Kinetics and mechanisms of oxidation of carbohydrazide by N-chloro and N-bromo benzenesulphonamides and hypochlorite ion in aqueous perchloric acid and buffered media

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Kinetics of oxidation of carbohydrazide (CH) by N-chloro- and N-bromo-benzenesulphonamides and hypochlorite ion have been studied in aqueous perchloric acid and buffered media under varying conditions. In aq. perchloric acid the rates first decrease, then remain nearly constant and finally increase with increase in $[H^+]$ giving inverted bell shaped rate—$[H^+]$ profiles in all the cases. The reaction is first order in [oxidant] in all the ranges of $[H^+]$, with all the three oxidants. But the rate dependence in [substrate] is $[H^+]$ dependent. It shows varying orders ranging from fractional to first order. Addition of benzenesulphonamide, or the variation in either ionic strength or dielectric constant of the medium has no significant effect on the rates of oxidations, in all the cases. In buffered media also the reaction is first order in [oxidant], fractional order to first order in [CH], but is independent of pH. Two-pathway mechanisms have been considered to explain the observed results. The rate-limiting steps have been identified and the coefficients of these steps are calculated at different temperatures and hence the corresponding activation parameters. The rate constants predicted from the rate laws are in reasonable agreement with the experimental values.

Although a lot of work has been reported on the solid complexes of hydrazine and its derivatives, very little is known of their reactions in solution, especially on mechanistic aspects. In continuation of our earlier work[1-7] on the kinetics of oxidation of hydrazine and its derivatives, we report herein the kinetic results on the oxidation of carbohydrazide by N-chloro- and N-bromo-benzenesulphonamides (chloramine-B and bromamine-B) and hypochlorite in aqueous perchloric acid and buffered media under varying conditions.

Materials and Methods

Chloramine-B (CAB) and bromamine-B (BAB) were prepared in the laboratory by literature methods. Aqueous solution of hypochlorite was obtained by the stoichiometric reaction between Cl_2 and NaOH under cold conditions and the resulting solution was standardised.

Carbohydrazide (CH) was prepared by mixing diethyl carbonate and 85% hydrazine hydrate in 1:2.2 molar ratio, removing alcohol and water formed by distillation. Crystals of carbohydrazide which separated out on cooling the residual liquid were purified by recrystallization from water. The purity of the compound was checked by determining its melting point (154°C) and by nitrogen estimation.

Aqueous stock solution (0.50 mol dm^{-3}) of carbohydrazide was used. All other reagents used were of AR grade. Preliminary studies of the reactions showed that the variation in ionic strength of the medium had no significant effect on the rates of the reactions.
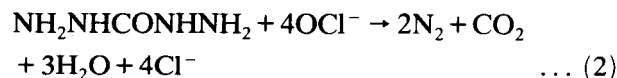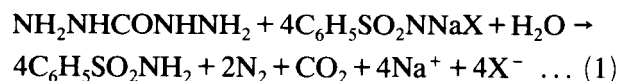
Kinetic measurement

The kinetic runs were carried out under pseudo-first order conditions with [substrate] > > [oxidant] (10-100 fold excess). The reactions were initiated by the quick addition of requisite amounts of thermally pre-equilibrated oxidant solutions (5×10^{-4} to 5×10^{-3} mol dm^{-3}), to solutions containing known amounts of carbohydrazide (0.02-0.40 mol dm^{-3}), perchloric acid (0.0001-0.15 mol dm^{-3}) or buffer and water thermostated at the same temperature. The progress of the reactions was monitored at least for two half-lives by the iodometric determination of unreacted oxidant at regular time intervals. The pseudo-first order rate constants (k_{obs}) were computed by the graphical methods and the values were reproducible within $\pm 3\%$. Activation parameters evaluated by computing the constants of rate limiting steps were also accurate with an error of about $\pm 4\%$.

Stoichiometry and product analysis

The stoichiometry of carbohydrazide-oxidant reaction was determined by thermally equilibrating

varying ratios of reactants at different $[HClO_4]$ (0.002-0.15 mol dm^{-3}) and buffered media. Determination of unreacted oxidant in the reaction mixture showed that one mole of the substrate reacts with four moles of oxidant. The observed 1:4 stoichiometry may be represented by Eqs (1 and 2).

$$NH_2NHCONHNH_2 + 4C_6H_5SO_2NNaX + H_2O \rightarrow$$
$$4C_6H_5SO_2NH_2 + 2N_2 + CO_2 + 4Na^+ + 4X^- \quad ... \quad (1)$$
$$NH_2NHCONHNH_2 + 4OCl^- \rightarrow 2N_2 + CO_2$$
$$+ 3H_2O + 4Cl^- \quad\quad\quad\quad ... \quad (2)$$

where X = Cl or Br.

