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Ru(III) Catalyzed And Uncatalyzed Oxidative Conversion of 5-Nitroquinoline To Its N-Oxide By Acidified N-Haloamines: A Comparative Kinetic And Mechanistic Approach

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Abstract: *Kinetics and mechanism Ru(III) catalyzed and uncatalyzed oxidation of 5-nitroquinoline has been carried out in HCl medium at 298 K by N-haloamines (CAT, CAB, BAT and BAB). Under comparable experimental conditions, reactions showed identical kinetics with all the oxidants studied with first order dependence each on $[oxidant]_o$, $[substrate]_o$ and [Ru(III)] and fractional-order dependence on [HCl]. Reactions were studied at different temperatures (288-308 K). Activation parameter for both Ru(III) catalyzed and uncatalyzed reactions were computed. Ru(III) catalyzed reactions were found to be 7-9 times faster. Under identical experimental conditions, the rates were higher with bromamines compared to chloramines by a factor of 3 the order: BAB > BAT > CAB > CAT. This is attributable to the difference in electrophilicities of the halo cations, Br^+ and Cl^+. Probable mechanism and related rate law have been elucidated.*

Keywords: *5-nitroquinolie, oxidation-kinetics, Ru(III), catalysis*

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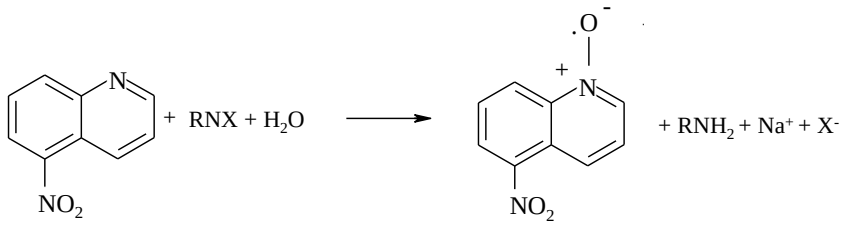
I. Introduction

Quinoline nucleus is a back bone of many natural products and pharmacologically significant compounds displaying a broad range of biological activity. Many functionalized quinolines are widely used as antimalarial, anti-inflammatory, anti-asthmatic, antibacterial, antihypertensive and thyrokinase inhibiting agents [1]. As they are increasingly useful and important in drugs, quinoline antibiotics has gained wide acceptance for the treatment of various bacterial infections to the larger extent. The new heterocycles show interesting chemical properties and they are attributed as potential antitumour reactants. Sadramycin and thiocoraline z natural depsi peptides which is 3 – hydroxyquinoline– 2-carboxylic acid plays a significant role in DNA binding properties of these compounds [2]. Quinolines have extremely vaired structure, due to various types of substitutions in their basic unit, which can influence their biological activity. Consequently, the biological activities of quinolines are highly dependent on the nature and position of the functional group [1-2]. For these reasons and in view of their medicinal importance, it is of immense interest to understand the redox chemistry of 5-nitro quinoline so as to explore the structure reactivity and mechanistic aspects of the reaction through the kinetic results. The literature survey shows that the information on the kinetics and mechanism of oxidation of quinolines is quite limited

Stoichiometry and product analysis

Different ratios of oxidant to 5NQ in presence of 1.0 x 10^{-2} mol dm^{-3} HCl and 1.0 x 10^{-7} mol dm^{-3} Ru(III) were equilibrated at 298 K for 24 hours. The unreacted oxidant in the reaction mixture was determined by iodometry. The analysis showed that one mole of 5NQ reacts with one mole of oxidant, leading to the following stoichiometry:



(1)

Here R = p-$CH_3C_6H_4SO_2$ for CAT and BAT and $C_6H_5SO_2$ for CAB and BAB; X = Cl or Br.

After completion of the reaction, the reaction products were neutralized with alkali and extracted with ether. The organic products were subjected to spot tests [6] and chromatographic analysis (TLC technique), which revealed the formation of oxidation as 5-nitroquinoline – N – oxide and its presence is confirmed by GC–MS analysis. GC–MS data was obtained on a 17A Shimadzu gas chromatograph with a QP-5050A Shimadzu mass spectrometer operating in electron-impact mode. The mass spectrum showed a molecular ion peak of 145 amu (Figure 1) confirming 5-nitroquinoline – N – oxide. It was also observed that there was no further oxidation of these products under the prescribed kinetic conditions.

The reduction product of CAT and BAT, p-toluenesulfonamide, was detected [7] by paper chromatography (R_f =0.905) and confirmed by mass spectral data (Figure 2). The reduction product of CAB and BAB, benzenesulfonamide, was detected by thin layer chromatography [8] and was confirmed by mass spectral analysis (Figure 3).

II. Results

The kinetics of oxidation of 5NQ by CAT, CAB, BAT, and BAB (henceforth abbreviated as oxidant) has been investigated at several initial concentrations of the reactants in the presence of HCl and Ru(III) catalyst at 298 K. Similar oxidation behavior is observe in the case of all the four oxidants under the identical experimental conditions.

Under the conditions $[oxidant]_o << [5NQ]_o$ and at constant $[oxidant]_o$, [HCl], [Ru(III)], and temperature, plots of log $k^/$ versus time were linear ($r > 0.9935$), indicated a first-order dependence on the rate of [oxidant]. The pseudo first-order rate constants ($k^/$) reported in Table 1 were found to be independent of $[oxidant]_o$ confirming the first-order dependence of rate on $[oxidant]_o$. Under the same experimental conditions, an increase in $[5NQ]_o$ led to an increase in the $k^/$ values (Table 1). Plots of log $k^/$ versus log [5NQ] were linear (Figure 4; $r > 0.9989$) with unit slopes, showing a first-order dependence of the rate on $[5NQ]_o$. Further, plots of $k^/$ versus [5NQ] were linear passing through the origin, confirming the first-order dependence on $[5NQ]_o$. When the [HCl] was increased, keeping the other experimental conditions constant, the rate of the reaction increased (Table 2). Plots of log $k^/$ versus log [HCl] were linear (Figure 5; $r > 0.9912$) with slopes of less than unity (0.61 – 0.66), showing a fractional-order dependence of rate on [HCl]. The rate increased with increase in [Ru(III)] (Table 2). Plots of log $k^/$ versus log [Ru(III)] were linear (Figure 6; $r > 0.9908$) with unit slopes, indicating a first-order dependence on [Ru(III)].

