

Kinetics and mechanism of oxidation of carbohydrazide by chloramine-T and bromamine-T in aqueous perchloric acid medium

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Abstract. Kinetics of oxidation of carbohydrazide by chloramine-T (CAT) and bromamine-T (BAT) have been studied in aqueous medium over a wide acid range, and are found to be $[H^+]$ dependent. At low $[H^+]$ (0.0005 – 0.0075 mol dm $^{-3}$), oxidation by both CAT and BAT shows first-order kinetics in [oxidant], fractional order in [substrate] and inverse fractional order in $[H^+]$. At $[HClO_4] > 0.005$ mol dm $^{-3}$, the rate dependence in $[H^+]$ is zero and fractional order for CAT and BAT oxidations respectively and the kinetics in [oxidant] and [substrate] are the same as before. Two pathways as well as Michaelis–Menten type mechanisms have been discussed to explain the observed kinetics and other effects. The rate controlling steps have been identified and the coefficients of these steps and the corresponding activation parameters are calculated. The rate constants are also predicted from the rate laws as [substrate] and $[H^+]$ are varied. The predicted values are in reasonable agreement with the experimental rate constants.

Keywords. Carbohydrazide; chloramine-T; bromamine-T; oxidation kinetics, oxidation mechanism.

1. Introduction

The chemistry of hydrazine and its derivatives is of great interest due to their wide synthetic and analytical applications and their biological activity (Audrieth and Ogg 1951; Kurzer and Wilkinson 1970; Campbell 1975). Carbohydrazide (ch) is the final member of the structural sequence urea, semicarbazide and carbohydrazide. It is a hydrazine derivative of carbonic acid. Both hydrazine groups of carbohydrazide display normal reactivity toward carbonyl compounds and give rise to a large variety of crystalline mono- and dihydrazones.

Recently we have initiated some work (Gowda and Bhat 1987, 1988, 1989; Gowda and Rao 1988; Gowda and Sherigara 1989; Gowda and Ramachandra 1989), to obtain some insight into the mechanism of their activity in solution. As part of these efforts, we have investigated the kinetics of oxidation of carbohydrazide by N-chloro and N-bromo *p*-toluenesulphonamides (chloramine-T and bromamine-T) in aqueous perchloric acid medium under varying conditions.

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2. Experimental

2.1 Materials and methods

Analytical grade chloramine-T (CAT) (Fluka, AG) was used. Bromamine-T (BAT) was prepared by the partial debromination of dibromamine-T (Nair *et al* 1978). The latter in turn was obtained by the bromination of chloramine-T (Nair and Indrasenan 1976). Aqueous stock solutions of the oxidants (0.1 mol dm^{-3}) were employed.

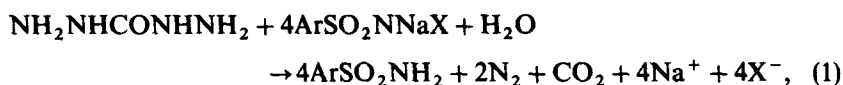
Carbohydrazide was prepared by the literature method (Kurzer and Wilkinson 1970). Aqueous stock solution (0.50 mol dm^{-3}) of carbohydrazide was employed. All other reagents used were of analytical grade. Preliminary studies of the reactions showed that the ionic strength of the medium has no significant effect on the rates.

2.2 Kinetic measurements

The kinetic studies were made in glass-stoppered pyrex boiling tubes under pseudo-first order conditions with $[\text{substrate}] \gg [\text{oxidant}]$ (5–100 fold excess). The reactions were initiated by the rapid addition of requisite amounts of oxidant solution (5×10^{-4} to $6 \times 10^{-3} \text{ mol dm}^{-3}$), thermally pre-equilibrated at a desired temperature, to solutions containing known amounts of carbohydrazide (0.01 – 0.20 mol dm^{-3}), perchloric acid (0.0005 – 0.10 mol dm^{-3}) and water thermostatted at the same temperature. The progress of the reactions was monitored for at least two half-lives by the iodometric estimation of unreacted oxidant at regular intervals of time. The pseudo-first order rate constants (k_{obs}) were computed by graphical methods and the values were reproducible within $\pm 4\%$ error. The activation parameters evaluated from the computed constants of rate limiting steps were also reproducible within $\pm 5\%$ error.

