9	13.5	19.5	19.0
1.0[b]	2.0	3.0	3.0	3.9	6.2	13.9	20.6	19.7
Effect of varying$[Asp]_0$								
1.0	0.5	3.0	2.1	2.5	3.0	8.6	11.1	13.3
1.0	1.0	3.0	2.4	2.9	3.7	9.9	13.3	16.4
1.0	2.0	3.0	2.7	3.7	6.0	13.7	20.1	19.3
1.0	4.0	3.0	4.4	5.0	7.5	16.4	27.2	25.1
Effect of varying $[HClO_4]$								
1.0	2.0	1.0	5.7	9.5	13.8	28.5	42.2	31.8
1.0	2.0	1.0	4.3	6.2	9.2	16.6	30.8	24.0
1.0	2.0	2.0	2.7	3.7	6.0	13.7	20.1	19.3
1.0	2.0	3.0	1.7	2.7	4.0	6.9	15.5	12.0
1.0	2.0	5.0	1.2	2.0	2.7	4.1	11.4	6.9

[a] $I = 0.10\ mol\ dm^{-3}$.
[b] $I = 0.50\ mol\ dm^{-3}$.

oxidations (Tables 1–8). The rates were measured at different temperatures with varying [AA]. The coefficients of the rate-limiting steps of the considered mechanisms were calculated at each temperature as described later. Activation parameters corresponding to these constants were also computed.

Sodium salts of *N*-chlorobenzenesulphonamide and its substituted compounds (NCSBS) are fairly strong electrolytes in aqueous solution and they furnish different reactive species depending on the pH of the medium.[1–9] The possible oxidizing species in acidic solutions of NCSBS are $ArSO_2NCl^-$, $ArSO_2NHCl$, HOCl and $ArSO_2NCl_2$ at low $[H^+]$ and $ArSO_2NH_2Cl^+$ and H_2OCl^+ at high $[H^+]$, where Ar = 4-XC_6H_4 (X = H, CH_3, C_2H_5, F, Cl or Br) and *i*-X-*j*-Y-C_6H_3 [*i*-X-*j*-Y = 2,3-$(CH_3)_2$, 2,4-$(CH_3)_2$, 2,5-$(CH_3)_2$, 2-CH_3-4-Cl, 2,4-Cl_2 and 3,4-Cl_2].

Table 3. Pseudo-second-order rate constants (k_{obs}) for the oxidation of glutamic acid (Glu) by the sodium salts of *p*-substituted *N*-chlorobenzenesulphonamides (NCSBS) in aqueous perchloric acid at 303 K ($I = 0.30\ mol\ dm^{-3}$)

$10^3[NCSBS]_0$ ($mol\ dm^{-3}$)	$10^2[Glu]_0$ ($mol\ dm^{-3}$)	$10^2[HClO_4]$ ($mol\ dm^{-3}$)	$10\,k_{obs}$ ($dm^3\ mol^{-1}\ s^{-1}$) for 4-X-$C_6H_4SO_2NaNCl$, where X =					
			H	CH_3	C_2H_5	F	Cl	Br
Effect of varying $[NCSBS]_0$								
0.5	2.0	3.0	2.7	3.0	2.5	3.6	4.2	8.0
1.0	2.0	3.0	2.4	2.7	2.4	3.5	4.0	7.9
2.0	2.0	3.0	2.2	2.4	2.4	3.5	4.0	7.9
4.0	2.0	3.0	2.0	2.3	2.3	3.4	4.0	7.8
1.0[a]	2.0	3.0	2.3	2.7	2.5	3.3	3.8	7.8
1.0[b]	2.0	3.0	2.5	3.2	2.7	3.6	4.2	8.3
Effect of varying $[Glu]_0$								
1.0	0.5	3.0	1.7	2.3	1.3	2.3	2.9	6.6
1.0	1.0	3.0	2.0	2.5	1.9	2.7	3.4	7.4
1.0	2.0	3.0	2.4	2.7	2.4	3.5	4.0	7.9
1.0	3.0	3.0	2.9	3.9	2.8	4.5	5.0	9.3
Effect of varying $[HClO_4]$								
1.0	2.0	1.0	7.0	10.7	8.0	11.7	24.0	30.8
1.0	2.0	2.0	3.9	5.1	4.1	7.4	13.4	16.6
1.0	2.0	3.0	2.4	2.7	2.4	3.5	4.0	7.9
1.0	2.0	5.0	1.5	1.7	1.6	2.4	2.4	3.7
1.0	2.0	10.0	0.7	0.9	0.8	1.2	1.5	1.8

[a] $I = 0.10\ mol\ dm^{-3}$.
[b] $I = 0.50\ mol\ dm^{-3}$.

Table 4. Pseudo-second-order rate constants (k_{obs}) for the oxidation of glutamic acid (Glu) by the sodium salts of disubstituted *N*-chlorobenzenesulphonamides (NCSBS) in aqueous perchloric acid at 303 K ($I = 0.30\ mol\ dm^{-3}$)

$10^3[NCSBS]_0$ ($mol\ dm^{-3}$)	$10^2[Glu]_0$ ($mol\ dm^{-3}$)	$10^2[HClO_4]$ ($mol\ dm^{-3}$)	$10\,k_{obs}$ ($dm^3\ mol^{-1}\ s^{-1}$) for *i*-X-*j*-Y-$C_6H_3SO_2NaNCl$, where *i*-X-*j*-Y =					
			2,3-$(CH_3)_2$	2,4-$(CH_3)_2$	2,5-$(CH_3)_2$	2-CH_3-4-Cl	2,4-Cl_2	3,4-Cl_2
Effect of varying $[NCSBS]_0$								
0.5	2.0	3.0	3.2	4.1	4.9	10.8	17.9	14.3
1.0	2.0	3.0	2.6	3.3	4.7	10.6	17.4	14.2
2.0	2.0	3.0	2.2	3.2	4.3	10.4	17.3	13.9
4.0	2.0	3.0	1.9	2.5	4.2	10.3	17.1	13.6
1.0[a]	2.0	3.0	2.4	3.1	4.5	10.4	17.1	14.0
1.0[b]	2.0	3.0	2.8	3.6	4.9	10.9	17.7	14.5
Effect of varying$[Glu]_0$								
1.0	0.5	3.0	1.9	2.1	2.7	6.9	12.1	8.7
1.0	1.0	3.0	2.2	2.7	3.1	8.8	13.3	11.7
1.0	2.0	3.0	2.6	3.3	4.7	10.6	17.4	14.2
1.0	4.0	3.0	3.5	4.3	6.3	12.7	22.6	18.5
Effect of varying $[HClO_4]$								
1.0	2.0	1.0	5.8	9.4	14.0	21.1	39.4	29.7
1.0	2.0	2.0	3.9	5.9	7.6	15.3	27.2	25.1
1.0	2.0	3.0	2.6	3.3	4.7	10.6	17.4	14.2
1.0	2.0	5.0	1.9	2.5	3.2	4.3	11.7	10.2
1.0	2.0	10.0	1.6	2.0	2.4	2.6	7.0	5.2

[a] $I = 0.10\ mol\ dm^{-3}$.
[b] $I = 0.50\ mol\ dm^{-3}$.

Amino acids exist in protonation equilibrium in acidic solutions as

$$\underset{(SH^+)}{RCH_2CH(N^+H_3)COOH} \rightleftharpoons \underset{(S)}{RCH_2CH(N^+H_3)COO^-} + H^+$$

where $R = CH_2COOH$ (Asp), CH_2CH_2COOH (Glu), CH_2CONH_2 (Asn) and $CH_2CH_2CONH_2$ (Gln).

The second-order kinetics in [NCSBS], fractional order in [AA] and higher inverse order dependence of the rate on $[H^+]$ and other effects for the oxidation of Asp, Glu, Asn and Gln by all the *N*-chloroarylsulphonamides may be explained by a two-pathway mechanism as shown in Scheme 1. It is supported by the fact that the direct plots of rate constants versus [AA] gave better correlations (Figs 1 and 2) than the double reciprocal plots (not shown). Further, in acidic aqueous solutions of the

Table 5. Pseudo-second-order rate constants (k_{obs}) for the oxidation of aspargine (Asn) by the sodium salts of *p*-substituted *N*-chlorobenzenesulphonamides (NCSBS) in aqueous perchloric acid at 303 K ($I = 0.30\ mol\ dm^{-3}$)

$10^3[NCSBS]_0$ ($mol\ dm^{-3}$)	$10^2[Asn]_0$ ($mol\ dm^{-3}$)	$10^2[HClO_4]$ ($mol\ dm^{-3}$)	$10\,k_{obs}$ ($dm^3\ mol^{-1}\ s^{-1}$) for 4-X-$C_6H_4SO_2NaNCl$, where X =					
			H	CH_3	C_2H_5	F	Cl	Br
Effect of varying $[NCSBS]_0$								
0.5	2.0	3.0	4.8	4.2	4.5	6.3	7.9	12.6
1.0	2.0	3.0	4.3	4.0	4.3	6.2	7.8	12.5
2.0	2.0	3.0	3.9	3.6	4.3	6.2	7.6	12.4
4.0	2.0	3.0	3.7	3.3	4.1	6.2	7.6	12.4
1.0[a]	2.0	3.0	4.2	3.4	4.1	6.1	7.6	12.4
1.0[b]	2.0	3.0	4.5	4.0	4.5	6.4	7.9	12.8
Effect of varying$[Asn]_0$								
1.0	0.5	3.0	2.5	2.3	2.5	4.0	5.8	9.2
1.0	1.0	3.0	3.2	2.9	3.1	4.7	6.3	10.4
1.0	2.0	3.0	4.3	4.0	4.3	6.2	7.8	12.5
1.0	4.0	3.0	6.8	5.3	6.9	8.4	10.5	15.8
Effect of varying $[HClO_4]$								
1.0	2.0	1.0	14.7	8.2	11.4	11.5	13.3	24.0
1.0	2.0	2.0	7.0	4.6	6.1	8.9	10.3	16.1
1.0	2.0	3.0	4.3	4.0	4.3	6.2	7.8	12.5
1.0	2.0	5.0	2.6	1.8	2.2	4.9	5.4	10.2
1.0	2.0	10.0	1.8	0.9	0.6	3.4	3.8	5.1

[a] $I = 0.10\ mol\ dm^{-1}$.
[b] $I = 0.50\ mol\ dm^{-1}$.