At constant $[H^+]$ of 1.0×10^{-2} mol dm^{-3} maintained with HCl, the addition of NaCl (1.0×10^{-3} - 4.0×10^{-3} mol dm^{-3}) did not alter the rate of the reaction. Therefore, the dependence of rate on [HCl] confirms the effect of $[H^+]$ only. Similarly, addition of NaBr (1.0×10^{-3} - 4.0×10^{-3} mol dm^{-3}) showed no effect on the rate (Table 3). These results indicate that there is no role for halide ions in the reaction. Addition of the reduction product of oxidants, p-toluenesulfonamide or benzenesulfonamide (1.0×10^{-3} – 4.0×10^{-3} mol dm^{-3}), to the reaction mixture did not affect the rate significantly. This indicates that neither PTS nor BSA is involved in any step prior to the rate determining step in the scheme proposed.

Rate studies were carried out in water-MeOH mixtures having different compositions (0 - 30 % v/v), thereby varying the dielectric constant of the solvent medium. The rate was found to increase with increase in MeOH content (Table 3) and plots of log $k^/$ versus 1 / D were linear (Figure 7; $r > 0.9919$) with positive slopes. Blank experiments performed with MeOH indicated that there was no oxidation of methanol by any of the four oxidants under the selected experimental conditions.

The effect of the temperature on the rate was studied by performing the kinetic experiments at various temperatures (288 – 308 K), keeping other experimental conditions constant. From the linear Arrhenius plots of log $k^/$ versus 1/T (Figure 8; $r > 0.9939$), the values of activation parameters for the overall reaction were evaluated. These data are summarized in Table 4. Rate studies in D_2O medium for CAT and BAB revealed that $k^/(H_2O) = 4.02 \times 10^{-4}$ s^{-1} and 26.7×10^{-4} s^{-1}, and $k^/(D_2O) = 5.58 \times 10^{-4}$ s^{-1} and 35.5×10^{-4} s^{-1} respectively. Test for the absence of free radicals was confirmed by acrylamide test.

III. Discussion

Aqueous solutions of organic haloamines act as strong electrolytes and, depending on the pH, they generate different types of reactive species [9]. The possible oxidizing species present in acid medium are RNHX, RNX_2, HOX and also perhaps H_2OX. In the present studies, the first-order dependence of rate on $[oxidant]_o$ and no effect of rate on $[RNH_2]$ clearly ruled out the possibility of both RNX_2 and HOX as reactive species. Further, Hardy and Johnston [10], who have studied the pH dependent relative concentrations of the reactive species present in acidified haloamine solutions of comparable molarities, have shown that RNHX is the likely oxidizing species in acid medium. Narayanan and Rao [11] and Subhashini *et al* [12] have reported that monochloramines can further get protonated. Because organic haloamines have similar chemical properties, the same equilibria can be expected for BAT and BAB also. In the present case, the fractional-order dependence

of rate on $[H^+]$ suggests that the protonation of RNHX results in the formation of RNH_2X, which is likely to be the active oxidizing species involved in the oxidation of 5NQ.

Although Cady and Connick [13] and Connick and Fine [14] have shown from absorption spectral studies in aqueous media that octahedral complexes such as $[RuCl_5(H_2O)]^{2-}$, $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, $[RuCl_2(H_2O)_4]^+$ and $[RuCl(H_2O)_5]^{2+}$ do not exist for $RuCl_3$, others [12-17] have shown that in acid solutions the following equilibria exists for Ru(III):

$$RuCl_3.xH_2O + 3HCl \longrightarrow [RuCl_6]^{3-} + xH_2O + 3H^+ \quad (2)$$

$$[RuCl_6]^{3-} + H_2O \rightleftharpoons [RuCl_5(H_2O)]^{2-} + Cl^- \quad (3)$$

Singh *et al* [18-19] used the above type of equilibrium in the case of Ru (III) chloride catalyzed oxidation of primary alcohols by chloramine-T and of glycols by N-bromoacetamide in acid medium. In the present study, however, the absence of the effect of chloride ion on the rate indicates that equilibrium (2) has no role in the reaction, hence, $[RuCl_5(H_2O)]^{2-}$ complex ion, has been assumed to be the reactive catalyzing species. Similar results were observed in Ru(III) catalyzed oxidation of chloroacetic acids [20], ethanols [21] and aliphatic primary amines [22] by bromamine-T.

In the present investigation, the absence of effect of chloride ion on the rate indicates that the equilibrium (2) does not play any role in the reaction and hence the complex ion, $[RuCl_5(H_2O)]^{2-}$, is assumed to be the reactive catalyst species that interacts with 5NQ to form an intermediate complex. Similar type of interactions have been reported in the Ru(III) catalyzed oxidation of several other substrates by organic haloamines [20, 23-25].

The complex formation between the substrate and catalyst was evidenced from the UV-Visible spectra of both 5NQ and 5NQ-Ru(III) mixture, in which a shift of 5NQ from 347 nm to 341 nm was observed, indicating the formation of a complex. Such type of substrate-catalyst complex formation has also been reported by others studies [24, 26-27].

In the light of above observations, a general mechanism (Scheme 1) is proposed for the Ru(III)-catalyzed oxidation of 5NQ by organic haloamines in HCl medium to account for the experimental observations:

$$RNHX + H^+ \overset{K_1}{\rightleftharpoons} RNH_2X \quad \text{(i) fast}$$

$$5NQ + RNH_2X \overset{K_2}{\rightleftharpoons} \text{complex} \quad \text{(ii) fast}$$

$$\text{complex} + Ru(III) \xrightarrow{k_3} \text{complex1} \quad \text{(iii) slow and rds}$$

$$\text{complex1} + RNH_2X \xrightarrow{+k_4} \text{Products} \quad \text{(iv) fast}$$

Scheme 1. General scheme for the oxidation of 5NQ by N-haloamines in acid medium.

In Scheme 1, complex and complex1 are complex intermediate species whose structures are shown in Scheme 2, where a detailed mechanistic interpretation of Ru(III) catalyzed 5NQ -haloamines reaction in acid medium is depicted.

The total effective concentration of oxidant is $[oxidant]_t$, then

$$[oxidant]_t = [RNHX] + [RN^+H_2X] \quad (4)$$

By substituting for [RNHX] from equilibrium (i) of Scheme 1 in equation (4) and solving for $[RN^+H_2X]$ one obtains:

$$[RN^+H_2X] = K_1[oxidant]_t [H^+] / K_1[H^+] + 1 \quad (5)$$

Solving for the [complex] from equilibrium (ii) of Scheme 1, one gets

$$[Y] = K_2 [5NQ] [Ru(III)] \quad (6)$$

From the slow step (iii) of Scheme 1,

$$Rate = k_3 [RN^+H_2X] [Y]_+ \quad (7)$$

Upon substituting for $[RN^+H_2X]$ from equation (5) and for [complex] from equation (6), equation (7) yields the following rate law (equation (7)):

$$\text{Rate} = \frac{K_1K_2k_3\,[\text{oxidant}]_t\,[5NQ]\,[H^+]\,[Ru(III)]}{K_1[H^+] + 1} \qquad (8)$$