2.3 Stoichiometry and product analysis

The stoichiometry of carbohydrazide–oxidant reactions was determined by thermally equilibrating varying ratios of reactants at different $[\text{HClO}_4]$ (0.001 – 0.10 mol dm^{-3}). Estimation of unreacted oxidant in the reaction mixture showed that one mole of the substrate reacts with four moles of oxidants. The observed stoichiometry may be represented by



where $\text{Ar} = \text{CH}_3\text{C}_6\text{H}_4$, $\text{X} = \text{Cl}$ or Br .

3. Results

The kinetics of oxidation of carbohydrazide by chloramine-T and bromamine-T were studied in aqueous perchloric acid medium under varying conditions. The results are shown in table 1 and figure 1.

Table 1. Pseudo-first order rate constants (k_{obs}) for the oxidation of carbohydrazide (ch) by chloramine-T (CAT) and bromamine-T (BAT) in aqueous perchloric acid medium at 303 K.

$10^2[\text{HClO}_4]$ (mol dm ⁻³)	$10^4 k_{\text{obs}}$ (s ⁻¹)		$10^3[\text{CAT}]_0$ (mol dm ⁻³)	$10^2[\text{ch}]_0$ (mol dm ⁻³)	$10^4 k_{\text{obs}}(\text{s}^{-1})$ at $[\text{HClO}_4](\text{mol dm}^{-3})$			
					CAT		BAT	
	CAT ^a	BAT ^b			0.001 ^c	0.01	0.002 ^d	0.01
<i>Effect of varying [CAT]₀</i>								
0.10	48.7	28.1	0.5	5.0(2.0)	10.2	15.3	3.6	6.0
0.20	27.6	15.8	1.0	5.0(2.0)	10.0	15.0	3.9	6.3
0.30	21.9	—	2.0	5.0(2.0)	10.3	15.2	—	6.4
0.50	15.7	7.5	3.0	5.0(2.0)	10.2	—	3.8	6.1
0.75	—	4.9	5.0	5.0(2.0)	10.2	15.0	3.8	6.3
1.0	15.0	6.3						
2.0	15.9	8.9	<i>Effect of varying [ch]₀</i>					
3.0	16.3	14.9	1.0	1.0	2.8	4.9	2.4	3.4
4.0	—	27.5	1.0	2.0	4.8	6.8	3.9	6.3
5.0	17.0	64.3	1.0	3.0	—	—	—	9.4
7.0	33.1	—	1.0	4.0	8.2	—	7.3	—
10.0	80.2	—	1.0	5.0	10.0	15.0	8.9	14.4
			1.0	7.0	—	—	12.3	—
			1.0	10.0	19.8	28.3	—	—
			1.0	20.0	—	52.5	—	—

^a $10^3[\text{CAT}]_0 = 20[\text{ch}]_0 = 1.0 \text{ mol dm}^{-3}$; ^b $10^3[\text{BAT}]_0 = 50[\text{ch}]_0 = 1.0 \text{ mol dm}^{-3}$; ^c 283 K; ^d 288 K