Nitrogen evolved was determined quantitatively by making use of Schiff's nitrometer. Benzenesulphonamide was detected by TLC employing ether-chloroform-*n*-butanol (2:2:1 v/v) as solvent and iodine as detecting reagent ($R_f = 0.88$).

Results

Kinetics of oxidation of carbohydrazide by chloramine-B (CAB), bromamine-B (BAB) and hypochlorite ion were investigated in aqueous perchloric acid and buffered media under varying conditions. The results are shown in Tables 1-4 and Figs 1-3.
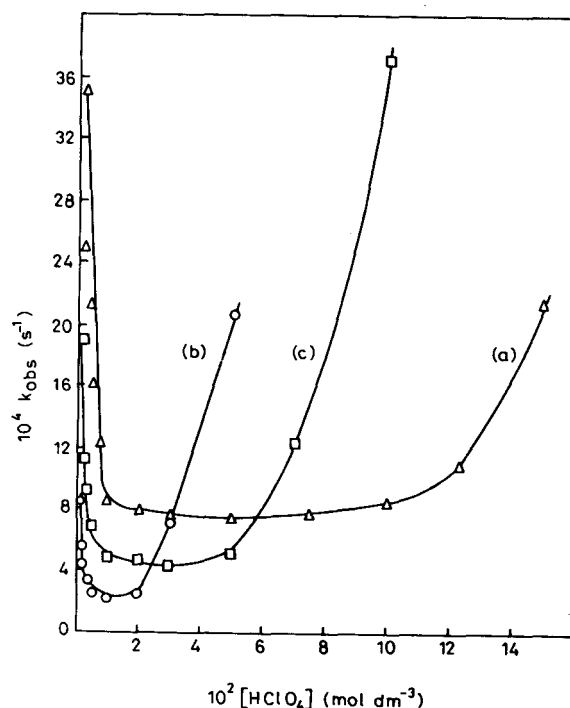

Fig. 1—Plots of k_{obs} versus $[HClO_4]$ ($10^3[CAB]_0 = 10[CH]_0 = 1.0$ mol dm^{-3}, temp. 283 K (a); $10^3[BAB]_0 = 50[CH]_0 = 1.0$ mol dm^{-3}, temp. 283 K (b), $10^3[HOCl]_0 = 20[CH]_0 = 1.0$ mol dm^{-3}, temp. 283 K (c)

Table 1—Pseudo-first order rate constants and pH values of the reaction mixtures as $[HClO_4]$ was varied for the oxidation of carbohydrazide (CH) by chloramine-B, bromamine-B and hypochlorite ion in aqueous perchloric acid at 283 K

$10^2[HClO_4]$ (mol dm^{-3})	$10^4\,k_{obs}\,(s^{-1})$			pH values		
	CAB[a]	BAB[b]	HOCl[c]	CAB[a]	BAB[b]	HOCl[c]
0.10	—	8.4	19.2	—	5.52	5.89
0.15	—	5.6	—	—	—	—
0.20	35.1	4.4	11.5	5.90	5.20	5.60
0.30	24.8	3.2	9.1	5.71	4.92	5.42
0.50	16.2	2.8	6.8	5.46	4.62	5.17
0.75	12.4	—	—	5.28	—	—
1.0	8.6	2.2	4.8	5.15	4.18	4.83
2.0	8.0	2.5	4.7	4.77	3.14	4.41
3.0	7.7	7.0	4.3	4.49	2.46	4.06
5.0	7.5	20.9	5.2	4.14	1.88	3.26
7.0	—	—	12.5	—	—	2.50
7.5	7.7	—	—	3.59	—	—
10.0	8.5	21.5	35.3	2.97	1.38	1.90
12.5	11.2	—	—	2.48	—	—
15.0	21.9	—	—	2.14	—	—

[a]$10^3[CAB]_0 = 10[CH]_0 = 1.0$ mol dm^{-3}; [b]$10^3[BAB]_0 = 50[CH]_0 = 1.0$ mol dm^{-3}; [c]$10^3[HOCl]_0 = 20[CH]_0 = 1.0$ mol dm^{-3}.