The rate law (8) is in agreement with the experimentally observed results.
Since rate = $k^{/}[\text{oxidant}]_t$, equation (8) can be transformed into equations (9) and (10):

$$k^{/} = \frac{K_1K_2k_3[5NQ]\,[H^+]\,[Ru(III)]}{K_1[H^+] + 1} \qquad (9)$$

$$\frac{1}{k^{/}} = \frac{1}{K_2k_3\,[5NQ]\,[Ru(III)]} + \frac{1}{K_1K_2k_3\,[5NQ]\,[Ru(III)]\,[H^+]} \qquad (10)$$

A plot of $1 / k^{/}$ versus $1 / [H^+]$ according to equation (10), with other experimental conditions held constant, was found to be linear for each oxidant (Figure 9; $r > 0.9851$). The protonation constant (K_1) of RNHX and K_2k_3 values have been calculated from the slope and intercept of such plots for the standard run, $[\text{oxidant}]_o = 1.0 \times 10^{-3}$ mol dm^{-3}; $[5NQ]_o = 1.0 \times 10^{-4}$ mol dm^{-3}; $[Ru(III)] = 1.0 \times 10^{-7}$ mol dm^{-3} at 298 K. Values of deprotonation constant $K^{/}_1 = 1 / K_1$ have also been calculated for each oxidant. These are given in Table 5. Nearly constant values of K_1 and $K^{/}_1$ forms an indirect proof for the formation of the reactive species RN^+H_2X from RNHX, substantiating the proposed mechanism. Scheme 1 and rate law (8) can explain the following observed results:

Reactions in aqueous medium that are susceptible to acid-base catalysis have been studied in heavy water (D_2O) after equilibrium. Since the majority oxidation reactions of organic compounds involve the cleavage of C-H bond, deuterium isotope effect on such reaction gives information regarding the nature of the rate determining step. In the present investigations, solvent isotope studies have shown that the rate of reaction is higher in D_2O medium. For a reaction involving a fast equilibrium H^+ or OH^- ion transfer, the rate increases in D_2O medium since D_3O^+ or OD^- are a stronger acid and a stronger base respectively, than H_3O^+ and OH^- ions [28]. The observed solvent isotope effect of $k^{/}$ (H_2O) and $k^{/}$ (D_2O) < 1 is due to the greater acidity of D_3O^+ compared to H_3O^+. However, the magnitude of increase in rate in D_2O is small (expected value is 2-3 times greater). This may be due to the fractional order dependence of rate on $[H^+]$. Hence, this observation supports the planned mechanism.

Addition of methanol to the reaction mixture increased the reaction rate. The positive dielectric effect observed in the present studies (Table 3) clearly supports [28] the involvement of dissimilar charges in the rate determining step in the mechanism proposed (Scheme 2).

Under comparable experimental conditions, the reactivity rates of organic haloamines towards 5NQ in the presence of $RuCl_3$ catalyst follow the order: BAB > BAT > CAB >CAT (Table 1.). The data in Table 4 also indicate that the energy of activation is highest for the slowest reaction and *vice versa*, as expected, indicating that the reaction is enthalpy controlled. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the oxidation of 5NQ with all the four oxidants are linearly related (Figure 10; $r = 0.9983$), with an isokinetic temperature of $\beta = 353$ K, indicating that a similar mechanism operates in the oxidation of 5NQ by all the four oxidants. Further, the genuinity of the isokinetic relationship was verified by the Exner criterion by plotting $\log k^{/}_{(298\ K)}$ versus $\log k^{/}_{(288\ K)}$; this plot is linear (Figure 11; $r = 0.9985$) and the value of β was found to be 360 K. The values of β evaluated from both the plots are much higher than the temperature range used in the present work. This indicates a common enthalpy controlled pathway for all the reactions. The proposed mechanism is also supported by the moderate values of energy of activation and other thermodynamic parameters. The fairly high positive values of the free energy of activation and of the enthalpy of activation suggest that the transition state is highly solvated, while the high negative entropy of activation indicates the formation of rigid associated transition states. The values of $\Delta G^{\neq}$ obtained in the cases of all the oxidants suggests that the oxidation of 5NQ by organic haloamines proceeds by a similar mechanism.

It was felt interesting to compare the reactivity of these four organic haloamines towards 5NQ in the absence of Ru(III) catalyst under identical experimental conditions in order to evaluate the catalytic efficiency of Ru(III). Hence, the reactions were studied at different temperatures (288-308 K). From the plots of $\log k^{/}$ versus $1 / T$ (Figure 12; $r > 0.9930$), activation parameters were evaluated for the uncatalyzed reactions (Table 4). The rate of reaction for uncatalyzed oxidation of 5NQ follows the order: BAB > BAT > CAB > CAT. A similar trend was also observed in the presence of Ru(III) catalyst. However, the Ru(III) catalyzed reactions

were found to be 7-9 times faster. This was also supported by the activation parameters calculated (Table 4). Thus, the observed rates of oxidation in the presence of Ru(III) catalyst justify the need of a catalyst for a facile oxidation of the 5NQ by the organic haloamines chosen. Further, the results suggest that Ru(III) has been an efficient catalyst in effecting the oxidation of 5NQ by organic haloamines in acidic medium also. The activation parameters evaluated for the catalyzed and uncatalyzed reactions explain the catalytic effect on the reaction. The catalyst Ru(III) forms a complex (Y) with the substrate, which increases the reducing property of the substrate than in absence of it. Further, the catalyst Ru(III) favourably modifies the reaction path by lowering the energy of activation (Table 4).

The values of catalytic constant (K_C) have been evaluated for each oxidant at different temperatures (288 K – 308 K) was found to vary with temperature. Further, plots of log K_C versus 1 / T were linear (Figure 13; r > 0.9901) and the values of energy of activation and other activation parameters for the catalyst were computed and are summarized in Table 5.