3.1 Chloramine-T oxidation

At fixed $[\text{HClO}_4]$, with several-fold excess of the substrate (10–100 times), the plots of $\log [\text{CAT}]_0/[\text{CAT}]$ versus time were linear for at least two half-lives and the pseudo-first order rate constants (k_{obs}) computed from the plots were almost unaffected by the changes in $[\text{CAT}]_0$ (table 1), establishing first-order kinetics in $[\text{CAT}]$. At constant $[\text{CAT}]$ and $[\text{ch}]$, the rate first decreased and then remained almost constant and finally increased with increase in $[\text{H}^+]$ (table 1). The plot of k_{obs} versus $[\text{H}^+]$ gave an inverted bell-shaped $[\text{H}^+]$ –rate profile (figure 1a). $[\text{ch}]$ and $[\text{CAT}]$ were varied in all three ranges of $[\text{H}^+]$ (0.0005–0.005, 0.005–0.05 and $\geq 0.05 \text{ mol dm}^{-3}$). The rate increased with increase in $[\text{ch}]$ in the first two ranges of $[\text{H}^+]$ with fractional-order dependence in $[\text{ch}]$ (0.86 and 0.77 respectively), while it decreased with increase in $[\text{ch}]$ at $[\text{H}^+] > 0.05 \text{ mol dm}^{-3}$.

3.2 Bromamine-T oxidation

At constant $[\text{HClO}_4]$ with several-fold excess of $[\text{ch}]$, the first-order plots were linear for at least two half-lives and the pseudo-first order rate constants (k_{obs}) calculated from the plots were unaffected by the changes in $[\text{BAT}]_0$ (table 1). At fixed $[\text{BAT}]$ and $[\text{ch}]$, the rate first decreased with increase in $[\text{HClO}_4]$ up to $0.0075 \text{ mol dm}^{-3}$ and increased thereafter. The rate– $[\text{H}^+]$ profile is almost inverted bell-shaped (figure 1b) with varying fractional order dependences in $[\text{H}^+]$ (–0.73, +0.73 etc.). $[\text{Substrate}]$ and $[\text{oxidant}]$ were varied in all the range of $[\text{H}^+]$. The rate showed first-order

