

## Mechanism of oxidation of *s*-butylamine by alkaline chloramine-T

Jyoti Gupta & M C Agrawal\*

Department of Post-Graduate Studies and  
Research in Chemistry, Rani Durgawati Vishwavidyalaya,  
Jabalpur 482 001

Received 7 November 1988; revised 13 March 1989; accepted  
30 March 1989

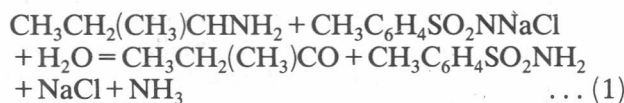
Oxidation of *s*-butylamine (SBA) by chloramine-T (CAT) is first order each in [CAT], [SBA] and the rate is proportional to  $1/[\text{OH}^-]$  at lower [amine] and higher [alkali]. Salt and solvent effects are negligible. Added toluene sulphonamide slightly accelerates the rate of reaction. A suitable mechanism involving the rate-determining reaction between *N*-chlorotoluene-*p*-sulphonamide and SBA has been proposed.

The kinetics of oxidation of some aromatic amines and their derivatives by chloramine-T (CAT), reported earlier<sup>1,2</sup>, have shown that these oxidations are independent of a change in  $[\text{OH}^-]$ . The kinetics of oxidation of *s*-butylamine (SBA) by CAT, reported herein, shows a retarding influence of alkali and this has prompted us to investigate the mechanism of this reaction.

### Experimental

All solutions were prepared in doubly distilled water using analytical grade reagents. The reaction was initiated by adding appropriate amount of CAT solution to the rest of the reaction mixture, pre-equilibrated at desired temperature. Progress of the reaction was followed by analysing CAT iodometrically at suitable time intervals.

Reaction mixtures containing known excess of CAT over SBA were kept at room temperature for 24 hr in the presence of  $0.02 \text{ mol dm}^{-3}$  NaOH. Estimation of unreacted CAT in these mixtures revealed that 1 mole of CAT consumed 1 mole of SBA according to Eq. (1).



The presence of a methyl ketone was detected by qualitative tests<sup>3</sup>.

### Results and discussion

The rate of oxidation was always first order in [CAT]. Pseudo-first order rate constants, ( $k_{\text{obs}}$ ) in

[CAT] were obtained from  $\log ([\text{CAT}]_0/[\text{CAT}])$  versus time plots. The  $k_{\text{obs}}$  initially increased proportionately with increase in [SBA] but later tended to attain a limiting value (Fig. 1A). The order in [SBA] is therefore unity only in lower [SBA] and  $< 1$  at higher [SBA].

Increase in [NaOH] at constant ionic strength ( $[\text{NaClO}_4] = 1.0 \text{ mol dm}^{-3}$ ) decreased  $k_{\text{obs}}$  values marginally at low [alkali]. But, at higher [alkali] the rate was nearly proportional to  $1/[\text{OH}^-]$  (Fig. 2A). At  $\text{NaOH} > 0.1 \text{ mol dm}^{-3}$  the observations could not be recorded because the reaction became quite slow and the reproducibility of the results was seriously affected. Addition of a neutral salt ( $[\text{NaClO}_4] = 0.16$  to  $0.80 \text{ mol dm}^{-3}$ ) or an inert solvent ( $[\text{methanol}] = 5$  to  $25\%$ ) had negligible effect on the rate of oxidation. Addition of the product, toluene sulphonamide (TSA), ( $1.2$  to  $4.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) slightly increased the rate constant ( $1.18$  to  $1.38 \times 10^{-4} \text{ s}^{-1}$ ). The  $E_a$  value from the Arrhenius plot (temp. range  $30$ - $50^\circ$ ) was obtained as  $73.9 \pm 0.3 \text{ kJ mol}^{-1}$ .