Under identical experimental conditions, the rates were higher with bromamines compared to chloramines by a factor of 3 (Table 1) and follow the order: BAB > BAT > CAB > CAT. This is attributable to the difference in electrophilicities of the halo cations, Br^+ and Cl^+, involved in the oxidation process and is also related to the ease with which these species are generated in reactions. In these reactions, the electronegativity values of Br^+ and Cl^+ play a vital role. Bromine has the electronegativity of 2.7 while chlorine has a higher value of 2.8. As the electronegativity increases, the electropositive nature decreases, since the halo cations are the reactive species in these oxidation reactions, and the electropositive nature of Br > Cl. This may also be due to the moderate differences in the van der Waal's radii of bromine and chlorine. Therefore, the reactivity of bromamines is greater than that of chloramines. This is consistent with the observed order of reactivity: BAB > BAT > CAB > CAT in the present work. Hence, it can be generalized that bromamines are stronger oxidants as compared to chloramines. Further, the observed oxidation rates are lower in BAT and in CAT compared to the rates in BAB and in CAB, the ratios $k^{/}$(BAB) / $k^{/}$(BAT) and $k^{/}$ (CAB) / $k^{/}$(CAT) were found to be nearly 2. This indicates the participation of a $–CH_3$ group in CAT and BAT, which exerts a strong inductive effect in enriching the electron density at the polar N-X bond, thereby reducing the electrophilicity of the X atom. This explains why the reactivity of benzenesulfonamide derivatives is higher than that of toluenesulfonamide derivatives of organic haloamines. It also substantiates the observed overall order of reactivity BAB > BAT > CAB > CAT towards the oxidation of 5NQ in the present work. It can be concluded therefore that Ru(III) act as an efficient catalyst in the oxidation of 5NQ by selected organic haloamines in acid medium.

Table 1

Effect of varying oxidant and substrate concentrations on the rate of reaction.

10^4[oxidant]$_o$ (mol dm^{-3})	10^3[5NQ]$_o$ (mol dm^{-3})	$10^5k^{/}$ (s^{-1})				$k^{/}_{BAT} / k^{/}_{CAT}$	$k^{/}_{BAB} / k^{/}_{CAB}$
		CAT	CAB	BAT	BAB		
0.50	1.00	2.14	3.88	6.45	12.8	2.8	3.2
1.00	1.00	4.02	8.03	12.7	26.3	3.1	3.5
2.00	1.00	8.22	15.8	25.9	53.9	3.1	3.5
4.00	1.00	17.2	34.9	49.7	103	2.7	23.0
5.80	1.00	24.3	49.8	80.2	157	3.4	3.1
1.00	0.20	3.92	8.05	12.8	26.6		
1.00	0.50	4.03	8.05	12.5	26.7		
1.00	1.00	4.05	7.97	12.7	26.8		
1.00	2.00	3.97	7.92	12.9	26.5		
1.00	4.00	4.04	8.06	13.1	26.2		

[HCl] = 1.00 x 10^{-2} mol dm^{-3}; [Ru(III)] = 1.00 x 10^{-5} mol dm^{-3}; T = 298 K.

Table 2

Effect of varying acid and catalyst concentrations on the rate of reaction.

10^2[HCl] (mol dm^{-3})	10^5[Ru(III)] (mol dm^{-3})	$10^5k^{/}$ (s^{-1})			
	CAT	CAB	BAT	BAB	
0.20	1.00	1.45	2.96	4.51	8.85

0.50	1.00	2.60	5.08	8.07	16.2
1.00	1.00	4.02	8.03	12.7	26.3
2.00	1.00	6.51	12.1	19.6	41.2
5.00	1.00	10.1	22.2	34.3	74.6
1.00	0.20	1.03	1.59	2.55	5.40
1.00	0.50	2.11	4.08	6.50	13.5
1.00	1.00	4.02	8.03	12.8	26.8
1.00	2.00	8.04	15.8	26.0	55.0
1.00	5.00	19.1	39.7	63.1	141

$[oxidant]_o$ = 1.00 x 10^{-3} mol dm^{-3}; $[5NQ]_o$= 1.00 x 10^{-4} mol dm^{-3}; T = 298 K.

Table 3

Effect of varying ionic strength and dielectric constant of the medium on the rate of reaction.

MeOH % (v/v)	$10^5 k^{/}$ (s^{-1}) CAT	CAB	BAT	BAB
0	4.02	8.03	12.7	26.3
10	5.05	9.22	15.1	28.5
20	7.01	11.5	18.5	34.0
30	10.1	14.2	24.0	40.0

$[oxidant]_o$ = 1.00 x 10^{-4} mol dm^{-3}; $[5NQ]_o$ = 1.00 x 10^{-3} mol dm^{-3};
[HCl] = 1.00 x 10^{-2} mol dm^{-3}; [Ru(III)] = 1.00 x 10^{-5} mol dm^{-3}; T = 298 K.

Table 4

Effect of varying temperature on the rate of reaction and values of activation parameters for the oxidation of 5NQ by CAT, CAB, BAT and BAB in presence and absence of Ru(III) catalyst.

Temperature (K)	$10^5 k^{/}$ (s^{-1}) CAT	CAB	BAT	BAB
288	1.52[a] (0.15)[b]	3.15(0.28)	5.25(0.57)	14.5(1.27)
293	2.62(0.26)	5.12(0.37)	7.81(0.93)	20.2(2.08)
298	4.02(0.51)	8.03(0.88)	12.7(1.57)	26.3(3.53)
303	5.27(0.91)	11.3(1.62)	17.5(3.07)	35.2(6.59)
308	9.57(1.55)	17.4(3.05)	26.5(5.58)	50.3(9.62)
E_a (kJ mol^{-1})	72.5 (97.8)	61.5(89.9)	55.3(79.1)	41.5 (68.8)
$\Delta H^{\neq}$ (kJ mol^{-1})	71.1±0.06 (94.1±0.05)	60.2±0.08 (87.8±0.07)	52.8±0.04 (77.5±0.32)	39.5±0.04 (66.7±0.07)
$\Delta G^{\neq}$ (kJ mol^{-1})	92.8±0.92 (98.3±0.45)	90.3±0.52 (95.9±0.75)	90.8±0.82 (95.3±0.66)	87.90±0.53 (92.8±0.56)
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	-73.8±0.56 (-13.0±0.55)	-105±0.35 (-28.9±0.51)	-125±0.45 (-63.1±0.53)	-165±0.51 (-87.3±0.35)
log A	9.32±0.05 (12.3±0.11)	7.58±0.04 (11.5±0.03)	6.78±0.06 (10.3±0.04)	4.78±0.04 (8.59±0.05)

Values in parentheses refer to oxidation of 5NQ in the absence of Ru(III) catalyst.
a : $[oxidant]_o$ = 1.00 x 10^{-4} mol dm^{-3}; $[5NQ]_o$= 1.00 x 10^{-3} mol dm^{-3};
[HCl] = 1.00 x 10^{-2} mol dm^{-3}; [Ru(III)] = 1.00 x 10^{-7} mol dm^{-3}.
b : Experimental conditions are the same as 'a' without Ru(III) catalyst.

Table 5

Data calculated from plots of $1/ k^{/}$ versus $1 / [H^+]$ using equation (9.8).

oxidant	$10^3 K_1$ (dm^3 mol^{-1})	$10^8 K_2 k_3$ (dm^3 mol^{-1} s^{-1})	$10^4 K^{/}_1$ (mol dm^{-3})
CAT	2.67	2.00	3.75
CAB	3.50	5.00	2.86

BAT	3.30	10.0	3.03
BAB	2.96	12.5	3.38

$[oxidant]_o$ = 1.00 x 10^{-4} mol dm^{-3}; $[5NQ]_o$= 1.00 x 10^{-3} mol dm^{-3};
[Ru(III)] = 1.00 x 10^{-7} mol dm^{-3}; T = 298 K.