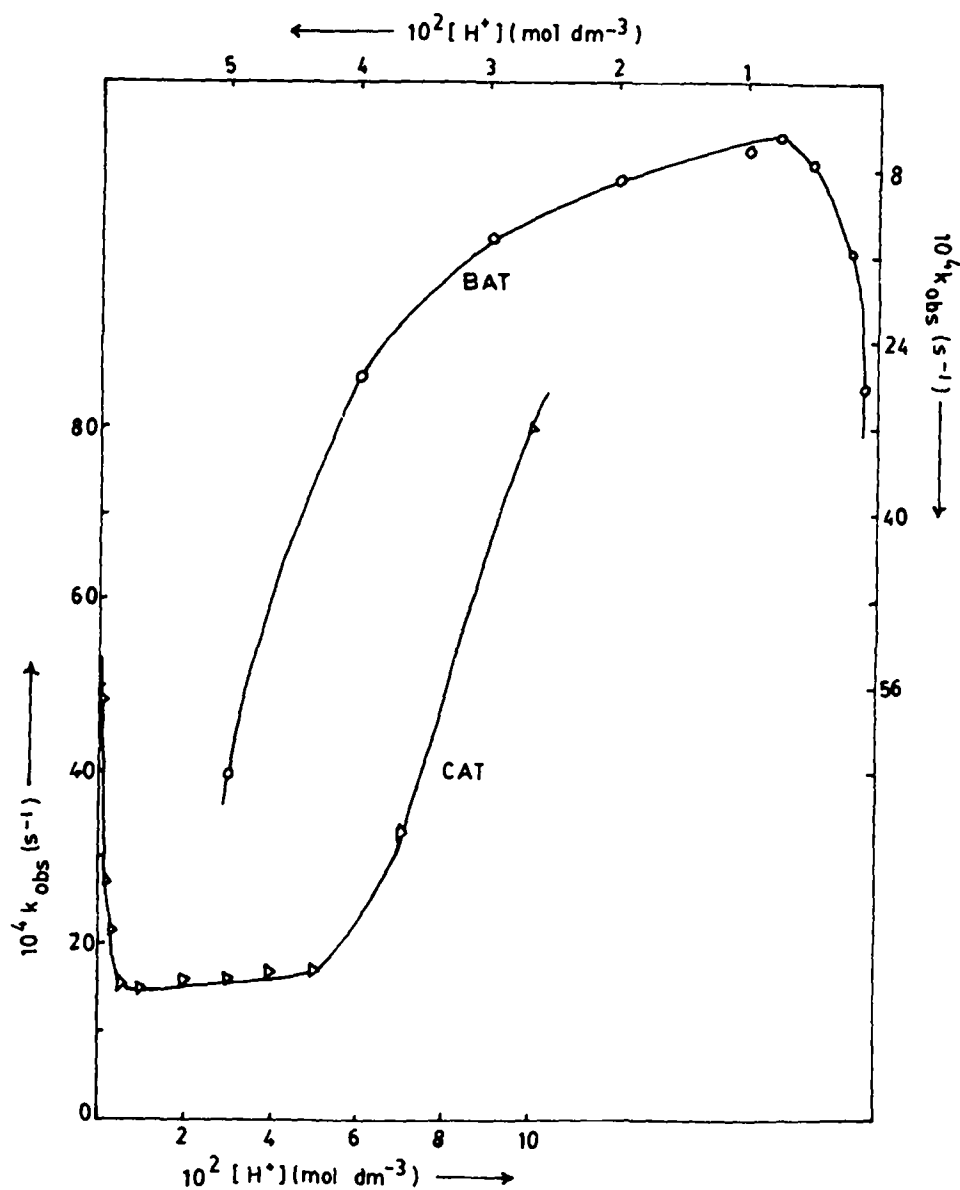


Figure 1. Plots of k_{obs} versus $[H^+]$: $10^3[\text{CAT}]_0 = 20[\text{ch}]_0 = 1.0 \text{ mol dm}^{-3}$, temperature - 303 K; $10^3[\text{BAT}]_0 = 50[\text{ch}]_0 = 1.0 \text{ mol dm}^{-3}$, temperature - 303 K.

kinetics in $[\text{oxidant}]$ for all the ranges of $[H^+]$, but it showed fractional-order dependence in $[\text{ch}]$ (~ 0.8) in the first two ranges of $[H^+]$ (table 1) and inverse dependence in $[\text{ch}]$ at high $[H^+]$.

The rates of both CAT and BAT oxidations were also studied under varying conditions of ionic strength and solvent compositions. Variations in either ionic strength or solvent composition of the medium had no significant effect on the rates of oxidation. Addition of the reduced product, *p*-toluenesulphonamide to the reaction

mixtures had also negligible effects on the rates of both oxidations (data not shown).

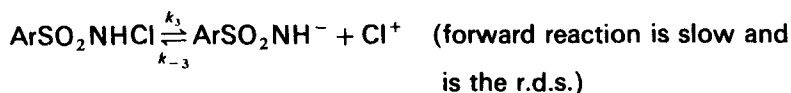
The rates were studied at varying temperatures (278–308 K) for various substrate concentrations and the constants for the rate controlling steps were calculated at each temperature as described under §4. Using the latter constants, the activation parameters were computed from the Arrhenius plots.

4. Discussion – mechanisms of oxidations

Chloramine-T and bromamine-T (ArSO_2NXNa , where $\text{Ar} = \text{CH}_3\text{C}_6\text{H}_4$ and $\text{X} = \text{Cl}$ or Br) are reasonably strong electrolytes in their aqueous solutions. They furnish different reactive species depending upon the pH of the reaction medium (Bishop and Jennings 1958; Campbell and Johnson 1978). The probable reactive oxidising species in acid solutions of CAT and BAT are ArSO_2NHX , ArSO_2NX_2 and HOX at low $[\text{H}^+]$ and $\text{ArSO}_2\text{NH}_2\text{X}^+$, and H_2OX^+ at high $[\text{H}^+]$.