Table 2—Pseudo-first order rate constants and pH values of the reaction mixtures and the effective rate constants as [CH] was varied for the oxidation of carbohydrazide by chloramine-B (CAB), bromamine-B (BAB) and hypochlorite ion in aqueous perchloric acid

10^2[CH] (mol dm^{-3})	$10^4\,k_{obs}$ (s^{-1})			pH values			$k^*_{eff} \times$		
							10^{7d}	10^{4d}	10^{2c}
				at 10^2[HClO$_4$] (mol dm^{-3})					
				CAB oxidation					
	0.50^a	3.0^b	12.5^a	0.50	3.0	12.5	0.50	3.0	12.5
2.0	2.7	—	—	4.65	—	—	0.31	—	—
3.0	—	6.5	—	—	3.02	—	—	5.3	—
5.0	7.4	7.9	—	5.17	4.06	—	0.30	6.0	—
10.0	16.2	13.1	11.2	5.46	4.49	2.48	0.37	9.6	1.8
20.0	38.4	20.2	16.7	5.74	5.01	2.62	0.51	14.3	3.7
40.0	—	—	29.0	—	—	3.22	—	—	7.6
				BAB oxidation					
	0.20^b	1.0^c	—	0.20	1.0	—	0.20	1.0	—
0.5	2.6	—	—	4.78	—	—	3.5	—	—
1.0	4.7	—	—	5.02	—	—	4.6	—	—
2.0	8.1	7.9	—	5.20	4.18	—	6.1	6.1	—
3.0	11.5	10.4	—	5.33	4.45	—	7.2	7.9	—
5.0	20.3	16.9	—	5.58	4.78	—	9.1	12.0	—
10.0	—	29.4	—	—	5.15	—	—	21.4	—
				HOCl oxidation					
	0.20^a	2.0^b	—	0.20	2.0	.	0.20	2.0	—
2.0	3.8	—	—	5.20	—	—	4.7	—	—
4.0	9.5	9.6	—	5.50	4.08	—	7.9	8.7	—
5.0	11.4	10.8	—	5.58	4.41	—	8.6	9.8	—
7.5	20.4	—	—	5.72	—	—	13.6	—	—
10.0	33.9	17.2	—	5.90	4.82	—	16.8	15.4	—
15.0	—	24.4	—	—	5.21	—	—	21.6	—

$^*k_{eff} = k_{obs}/[H^+]^n$ (please see text), ^{a}at 283 K, ^{b}at 293 K, ^{c}at 303 K, ^{d}(mol^n dm^{-3n} s^{-1}), ^{e}(mol^{-n} dm^{3n} s^{-1}).

(a) Oxidations in acid medium

(i) Chloramine-B oxidation

At fixed [HClO$_4$] with several fold excess (25-500) of [substrate] (CH), the plots of log [CAB]$_0$/[CAB] versus time were linear for at least two half-lives and the pseudo-first order rate constants (k_{obs}) were generally insensitive to changes in [CAB]$_0$, establishing first order kinetics in [CAB]. At constant [CAB] and [CH], the rate first decreased and then remained constant and finally increased with increase in [H$^+$] (Table 1). The plot of k_{obs} versus [H$^+$] gave an inverted bell shaped [H$^+$]-rate profile (Fig. 1). The [substrate] and [oxidant] were varied in all the three ranges of [H$^+$] (0.002-0.01, 0.01-0.075 and >0.05 mol dm^{-3}) (Table 2). The rate increased with increase in [CH] in all the ranges, showing varying orders in [CH] (Table 4).

(ii) Bromamine-B oxidation

At constant [H$^+$] with several fold excess of [CH], the first order plots were linear for two half-lives and the pseudo-first order rate constants computed from the plots were unaffected by the changes in [BAB]$_0$. Variation in [HClO$_4$], at constant [BAB] and [CH], also showed an inverted bell shaped [H$^+$]-rate profile (Fig. 1). [BAB] and [CH] were varied only in the first two ranges of [H$^+$] as the rate showed inverse dependence in [CH] at high acidities (Table 2). The reaction showed fractional order kinetics in [CH] in both the ranges of acid concentrations (Table 4).

(iii) Hypochlorite oxidation

The behaviour of hypochlorite −CH reaction and its kinetics were almost similar to CAB and BAB oxidations (Tables 1, 2 and 4).