In aqueous alkaline solutions of CAT, equilibria (2) and (3) become operative<sup>4,5</sup>,

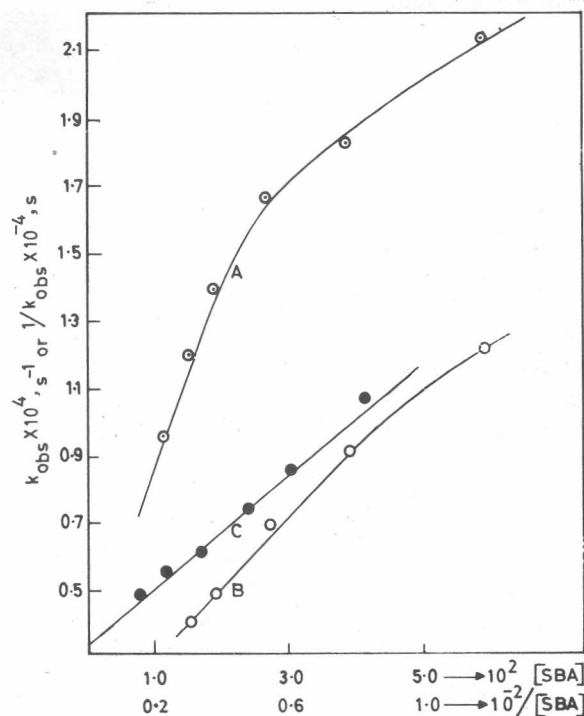


Fig. 1—A and B, plot of  $k_{\text{obs}}$  versus [SBA] in presence of  $[\text{NaOH}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$  in A and  $6.0 \times 10^{-2} \text{ mol dm}^{-3}$  in B; C—Plot of  $1/k_{\text{obs}}$  versus  $1/[\text{SBA}]$  under conditions of A above.

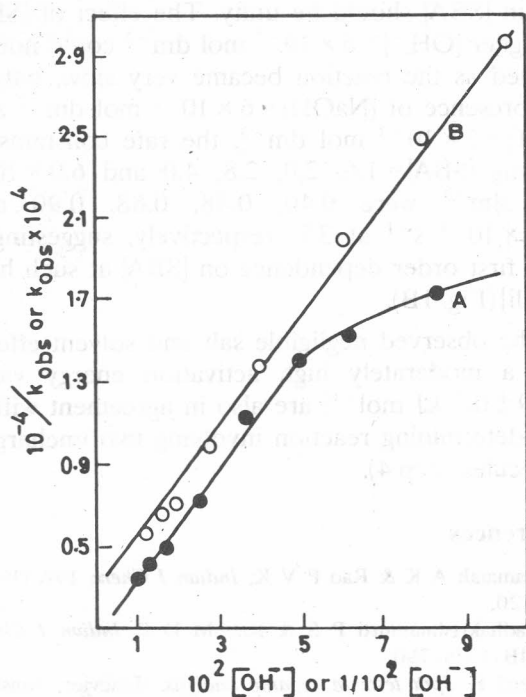
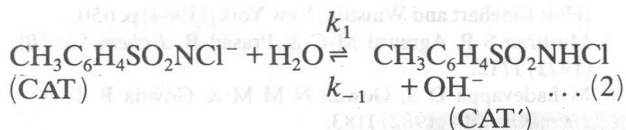
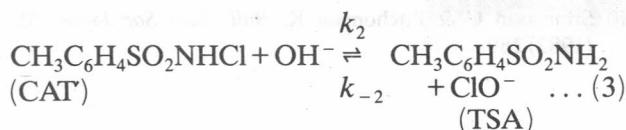


Fig. 2 - A, Plot of  $k_{\text{obs}}$  versus  $1/[\text{OH}^-]$  and B, Plot of  $1/k_{\text{obs}}$  versus  $[\text{OH}^-]$



$[K_1 = 3.0 \times 10^{-5}$  at  $25^\circ\text{C}$  (ref. 6)]



$K_2 = 4.9 \times 10^{-8}$  at  $25^\circ\text{C}$  (ref. 6)]

