Ruthenium(III)-Catalyzed Mechanistic Studies of Oxidation of Benzhydrols by Sodium *N*-Chloro-*p*-Toluenesulfonamide in HCl Medium

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ABSTRACT: The kinetics of oxidation of benzhydrol and its *p*-substituted derivatives (YBH, where Y = H, Cl, Br, NO_2, CH_3, and OCH_3) by sodium *N*-chloro-*p*-toluenesulfonamide or chloramine-T (CAT), catalyzed by ruthenium(III) chloride, in the presence of hydrochloric acid in 30% (v/v) MeOH medium has been studied at 35°C. The reaction rate shows a first-order dependence on $[CAT]_O$ and a fractional-order each on $[YBH]_O$, [Ru(III)], and $[H^+]$. The reaction also has a negative fractional-order (-0.35) behavior in the reduction product of CAT, *p*-toluenesulfonamide (PTS). The increase in MeOH content of the solvent medium retards the rate. The variation of ionic strength of the medium has negligible effect on the rate. Rate studies in D_2O medium show that the solvent isotope effect, $k'H_2O/k'D_2O$, is equal to 0.60. Proton inventory studies have been made in $H_2O—D_2O$ mixtures. The rates correlate satisfactorily with Hammett σ relationship. The LFE relationship plot is biphasic and the reaction constant $\rho = -2.3$ for electron donating groups and $\rho = -0.32$ for electron withdrawing groups at 35°C. Activation parameters $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$ have been calculated. The parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, are linearly related with an isokinetic temperature $\beta = 334$ K indicating enthalpy as a controlling factor. A mechanism consistent with the observed kinetics has been proposed. © 1997 John Wiley & Sons, Inc. Int J Chem Kinet **29:** 773–780, 1997.

INTRODUCTION

Considerable attention has centered around the chemistry of *N*-metallo-*N*-haloarylsulfonamides because of their versatile ability to act as mild oxidants, halogenating agents, and *N*-anions. They can behave as both electrophiles and nucleophiles depending on the reaction conditions. Chloramine-T or CAT (p-Me—$C_6H_4SO_2NClNa$ 1.5 H_2O), which is a prominent chlorine derivative of this class of organic haloamines and a byproduct in saccharin manufacture, is a well-known analytical reagent. Mechanistic aspects of many of its reactions have been reported [1-4]. Chloramine-T has been found to specifically oxidize pri-

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mary and secondary alcohols to corresponding aldehydes and ketones in good yields in aqueous solutions under mild conditions [5,6]. Mild oxidation of alcohols to carbonyl compounds is a very important synthetic tool in organic synthesis [7,8]. A significant amount of work has been done on the mechanistic studies of oxidation of alcohols by transition metal ions such as chromium(VI), vanadium(V), cobalt(III), manganese(VII), and cerium(IV) in acid medium [9] and copper(II) [10], ruthenium tetroxide, and ferrate(VI) ions in alkaline medium [11,12]. However, there is no report in the literature on the oxidation kinetics of secondary aromatic alcohols by *N*-metallo-*N*-haloarylsulfonamides. Preliminary experiments involving several *N*-haloarylsulfonamides have shown that CAT is an excellent oxidant which allows controlled conversion of alcohols to corresponding carbonyl products in the presence of the catalyst ruthenium(III) chloride in acid medium. Furthermore, this redox system is adoptable for large scale operations. In an effort to understand the mechanism of alcohol-CAT redox reaction, we have studied the kinetics of oxidation of six substituted benzhydrols or diphenyl carbinols by CAT. Optimum conditions of the reaction have been devised for the formation of benzophenone which, in addition to being an important constituent of perfumes, finds applications in the manufacture of antihistamines, hypnotics, and insecticides. Activation parameters have been calculated and a Hammett-free energy relationship has been tested. An isokinetic relationship has also been deduced.

EXPERIMENTAL

Oxidant

Chloramine-T or CAT (N. R. Chem., Bombay) was purified by the method of Morris et al. [13]. An aqueous solution of CAT was prepared, standardized iodometrically, and stored in amber colored stoppered bottles until further use. The concentration of the stock solution was periodically checked.

Substrates (YBH)

Benzhydrol, 4-chlorobenzhydrol, 4-bromobenzhydrol, 4-nitrobenzhydrol, 4-methylbenzhydrol, and 4-methoxybenzhydrol (Aldrich Chemical Co., USA) were of acceptable grades of purity and used without further purification to prepare solutions in 30% MeOH (v/v).