4.1 Chloramine-T oxidation

4.1a In the $[\text{HClO}_4]$ range $0.0005\text{--}0.005\text{ mol dm}^{-3}$: The kinetics of oxidation of carbohydrazide by CAT is $[\text{H}^+]$ -dependent. At low $[\text{H}^+]$ ($0.0005\text{--}0.005\text{ mol dm}^{-3}$) the rate shows first-order kinetics in $[\text{CAT}]$, fractional-order in $[\text{ch}]$ and inverse fractional-order in $[\text{H}^+]$ and is unaffected by the addition of reduced product of the oxidant. The plots of k_{obs} versus $[\text{ch}]$ and k_{obs} versus $1/[\text{H}^+]$ are linear with finite intercepts on the ordinates. These results may be explained by a mechanism shown in scheme 1. This leads to the rate law (4).



followed by fast steps,



where S = substrate (ch).

Scheme 1.

$$-\frac{d[\text{CAT}]}{dt} = \frac{K_1 k_2 [\text{CAT}][\text{S}]}{[\text{H}^+]} + k_3 [\text{CAT}], \quad (4)$$

but

$$-\frac{1}{[\text{CAT}]} \frac{d[\text{CAT}]}{dt} = -\frac{d \ln [\text{CAT}]}{dt} = k_{\text{obs}}.$$

Therefore the rate law (4) becomes

$$k_{\text{obs}} = \frac{K_1 k_1 [\text{S}]}{[\text{H}^+]} + k_3. \quad (5)$$

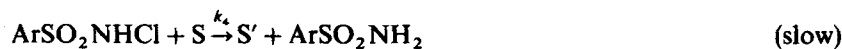
The rate laws are consistent with the observed results. Two sets of K_1, k_2 and k_3 were calculated from the plots of k_{obs} vs $[\text{S}]$ and k_{obs} vs $1/[\text{H}^+]$. The constants computed from the former plot were used to predict the rate constants from the rate law (5) as $[\text{H}^+]$ was varied and vice versa. Reasonable agreement between the predicted values and experimental constants (table 2) tests the consistency of the rate law (5) and thus provides support to the suggested mechanisms. The constant $K_1 k_2$ was also calculated at different temperatures by varying $[\text{S}]$ at each temperature and these values were used to compute the activation parameters. The values of $\log A, E_a, \Delta H^\ddagger, \Delta G^\ddagger$ (all in kJ mol^{-1}) and ΔS^\ddagger (JK^{-1}) are 3.8, 36.8, 32.3, 72.2 and -142 respectively (Reference temperature: 283 K).

Table 2. Comparison of predicted (pred.) and experimental (expt.) rate constants for the oxidation of carbohydrazide by chloramine-T and bromamine-T as $[\text{H}^+]$ and $[\text{ch}]$ were varied.

$10^2 [\text{H}^+]$ (mol dm^{-3})	$10^4 k_{\text{obs}} (\text{s}^{-1})$		$10^2 [\text{ch}]$ (mol dm^{-3})	$10^4 k_{\text{obs}} (\text{s}^{-1})$	
	Pred.	Expt.		Pred.	Expt.
<i>CAT oxidation</i> ^a ($[\text{H}^+] = 0.0005-0.005 \text{ mol dm}^{-3}$)					
0.05	19.4	19.4	1.0	3.4	2.8
0.10	10.0	10.0	2.0	5.1	4.8
0.20	5.6	6.4	4.0	8.7	8.2
0.50	2.8	3.2	5.0	10.2	10.0
			10.0	19.2	19.8
<i>BAT oxidation</i> ($[\text{H}^+] = 0.001-0.0075 \text{ mol dm}^{-3}$)					
0.10	7.2	7.0	1.0	2.3	2.4
0.20	3.9	3.9	2.0	3.8	3.9
0.30	2.7	2.6	4.0	7.0	7.3
0.50	1.9	2.1	5.0	8.5	8.9
			7.0	11.6	12.3
<i>BAT oxidation</i> ^b ($[\text{H}^+] = 0.0075-0.03 \text{ mol dm}^{-3}$)					
0.75	4.9	4.9	1.0	5.0	3.4
1.0	6.4	6.3	2.0	5.8	6.3
2.0	7.4	8.9	3.0	6.5	9.4
			5.0	9.9	14.4