It is evident that the formation of CAT and  $\text{ClO}^-$  is base-catalysed while that of N-chlorotoluene-*p*-sulphonamide (CAT) is retarded by alkali. Although, the  $[\text{CAT}]$  will be quite small in the alkali range employed, it should be sufficient to carry the reaction forward. During the oxidation of  $\alpha$ -hydroxy acids<sup>7</sup>,  $\alpha$ -amino acids<sup>8,9</sup> and substituted phenylthioacetic acids<sup>10</sup> at similar [alkali], CAT has been reported to act as the effective oxidant. Further, addition of TSA should favour formation of CAT' but should retard the formation of  $\text{ClO}^-$ . In the present investigation, the rate retardation with increase in  $[\text{OH}^-]$  and slight rate acceleration by added TSA, leads to the inference that the main oxidising species is essentially N-chlorotoluene-*p*-sulphonamide, i.e. CAT'.

As the reaction shows first order dependence in  $[\text{SBA}]$ , a rate-determining reaction between CAT

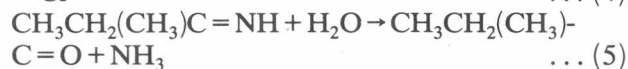
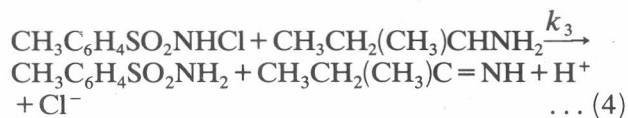
Table 1 - Effect of varying [reactants] on reaction rate at  $35^\circ$

$[\text{OH}^-] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$		
$10^3 [\text{CAT}]$ ( $\text{mol dm}^{-3}$ )	$10^2 [\text{SBA}]$ ( $\text{mol dm}^{-3}$ )	$k_{\text{obs}} \times 10^4$ ( $\text{s}^{-1}$ )
1.2	2.0	1.09
1.6	2.0	1.30
2.0	2.0	1.38
2.8	2.0	1.32
4.0	2.0	1.15
2.0	1.2	0.95
2.0	1.6	1.19
2.0	2.8	1.65
2.0	4.0	1.81
2.0	6.0	2.10

Table 2 - Effect of varying  $[\text{OH}^-]$  on reaction rate at  $35^\circ$   
 $[\text{CAT}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{SBA}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$  and  
 $\mu = 1.0 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ )

$10^2 [\text{OH}^-]$ ( $\text{mol dm}^{-3}$ )	$k_{\text{obs}} \times 10^4$ ( $\text{s}^{-1}$ )	$10^6 k_{\text{obs}} \times [\text{OH}^-]$ ( $\text{mol dm}^{-3} \text{ s}^{-1}$ )
1.2	1.74	2.09
1.6	1.54	2.46
2.0	1.42	2.84
2.8	1.02	2.86
4.0	0.72	2.88
6.0	0.50	3.00
8.0	0.40	3.2
10	0.335	3.35

and the reducing substrate is proposed (see Eqs 4 and 5)



CAT' might abstract two hydrogen atoms from SBA to give an intermediate imine type compound which is subsequently hydrolysed to give the products (Eq. 5).

In the absence of initial TSA, the reverse of step (3) is of little consequence as is also evidenced by the observed small positive effect of TSA. Thus, assuming  $k_{-2}$  to be small,  $-(d[\text{CAT}]/dt)$  from steps (2)-(5) is given by Eq. (6)

$$-\frac{d[\text{CAT}]}{dt} = \frac{k_1 k_3 [\text{CAT}][\text{SBA}][\text{H}_2\text{O}]}{(k_{-1} + k_2)[\text{OH}^-] + k_3[\text{SBA}]} \quad (6)$$

The rate law (6) is in agreement with the experimental observations including decrease in order in

[SBA] and increase in dependence on  $[\text{OH}^-]$  in their higher concentration regions (Tables 1 & 2).

The rate law (6) in terms of  $1/k_{\text{obs}}$  may be expressed by Eq. (7).