Catalyst

A solution of $RuCl_3$ (Arora Mathey, Bombay), prepared in 0.50 mol dm^{-3} hydrochloric acid, was used as the catalyst. Allowance was made for the amount of acid present in the catalyst solution while preparing the solutions for kinetic runs.

All other reagents used were of analytical grade. Solvent isotope studies were made with D_2O (99.2%) supplied by the Bhabha Atomic Research Centre, Bombay, India. Triple distilled water was used for preparing all aqueous solutions. The ionic strength of the reaction mixtures was kept at a constant value (0.40 mol dm^{-3}) using a concentrated solution of sodium perchlorate. Regression analysis of experimental data was carried out on an EC-72 Statistical Calculator (Electronic Corporation, India).

Kinetic Measurements

The reaction was carried out in stoppered Pyrex boiling tubes whose outer surfaces were coated black to eliminate photochemical effects. Kinetic runs were performed under pseudo-first-order conditions with a known excess of [YBH] over [CAT] at 35°C. For each run, requisite amounts of solutions of YBH, HCl, $NaClO_4$, and $RuCl_3$ were taken in the tube. Required amounts of MeOH and water (to maintain a 30% MeOH medium and a constant total volume) were added. The tube was thermostated in a water bath at a set temperature (35°C). A measured amount of CAT solution, also preequilibrated at the same temperature, was added to the above mixture to initiate the reaction. The reaction mixture was periodically shaken for uniform concentration. The progress of the reaction was monitored by withdrawing known aliquots from the reaction mixture at regular time intervals and determining the unreacted CAT concentration iodometrically. The reaction was followed for at least two half-lives. The pseudo-first-order rate constants, k_1' or k_{obs}, calculated were reproducible within ±3%.

Reaction Stoichiometry

Preliminary studies were performed with mixtures of varying mole ratios of CAT to YBH (CAT $\gg$ YBH), in the presence of 0.50 molar HCl and 4.82×10^{-5} molar $RuCl_3$ in 30% MeOH, thermostated for 24 h or longer at 35°C.

Product Analysis

The reaction products were analyzed by column chromatography with silica gel (60–200 mesh) using gra-

Table I Effect of Varying Reactant Concentrations on the Rate[a]

$[CAT]_0 \times 10^3$ (mol dm^{-3})	$[YBH]_0 \times 10^2$ (mol dm^{-3})[b]	$k' \times 10^4$ (s^{-1})	$[CAT]_0 \times 10^3$ (mol dm^{-3})	$[YBH]_0 \times 10^2$ (mol dm^{-3})[b]	$k' \times 10^4$ (s^{-1})
0.50	1.00	3.74	1.00	0.50	1.69
1.00	1.00	3.36	1.00	0.75	2.29
1.50	1.00	3.26	1.00	1.00	3.36
2.00	1.00	3.09	1.00	1.50	4.17
2.50	1.00	3.39	1.00	2.00	6.39
3.00	1.00	3.56	1.00	3.00	9.56
3.50	1.00	3.62	1.00	4.00	11.26
4.00	1.00	3.46	1.00	5.00	12.92
5.00	1.00	3.71	1.00	6.00	12.86

[a] [HCl] = 0.100 mol dm^{-3}, $[RuCl]_3$ = 4.82 × 10^{-5} mol dm^{-3}, μ = 0.40 mol dm^{-3}, MeOH = 30% v/v, and Temp = 308 K.

[b] YBH = benzhydrol where Y = H.

dient elution (dichloromethane). After initial separation, the products were further purified by recrystallization and characterized by comparing their data with that of authentic samples available commercially.

Benzophenone: The sample recrystallized from ethanol has an uncorrected m.p. of 49–50°C (lit. m.p. = 49–51°C, Merck Index 11, 1108). The R_f value of 0.82 was obtained from TLC using dichloromethane as solvent and iodine as developing agent. Benzophenone was further identified by preparing its 2,4-dinitrophenylhydrazone (2,4-DNP) derivative which, after recrystallization from ethanol (recovery 72.2%), was found to be identical with the 2,4-DNP of the authentic sample with m.p. = 237–238°C (lit. m.p. = 238) [14].

p-Toluenesulfonamide (PTS): The sample recrystalized from dichloromethane and petroleum ether was found to have an uncorrected m.p. of 137–139°C (lit. m.p. = 137–140°C, Beil 11, 104). An R_f value of 0.26 was obtained from TLC using dichloromethane as solvent and iodine as developing agent [6,14].