Table 6. Pseudo-second-order rate constants (k_{obs}) for the oxidation of aspargine (Asn) by the sodium salts of disubstituted *N*-chlorobenzenesulphonamides (NCSBS) in aqueous perchloric acid at 303 K ($I = 0.30\ mol\ dm^{-3}$)

10^3[NCSBS]$_0$ (mol dm^{-3})	10^2[Asn]$_0$ (mol dm^{-3})	10^2[$HClO_4$] (mol dm^{-3})	$10\,k_{obs}$ (dm^3 mol^{-1} s^{-1}) for *i*-X-*j*-Y-$C_6H_3SO_2NaNCl$, where *i*-X-*j*-Y =					
			2,3-$(CH_3)_2$	2,4-$(CH_3)_2$	2,5-$(CH_3)_2$	2-CH_3 -4Cl	2,4-Cl_2	3,4Cl_2
Effect of varying [NCSBS]$_0$								
0.5	2.0	3.0	4.4	5.1	4.9	7.7	18.5	18.1
1.0	2.0	3.0	3.3	4.0	4.3	7.2	18.4	17.8
2.0	2.0	3.0	3.2	3.5	4.2	7.1	18.1	17.4
4.0	2.0	3.0	3.0	3.2	3.8	6.9	17.9	17.4
1.0[a]	2.0	3.0	3.0	3.8	4.2	7.1	18.3	17.3
1.0[b]	2.0	3.0	3.5	4.4	4.5	7.5	18.7	18.4
Effect of varying[Asn]$_0$								
1.0	0.5	3.0	2.5	2.5	3.2	4.9	12.4	7.7
1.0	1.0	3.0	2.8	3.2	3.6	5.9	13.7	13.0
1.0	2.0	3.0	3.2	4.0	4.3	7.2	18.4	17.8
1.0	4.0	3.0	3.8	4.8	6.3	8.6	28.2	23.5
Effect of varying [$HClO_4$]								
1.0	2.0	1.0	5.8	11.2	12.1	20.4	33.3	31.7
1.0	2.0	2.0	4.4	5.5	7.9	12.2	28.4	22.6
1.0	2.0	3.0	3.2	4.0	4.3	7.2	18.4	17.8
1.0	2.0	5.0	2.1	3.2	2.7	4.1	9.7	12.5
1.0	2.0	10.0	1.4	2.0	1.5	2.7	6.4	6.3

[a] $I = 0.10\ mol\ dm^{-3}$.
[b] $I = 0.50\ mol\ dm^{-3}$.

N-chloroarylsulphonamides, the corresponding *N*,*N*-dichloro compounds are produced, which are insoluble in water but soluble in organic solvents.

Applying the steady-state approximation to the intermediate Y in path 1, we have

$$[Y] = k_2[ArSO_2NH_2Cl^+]_0[S]/\{k_{-2} + k_3[ArSO_2NH_2Cl^+]_0 + k_2[S]\} \quad (1)$$

where $[ArSO_2NH_2Cl^+] = [ArSO_2NH_2Cl^+]_0 - [Y]$ and $[S]_0 \approx [S]$. Since k_3 is small and $[S] \gg [ArSO_2NH_2Cl^+]_0$, $k_3[ArSO_2NH_2Cl^+]_0$ is negligibly small compared with other terms in the denominator, hence Eqn (1) becomes

$$[Y] = k_2[ArSO_2NH_2Cl^+]_0[S]/(k_{-2} + k_2[S]) = K_2[NCSBS]_0[S]/(1 + K_2[S]) \quad (2)$$

Table 7. Pseudo-second-order rate constants (k_{obs}) for the oxidation of glutamine (Gln) by the sodium salts of *p*-substituted *N*-chlorobenzenesulphonamides (NCSBS) in aqueous perchloric acid at 303 K ($I = 0.30\ mol\ dm^{-3}$)

10^3[NCSBS]$_0$ (mol dm^{-3})	10^2[Gln]$_0$ (mol dm^{-3})	10^2[$HClO_4$] (mol dm^{-3})	$10\,k_{obs}$ (dm^3 mol^{-1} s^{-1}) for 4-X-$C_6H_4SO_2NaNCl$, where X =					
			H	CH_3	C_2H_5	F	Cl	Br
Effect of varying [NCSBS]$_0$								
0.5	2.0	3.0	3.0	2.9	3.4	4.9	7.8	9.3
1.0	2.0	3.0	2.7	2.9	3.1	4.8	7.6	9.2
2.0	2.0	3.0	2.5	2.8	3.1	4.7	7.6	9.2
4.0	2.0	3.0	2.2	2.7	3.0	4.7	7.6	9.2
1.0[a]	2.0	3.0	2.2	2.8	3.2	4.6	7.5	9.0
1.0[b]	2.0	3.0	2.8	3.2	3.4	5.0	7.9	9.4
Effect of varying [Gln]$_0$								
1.0	0.5	3.0	1.8	2.2	2.0	3.2	5.3	7.1
1.0	1.0	3.0	2.1	2.5	2.4	3.9	6.1	8.4
1.0	2.0	3.0	2.7	2.9	3.1	4.8	7.6	9.2
1.0	4.0	3.0	3.4	5.0	4.5	6.9	9.8	12.0
Effect of varying [$HClO_4$]								
1.0	2.0	1.0	8.1	9.7	7.7	20.5	18.7	29.3
1.0	2.0	2.0	4.2	4.7	4.9	10.4	11.1	16.6
1.0	2.0	3.0	2.7	2.9	3.1	4.8	7.6	9.2
1.0	2.0	5.0	1.3	1.6	1.6	2.9	4.3	8.7
1.0	2.0	10.0	0.8	0.7	0.8	1.2	2.1	4.1

[a] $I = 0.10\ mol\ dm^{-3}$.
[b] $I = 0.50\ mol\ dm^{-3}$.

Table 8. Pseudo-second-order rate constants (k_{obs}) for the oxidation of glutamine (Gln) by the sodium salts of disubstituted *N*-chlorobenzenesulphonamides (NCSBS) in aqueous perchloric acid at 303 K ($I = 0.30\ mol\ dm^{-3}$)

10^3[NCSBS]$_0$ (mol dm^{-3})	10^2[Gln]$_0$ (mol dm^{-3})	10^2[$HClO_4$] (mol dm^{-3})	$10\,k_{obs}$ (dm^3 mol^{-1} s^{-1}) for *i*-X-*j*-Y-$C_6H_3SO_2NaNCl$, where *i*-X-*j*-Y =					
			2,3-$(CH_3)_2$	2,4-$(CH_3)_2$	2,5-$(CH_3)_2$	2-CH_3-4-Cl	2,4-Cl_2	3,4-Cl_2
Effect of varying [NCSBS]$_0$								
0.5	2.0	3.0	4.6	4.8	5.9	6.8	15.9	14.3
1.0	2.0	3.0	2.8	4.0	4.7	5.4	15.5	13.7
2.0	2.0	3.0	2.5	3.7	4.5	5.3	14.9	13.4
4.0	2.0	3.0	1.9	3.0	4.3	5.0	14.8	13.3
1.0[a]	2.0	3.0	2.6	3.6	4.6	5.2	15.2	13.3
1.0[b]	2.0	3.0	3.2	4.2	4.9	5.6	15.8	14.7
Effect of varying [Gln]$_0$								
1.0	0.5	3.0	2.0	2.6	3.2	4.2	10.4	7.6
1.0	1.0	3.0	2.3	3.2	3.6	4.6	13.3	9.8
1.0	2.0	3.0	2.8	4.0	4.7	5.4	15.5	13.7
1.0	4.0	3.0	3.8	5.5	6.4	8.2	18.9	20.9
Effect of varying [$HClO_4$]								
1.0	2.0	1.0	7.4	10.0	10.6	11.8	28.6	28.3
1.0	2.0	2.0	4.9	6.2	6.9	7.9	21.4	17.1
1.0	2.0	3.0	2.8	4.0	4.7	5.4	15.5	13.7
1.0	2.0	5.0	2.3	2.7	3.0	4.2	9.7	9.5
1.0	2.0	10.0	1.7	1.9	2.2	2.8	6.4	6.1

[a] $I = 0.10\ mol\ dm^{-3}$.
[b] $I = 0.50\ mol\ dm^{-3}$.

where $K_2 = k_2/k_{-2}$. Then the rate of the reaction going through path 1 is given by

$$-d[NCSBS]/dt = k_3[NCSBS][Y] = K_2k_3[NCSBS]_0[NCSBS][S]/(1 + K_2[S]) \quad (3)$$

Table 9. Kinetic data for the oxidation of amino acids (AA) by the sodium salts of mono- and disubstituted *N*-chlorobenzenesulphonamides (NCSBS) in aqueous perchloric acid (the kinetic order in [NCSBS] was 2 in all the oxidations)

Oxidant	Order in	Asp	Glu	Asn	Gln
NCBS	[AA]	0.3	0.3	0.4	0.2
	[$HClO_4$]	−1.2	−1.0	−1.0	−1.1
NC4MBS	[AA]	0.3	0.3	0.4	0.3
	[$HClO_4$]	−1.1	−1.1	−1.0	−1.1
NC4EBS	[AA]	0.3	0.4	0.4	0.3
	[$HClO_4$]	−1.1	−1.0	−1.1	−1.1
NC4FBS	[AA]	0.3	0.3	0.3	0.3
	[$HClO_4$]	−1.2	−0.9	−0.5	−1.3
NC4CBS	[AA]	0.3	0.3	0.2	0.3
	[$HClO_4$]	−1.2	−1.4	−0.6	−1.0
NC4BBS	[AA]	0.4	0.2	0.2	0.2
	[$HClO_4$]	−0.8	−1.2	−0.6	−0.8
NC23DMBS	[AA]	0.3	0.3	0.2	0.3
	[$HClO_4$]	−1.2	−0.9	−0.8	−0.8
NC24DMBS	[AA]	0.4	0.3	0.3	0.3
	[$HClO_4$]	−0.8	−0.9	−0.8	−0.8
NC25DMBS	[AA]	0.5	0.4	0.3	0.3
	[$HClO_4$]	−1.2	−0.9	−0.9	−1.0
NC2M4CBS	[AA]	0.3	0.3	0.3	0.3
	[$HClO_4$]	−0.9	−1.0	−0.9	−0.8
NC24DCBS	[AA]	0.4	0.4	0.3	0.3
	[$HClO_4$]	−1.0	−1.0	−1.1	−1.0
NC34DCBS	[AA]	0.3	0.3	0.6	0.5
	[$HClO_4$]	−0.9	−0.8	−0.8	−0.8