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_1[\text{H}_2\text{O}]} + \frac{(k_{-1} + k_2)[\text{OH}^-]}{k_1 k_3 [\text{SBA}][\text{H}_2\text{O}]} \quad \dots(7)$$

where  $-d[\text{CAT}]/dt = k_{\text{obs}}[\text{CAT}]$ . According to Eq. (7) plots of  $1/k_{\text{obs}}$  versus  $1/[\text{SBA}]$  at constant  $[\text{OH}^-]$  and of  $1/k_{\text{obs}}$  versus  $[\text{OH}^-]$  at constant  $[\text{SBA}]$  should be linear with intercepts on  $1/k_{\text{obs}}$  axis. The magnitude of these intercepts should be same, i.e.  $1/k_1[\text{H}_2\text{O}]$  for both these plots. The experimental values of these intercepts obtained from Figs 1C and 2B are:  $0.33 \times 10^{-4}$  and  $0.29 \times 10^{-4}$  respectively. These are in fair agreement, and thus supporting the proposed mechanism.

The slope of the plot of  $1/k_{\text{obs}}$  versus  $1/[\text{SBA}]$  from Eq. (7) should be equal to  $(k_{-1} + k_2)[\text{OH}^-]/k_1 k_3$ . Assuming  $k_2$  to be small in comparison to  $k_{-1}$  and  $[\text{OH}^-] = 0.02 \text{ mol dm}^{-3}$  the value of this slope should be  $0.02/K_1 k_3$ . The experimental slope at  $35^\circ$  (Fig. 1C) is equal to  $0.81 \times 10^2$ . From the observed value of temperature coefficient ( $\sim 2.3$ ) the corresponding value of slope is expected to be  $1.86 \times 10^2$  at  $25^\circ$ . Accordingly, the constant  $k_3$  for the rate-determining reaction (4) may be obtained as  $0.02/(3 \times 10^{-5}) \times (1.86 \times 10^2) \approx 3.6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at  $25^\circ$ .

The proposed rate law (6) further predicts that at higher [alkali], the rates should be proportional to  $1/[\text{OH}^-]$  (Fig. 2B) and at the same time the or-

der in [SBA] should be unity. The effect of [SBA] at higher  $[\text{OH}^-] > 6 \times 10^{-2} \text{ mol dm}^{-3}$  could not be studied as the reaction became very slow, but, in the presence of  $[\text{NaOH}] = 6 \times 10^{-2} \text{ mol dm}^{-3}$  and  $[\text{CAT}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$ , the rate constants at varying  $[\text{SBA}] = 1.6, 2.0, 2.8, 4.0$  and  $6.0 \times 10^{-2} \text{ mol dm}^{-3}$  were  $0.40, 0.48, 0.68, 0.90$  and  $1.20 \times 10^{-4} \text{ s}^{-1}$  at  $35^\circ$  respectively, suggesting a near first order dependence on [SBA] at such high [alkali] (Fig. 1B).

The observed negligible salt and solvent effects and a moderately high activation energy value ( $73.9 \pm 0.3 \text{ kJ mol}^{-1}$ ) are also in agreement with a rate-determining reaction involving two uncharged molecules (step 4).

## References

- 1 Ramaiah A K & Rao P V K, *Indian J Chem*, 19A (1980) 1120.
- 2 Radhakrishnamurti P S & Rao M D P, *Indian J Chem*, 14B (1976) 790.
- 3 Feigl F, *Spot tests in organic analysis*, (Elsevier, Amsterdam) (1975) p. 208.
- 4 Dietzel R & Tafel K, *Apotheker Ztg*, 44 (1929) 989.
- 5 Agrawal M C & Mushran S P, *J chem Soc Perkin Transactions II*, (1973) 762.
- 6 Gould E S, *Mechanism and structure in organic chemistry*, (Holt Rinehart and Winston, New York) (1964) p. 650.
- 7 Mushran S P, Agrawal M C & Prasad B, *J chem Soc (B)*, (1971) 1712.
- 8 Mahadevappa D S, Gowda N M M & Gowda B T, *Int J chem Kinet*, 14 (1982) 1183.
- 9 Gupta K C & Kumkum Gupta, *Int J chem Kinet*, 17 (1985) 769.
- 10 Srinivasan C & Pitchomani K, *Bull chem Soc Japan*, 55 (1982) 289.