RESULTS

Reaction Stoichiometry

Results of preliminary experiments, performed with varying compositions of CAT and YBH, showed that one mole of CAT reacted with one mole of the substrate.

The oxidation of YBH by the haloamine, CAT, in HCl medium in the presence of ruthenium(III) chloride catalyst follows a pseudo-first-order kinetics.

Kinetics

Effect of Reactants on the Rate: Under pseudo-first-order conditions of $[YBH]_O \gg [CAT]_O$ at constant $[YBH]_O$, [HCl], $[RuCl_3]$, and temperature, plots of log [CAT] vs. time were linear indicating a first-order dependence of the reaction rate on [CAT]. The values of pseudo-first-order rate constant, k_1', are given in Table I. Furthermore, the rate constant did not change with the change in $[CAT]_O$ confirming the first-order dependence on $[CAT]_O$.

The rate increased initially with increase in $[YBH]_O$ and a plot of log k_1' vs. log $[YBH]_O$ was linear (r = 0.9989, Table I) with a fractional slope of 0.87 showing a fractional-order dependence of the rate on $[YBH]_O$. The rate, however, levels off at higher $[YBH]_O$.

Effects of HCl and H$^+$ Concentrations on the Rate: When the [HCl] was increased, keeping the other experimental conditions the same, the rate increased. A plot of log k_1' vs. log [HCl] was linear with a fractional slope of 0.87 (r = 0.998, Table II). At constant [Cl$^-$] of 0.40 mol dm^{-3}, maintained by adding NaCl, the rate increased with increasing [H$^+$] which was caused by the addition of HCl. A plot of log k_1' vs. log [H$^+$] was linear with a fractional slope of 0.88 (r = 0.9998, Table II) indicating that the effect of HCl was due to [H$^+$] only.

Effect of Ruthenium(III) Concentration: The increase in $[RuCl_3]$, when the other conditions are kept constant, increased the reaction rate. A plot of log k_1' vs. log $[RuCl_3]$ was linear (r = 0.9988), with a fractional slope (0.56), indicating a positive fractional-order dependence on $[RuCl_3]$ (Table II).

Effects of Halide Ions and Ionic Strength on the Rate: Addition of the halide ions, Cl$^-$ or Br$^-$, in the form of their sodium salts (5.0 × 10^{-4} −2.0 × 10^{-3}

Table II Effect of Varying HCl, H^+, and $RuCl_3$ Concentrations on the Rate[a]

[HCl] × 10 (mol dm^{-3})	k' × 10^4 (s^{-1})	$[H^+]^a$ × 10 (mol dm^{-3})	k' × 10^4 (s^{-1})	$[RuCl]_3$ × 10^{5c} (mol dm^{-3})	k' × 10^4 (s^{-1})
0.50	1.74	1.00	3.36	1.96	2.02
0.80	2.75	1.50	4.89	2.52	2.39
1.00	3.36	2.00	5.88	3.64	2.85
1.50	4.78	2.50	7.58	4.82	3.36
2.00	6.30	3.00	8.91	7.24	3.94
3.00	8.71	4.00	11.22	9.26	4.46
4.00	10.96	5.00	13.48	11.22	5.59

[a] $[CAT]_0 = 1.00 \times 10^{-3}$ mol dm^{-3}, $[YBH]_0 = 1.00 \times 10^{-2}$ mol dm^{-3} where Y = H, $\mu = 0.40$ mol dm^{-3}, MeOH = 30% v/v, and Temp = 308 K.

[b] At constant $[Cl^-] = 0.40$ mol dm^{-3}.

[c] [HCl] = 0.100 mol dm^{-3}.

mol dm^{-3}), to the reaction mixture had no effect on the rate. Also, the ionic strength of the reaction medium varied by adding $NaClO_4$ (0.20–1.00 mol dm^{-3}) did not influence the rate.

Effect of p-Toluenesulfonamide (PTS) on the Rate: Addition of the reaction product, PTS ($2.0 \times 10^{-4} - 1.5 \times 10^{-3}$ mol dm^{-3}), to the reaction mixture decreased the rate. A plot of log k'_1 vs. log $[PTS]_O$ was linear with a fractional slope of −0.35 (r = 0.989, Table III) indicating that PTS is involved in a fast preequilibrium to the rds.