If it is assumed that [NCSB]$_0$ [NCSBS] ≈ [NCSBS]^2, then the rate law (3) becomes

$$-d[NCSBS]/dt = K_2k_3[NCSBS]^2[S]/(1 + K_2[S]) \quad (4)$$

Rearranging Eqn (4), we have

$$-(d[NCSBS]/[NCSBS]^2)/dt = K_2k_3[S]/(1 + K_2[S]) \quad (5)$$

However, the left-hand side of Eqn (5) may be written as

$$-(d[NCSBS]/[NCSBS]^2)/dt = d(1/[NCSBS])/dt = k_{p1}$$

Hence Eqn (5) becomes

$$k_{p1} = K_2k_3[S]/(1 + K_2[S]) \quad (6)$$

We also have

$$[S] = K_1[SH^+]/[H^+] \quad (7)$$

Therefore, Eqn (6) takes the form

$$k_{p1} = K_1K_2k_3[SH^+]/([H^+] + K_1K_2[SH^+]) \quad (8)$$

If K_2 is small, then the rate law (6) will take the form

$$k_{p1} = K_2k_3[S] = K_1K_2k_3[SH^+]/[H^+] \quad (9)$$

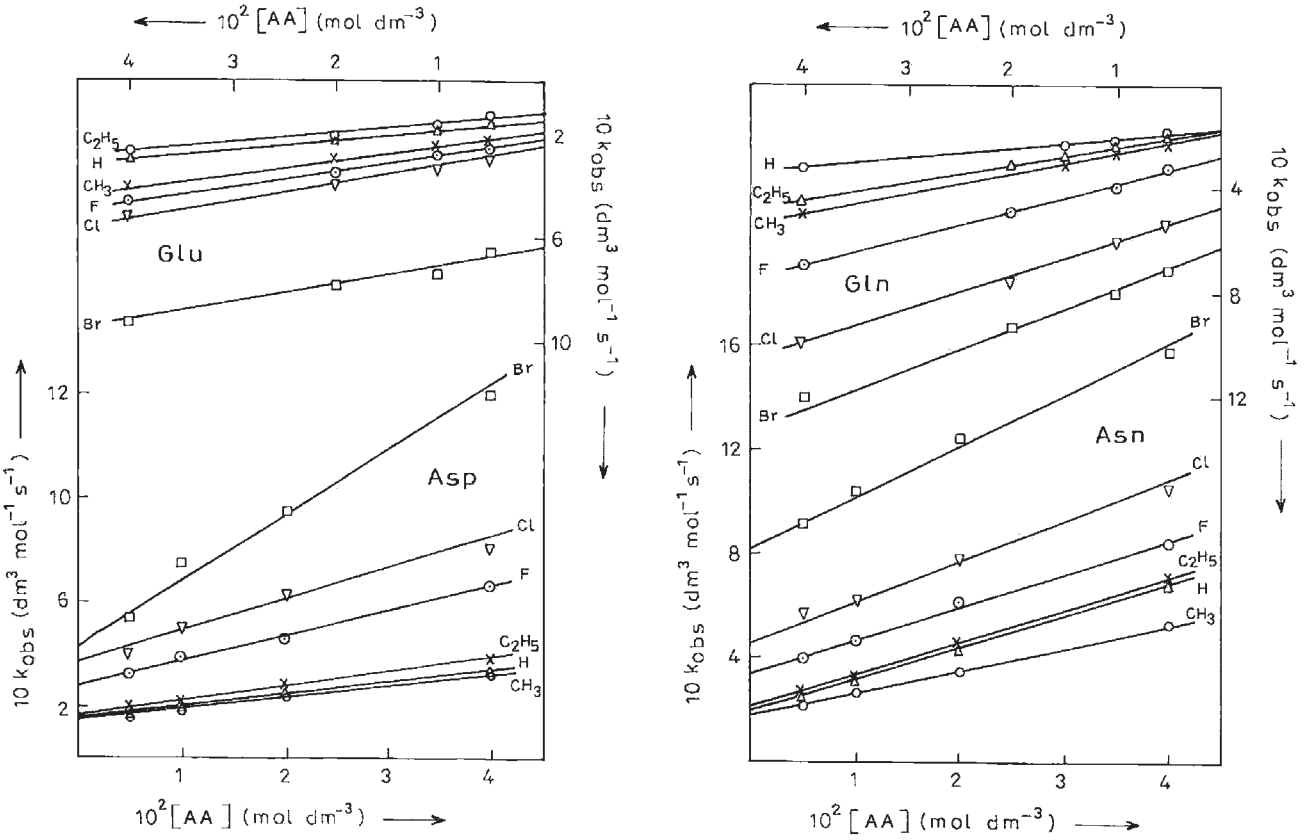

Figure 1. Plots of k_{obs} versus [AA]. 10^3[NCSBS] = 33.3[$HClO_4$] = 3.33I = 1.0 mol dm^{-3}; temperature = 303 K. NCSBS: 4-X-$C_6H_4SO_2NaNCl$, where X = H, CH_3, C_2H_5, F, Cl, Br

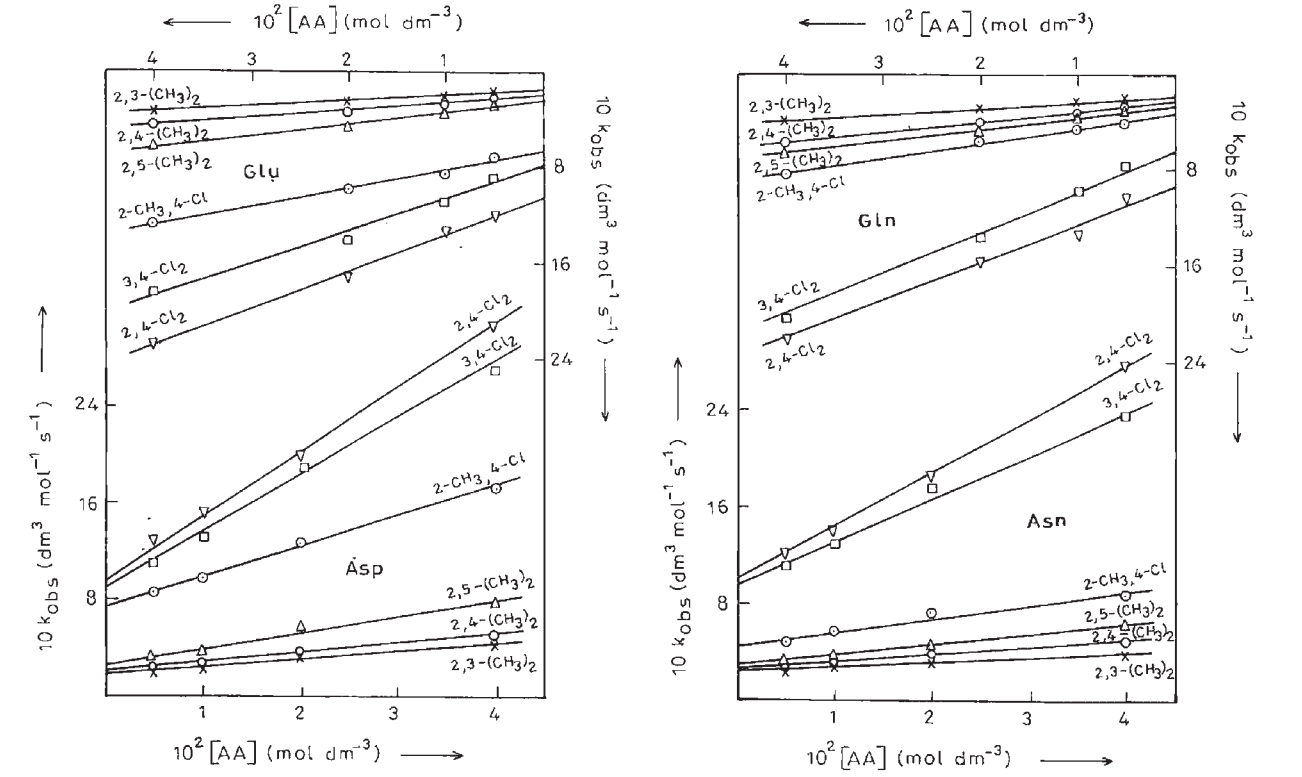

Figure 2. Plots of k_{obs} versus [AA]. 10^3[NCSBS] = 33.3[$HClO_4$] = 3.33I = 1.0 mol dm^{-3}; temperature = 303 K. NCSBS: *i*-X-*j*-Y-$C_6H_3SO_2NaNCl$, where *i*-X-*j*-Y = 2,3-$(CH_3)_2$, 2,4-$(CH_3)_2$, 2,5-$(CH_3)_2$, 2-CH_3-4-Cl, 2,4-Cl_2, 3,4-Cl_2

Path 1:

$$SH^+ \overset{K_1}{\rightleftharpoons} S + H^+ \quad \text{(fast)}$$

$$(ArSO_2NH_2Cl)^+ + S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{intermediate(Y)} \quad \text{(fast)}$$

$$Y + (ArSO_2NH_2Cl)^+ \overset{k_3}{\rightarrow} \text{products} \quad \text{(slow)}$$

Path 2:

$$2(ArSO_2NH_2Cl) + \overset{K_4}{\rightleftharpoons} \text{intermediate(Y')} + 2H^+ \quad \text{(fast)}$$

$$Y' \overset{k_5}{\rightarrow} ArSO_2NCl_2 + ArSO_2NH_2 \quad \text{(slow)}$$

$$ArSO_2NCl_2 + H_3O^+ \rightarrow H_2OCl^+ + ArSO_2NHCl \quad \text{(fast)}$$

$$H_2OCl^+ + S \rightarrow \text{products} \quad \text{(fast)}$$

$$ArSO_2NHCl + H^+ \rightarrow (ArSO_2NH_2Cl)^+ \quad \text{(fast)}$$

Scheme 1

The rate law for the reaction in path 2 was deduced in a similar way:

$$-(d[NCSBS]/[NCSBS]^2)/dt = K_4k_5/[H^+]^2$$

or

$$k_{p2} = K_4k_5/[H^+]^2 \quad (10)$$

The combined rate law for both the pathways is therefore given by

$$k_{obs} = (K_1K_2k_3[SH^+]/[H^+]) + (K_4k_5/[H^+]^2) \quad (11)$$

or

$$k_{obs} = (k[SH^+]/[H^+]) + (k'/[H^+]^2) \quad (12)$$

where $k = K_1K_2\ k_3$ and $k' = K_4\ k_5$

Table 10. Calculated constant *k* for path 1 of the oxidation of amino acids (AA) by the sodium salts of mono- and disubstituted *N*-chlorobenzenesulphonamides in aqueous perchloric acid

		$10\,k$ ($dm^3\,mol^{-1}\,s^{-1}$) for 4-X-$C_6H_4SO_2NaNCl$, where X =					
AA	Temperature (K)	H	CH_3	C_2H_5	F	Cl	Br
Asp	298	1.3	1.8	1.1	1.6	2.4	6.3
	303	1.8	2.1	2.2	3.9	4.4	7.5
	308	2.2	3.0	3.1	5.3	5.2	9.5
	313	3.6	4.1	5.2	6.3	8.4	10.4
Glu	298	1.2	1.4	1.4	1.4	1.6	3.9
	303	1.5	1.8	1.9	2.5	2.9	6.0
	308	3.1	3.4	3.3	4.7	5.0	9.0
	313	3.6	5.1	3.7	5.7	6.2	11.8
Asn	298	1.5	2.3	1.6	3.3	3.3	5.5
	303	2.6	2.7	2.2	4.6	5.2	8.0
	308	5.2	3.4	3.2	6.7	6.6	12.0
	313	6.4	3.9	3.6	8.4	8.2	16.0
Gln	298	1.2	2.0	1.3	2.5	2.1	2.9
	303	1.7	2.2	2.1	3.6	4.8	6.9
	308	2.4	3.2	2.4	5.7	6.3	8.5
	313	3.1	3.6	3.4	7.7	8.4	11.2
		$10\,k$ ($dm^3\,mol^{-1}\,s^{-1}$) for *i*-X-*j*-Y-$C_6H_3SO_2NaNCl$, where *i*-X-*j*-Y =					
		2,3-$(CH_3)_2$	2,4-$(CH_3)_2$	2,5-$(CH_3)_2$	2-CH_3-4-Cl	2,4-Cl_2	3,4-Cl_2
Asp	298	1.7	1.6	1.6	4.5	5.6	8.5
	303	2.0	2.3	3.9	7.3	12.5	10.3
	308	2.7	4.3	4.3	8.5	21.5	12.2
	313	4.2	4.7	5.1	9.2	29.8	18.1
Glu	298	1.3	1.3	2.3	1.9	12.6	4.3
	303	1.5	1.8	3.3	4.4	14.6	8.2
	308	2.6	3.0	3.9	5.9	17.6	10.2
	313	3.5	6.0	5.4	8.4	23.9	15.4
Asn	298	0.9	1.8	1.5	2.3	10.1	7.0
	303	1.4	2.3	2.8	3.9	13.8	11.8
	308	2.0	4.1	4.6	5.1	16.7	15.5
	313	4.4	6.5	6.2	9.8	22.9	20.2
Gln	298	2.0	1.6	1.9	3.1	6.0	6.2
	303	2.3	2.4	2.9	4.1	8.9	8.8
	308	3.2	4.7	4.6	4.9	10.4	10.2
	313	4.4	5.8	6.3	10.3	15.0	11.6