Table 6

Values of catalytic constant (K_C) at different temperatures and activation parameters calculated using K_C values.

Temperature (K)	10^{-3} K_C			
	CAT	CAB	BAT	BAB
288	1.37	2.91	4.74	13.2
293	2.35	4.75	6.82	18.1
298	4.49	7.11	11.2	22.5
303	4.35	9.65	14.7	29.5
308	8.03	14.1	20.7	40.6
E_a (kJ mol^{-1})	58.6	57.3	52.5	44.3
$\Delta H^{\neq}$ (kJ mol^{-1})	56.1±0.06	54.8±006	50.0±0.09	41.8±0.06
$\Delta G^{\neq}$ (kJ mol^{-1})	57.3±0.40	57.1±0.81	56.4±0.60	56.5±0.61
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	-5.02±0.80	-7.56±0.71	-14.8±0.71	-49.2±0.21
log A	13.8±0.02	13.4±0.02	13.1±0.04	12.1±0.03

$[oxidant]_o$ = 1.00 x 10^{-4} mol dm^{-3}; $[5NQ]_o$ = 1.00 x 10^{-3} mol dm^{-3};
[HCl] = 1.00 x 10^{-2} mol dm^{-3}.

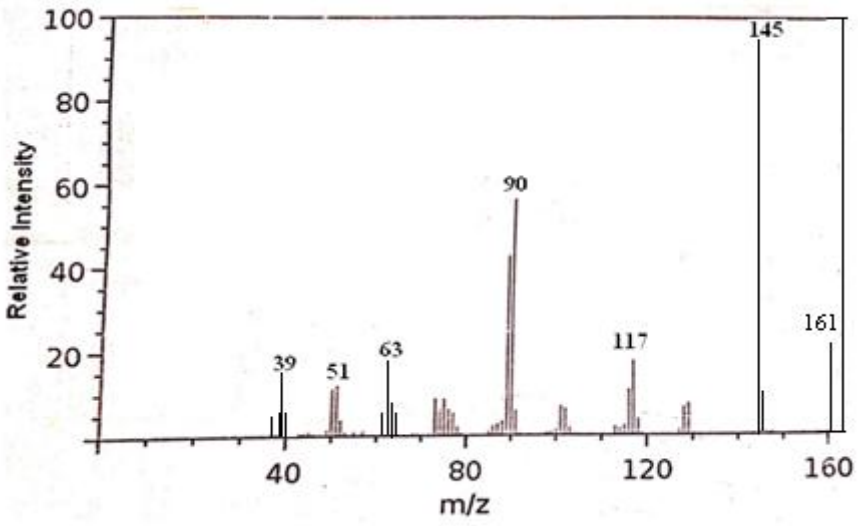


Figure 1 GC-Mass spectrum of 5-nitroquinoline-N-oxide with its molecular ion peak at 161 amu.

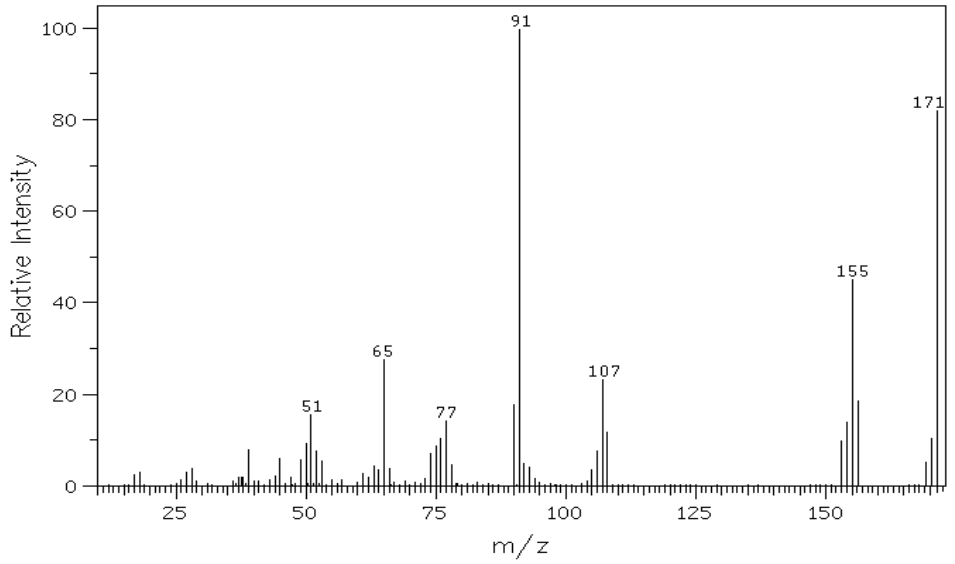


Figure 2 GC-Mass spectrum of p-toluenesulfonamide with its molecular ion peak at 171 amu.

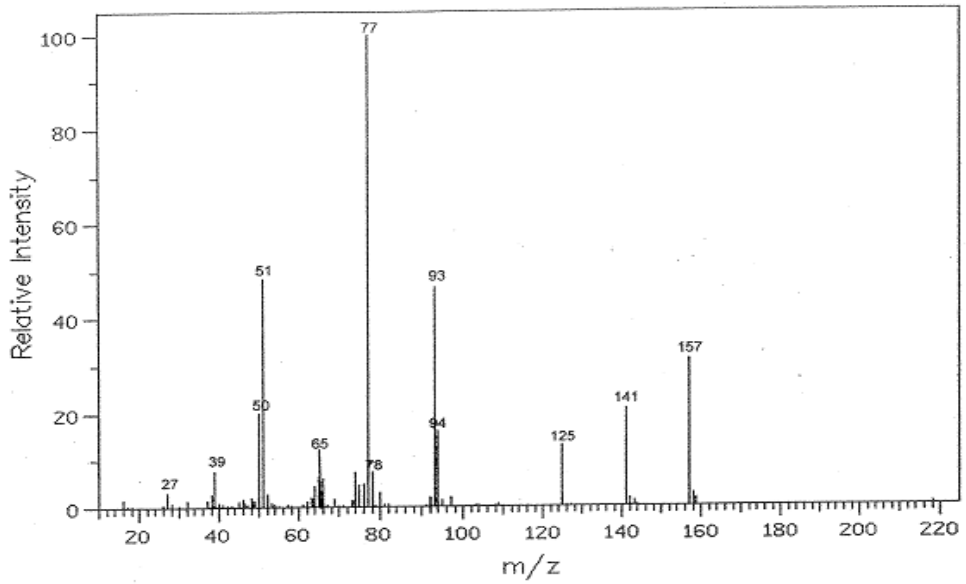


Figure 3 GC-Mass spectrum of benzenesulfonamide with its molecular ion peak at 157 amu.