Effect of Varying Dielectric Constant on the Rate: The dielectric constant (D) of the solvent medium was varied by adding MeOH (30–60%). The rate decreased with increase in MeOH content and gave a linear plot of log k'_1 vs. 1/D with a negative slope (r = 0.999, Table III) supporting a rate-limiting step involving partial ionization [15]. As the control experiments with MeOH showed a slight decomposition of MeOH, under the experimental conditions, the rate constants were corrected to represent only the oxidation of YBH.

Solvent Isotope Studies: As the rate was dependent on $[H^+]$, solvent isotope studies were made using D_2O as the solvent medium. The oxidation of YBH by CAT was faster in D_2O medium ($k'_1H_2O = 3.36 \times 10^{-4}$ s^{-1} and $k'_1D_2O = 5.60 \times 10^{-4}$ s^{-1}) showing a solvent isotope effect, k'_1H_2O/k'_1D_2O, of 0.60. The proton inventory studies were made in H_2O—D_2O mixtures with varying deuterium atom fraction 'n' in the solvent (Table IV). A plot of the rate constant $k_{obs}{}^n$ vs. 'n' is shown in Figure 1.

Effect of Temperature on the Rate: The reaction was studied with varying temperature, 303 K to 318 K, keeping the other experimental conditions constant. The determined rate constants are presented in Table V. Activation parameters calculated from the Arrhenius and Eyring plots of log k'_1 vs. $1/T$ and log (k'_1/T) vs. $1/T$, respectively, are given in Table VI.

Test for Free Radicals: Addition of the reaction mixture to the acrylamide monomer in the dark did not initiate polymerization indicating the absence of free radicals. Proper control experiments were also simultaneously performed.

DISCUSSION

Reaction Stoichiometry

The 1:1 stoichiometry of the reaction of Chloramine-T (TsNClMa or CAT) with the substrate (YBH) is as shown in eq. (1).

Table III Effect of Varying *p*-Toluenesulfonamide (PTS) Concentration and Dielectric Constant on the Rate[a]

[PTS] × 10^4 (mol dm^{-3})	k' × 10^4 (s^{-1})	% MeOH (v/v)	Dielectric Constant (D)	k' × 10^4 (s^{-1})
2.0	3.07	30.0	56.73	3.36
4.0	2.54	40.0	51.08	2.56
6.0	2.18	50.0	45.30	1.92
10.0	1.86	55.0	42.66	1.51
15.0	1.54	60.0	40.40	1.27

[a] $[CAT]_0 = 1.00 \times 10^{-3}$ mol dm^{-3}, $[YBH]_0 = 1.00 \times 10^{-2}$ mol dm^{-3} where Y = H, [HCl] = 0.100 mol dm^{-3}, $[RuCl_3] = 4.82 \times 10^{-5}$ mol dm^{-3}, $\mu = 0.40$ mol dm^{-3}, and Temp = 308 K.

Table IV Proton Inventory Studies of Benzhydrols (YBH) in H_2O—D_2O Mixtures at 308 K[a]

Atom Fraction of Deuterium (n)	$k_{obs}{}^{n} \times 10^4/(s^{-1})$
0.00	3.36
0.15	3.65
0.30	4.20
0.45	4.75
0.56	5.60

[a] $[CAT]_0 = 1.00 \times 10^{-3}$ mol dm^{-3}, $[YBH]_0 = 1.00 \times 10^{-2}$ mol dm^{-3} where Y = H, [HCl] = 0.100 mol dm^{-3}, $[RuCl_3] = 4.82 \times 10^{-5}$ mol dm^{-3}, $\mu = 0.40$ mol dm^{-3}, MeOH = 30% v/v, and Temp = 308 K.

$$\begin{aligned} &Y—C_6H_4—CH(OH)—C_6H_5 + TsNClNa \longrightarrow \\ &\quad Y—C_6H_4—CO—C_6H_5 + TsNH_2 \\ &\qquad + Na^+ + Cl^- \qquad (1) \end{aligned}$$

Kinetics and Mechanism

Chloramine-T acts as a mild oxidant in both acidic and alkaline media. In general, CAT undergoes a two-electron change in its reactions. The oxidation potential of CAT-$TsNH_2$ couple is pH dependent and decreases with increase in the pH of the medium (E_o is 1.14 V at pH 0.65 and 0.50 V at pH 12). Depending on the pH, CAT furnishes different types of reactive species (eqs. (2)–(7)) such as TsNHCl, $TsNCl_2$, HOCl, and possibly H_2OCl^+ in acid solutions [5,16,17].