Table 11. Calculated constant k' for path 2 of the oxidation of amino acids (AA) by the sodium salts of mono- and disubstituted *N*-chlorobenzenesulphonamides in aqueous perchloric acid

AA	Temperature (K)	$10^4\ k'$ ($dm^3\ mol^{-1}\ s^{-1}$) for 4-X-$C_6H_4SO_2NaNCl$, where X =					
		H	CH_3	C_2H_5	F	Cl	Br
Asp	298	0.8	0.9	0.8	1.8	2.1	2.5
	303	1.4	1.3	1.4	2.2	2.9	3.1
	308	1.8	2.3	2.0	3.2	4.4	5.0
	313	2.2	2.7	3.1	4.3	5.4	6.0
Glu	298	0.9	0.8	0.7	1.3	1.1	3.6
	303	1.3	1.5	1.1	1.6	2.1	4.6
	308	1.7	2.1	2.0	2.7	3.0	6.2
	313	2.5	2.9	2.7	4.0	4.1	9.0
Asn	298	1.1	0.8	0.7	1.8	2.2	4.7
	303	1.7	1.4	1.4	2.7	4.1	6.3
	308	2.0	1.9	1.9	4.0	5.4	7.8
	313	2.4	2.3	2.6	5.2	7.7	11.5
Gln	298	0.9	0.7	0.9	1.2	2.3	4.1
	303	1.4	1.5	1.5	2.2	3.8	5.5
	308	2.0	2.2	2.2	4.0	4.4	9.0
	313	2.4	3.0	2.8	5.2	5.8	10.6
		$10^4\ k'$ ($dm^3\ mol^{-1}\ s^{-1}$) for *i*-X-*j*-Y-$C_6H_3SO_2NaNCl$, where *i*-X-*j*-Y =					
		2,3-$(CH_3)_2$	2,4-$(CH_3)_2$	2,5-$(CH_3)_2$	2-CH_3-4-Cl	2,4-Cl_2	3,4-Cl_2
Asp	298	1.0	1.5	1.7	4.2	7.2	7.2
	303	1.5	1.8	2.2	6.2	8.6	8.4
	308	2.1	3.0	2.9	9.7	16.3	13.3
	313	2.9	3.9	4.6	13.4	22.9	18.4
Glu	298	1.1	1.4	1.6	4.1	3.6	3.6
	303	1.4	1.7	2.0	4.4	6.9	6.3
	308	2.5	2.3	2.7	5.7	10.2	9.1
	313	4.1	3.8	3.2	8.5	15.0	11.7
Asn	298	1.5	1.5	2.1	2.7	4.8	5.1
	303	2.0	2.2	2.3	3.8	8.6	7.3
	308	3.1	2.7	2.7	6.0	13.2	13.1
	313	7.6	4.2	4.0	7.7	16.8	15.6
Gln	298	1.3	1.7	1.8	2.3	5.9	5.9
	303	1.5	2.0	2.5	2.7	9.2	6.5
	308	1.7	2.5	3.1	3.4	11.3	8.7
	313	3.5	3.4	4.0	5.0	14.9	13.4

The plots of k_{obs} versus [AA] were linear with finite intercepts on the ordinate (Figs 1 and 2), in conformity with the rate law (12). The constants k and k' were calculated from the slopes and intercepts of the plots, respectively, by inserting the values of $[H^+]$. These constants were used to recalculate the rate constants from the rate law (12) as $[H^+]$ was varied. The recalculated values agreed reasonably well with the experimental constants (data not shown), testing the validity of the rate law and providing support for the suggested mechanism. Further, k and k' were calculated at different temperatures by varying [AA] at each temperature (Tables 10 and 11). The activation parameters corresponding to these constants were also calculated from the plots of $\log k$ or $\log k'$ versus $1/T$ and $\log (k/T)$ or $\log (k'/T)$ versus $1/T$ (Tables 12–15).

The applicability of the Hammett equation was tested for the oxidation of all four amino acids by all of the monosubstituted oxidants. The plots of $\log k_i$ versus σ_p were reasonably linear (Figs 3–6) and the following relations were found to be valid:

Asp: $\log k = -0.551 + 1.270\sigma\ (r = 0.855)$
$\log k' = -3.752 + 1.011\sigma\ (r = 0.947)$

Glu: $\log k = -0.655 + 1.050\sigma\ (r = 0.784)$
$\log k' = -3.790 + 1.123\sigma\ (r = 0.817)$

Asn: $\log k = -0.477 + 1.24\sigma\ (r = 0.923)$
$\log k' = -3.670 + 1.607\sigma\ (r = 0.957)$

Gln: $\log k = -0.561 + 1.282\sigma\ (r = 0.874)$
$\log k' = -3.702 + 1.402\sigma\ (r = 0.917)$

The constancy of the $\Delta G^{\ddagger}$ values for paths 1 and 2 (Tables 12–15) indicated the operation of similar mechanisms in all cases. The formation of more ordered activated complexes is evident from the negative $\Delta S^{\ddagger}$

Table 12. Activation parameters for path 1 of the mechanism for the oxidations of amino acids (AA) by the sodium salts of *p*-substituted *N*-chlorobenzenesulphonamides in aqueous perchloric acid

		4-X-$C_6H_4SO_2NaNCl$, where X =					
AA	Parameter	H	CH_3	C_2H_5	F	Cl	Br
Asp	E_a (kJ mol^{-1})	51.3	40.4	75.5	62.8	65.6	29.9
	Log *A*	8.1	6.2	12.3	10.5	11.0	5.1
	$\Delta H^{\ddagger}$ (kJ mol^{-1})	48.8	38.4	75.0	61.9	63.4	29.3
	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	−98.4	−130.5	−10.5	−48.5	−42.5	−152.9
	$\Delta G^{\ddagger}$ (kJ mol^{-1})	78.6	78.0	78.1	76.6	76.3	74.9
Glu	E_a (kJ mol^{-1})	47.7	70.6	55.9	84.1	75.1	59.0
	Log *A*	7.4	11.5	8.9	13.9	12.4	9.8
	$\Delta H^{\ddagger}$ (kJ mol^{-1})	46.8	66.2	54.3	82.2	73.5	57.0
	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	−106.3	−40.7	−77.8	+14.5	−15.8	−58.7
	$\Delta G^{\ddagger}$ (kJ mol^{-1})	79.0	78.5	78.3	77.7	77.4	75.5
Asn	E_a (kJ mol^{-1})	70.1	65.0	47.9	60.0	54.9	57.9
	Log *A*	11.5	10.6	7.5	10.0	9.0	9.9
	$\Delta H^{\ddagger}$ (kJ mol^{-1})	69.0	65.5	46.3	59.6	54.7	55.5
	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	−28.6	−39.0	−89.8	−55.7	−75.7	−63.9
	$\Delta G^{\ddagger}$ (kJ mol^{-1})	78.1	77.5	73.4	76.2	75.6	74.9
Gln	E_a (kJ mol^{-1})	56.6	40.7	49.7	56.6	79.0	79.9
	Log *A*	9.0	6.5	7.9	9.3	13.3	13.7
	$\Delta H^{\ddagger}$ (kJ mol^{-1})	54.3	35.3	49.0	52.0	78.6	78.0
	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	−80.8	−139.2	−96.1	−81.9	+ 8.3	+ 9.4
	$\Delta G^{\ddagger}$ (kJ mol^{-1})	79.0	78.1	78.2	76.9	76.1	75.2

values. Further, the enthalpies and entropies of activations for the oxidations of all the four amino acids by all the *N*-chloroarylsulphonamides were correlated. The plots of $\Delta H^{\ddagger}$ (kJ mol^{-1}) versus $\Delta S^{\ddagger}$ (J K^{-1} mol^{-1}) corresponding to both *k* and *k*′ were linear (Figs 7–10). The following relations were found to be valid with isokinetic temperatures of 297 and 273 K (for Asp), 312 and 293 K (for Glu), 314 and 303 K (for Asn) and 298 and 311 K (for Gln), respectively, which are more or less in the temperature ranges employed in the present investigations (298–313 K):

Asp: Path 1: $\Delta H^{\ddagger} = 76.17 + 297\Delta S^{\ddagger}$ ($r = 0.997$)
Path 2: $\Delta H^{\ddagger} = 90.81 + 273\Delta S^{\ddagger}$ ($r = 0.966$)

Table 13. Activation parameters for path 1 of the mechanism for the oxidations of amino acids (AA) by the sodium salts of disubstituted *N*-chlorobenzenesulphonamides in aqueous perchloric acid

		i-X-*j*-Y-$C_6H_3SO_2NaNCl$, where *i*-X-*j*-Y =					
AA	Parameter	2,3-$(CH_3)_2$	2,4-$(CH_3)_2$	2,5-$(CH_3)_2$	2-CH_3-4-Cl	2,4-Cl_2	3,4-Cl_2
Asp	E_a (kJ mol^{-1})	52.8	62.1	81.6	43.6	103.0	48.7
	Log *A*	8.4	10.1	13.6	7.4	17.8	8.4
	$\Delta H^{\ddagger}$ (kJ mol^{-1})	50.9	61.0	78.9	40.7	102.4	44.8
	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	−90.5	−55.8	+ 7.7	−113.2	+ 94.8	−96.8
	$\Delta G^{\ddagger}$ (kJ mol^{-1})	78.3	77.9	76.5	75.0	73.7	74.1
Glu	E_a (kJ mol^{-1})	80.4	70.9	41.4	86.1	36.1	68.0
	Log *A*	13.0	11.5	6.7	14.5	6.4	11.7
	$\Delta H^{\ddagger}$ (kJ mol^{-1})	76.3	67.7	38.4	85.1	35.7	67.4
	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	−9.0	−35.8	−127.5	+29.1	−124.0	−24.6
	$\Delta G^{\ddagger}$ (kJ mol^{-1})	79.0	78.6	77.0	76.3	73.2	74.8
Asn	E_a (kJ mol^{-1})	78.0	70.6	78.0	73.6	42.2	64.3
	Log *A*	12.6	11.5	12.6	12.1	7.4	11.1
	$\Delta H^{\ddagger}$ (kJ mol^{-1})	77.2	70.5	77.6	71.6	39.4	57.7
	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	−6.6	−24.5	+ 0.6	−16.6	−112.4	−53.4
	$\Delta G^{\ddagger}$ (kJ mol^{-1})	79.2	77.9	77.4	76.6	73.5	73.9
Gln	E_a (kJ mol^{-1})	37.7	80.3	66.9	73.9	48.0	48.2
	Log *A*	5.9	13.2	11.0	12.3	8.1	8.1
	$\Delta H^{\ddagger}$ (kJ mol^{-1})	36.3	79.3	64.8	73.1	47.9	47.9
	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	−137.4	+4.6	−41.4	−10.9	−87.9	−88.2
	$\Delta G^{\ddagger}$ (kJ mol^{-1})	77.9	77.8	77.3	76.4	74.6	74.7