Table 3—Pseudo-first order rate constants (k_{obs}) for the oxidation of carbohydrazide (CH) by chloramine-B (CAB), bromamine-B (BAB) and hypochlorite ion in buffered media at 293 K (values in parentheses are [CH] for BAB oxidations)

pH	$10^4 k_{obs}$ (s⁻¹) CAB	BAB	HOCl	10^3[oxi] (mol dm⁻³)	10^2[CH] (mol dm⁻³)	CAB 1.80[a]	3.0[b]	4.05[cd]	4.45[d]	BAB 1.80	3.0	HOCl 4.05[d]
1.50[a]	5.8	—	11.5	0.5	5.0(2.0)	5.0	7.8	5.4	6.4	11.4	15.7	10.1
1.80[a]	5.4	—	11.5	1.0	5.0(2.0)	5.4	8.3	5.2	6.1	11.5	15.5	10.6
2.00[a]	5.6	—	11.5	2.0	5.0(2.0)	5.6	8.2	5.3	6.5	11.3	15.8	10.5
2.20[a]	6.2	—	11.5	4.0	5.0(2.0)	5.4	9.0	5.7	6.7	11.8	16.0	—
2.40[b]	8.5	—	16.1	1.0	3.0(1.0)	3.3	6.5	3.7	5.3	7.6	12.3	8.2
2.70[b]	8.4	—	15.6	1.0	5.0(2.0)	5.4	8.3	5.2	6.1	11.5	15.5	10.6
3.00[b]	8.3	—	15.5	1.0	7.0(−)	—	—	—	—	—	18.4	13.0
3.40[b]	8.1	—	15.6	1.0	10.0(5.0)	9.6	11.5	6.6	7.9	21.8	23.3	15.8
3.42[cd]	5.4	—	—	1.0	20.0(10.0)	20.4	18.1	10.4	10.5	46.9	—	—
4.05[cd]	5.3	5.6	10.6									
4.45[cd]	5.3	6.1	10.8									
4.99[cd]	5.7	7.0	10.7									
5.23[cd]	—	7.4	10.8									

[a]KCl-HCl buffer, [b]biphthalate-HCl buffer, [c]acetate buffer, [d]at 283 K

Table 4—Kinetic data for the oxidation of carbohydrazide (CH) by chloramine-B (CAB), bromamine-B (BAB) and hypochlorite ion (computed from the effective rate constants (k_{eff}) in aqueous perchloric acid and from the observed rate constants (k_{obs}) in aqueous buffered media)

In 10^2[HClO₄] (mol dm⁻³) range

Orders (n) observed in	CAB 0.10-0.75	CAB 1.0-7.5	CAB 7.5-15.0	BAB 0.10-0.50	BAB 0.50-2.0	HOCl 0.10-1.0	HOCl 1.0-5.0
[oxidant]	1.0(1.0)	1.0(1.0)	1.0(1.0)	1.0(1.0)	1.0(1.0)	1.0(1.0)	1.0(1.0)
[CH]	0.18(1.2)	0.64(0.70)	1.0(0.70)	0.43(0.80)	0.80(0.80)	0.77(1.4)	0.70(0.70)
[H⁺]	−0.85(−0.90)	−0.03(−0.08)	0.49(0.90)	−0.60(−0.90)	−0.03(0.0)	−0.56(−0.70)	−0.01(−0.10)

In buffered media in the pH range

Orders (n) observed in	CAB 1.5-2.2[a]	CAB 2.4-3.4[b]	CAB 3.4-5.2[c]	BAB 3.4-5.2	HOCl 1.5-2.2	HOCl 2.4-3.4	HOCl 3.4-5.2
[oxidant]	1.0	1.0	1.0	1.0	1.0	1.0	1.0
[CH]	1.0	0.54	0.49	0.25	1.0	0.53	0.54
[H⁺]	0	0	0	0	0	0	0

Values in the parentheses were computed from the observed rate constants (k_{obs}).
[a]KCl-HCl buffer, [b]biphthalate-HCl buffer, [c]acetate buffer.

Variation in either ionic strength or solvent composition of the medium had no significant effect on the rates of oxidations, in all the cases. Addition of benzene-sulphonamide to the reaction mixture had negligible effect on the rates of CAB and BAB oxidations.

The rates of reactions were measured at different temperatures under varying [substrate]. The activation parameters have been computed from the Arrhenius and Eyring plots by computing the constants of rate limiting steps (Table 5).