$$\underset{(CAT)}{TsNClNa} \rightleftharpoons TsNCl^- + Na^+ \qquad (2)$$

$$TsNCl^- + H^+ \overset{K_a}{\rightleftharpoons} TsNHCl; \quad K_a = 2.82 \times 10^{-5}\text{ M at } 25°C \qquad (3)$$

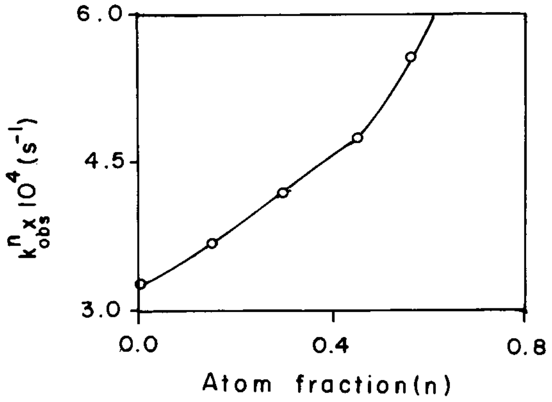


Figure 1 Proton inventory plot of $k_{obs}{}^{n}$ vs. the deuterium atom fraction (n) in H_2O—D_2O solvent mixtures: $[CAT]_O = 1.00 \times 10^{-3}$ mol dm^{-3}; $[YBH]_0 = 1.00 \times 10^{-2}$ mol dm^{-3} where Y = H; [HCl] = 0.100 mol dm^{-3}; $[RuCl_3] = 4.82 \times 10^{-5}$ mol dm^{-3}; μ = 0.40 mol dm^{-3}; MeOH = 30% v/v; and Temp. = 308 K.

Table V Temperature Dependence of the Oxidation of Substituted Benzhydrols by CAT

Substrate (YBH) Y =	$k' \times 10^4/(s^{-1})$ 303 K	308 K	313 K	318 K
4-NO_2	1.26	1.52	1.78	2.14
4-Cl	1.55	2.10	2.39	3.02
4-Br	1.74	2.39	3.06	3.71
4-H	2.51	3.36	5.00	6.94
4-CH_3	4.26	7.76	12.30	19.95
4-OCH_3	7.08	13.80	22.38	39.81

$[CAT]_0 = 1.00 \times 10^{-3}$ mol dm^{-3}, $[YBH]_0 = 1.00 \times 10^{-2}$ mol dm^{-3}, [HCl] = 0.100 mol dm^{-3}, $[RuCl_3] = 4.82 \times 10^{-5}$ mol dm^{-3}, μ = 0.40 mol dm^{-3}, and MeOH = 30% v/v.

$$2TsNHCl \overset{K_d}{\rightleftharpoons} TsNCl_2 + \underset{(PTS)}{TsNH_2}; \quad K_d = 6.1 \times 10^{-2} \text{ at } 25°C \qquad (4)$$

$$TsNHCl + H_2O \rightleftharpoons TsNH_2 + HOCl \qquad (5)$$

$$TsNHCl + H^+ \rightleftharpoons TsNH_2Cl^+ \qquad (6)$$

$$TsNH_2Cl^+ + H_2O \rightleftharpoons TsNH_2 + H_2OCl^+ \qquad (7)$$

Since the involvement of $TsNCl_2$ as the reactive species predicts a second-order dependence of the rate on $[CAT]_O$, contrary to the experimental observation of first-order, $TsNCl_2$ is ruled out in the mechanism. As the rate increases with increase in $[H^+]$ and with decrease in [PTS], eqs. (6) and (7) should play a dominant role in the oxidation of YBH by CAT.

Electronic spectral studies of Cady and Connick [18], and Connick and Fine [19] have shown that the complex species 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 in aqueous solutions of $RuCl_3$. A study on the oxidation states of ruthenium has shown that Ru(III) exists in the following equilibrium in acidic solutions [20–22]:

$$[RuCl_6]^{-3} + H_2O \rightleftharpoons [RuCl_5(H_2O)]^{-2} + Cl^- \qquad (8)$$

Singh et al. [23,24] used the above equilibrium in Ru(III)-catalyzed oxidation of primary alcohols by bromamine-T in acid medium and ethylene glycols by *N*-bromoacetamide in $HClO_4$ medium. However, in the present study, the zero effect of chloride ion on the rate indicates that the complex ion, $[RuCl_6]^{-3}$, is the catalyzing species.