Table 14. Activation parameters for path 2 of the mechanism for the oxidations of amino acids (AA) by the sodium salts of *p*-substituted *N*-chlorobenzenesulphonamides in aqueous perchloric acid

		4-X-$C_6H_4SO_2NaNCl$, where X =					
AA	Parameter	H	CH_3	C_2H_5	F	Cl	Br
Asp	E_a (kJ mol^{-1})	52.7	54.7	64.7	50.5	47.5	52.5
	Log A	5.2	5.5	7.3	5.0	4.7	5.6
	$\Delta H^{\ddagger}$ (kJ mol^{-1})	50.3	48.5	62.5	42.3	43.5	47.9
	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	−153.5	−160.1	−112.5	−175.2	−170.5	−154.5
	$\Delta G^{\ddagger}$ (kJ mol^{-1})	96.7	96.9	96.7	95.5	94.7	94.4
Glu	E_a (kJ mol^{-1})	50.8	64.7	68.2	54.4	73.6	47.2
	Log A	4.9	7.3	7.8	5.6	8.9	4.8
	$\Delta H^{\ddagger}$ (kJ mol^{-1})	49.9	58.0	65.1	52.4	73.5	47.1
	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	−154.6	−126.6	−106.6	−144.6	−73.3	−153.5
	$\Delta G^{\ddagger}$ (kJ mol^{-1})	96.8	96.5	97.4	96.2	95.7	93.5
Asn	E_a (kJ mol^{-1})	56.9	53.3	74.8	49.8	71.4	42.6
	Log A	6.1	5.4	9.1	5.0	8.9	4.1
	$\Delta H^{\ddagger}$ (kJ mol^{-1})	55.7	51.6	73.0	47.9	67.4	40.0
	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	−134.5	−149.5	−78.2	−155.6	−87.8	−174.4
	$\Delta G^{\ddagger}$ (kJ mol^{-1})	96.2	96.6	96.6	95.0	94.0	92.9
Gln	E_a (kJ mol^{-1})	54.9	89.7	65.7	90.5	54.9	54.1
	Log A	5.6	11.7	7.5	11.9	6.1	6.1
	$\Delta H^{\ddagger}$ (kJ mol^{-1})	52.9	84.1	64.9	90.4	53.7	48.9
	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	−145.0	−39.0	−104.0	−16.8	−133.4	−147.0
	$\Delta G^{\ddagger}$ (kJ mol^{-1})	96.7	96.5	96.5	95.5	94.1	93.2

Glu: Path 1: $\Delta H^{\ddagger} = 77.52 + 312\Delta S^{\ddagger}$ ($r = 0.994$)
Path 2: $\Delta H^{\ddagger} = 94.12 + 293\Delta S^{\ddagger}$ ($r = 0.993$)
Asn: Path 1: $\Delta H^{\ddagger} = 78.00 + 314\Delta S^{\ddagger}$ ($r = 0.994$)
Path 2: $\Delta H^{\ddagger} = 94.78 + 303\Delta S^{\ddagger}$ ($r = 0.994$)
Gln: Path 1: $\Delta H^{\ddagger} = 76.36 + 298\Delta S^{\ddagger}$ ($r = 0.996$)
Path 2: $\Delta H^{\ddagger} = 95.98 + 311\Delta S^{\ddagger}$ ($r = 0.996$)

CONCLUSION

The effect of substituents in the benzene ring of the oxidant on the E_a for the oxidation of amino acids was analysed by optimizing E_a values with reference to log A of the parent oxidant (NCSBS) according to the equation $E_a = 2.303RT(\log A - \log k)$. Similarly, log A values were

Table 15. Activation parameters for path 2 of the mechanism for the oxidations of amino acids (AA) by the sodium salts of disubstituted *N*-chlorobenzenesulphonamides in aqueous perchloric acid

		i-X-*j*-Y-$C_6H_3SO_2NaNCl$, where *i*-X-*j*-Y =					
AA	Parameter	2,3-$(CH_3)_2$	2,4-$(CH_3)_2$	2,5-$(CH_3)_2$	2-CH_3-4-Cl	2,4-Cl_2	3,4-Cl_2
Asp	E_a (kJ mol^{-1})	49.2	57.2	54.4	59.5	64.4	49.2
	Log A	4.7	6.1	5.7	7.1	8.0	5.4
	$\Delta H^{\ddagger}$ (kJ mol^{-1})	49.1	57.1	52.1	59.4	57.6	47.2
	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	−156.2	−128.2	−143.0	−110.4	−113.7	−148.2
	$\Delta G^{\ddagger}$ (kJ mol^{-1})	96.4	96.0	95.4	92.9	92.0	92.1
Glu	E_a (kJ mol^{-1})	73.5	60.7	32.5	49.3	80.7	71.0
	Log A	8.8	6.7	1.9	5.2	10.8	9.1
	$\Delta H^{\ddagger}$ (kJ mol^{-1})	69.8	60.5	31.4	44.7	76.0	70.6
	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	−88.4	−118.1	−212.3	−161.8	−53.8	−73.4
	$\Delta G^{\ddagger}$ (kJ mol^{-1})	96.6	96.3	95.7	93.7	92.1	92.9
Asn	E_a (kJ mol^{-1})	101.0	55.5	61.4	56.9	72.2	63.8
	Log A	13.7	5.9	7.0	6.4	9.4	7.9
	$\Delta H^{\ddagger}$ (kJ mol^{-1})	100.9	52.8	56.1	53.6	71.8	59.6
	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	+17.1	−140.7	−129.8	−133.5	−66.7	−108.1
	$\Delta G^{\ddagger}$ (kJ mol^{-1})	95.7	95.4	95.3	94.0	92.0	92.4
Gln	E_a (kJ mol^{-1})	68.8	40.8	44.0	46.4	51.6	50.1
	Log A	8.0	3.3	4.0	4.5	5.9	5.5
	$\Delta H^{\ddagger}$ (kJ mol^{-1})	63.6	40.7	40.5	45.1	49.4	46.5
	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	−108.3	−181.7	−180.3	−164.6	−140.1	−152.6
	$\Delta G^{\ddagger}$ (kJ mol^{-1})	96.4	95.7	95.1	95.0	91.9	92.7

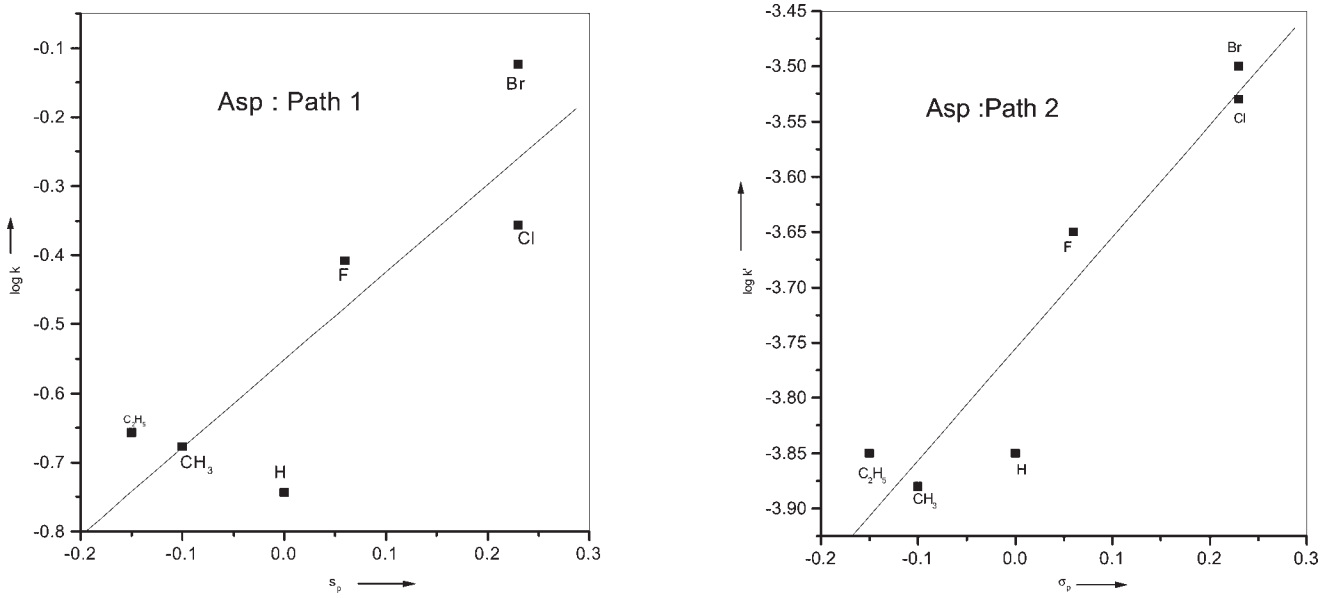

Figure 3. Plots of log k versus σ_p and log k' versus σ_p for oxidation of Asp by NCSBS. NCSBS: 4-X-$C_6H_4SO_2NaNCl$, where X = H, CH_3, C_2H_5, F, Cl, Br

optimized with reference to E_a of the parent oxidant through the equation $\log A = \log k + E_a/2.303RT$. The optimized values are shown in Tables 16 and 17. It is evident from the data that the the rates of oxidation and the E_a values are least affected by the introduction of electron-donating groups into the benzene ring, whereas the introduction of electron-withdrawing groups such as halides into the ring increase the rates of oxidation and lower E_a. Enthalpies of activation have similar trends. The log A values have the reverse trend. Hence the study revealed that the introduction of electron-withdrawing groups such as halides into the benzene ring eased the release of Cl^+ from the reagent and hence increased the oxidizing strengths of the *N*-chloroarylsulphonamides.