(b) *Oxidations in buffered medium*

We have observed in the oxidation of carbohydrazide by dichlorosulphonamides[6] that pH of the medium varied as [CH] was varied. The effect was more pronounced at low [H⁺]. Hence, to make sure that the kinetics determined were reliable, pH of the reaction mixtures were measured as [HClO₄] and [CH] were varied (Tables 1 and 2). The rate dependences in [H⁺]$_{eff}$ (n) were calculated from the measured pH values as [HClO₄] was varied (Table 4). The n values so computed were used to compensate

Table 5—Activation parameters corresponding to the rate limiting steps for the oxidation of carbohydrazide (CH) by chloramine-B (CAB), bromamine-B (BAB) and hypochlorite ion in aqueous medium under various conditions

In $[HClO_4]$ (mol dm^{-3}) range

	CAB	BAB			HOCl	
	0.01-0.075	0.001-0.005	0.005-0.02		0.01-0.05	
	Calculated using the values of					
	k_4	k'	k_3	k_4	k_3	k_4
E_a (kJ mol^{-1})	28.6	42.7	95.7	33.5	36.2	33.2
log A	2.8	2.9	12.8	4.1	3.2	3.9
$\Delta H^{\neq}$ (kJ mol^{-1})	25.4	38.3	80.7	35.0	39.6	32.2
$\Delta S^{\neq}$ (JK^{-1})	-201.4	-206.6	-49.7	-162.1	-173.8	-172.1
$\Delta G^{\neq}$ (kJ mol^{-1})	84.5	98.8	95.7	84.1	90.5	82.6

In buffered medium in the pH range

	CAB				BAB		HOCl			
	2.4-3.4		3.4-5.2		3.4-5.2		2.4-3.4		3.4-5.2	
	k_3	k_4	k_3	k_4	k_3	k_4	k_3	k_4	k_3	k_4
E_a (kJ mol^{-1})	42.6	47.3	69.3	52.0	39.9	65.9	43.1	69.2	24.7	67.3
log A	4.3	6.3	9.3	7.2	4.1	9.9	4.6	10.5	4.6	10.7
$\Delta H^{\neq}$ (kJ mol^{-1})	41.4	46.2	63.2	49.8	38.6	62.3	39.4	67.9	23.4	67.9
$\Delta S^{\neq}$ (JK^{-1})	-166.4	-128.9	-90.4	-115.6	-171.4	-67.1	-169.5	-47.8	-223.7	-42.1
$\Delta G^{\neq}$ (kJ mol^{-1})	90.2	84.0	88.5	82.3	87.1	81.3	89.1	82.0	86.7	80.0

the changes in rate constant due to changes in $[H^+]$ as [CH] was varied ($k_{obs}/[H^+]^n$) (Table 2). The rate dependences in [CH] were calculated from the effective or compensated rate constants. In addition to these, kinetics have been investigated in buffered aqueous medium. KCl-HCl, HCl-biphthalate and acetate buffers were employed (Table 3). The kinetic data for the oxidation of carbohydrazide by chloramine-B, bromamine-B and HOCl under various conditions are summarised in Table 4.

As can be seen, in acid medium there are differences between the orders computed from k_{obs} and k_{eff} values, especially at low $[HClO_4]$. It is also evident from the rate dependences in [CH] that under $[H^+]$ dependent oxidation conditions, the kinetic orders in [CH] have to be calculated after neutralising $[H^+]$ effect on the rate constant, as the effect is more pronounced.
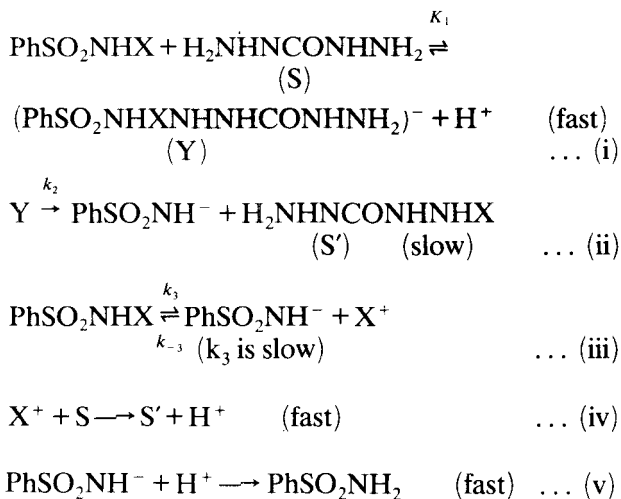
Discussion

Chloramine-B ($C_6H_5SO_2NClNa$), like chloramine-T[8,9] and bromamine-B[10] are fairly strong electrolytes in aqueous solution and they furnish different reactive species depending upon pH of the medium. The possible oxidising species in acid solutions of CAB and BAB are $C_6H_5SO_2NX^-$,

$C_6H_5SO_2NHX$, HOX and $C_6H_5SO_2NX_2$ at low $[H^+]$ and $C_6H_5SO_2NH_2X^+$ and H_2OX^+ at high acidities.