Ultraviolet spectral measurements showed that benzhydrol solution has two sharp absorption bands at 255.2 and 222.4 nm while Ru(III) and CAT solutions have bands at 204.0 and 227.2 nm, respectively, in the presence of 0.10 molar HCl. Mixtures of (a) benzhy-

Table VI Activation Parameters for the Oxidation of Substituted Benzhydrols by CAT[a]

Substrate (YBH) Y =	E_a (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})	log A
4-NO_2	25.8	20.4	−252.0	98.5	5.8
4-Cl	31.6	24.1	−236.9	97.8	6.9
4-Br	36.3	30.8	−213.8	97.3	7.8
4-H	49.7	47.2	−158.0	96.2	10.3
4-CH_3	88.9	86.6	− 23.9	93.9	17.2
4-OCH_3	93.9	89.9	− 10.4	92.5	18.1

[a] $[\text{CAT}]_0 = 1.00 \times 10^{-3}$ mol dm^{-3}, $[\text{YBH}]_0 = 1.00 \times 10^{-2}$ mol dm^{-3}, [HCl] = 0.100 mol dm^{-3}, $[\text{RuCl}_3] = 4.82 \times 10^{-5}$ mol dm^{-3}, $\mu = 0.40$ mol dm^{-3}, and MeOH = 30% v/v.

drol and Ru(III) and (b) CAT and Ru(III) in the presence of 0.10 molar HCl showed no changes in the $\lambda_{\max}$, whereas CAT-YBH mixtures in the presence of 0.100 molar HCl exhibited a sharp band at 216.8 nm. This suggests that a complexation occurs only between CAT and YBH. In view of the preceding facts, a mechanism, Scheme I, is proposed for the oxidation of YBH by CAT.

$$\underset{\text{(oxidant)}}{\text{TsNHCl}} + \text{H}_3\text{O}^+ \overset{K_1}{\rightleftharpoons} \text{TsNH}_2 + (\text{H}_2\text{OCl})^+ \quad \text{fast} \quad \text{(i)}$$

$$\underset{\text{(substrate)}}{\text{YBH}} + (\text{H}_2\text{OCl})^+ \overset{K_2}{\rightleftharpoons} \underset{\text{(complex I)}}{\text{X}} \quad \text{fast} \quad \text{(ii)}$$

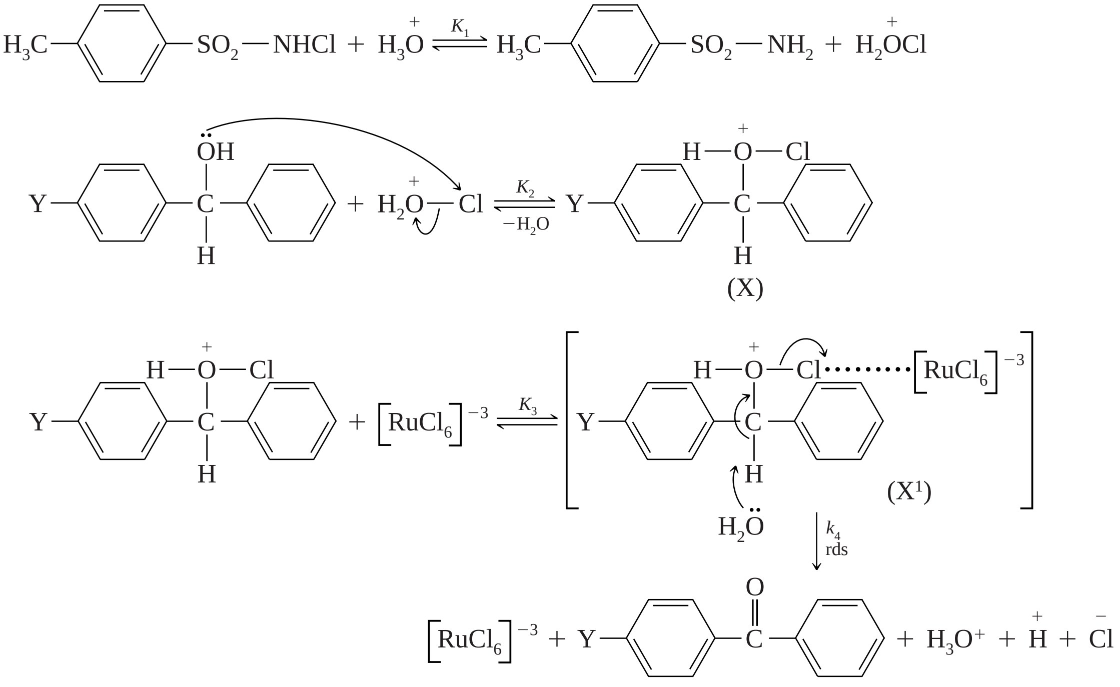
$$\text{X} + \underset{\text{(catalyst)}}{[\text{RuCl}_6]^{-3}} \overset{K_3}{\rightleftharpoons} \underset{\text{(complex II)}}{\text{X}'} \quad \text{fast} \quad \text{(iii)}$$