EXPERIMENTAL

Materials and methods

Benzenesulphonamide (BSA) and substituted benzenesulphonamides (SBSA), namely 4-methylbenzenesulphonamide (4MBSA), 4-ethylbenzenesulphonamide (4EBSA),

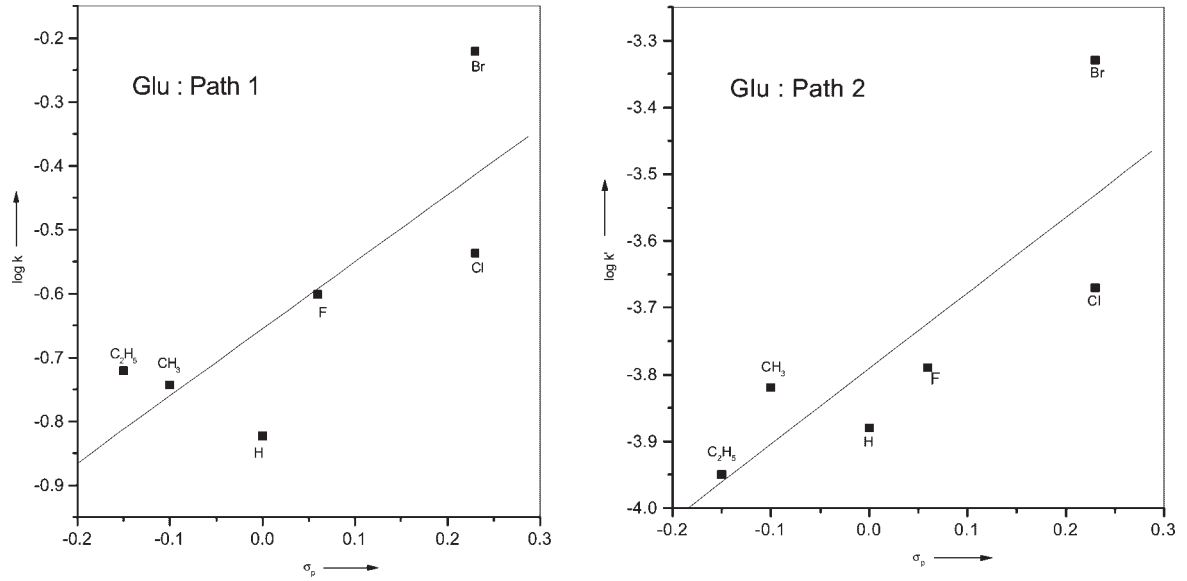

Figure 4. Plots of log k versus σ_p and log k' versus σ_p for oxidation of Glu by NCSBS. NCSBS: 4-X-$C_6H_4SO_2NaNCl$, where X = H, CH_3, C_2H_5, F, Cl, Br

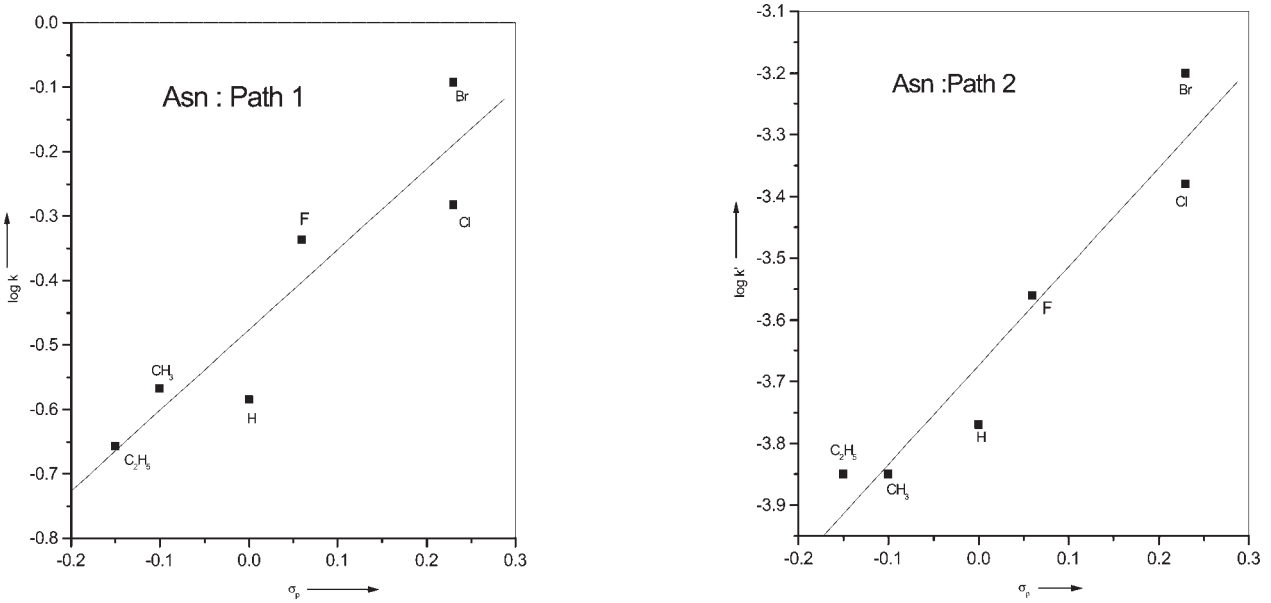

Figure 5. Plots of log k versus σ_p and log k' versus σ_p for oxidation of Asn by NCSBS. NCSBS: 4-X-$C_6H_4SO_2NaNCl$, where X = H, CH_3, C_2H_5, F, Cl, Br

4-fluorobenzenesulphonamide (4FBSA), 4-chlorobenzenesulphonamide (4CBSA), 4-bromobenzenesulphonamide (4BBSA) 2,3-dimethylbenzenesulphonamide (23DMBSA), 2,4-dimethylbenzenesulphonamide (24DMBSA), 2,5-dimethylbenzenesulphonamide (25DMBSA), 2-methyl-4-chlorobenzenesulphonamide (2M4CBSA), 2,4-dichlorobenzenesulphonamide (24DCBSA) and 3,4-dichlorobenzenesulphonamide (34DCBSA), were prepared by chlorosulphonation of the respective substituted benzenes to the corresponding sulphonyl chlorides and subsequent conversion of the latter to the respective substituted benzenesulphonamides by procedures reported earlier[10–13]. The sulphonamides were recrystallized to constant melting-points from dilute ethanol. The purities of all the sulphonamides were further checked by estimating the amount of sulphur present in them. The observed melting-points (°C)

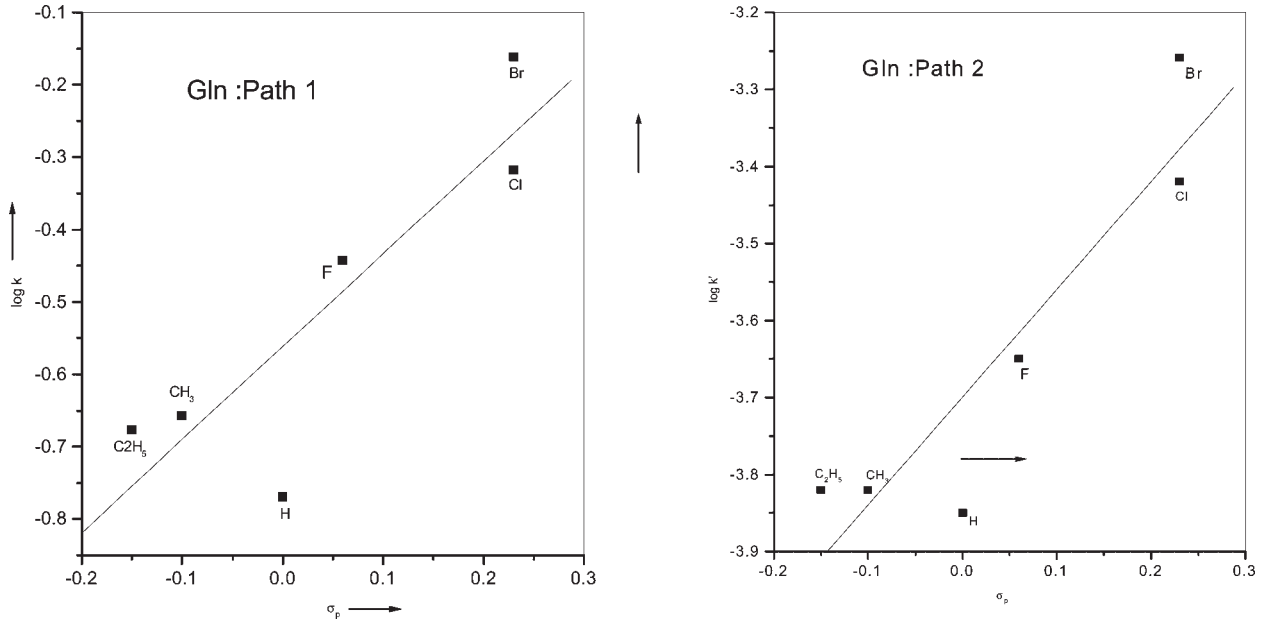

Figure 6. Plots of log k versus σ_p and log k' versus σ_p for oxidation of Gln by NCSBS. NCSBS: 4-X-$C_6H_4SO_2NaNCl$, where X = H, CH_3, C_2H_5, F, Cl, Br

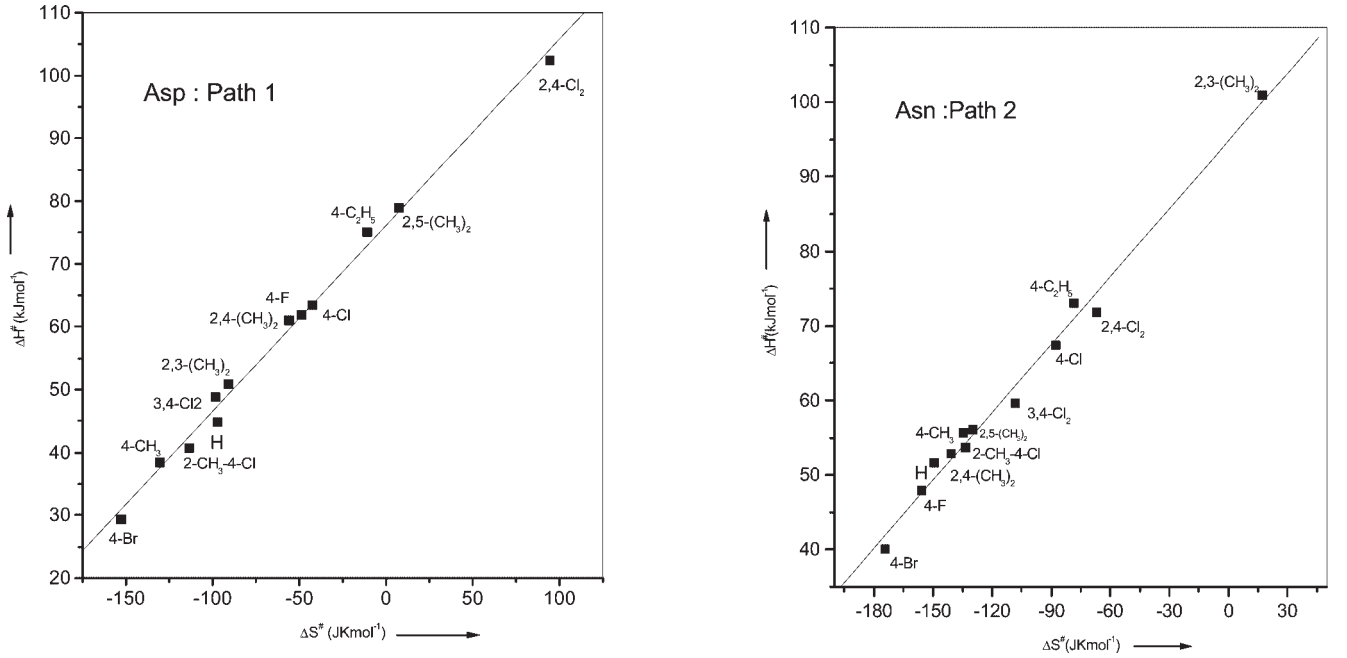

Figure 7. Plot of $\Delta H^{\neq}$ versus $\Delta S^{\neq}$ for oxidation of Asp by NCSBS. NCSBS: *i*-X-$C_6H_4SO_2NaNCl$, where *i*-X = 4-H, 4-CH_3, 4-C_2H_5, 4-F, 4-Cl 4-Br, and *i*-X-*j*-Y-$C_6H_3SO_2NaNCl$, where *i*-X-*j*-Y = 2,3-$(CH_3)_2$, 2,4-$(CH_3)_2$, 2,5-$(CH_3)_2$, 2-CH_3-4-Cl, 2,4-Cl_2, 3,4-Cl_2