Mechanism of oxidations: (a) *Acid medium*

The observed kinetics for the oxidation of carbohydrazide by chloramine-B, bromamine-B and hypochlorite ion in all the ranges of $[H^+]$ (Table 4) may be explained by a comprehensive mechanism shown in Scheme 1.
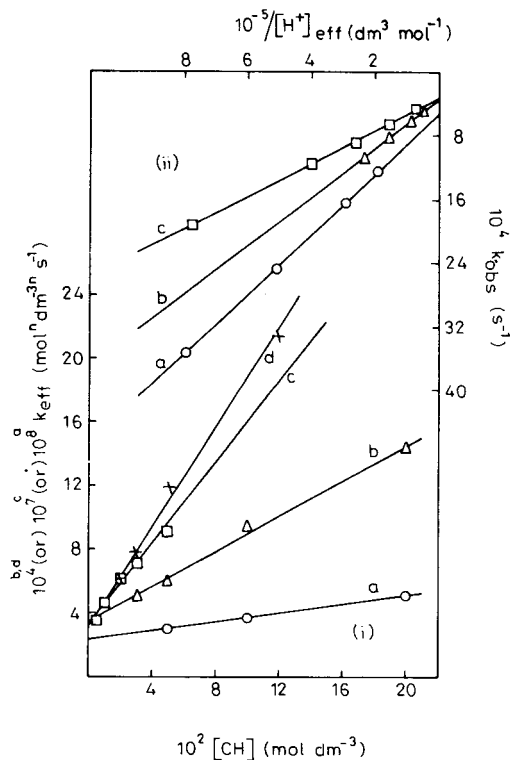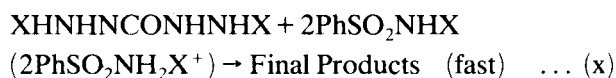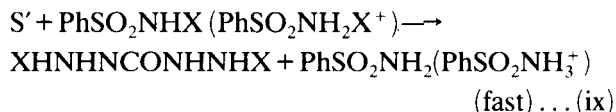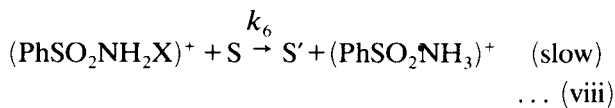
$$PhSO_2NHX + H_2NHNCONHNH_2 \overset{K_1}{\rightleftharpoons}$$
$$(S)$$

$$(PhSO_2NHXNHNHCONHNH_2)^- + H^+ \quad \text{(fast)}$$
$$(Y) \qquad \qquad \ldots \text{(i)}$$

$$Y \overset{k_2}{\rightarrow} PhSO_2NH^- + H_2NHNCONHNHX$$
$$(S') \quad \text{(slow)} \qquad \ldots \text{(ii)}$$

$$PhSO_2NHX \overset{k_3}{\underset{k_{-3}}{\rightleftharpoons}} PhSO_2NH^- + X^+$$
$$(k_3 \text{ is slow}) \qquad \ldots \text{(iii)}$$

$$X^+ + S \longrightarrow S' + H^+ \quad \text{(fast)} \qquad \ldots \text{(iv)}$$

$$PhSO_2NH^- + H^+ \longrightarrow PhSO_2NH_2 \quad \text{(fast)} \ldots \text{(v)}$$

Fig. 2—(i) Plots of k_{eff} versus $[CH]_0$ ($10^3[CAB]_0 = 1.0$ mol dm^{-3}, $10^2[HClO_4]$ (mol dm^{-3}) = 0.5, temp. 283 K (a), 3.0, temp. 293 K (b); $10^3[BAB]_0 = 1.0$ mol dm^{-3}, $10^2[HClO_4]$ (mol dm^{-3}) = 0.2, temp. 293 K (c), 1.0, temp. 303 K (d)).