$$\text{X}' + \text{H}_2\text{O} \xrightarrow{k_4} \text{products} \quad \text{slow/rds} \quad \text{(iv)}$$

Scheme I

In Scheme I, the protonation and hydrolysis of TsNHCl form the reactive oxidant species, $(\text{H}_2\text{OCl})^+$, which interacts with the substrate to form complex I (X). Complex I reacts with the active catalyst species, $[\text{RuCl}_6]^{-3}$, in an equilibrium step to form complex II (X′) which hydrolyzes to form products. The fractional order in $[\text{RuCl}_6]^{-3}$ supports a fast preequilibrium, step (iii), in the mechanism.

A detailed mechanistic scheme, involving structures of the participating species including YBH, CAT, and complexes X and X′, for the CAT oxidation of benzhydrols catalyzed by RuCl_3 in HCl medium is presented in Scheme II.



Scheme II

$$\text{rate} = k_4\,[\mathrm{X}']\,[\mathrm{H_2O}]$$
$$= k_4'\,[\mathrm{X}'],\ \text{based on the rds in Scheme I} \quad (9)$$

Since the total effective concentration of the oxidant CAT is given by eq. (10), the rate law (eq. (11) can be derived.

$$[\mathrm{CAT}]_t = [\mathrm{TsNHCl}] + [\mathrm{H_2OCl^+}] + [\mathrm{X}] + [\mathrm{X}'] \quad (10)$$

$$\text{rate} = \frac{-\,d[\mathrm{CAT}]}{dt} = \frac{K_1K_2K_3k_4'\,[\mathrm{CAT}]_t\,[\mathrm{YBH}]\,[\mathrm{H_3O^+}]\,[\mathrm{Ru(III)}]}{[\mathrm{TsNH_2}] + K_1\,[\mathrm{H_3O^+}] + K_1K_2[\mathrm{H_3O^+}]\,[\mathrm{YBH}]\,\{1 + K_3\,[\mathrm{Ru(III)}]\}} \quad (11)$$

where $k_4' = k_4\,[\mathrm{H_2O}]$.

It is interesting to note that the rate in D_2O medium is faster than that in H_2O. Since the D_3O^+ ion is a stronger acid than H_3O^+ by a factor of 2–3, a solvent isotope effect of this magnitude is to be expected. But the observed inverse solvent isotope effect, k'_{D_2O}/k'_{H_2O}, is 1.66. This probably shows that since the protonation is followed by hydrolysis in the rds which involves O—H bond rupture, the normal kinetic isotope effect $k'_H/k'_D > 1$ could counterbalance the solvent isotope effect. The proton inventory studies made in H_2O—D_2O mixtures could throw light on the nature of the transition state. The dependence of the rate constant, $k_{obs}{}^{n}$, on the deuterium-atom fraction 'n' in the solvent mixture is given by the following form of Gross–Butler equation [25,26]:

$$k_{obs}{}^{o}/k_{obs}{}^{n} = \Pi^{TS}\,(1 - n + n\,\Phi_i)/\Pi^{RS}\,(1 - n + n\,\Phi_j) \quad (12)$$

where Φ_i and Φ_j are isotopic fractionation factors for isotopically exchangeable hydrogen sites in the transition state (TS) and in the ground/reactant state (RS), respectively. The Gross–Butler equation (eq. 12) permits the evaluation of Φ_i when the value of Φ_j is known. However, the curvature of the proton inventory plot could reflect the number of exchangeable protons in the reaction [25]. A plot of $k_{obs}{}^{n}$ vs. n (Fig. 1, Table IV) is a curve, in the present case, which in comparison with the standard curves indicates the involvement of a single proton or H—D exchange in the reaction sequence [27]. This proton exchange infers the participation of hydrogen ion in the formation of transition state.