of the arylsulphonamides and the literature values (in parentheses) are BSA 152 (150–152), 4MBSA 138 (138–139), 4EBSA 99 (99–100), 4FBSA 125 (124–127), 4CBSA 145 (145–147), 4BBSA 162 (162), 23DMBSA 138–140, 24DMBSA 140–142, 25DMBSA 149–151, 2M4CBSA 180–182 (184–185), 24DCBSA 178 (179–180) and 34DCBSA 141.

The SBSA were then *N*-chlorinated as follows to give sodium salts of substituted *N*-chlorobenzenesulphonamides (NCSBS), namely, the sodium salts of *N*-chlorobenzenesulphonamide (NCBS), *N*-chloro-4-methylbenzenesulphonamide (NC4MBS), *N*-chloro-4-ethylbenzenesulphonamide (NC4EBS), *N*-chloro-4-fluorobenzenesulphonamide (NC4FBS), *N*-chloro-4-chloro-

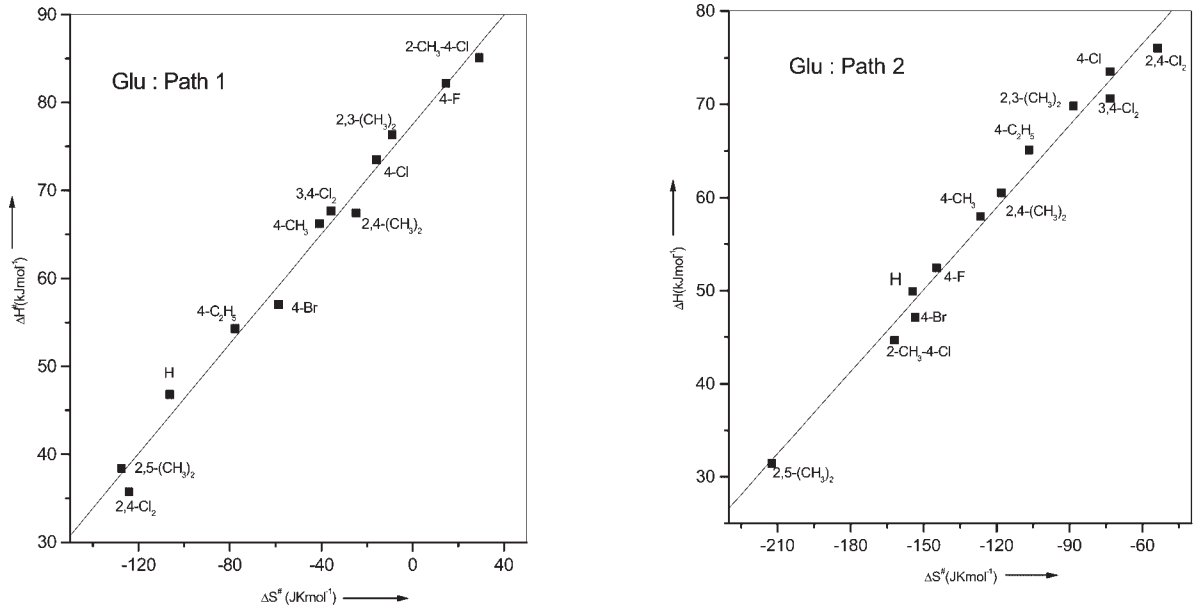

Figure 8. Plot of $\Delta H^{\neq}$ versus $\Delta S^{\neq}$ for oxidation of Glu by NCSBS. NCSBS: *i*-X-$C_6H_4SO_2NaNCl$, where *i*-X = 4-H, 4-CH_3, 4-C_2H_5, 4-F, 4-Cl 4-Br, and *i*-X-*j*-Y-$C_6H_3SO_2NaNCl$, where *i*-X-*j*-Y = 2,3-$(CH_3)_2$, 2,4-$(CH_3)_2$, 2,5-$(CH_3)_2$, 2-CH_3-4-Cl, 2,4-Cl_2, 3,4-Cl_2

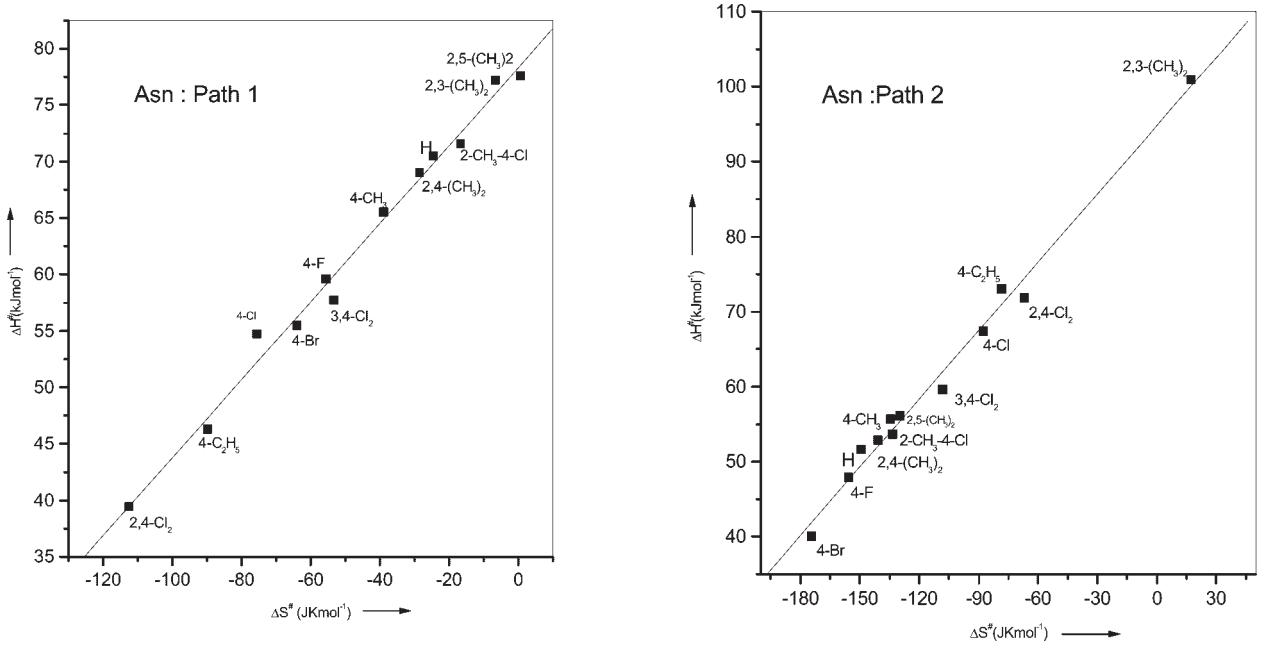

Figure 9. Plot of $\Delta H^{\neq}$ versus $\Delta S^{\neq}$ for oxidation of Asn by NCSBS. NCSBS: *i*-X-$C_6H_4SO_2NaNCl$, where *i*-X = 4-H, 4-CH_3, 4-C_2H_5, 4-F, 4-Cl 4-Br, and *i*-X-*j*-Y-$C_6H_3SO_2NaNCl$, where *i*-X-*j*-Y = 2,3-$(CH_3)_2$, 2,4-$(CH_3)_2$, 2,5-$(CH_3)_2$, 2-CH_3-4-Cl, 2,4-Cl_2, 3,4-Cl_2

benzenesulphonamide (NC4CBS), *N*-chloro-4-bromobenzenesulphonamide (NC4BBS), *N*-choro-2,3-dimethylbenzenesulphonamide (NC23DMBS), *N*-choro-2,4-dimethylbenzenesulphonamide (NC24DMBS), *N*-chloro-2,5-dimethylbenzenesulphonamide (NC25DMBS), *N*-chloro-2-methyl-4-chlorobenzenesulphonamide (NC2M4 CBS), *N*-chloro-2,4-dichlorbenzene-sulphonamide (NC24 DCBS) and *N*-chloro-3,4-dichlorobenzenesulphonamide (NC34DCBS). Pure chlorine gas was bubbled through clear solutions of SBSA in 4 M NaOH at 70 °C for about 1 h. The precipitated sodium salts of NCSBS were filtered, washed, dried and recrystallized from water. The purity of