(ii) Plots of k_{obs} versus $1/[H^+]_{eff}$ ($10^3[CAB]_0 = 10[CH]_0 = 1.0$ mol dm^{-3}, temp. 283 K (a); $10^3[BAB]_0 = 50[CH]_0 = 1.0$ mol dm^{-3}, temp. 293 K (b) and $10^3[HOCl]_0 = 20[CH]_0 = 1.0$ mol dm^{-3}, temp. 283 K (c)).

$$PhSO_2NHX + S \xrightarrow{k_4} S' + PhSO_2NH_2 \quad (slow) \quad \ldots (vi)$$

$$PhSO_2NHX + H^+ \underset{K_5}{\rightleftharpoons} (PhSO_2NH_2X)^+ \quad (fast) \ldots (vii)$$

$$(PhSO_2NH_2X)^+ + S \xrightarrow{k_6} S' + (PhSO_2NH_3)^+ \quad (slow)$$
$$\ldots (viii)$$

$$S' + PhSO_2NHX (PhSO_2NH_2X^+) \longrightarrow$$
$$XHNHNCONHNHX + PhSO_2NH_2(PhSO_2NH_3^+)$$
$$(fast) \ldots (ix)$$

$$XHNHNCONHNHX + 2PhSO_2NHX$$
$$(2PhSO_2NH_2X^+) \rightarrow Final Products \quad (fast) \quad \ldots (x)$$
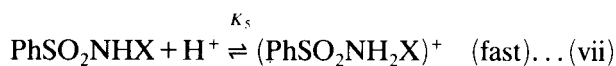
Scheme 1

The observed results at low $[H^+]$ can be explained by a two-pathway mechanism (steps (i) and (ii), and steps (iii) and (iv)) and subsequent fast steps (ix and x) leading to final products. Based on these steps the combined rate law (3) has been deduced.
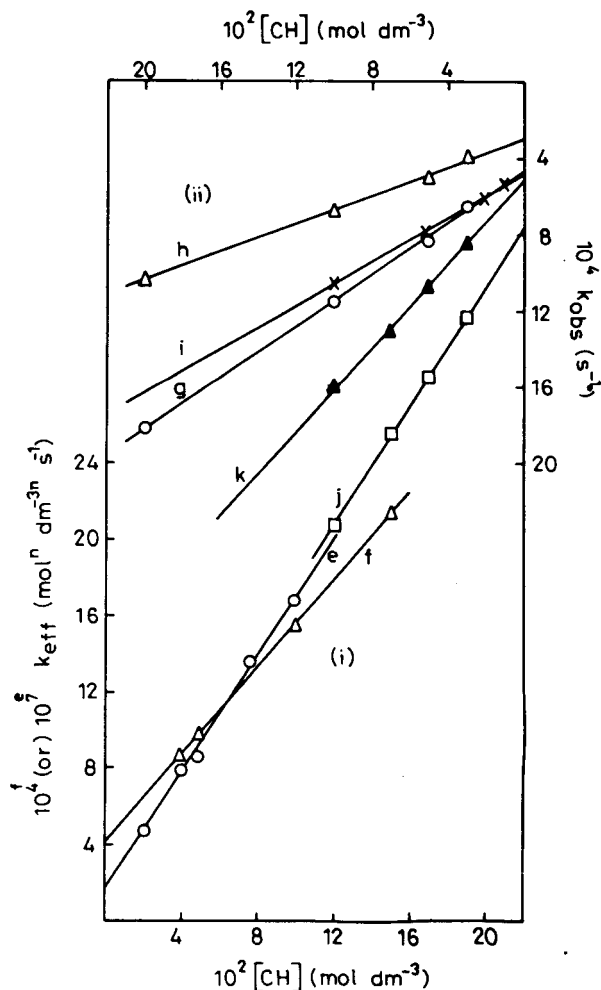

Fig. 3—(i) Plots of k_{eff} versus $[CH]_0$ ($10^3[HOCl]_0 = 1.0$ mol dm^{-3}, $10^2[HClO_4]$ (mol dm^{-3}) = 0.2, temp. 283 K (e), 2.0 temp. 293 K (f)).

(ii) Plots of k_{obs} versus $[CH]_0$ ($10^3[CAB]_0 = 1.0$ mol dm^{-3}, $pH = 3.0$, temp. 293 K (g), 4.05, temp. 283 K (h); $10^3[BAB]_0 = 1.0$ mol dm^{-3}, $pH = 4.45$, temp. 283 K (i), $10^3[HOCl]_0 = 1.0$ mol dm^{-3}, $pH = 3.0$, temp. 293 K (j) 4.05, temp. 283 K (k)).

$$-\frac{d[\text{oxidant}]}{dt} = \frac{K_1 k_2[\text{oxidant}][S]}{[H^+]} + k_3[\text{oxidant}] \ldots (3)$$

or

$$k_{obs} = K_1 k_2 \frac{[S]}{[H^+]} + k_3 = k' \frac{[S]}{[H^+]} + k_3 \quad \ldots (4)$$

where $k' = K_1 k_2$.