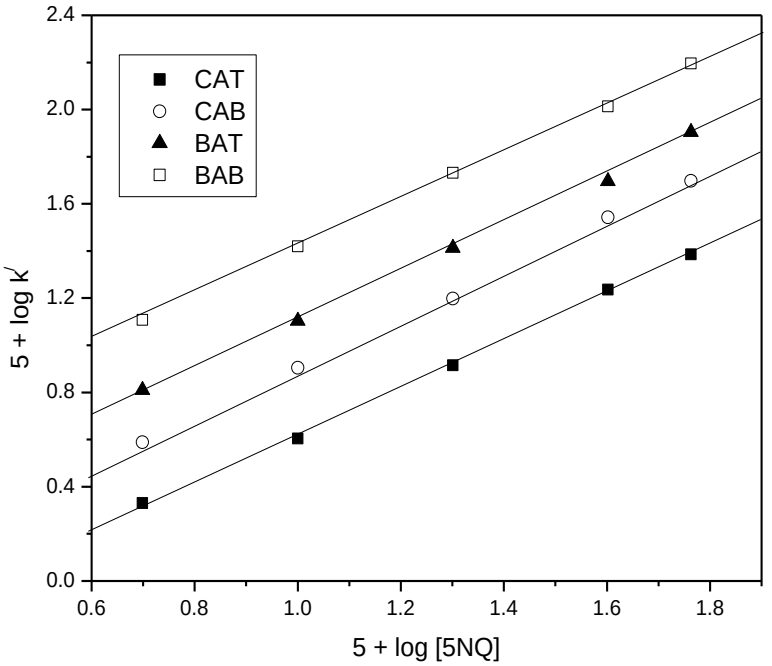


Figure 4 Plots of log k/ versus log [5NQ]

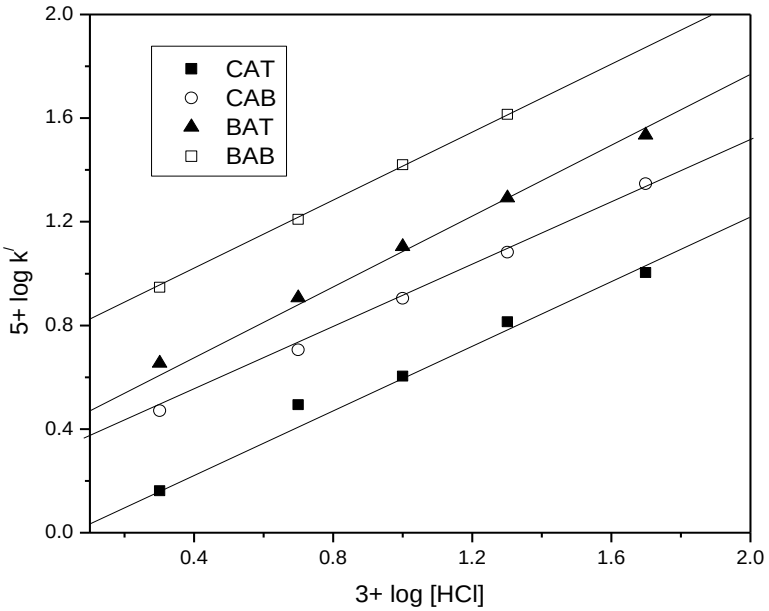


Figure 5. Plots of log k/ versus log [HCl].

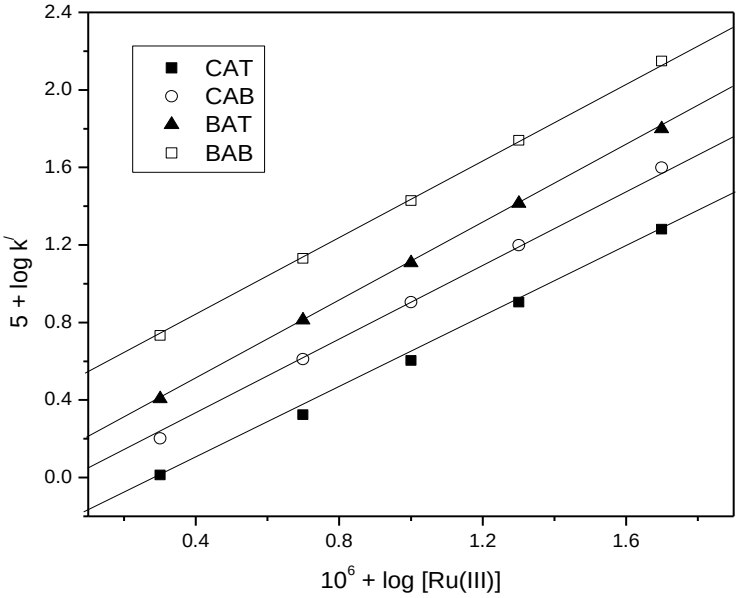


Figure 6. Plots of log k/ versus log [Ru(III)].

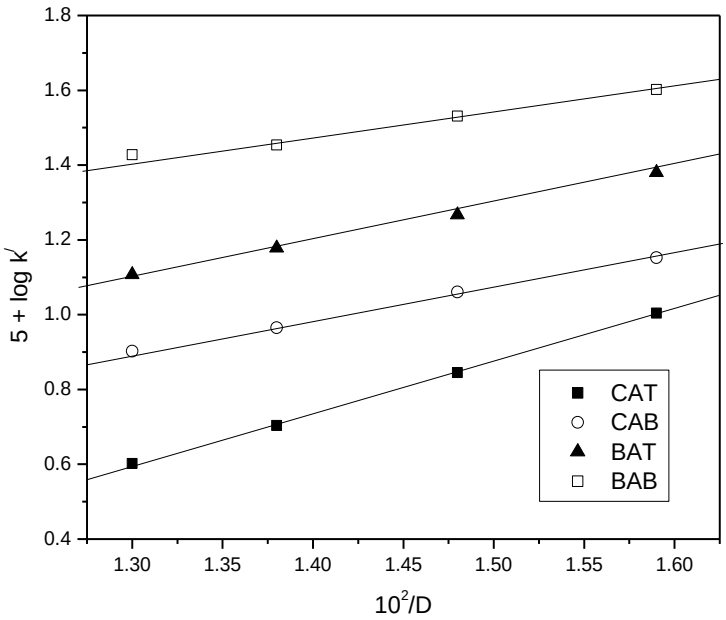


Figure 7. Plots of log k/ versus 1/D.