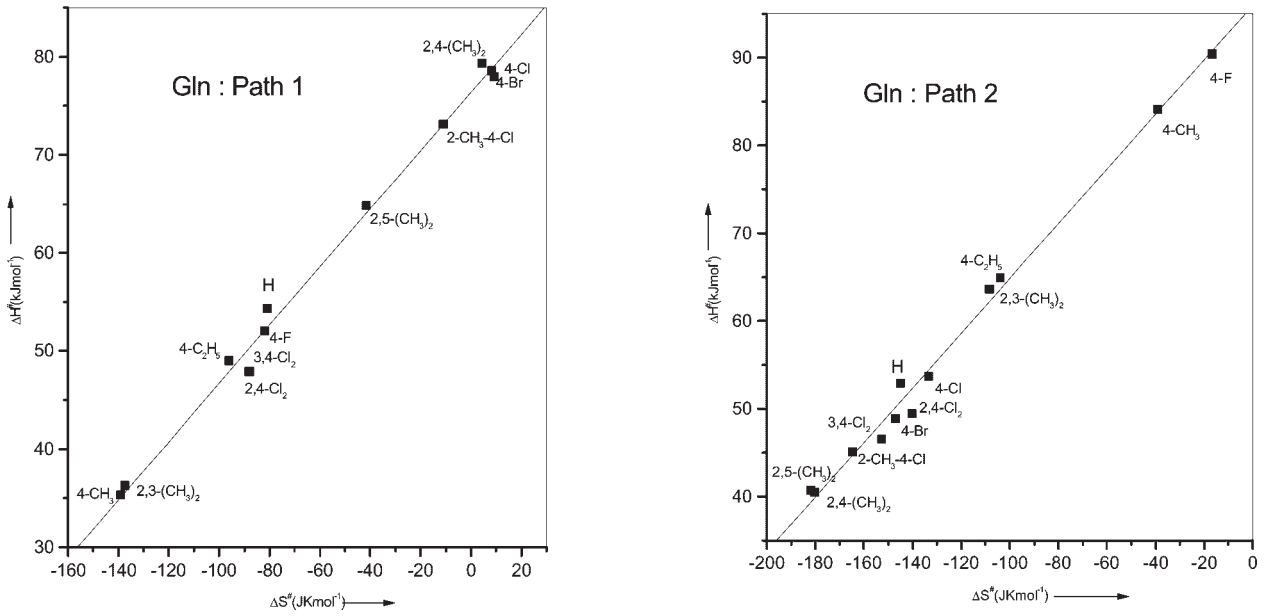

Figure 10. Plot of $\Delta H^{\neq}$ versus $\Delta S^{\neq}$ for oxidation of Gln by NCSBS. NCSBS: *i*-X-$C_6H_4SO_2NaNCl$, where *i*-X = 4-H, 4-CH_3, 4-C_2H_5, 4-F, 4-Cl 4-Br, and *i*-X-*j*-Y-$C_6H_3SO_2NaNCl$, where *i*-X-*j*-Y = 2,3-$(CH_3)_2$, 2,4-$(CH_3)_2$, 2,5-$(CH_3)_2$, 2-CH_3-4-Cl, 2,4-Cl_2, 3,4-Cl_2

Table 16. Optimized values of E_a, Log A and $\Delta S^{\ddagger}$ for path 1 of the mechanism for the oxidation of amino acids (AA) by the sodium salts of mono- and disubstituted *N*-chlorobenzenesulphonamides in aqueous perchloric acid

		4-X-$C_6H_4SO_2NaNCl$, where X =					
Parameter	AA	H	CH_3	C_2H_5	F	Cl	Br
E_a (kJ mol^{-1})	Asp	51.3	50.9	50.8	49.3	49.0	47.7
	Glu	47.7	47.2	47.1	46.4	46.0	44.2
	Asn	70.1	70.0	70.5	68.7	68.4	67.3
	Gln	56.6	56.0	56.1	54.8	54.1	53.1
Log A	Asp	8.1	8.2	8.2	8.4	8.5	8.7
	Glu	7.4	7.5	7.5	7.6	7.7	8.0
	Asn	11.5	11.5	11.4	11.7	11.8	12.0
	Gln	9.0	9.1	9.1	9.3	9.4	9.6
$\Delta S^{\ddagger}$ (JK^{-1} mol^{-1})	Asp	−98.4	−96.2	−97.0	−91.9	−90.5	−86.3
	Glu	−106.3	−104.8	−104.4	−101.8	−101.2	−94.8
	Asn	−28.6	−28.3	−31.7	−23.9	−22.7	−19.3
	Gln	−80.8	−77.7	−78.3	−74.0	−71.7	−68.3
		i-X-*j*-Y-$C_6H_3SO_2NaNCl$, where *i*-X-*j*-Y =					
		2,3-$(CH_3)_2$	2,4-$(CH_3)_2$	2,5-$(CH_3)_2$	2-CH_3-4-Cl	2,4-Cl_2	3,4-Cl_2
E_a (kJ mol^{-1})	Asp	51.1	50.6	49.4	47.8	46.5	46.9
	Glu	47.7	47.2	45.7	45.0	42.0	42.4
	Asn	72.2	70.4	69.9	69.2	65.9	66.3
	Gln	55.9	55.8	55.3	54.4	52.5	52.5
Log A	Asp	8.1	8.2	8.4	8.7	8.9	8.8
	Glu	7.4	7.5	7.7	7.9	8.4	8.1
	Asn	11.3	11.5	11.6	11.7	12.3	12.2
	Gln	9.0	9.0	9.1	9.3	9.6	9.6
$\Delta S^{\ddagger}$ (JK^{-1} mol^{-1})	Asp	−97.4	−96.1	−91.9	−86.5	−82.1	−83.6
	Glu	−105.2	−103.5	−98.6	−95.6	−86.3	−91.1
	Asn	−32.2	−28.1	−26.5	−23.7	−13.2	−14.5
	Gln	−77.5	−77.4	−75.6	−72.6	−66.3	−66.3

all the *N*-chloro compounds was checked by estimating the amounts of active chlorine present in them and by determining their melting-points. The observed melting-points (°C) and the literature values (in parentheses) are NCBS 172–173 (170–173), NC4MBS 168–169 (167–170), NC4EBS 194, NC4FBS 198, NC4CBS 191 (190), NC4BBS 179 (178), NC23DMBS 167, NC24DMBS 154, NC25DMBS 192, NC2M4CBS 172, NC24DCBS 210 and NC34DCBS 192. Both the SBSA and NCSBS were characterized by their infrared and NMR spectra.[10,11] Aqueous stock solutions of these compounds (0.01 mol dm^{-3}) were prepared in doubly distilled water, standardized by the iodimetric method and preserved in dark bottles to prevent their photochemical deterioration.

Pure samples of amino acids (aspartic acid, glutamic acid, aspargine and glutamine) (CDH, India) were employed. They were further assayed by the acetic acid–perchloric acid method.[12] Aqueous stock solutions of these compounds (0.10 mol dm^{-3}) were used. All other reagents employed were of the accepted grades of purity. The ionic strength of the medium was maintained at 0.30 mol dm^{-3} using a concentrated aqueous solution of sodium nitrate (Merck).

Stoichiometry and product analysis

The stoichiometry of amino acid–NCSBS oxidations was determined by equilibrating varying ratios of [NCSBS] to [AA] in aqueous $HClO_4$ at room temperature. The major products of the oxidations were the corresponding aldehydes. The observed 1:1 stoichiometry may be represented by the following equation:

$$ArSO_2NCl^- + RCH(NH_3^+)COO^- + H_2O \rightarrow ArSO_2NH_2 + RCHO + Cl^- + NH_3 + CO_2$$

where Ar = 4-XC_6H_4 (X = H, CH_3, C_2H_5, F, Cl or Br) and *i*-X-*j*-Y-C_6H_3 [*i*-X-*j*-Y = 2,3-$(CH_3)_2$, 2,4-$(CH_3)_2$, 2,5-$(CH_3)_2$, 2-CH_3-4-Cl, 2,4-Cl_2 or 3,4-Cl_2] and R = CH_2COOH (Asp), CH_2CH_2COOH (Glu), CH_2CONH_2 (Asn) or $CH_2CH_2CONH_2$ (Gln).

In a typical experiment, a mixture of aspartic acid (0.02 mol dm^{-3}), *N*-chloro-4-chlorobenzenesulphonamide (0.001 mol dm^{-3}) and perchloric acid (0.03 mol dm^{-3}) was made up to 50 ml with water. The mixture was allowed to stand for 24 h in the dark to ensure completion of reaction. It was then treated with an

Table 17. Optimized values of E_a Log A and $\Delta S^{\ddagger}$ for path 2 of the mechanism for the oxidation of amino acids (AA) by the sodium salts of mono- and disubstituted *N*-chlorobenzenesulphonamides in aqueous perchloric acid

Parameter	AA	4-X-$C_6H_4SO_2NaNCl$, where X = H	CH_3	C_2H_5	F	Cl	Br
E_a (kJ mol^{-1})	Asp	52.7	52.6	52.7	50.9	50.3	50.1
	Glu	50.8	50.4	51.5	50.4	49.7	47.5
	Asn	56.9	57.1	57.1	55.5	54.5	53.4
	Gln	54.9	54.7	54.7	53.7	52.3	51.4
Log A	Asp	5.2	5.1	5.2	5.4	5.5	5.5
	Glu	4.9	4.9	4.7	5.0	5.1	5.4
	Asn	6.1	5.9	5.9	6.2	6.4	6.6
	Gln	5.6	5.7	5.6	5.8	6.0	6.2
$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	Asp	−153.5	−154.1	−153.5	−148.5	−146.6	−146.2
	Glu	−154.6	−153.5	−157.0	−152.9	−151.2	−143.9
	Asn	−134.6	−135.7	−135.7	−130.4	−126.9	−123.3
	Gln	−145.0	−143.8	−143.8	−140.5	−133.5	−133.0
	AA	*i*-X-*j*-Y-$C_6H_3SO_2NaNCl$, where *i*-X-*j*-Y = 2,3-$(CH_3)_2$	2,4-$(CH_3)_2$	2,5-$(CH_3)_2$	2-CH_3-4-Cl	2,4-Cl_2	3,4-Cl_2
E_a (kJ mol^{-1})	Asp	51.8	51.3	50.8	48.1	47.3	47.4
	Glu	50.8	50.4	49.8	47.9	46.7	47.0
	Asn	57.4	56.0	55.9	54.7	52.6	53.0
	Gln	54.7	53.9	53.4	53.1	50.1	50.9
Log A	Asp	5.2	5.3	5.4	5.8	6.0	6.0
	Glu	4.9	5.0	5.1	5.4	5.6	5.6
	Asn	6.1	6.1	6.1	6.3	6.7	6.6
	Gln	5.6	5.8	5.9	5.9	6.4	6.3
$\Delta S^{\ddagger}$ (JK^{-1} mol^{-1})	Asp	−152.2	−150.6	−148.9	−140.3	−137.6	−138.0
	Glu	−154.1	−152.9	−151.2	−144.5	−140.8	−141.7
	Asn	−132.8	−132.8	−131.7	−127.5	−120.6	−121.9
	Gln	−143.6	−141.5	−139.5	−139.0	−128.6	−131.5

excess of a saturated solution of 2,4-dinitrophenylhydrazine and set aside for 10 h. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried and recrystallized from ethanol. The product was found to be identical (melting-point) with an authentic sample of the DNP of formylacetic acid. In similar experiments with other amino acids, the corresponding carbonyl compounds were identified as their DNPs of carbonyl compounds. In all cases, carbon dioxide and ammonia were detected using baryta water and Nessler's reagent, respectively. The presence of aldehydes or ketones were also confirmed by spot tests. The reduction products, SBSA, were identified by TLC using light petroleum–chloroform–butanol (2:2:1, v/v/v) as the solvent system and iodine as spray reagent.[14] The R_f values were 0.88, 0.91, 0.94, 0.93, 0.91, 0.84, 0.91, 0.96, 0.93, 0.95, 0.91 and 0.94 for BSA, 4MBSA, 4EBSA, 4FBSA, 4CBSA, 4BBSA, 23DMBSA, 24DMBSA, 25DMBSA, 2M4CBSA, 24DCBSA and 34DCBSA, respectively. These R_f values of the reduced SBSA were virtually identical with the values of the corresponding pure SBSA.

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