^a From (5); ^b from (9)

4.1b In the $[H^+]$ range, 0.005 to 0.05 mol dm⁻³: Under these conditions the reaction was first order in [CAT] and fractional-order in [S], but almost independent of $[H^+]$. These results can be explained by a mechanism resulting from the combination of the first two steps of scheme 1 (as the backward reaction of step 1 of scheme 1 lies towards the left under these conditions), i.e. replacing the first two steps by the following step.



The combined rate law (6), based on this modified scheme accounts for the observed results.

$$-\frac{d[\text{CAT}]}{dt} = k_3[\text{CAT}] + k_4[\text{CAT}][\text{S}] \quad (6)$$

or

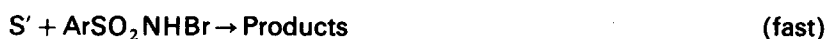
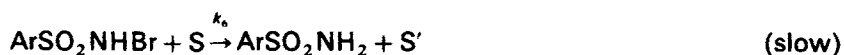
$$k_{\text{obs}} = k_3 + k_4[\text{S}]. \quad (7)$$

The plot of k_{obs} versus [S] was linear in conformity with the rate law (7). The [S] was varied at different temperatures, even under these conditions, and k_3 values were calculated at each temperature ($10^3 k_3 = 10.5, 13.5, 18.3, 24.8$ dm³ mol⁻¹ s⁻¹ at $T = 278, 283, 288$ and 293 K, respectively). These values were used to compute the activation parameters. The values are 4.3, 41.1, 40.1, 76.3 and -120 for log A , E_a , ΔH^\ddagger , ΔG^\ddagger (all in kJ mol⁻¹) and ΔS^\ddagger (JK⁻¹), respectively (reference temperature: 303 K).

4.2 Bromamine-T oxidation

4.2a In the $[\text{HClO}_4]$ range 0.001–0.0075 mol dm⁻³: Kinetics of oxidation of carbonylhydrazide by BAT at low $[H^+]$ were similar to those for CAT oxidation at low $[H^+]$. Hence these results may be explained by a similar mechanism and the related combined rate law (4) or (5). The plots of k_{obs} versus [S] and k_{obs} versus $1/[H^+]$ were linear. The rate constants were also predicted from the rate law as [S] and $[H^+]$ were varied. There is good agreement between the predicted and experimental values (table 2). The activation parameters were computed by a similar method. The values are 2.8, 34.4, 31.6, 75.7 and -152 for log A , E_a , ΔH^\ddagger , ΔG^\ddagger (all in kJ mol⁻¹) and ΔS^\ddagger (JK⁻¹) respectively (reference temperature: 288 K).

4.2b In the $[\text{HClO}_4]$ range 0.0075–0.030 mol dm⁻³: The kinetic observations in the middle acid range can be explained by the mechanism shown in scheme 2.



Scheme 2.