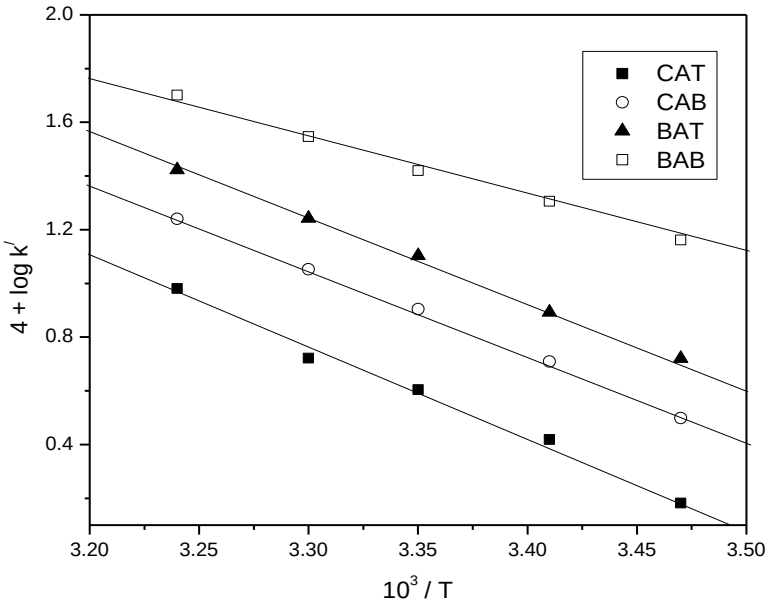


Figure 8. A plot of log $k^{/}$ versus 1/T.

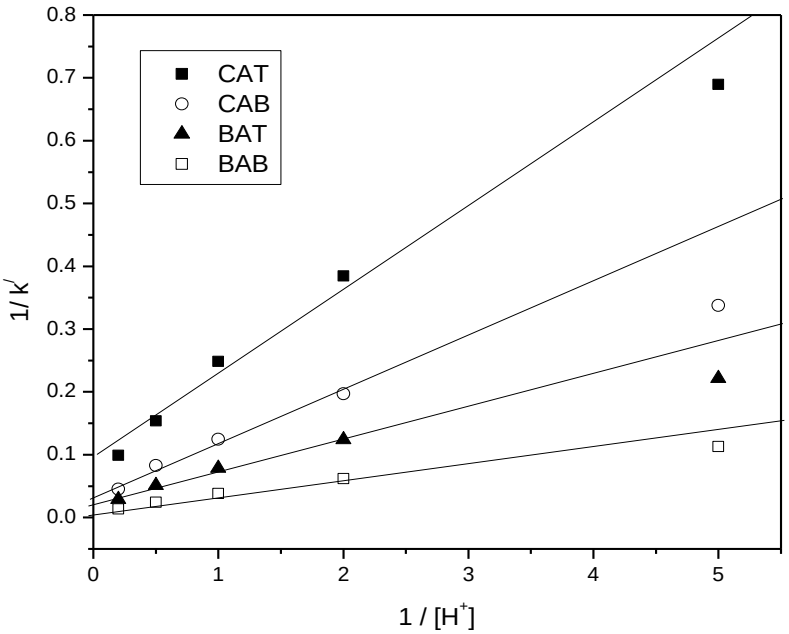


Figure 9. A plot of $1/k^{/}$ versus $1/[H^{+}]$.