Rate law (4) is consistent with the observed results. Two sets of k' and k_3 were calculated from the plots of k_{eff} versus $[S]$ and k_{obs} versus $1/[H^+]$. The constants computed from the former plot were used to predict the rate constants from rate law (4) as $[H^+]$ was varied and vice versa. There was a reason-

able agreement between the experimental constants and calculated values (values not shown), supporting the suggested reaction pathways. Further, the constants k' and k_3 were calculated at different temperatures by varying [substrate] at each temperature and the latter values were employed to compute the activation parameters (Table 5).

As the [H$^+$] is increased further, equilibrium of step (i) lies towards left and steps (i) and (ii) get transformed into step (vi). This is evident from the observed virtual non-dependence of rate on [H$^+$]. Hence, the kinetics in the second acid range can also be accounted by two pathway mechanism i.e., by the two competitive steps (iii) and (vi) followed by a number of fast steps as shown in Scheme 1. The related combined rate law is given by Eq. (5).

$$-\frac{d[\text{oxidant}]}{dt} = k_3[\text{oxidant}] + k_4[\text{oxidant}][S] \quad \dots (5)$$

or

$$k_{\text{obs}} = k_3 + k_4[S] \quad \dots (6)$$

The plot of k_{eff} versus [S] was linear in conformity with the rate law (6) (Fig. 2). From the slope and intercept of the plot, the constants k_3 and k_4 were calculated. Further, the substrate concentrations were varied at different temperatures even under these conditions and hence k_3 and k_4 were evaluated at each temperature. The latter values were employed to compute the activation parameters (Table 5).

At high [H$^+$]([HClO$_4$] > 0.05 mol dm^{-3}) protonation of the oxidant and substrate becomes significant. Under these conditions, the reaction is first order each in [CAB] and [CH], and fractional order in [H$^+$]. The observed results may be explained by steps (vii) and (viii). Further oxidation of the substrate takes place in subsequent fast steps. Based on steps (vii) and (viii), Eq. (7) has been deduced.

$$-\frac{d[\text{CAB}]}{dt} = \frac{K_5 k_6 [\text{CAB}]_{\text{tot}}[S][H^+]}{1 + K_5[H^+]} \quad \dots (7)$$

or

$$k_{\text{obs}} = \frac{K_5 k_6 [S][H^+]}{1 + K_5[H^+]} \quad \dots (8)$$

The plot of k_{eff} (Table 2) versus [S] was linear in accordance with rate law (8).

(b) *Buffered media*

Oxidation of carbohydrazide by the oxidants in buffered media followed first order kinetics in [oxidant], fractional to first order in [substrate]. But the rate was independent of pH. The kinetics of oxidation in the buffered medium at low pH were similar to those in acid medium in the third [H$^+$] range (Table 4) in CAB oxidation and those for oxidation

at other pH were similar to those in second [H$^+$] range in acid medium. Hence the results in the pH range 1.5 to 2.2 (HCl-KCl buffer) may be explained by step (vi) and other subsequent fast steps shown in Scheme 1, whereas results in other buffered media can be explained by two-pathway mechanism, i.e. through two competitive steps (iii) and (vi) followed by a number of fast steps as shown in Scheme 1. Similar calculations of the coefficients of the rate limiting steps and the related activation parameters were made even under these conditions (Table 5).

Conclusions

Comparison of the values of k_4 reveals that bromamine-B ($10^4 k_4 = 16.1$ mol dm^{-3} at 298 K), is a better oxidant than chloramine-B (7.5 mol dm^{-3} at 298 K), i.e., BAB donates Br$^+$ species much more readily than CAB does Cl$^+$ species. Similar trends have been observed for oxidations of other substrates by these oxidants and by toluene analogues of them namely, chloramine-T and bromamine-T[1-7]. There is also reasonable agreement between the values of the constants computed in the different ranges of [H$^+$] or pH values in buffered media.

Oxidation of thiocarbohydrazide (TCH), thio-analogue of carbohydrazide, by chloramine-B, chloramine-T and hypochlorite ion under identical conditions showed simple and straight forward kinetics[4,5]. The rate was first order in [oxidant] and fractional order in [TCH] in both the cases. But the rate was independent of [H$^+$] in CAB oxidation[5] and fractional order in [H$^+$] for chloramine-T and hypochlorite oxidations.

Negative $\Delta S^{\neq}$ values (Table 5) indicate that the transition states are more ordered than reactants due to decrease in the number of degrees of freedom. Relatively high positive values for free energy of activation may signal bond breaking in the formation of transition states.

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