The related combined rate law is

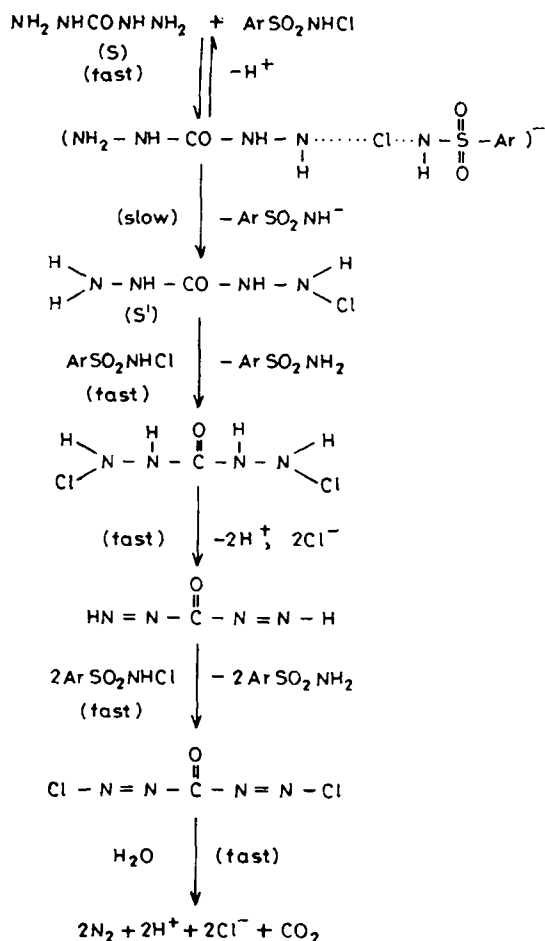
$$-\frac{d[\text{BAT}]}{dt} = k_5[\text{BAT}][\text{H}^+] + k_6[\text{BAT}][\text{S}] \quad (8)$$

or

$$k_{\text{obs}} = k_5[\text{H}^+] + k_6[\text{S}]. \quad (9)$$

The plots of k_{obs} versus $[\text{S}]$ and k_{obs} versus $[\text{H}^+]$ were linear in conformity with rate law (9). The rate constants were also predicted from the latter for the variation of $[\text{S}]$ and $[\text{H}^+]$ by the method described earlier. Unlike in other cases, the agreement between the predicted and experimental values is poor under these conditions, probably because BAT oxidations are more sensitive to $[\text{H}^+]$ variation (table 2). The activation parameters were computed from the calculated values of k_6 at different temperatures ($10^3 k_6 = 15.8, 24.2, 26.9$ and $35.4 \text{ dm}^3/\text{m mol}^{-1} \text{ s}^{-1}$ at temperatures 293, 298, 303 and 308 K respectively). Log A , E_a , ΔH^\ddagger , ΔG^\ddagger (all in kJ mol^{-1}) and ΔS^\ddagger (JK^{-1}) values are 3.9, 41.1, 36.6, 78.4 and -138 , respectively (reference temperature: 303 K).

A typical detailed mechanism of oxidation of carbohydrazide by chloramine-T is shown in scheme 3.



Scheme 3. A typical detailed mechanism of oxidation of carbohydrazide is shown.

The free energies of activation are almost constant indicating that similar mechanisms are operative in all the cases. Relatively larger negative entropies of activation may indicate that the transition states are more ordered than reactants due to decrease in the number of degrees of freedom. Discrepancies noted in the E_a and ΔS^\ddagger values are due to change of the form of reactive species as $[H^+]$ is varied.

The rates first decreased with increase in $[H^+]$ and then increased. Further it is interesting to note that oxidations by BAT are more sensitive to increase in $[H^+]$ than are oxidations by CAT. The latter may be due to the fact that BAT donates Br^+ species much more readily than CAT does Cl^+ species.

Similar trends were observed for the oxidations of thiosemicarbazide (Gowda and Rao 1988), and thiocarbohydrazide (Gowda and Sherigara 1989). Increase of rate with increase in $[H^+]$ may be due to change in the form of oxidising species. At low $[H^+]$, oxidants mostly react in the undissociated forms $ArSO_2NHX$ ($X = Cl$ or Br) whereas at high $[H^+]$, it is likely that they react mostly in the form of the X^+ species, produced in the pre-equilibrium disproportionation step.

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