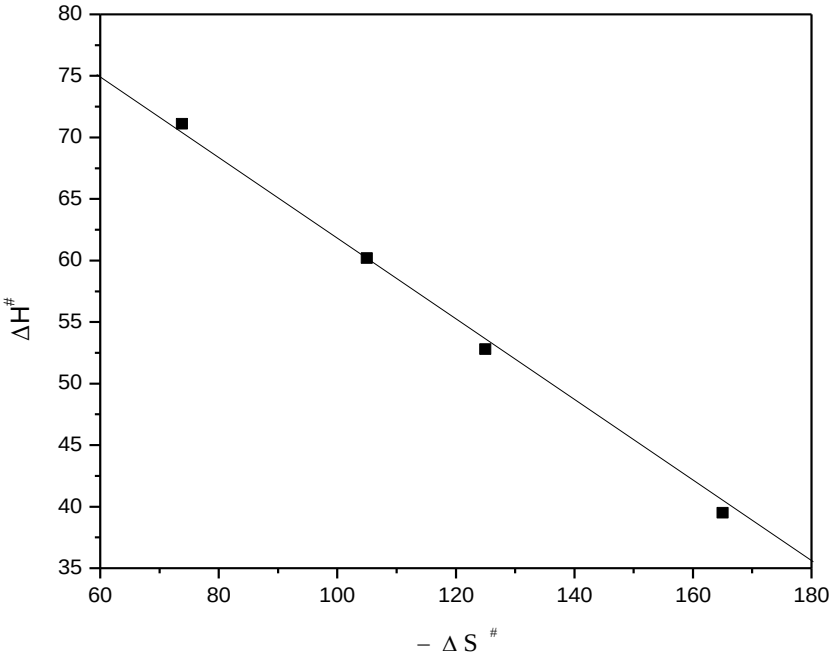


Figure 10. A plot of $\Delta H^{\#}$ *versus* - $\Delta S^{\#}$

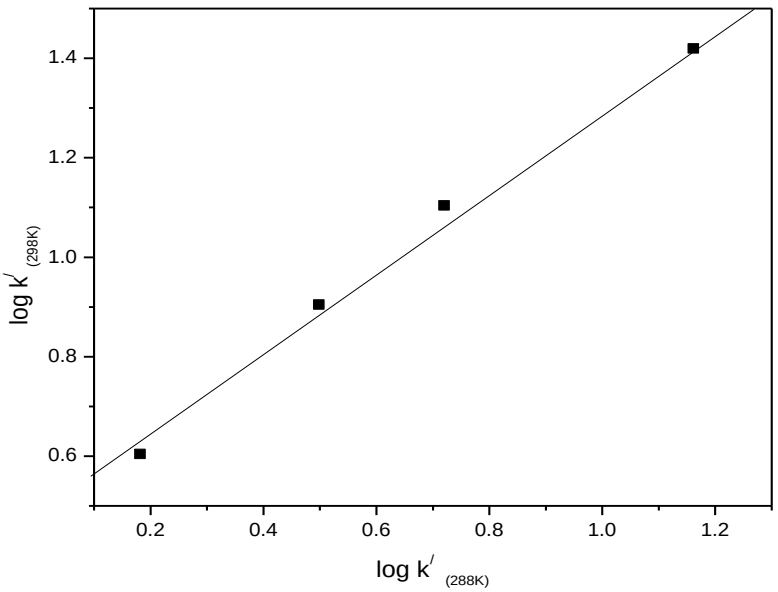


Figure 11. A plot of log $k^{/}_{(298K)}$ versus log $k^{/}_{(288K)}$

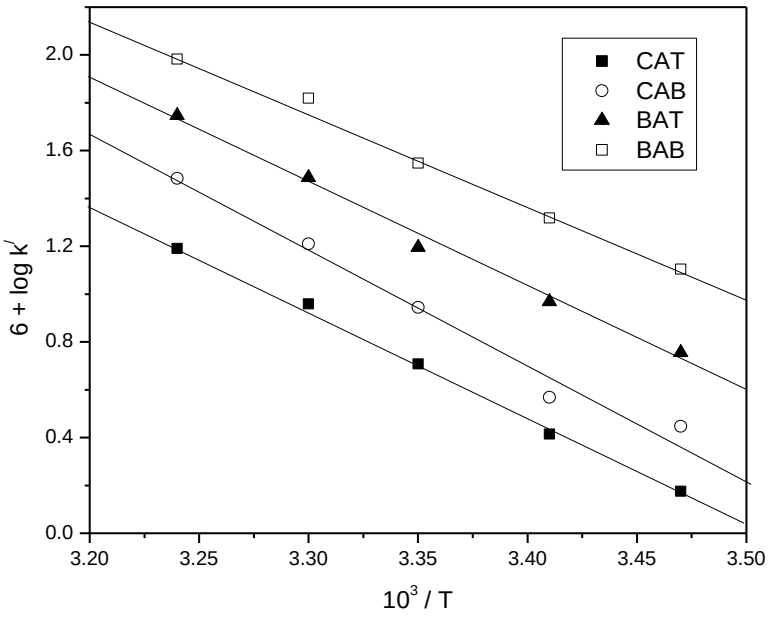


Figure 12. A plot of log $k^{/}$ versus 1/T for uncatalyzed reactions.

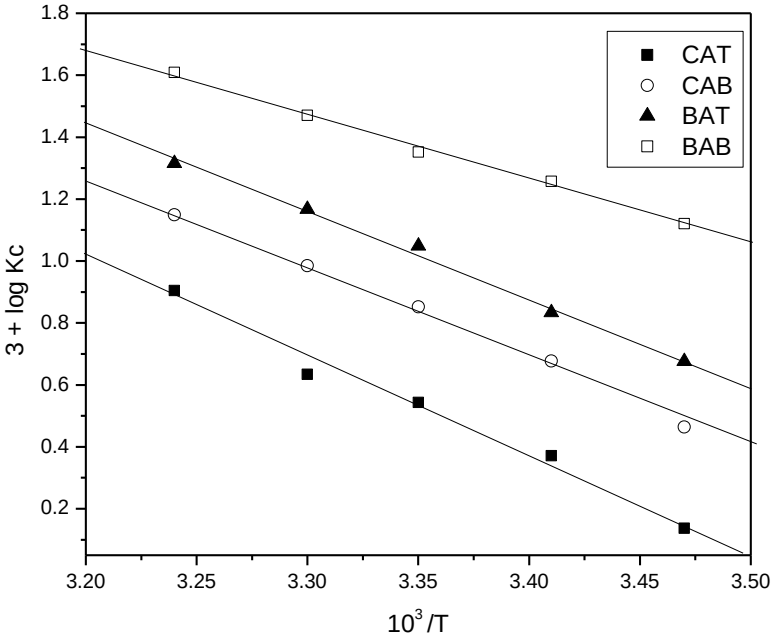
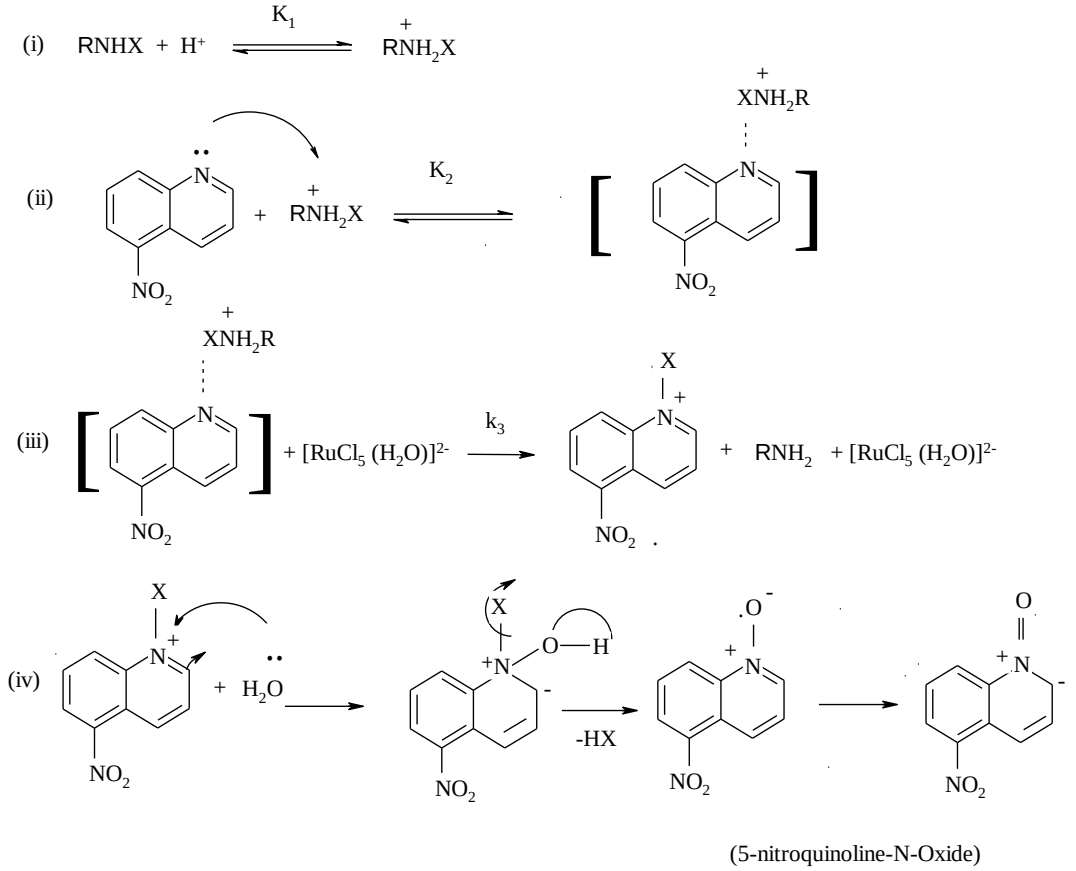


Figure 13. A plot of log K_C versus 1/T



Scheme 2 A detailed mechanistic interpretation for the oxidation of 5NQ by N-haloamines in HCl medium.

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