The moderate values of enthalpy of activation ($\Delta H^{\neq}$), entropy of activation ($\Delta S^{\neq}$), and free energy of activation ($\Delta G^{\neq}$), obtained for the oxidation of benzhydrols by CAT support the reaction mechanism (Schemes I and II) (Table VI). For each YBH reaction, the negative $\Delta S^{\neq}$ value suggests the formation of an associative rigid transition state. In addition, the near constancy of $\Delta G^{\neq}$ values are indicative of a similar solvated transition state. The values of both $\Delta S^{\neq}$ and $\Delta G^{\neq}$ support the existence of a similar mechanism for the oxidation of all benzhydrols.

Structure-Reactivity Correlations

A plot of log k_2 (second-order rate constant) vs. σ_P parameters for the ring substituents was obtained (Fig. 2). This Hammett plot shows two distinct lines for each of which there is a good correlation between the substituent constants and log of rate constant, particularly when the McDaniel–Brown constant, σ_P, is used [28]. Of these, one has a much lower value for the reaction constant ($\rho = -2.3$) for electron-releasing groups while the other line has a relatively high value ($\rho = -0.32$) for electron-withdrawing groups at 35°C. The break in the Hammett plot could suggest a concerted mechanism, the degree of concertedness depending on whether the hydride transfer from C—H bond to the oxidant is synchronous with the removal of a proton from the O—H group of YBH by a water molecule. Puttaswamy and Mahadevappa [29], have studied the kinetics of oxidation of primary alcohols by organic haloamines and noted that the electron-donating groups tend to increase the rate. This

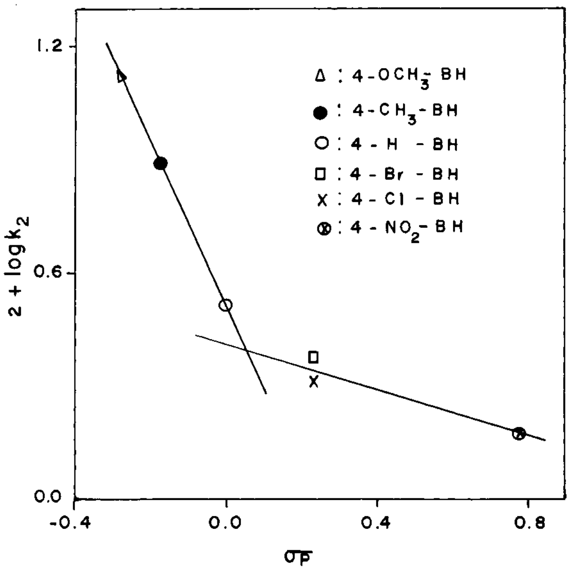


Figure 2 A Hammett plot of log k_2 vs. σ_p parameters for benzhydrols: $[\mathrm{CAT}]_O = 1.00 \times 10^{-3}$ mol dm^{-3}; $[\mathrm{YBH}]_O = 1.00 \times 10^{-2}$ mol dm^{-3}; [HCl] = 0.100 mol dm^{-3}; $[\mathrm{RuCl_3}] = 4.82 \times 10^{-5}$ mol dm^{-3}; $\mu = 0.40$ mol dm^{-3}; MeOH = 30% v/v; and Temp. = 308 K.

indicates the formation of a carbonium ion or a positive character in the transition state which is stabilized by electron-donating groups. The complex X′ can develop a positive character due to the cleavage of the O—Cl bond which begins ahead of other bond ruptures. In the present case, the increase in the rate due to the presence of electron-donating groups is in agreement with the above observation.

Isokinetic Relationship

The values of $\Delta H^{\neq}$ are low for the oxidation of benzhydrols by CAT (Table VI). The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are linearly related (r = 0.9996) giving an isokinetic temperature β. The genuine nature of the isokinetic relationship was verified by the Exner criterion [30] by plotting log k' (318 K) vs. log k' (303 K). The value of β was calculated from the equation, $\beta = T_1 (1 - q)/(T_1/T_2) - q$, where q is the slope of the Exner plot and $T_1 > T_2$. The calculated value of β is 346 K. It is seen that the β value is higher than the experimental temperature (308 K) indicating a common enthalpy-controlled pathway for the reactions (Table VI).

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