



Kinetic Studies on Tetrabutylammonium Bromochromate Oxidation of Some Mono- and Di-substituted Benzhydrols

S. HEMALATHA¹, BASIM H. ASGHAR² and S. SHEIK MANSOOR^{3,*}

¹Research and Development Centre, Bharathiar University, Coimbatore-641 046, India

²Department of Chemistry, Faculty of Applied Sciences, Umm Al-Qura University, P.O. Box: 9569, Makkah, Saudi Arabia

³Department of Chemistry, C. Abdul Hakeem College (Autonomous), Melvisharam-632 509, India

*Corresponding author: E-mail: smansoors2000@yahoo.co.in

Received: 28 September 2017;

Accepted: 5 January 2018;

Published online: 28 February 2018;

AJC-18793

The oxidation of 12 mono- and di-substituted benzhydrols (BH) by tetrabutylammonium bromochromate (TBABC) have been studied in aqueous acetic acid medium. Absence of any effect of added acrylonitrile on the reaction discounts the possibility of a one-electron oxidation, leading to the formation of free radicals. The tetrabutylammonium bromochromate oxidation of 12 mono- and di-substituted benzhydrols complies with the isokinetic relationship and Hammett relationship. The overall mechanism is proposed to involve a cyclic concerted symmetrical transition state leading to the product.

Keywords: Tetrabutylammonium bromochromate, Benzhydrol, Thermodynamic parameters, Isokinetic relationship, Kinetics.

INTRODUCTION

Chromium(VI) based reagents are widely used in modern organic synthesis for the oxidation of a variety of compounds under anhydrous and aprotic conditions, including primary and secondary alcohol [1]. Extensive work has led to the development of a good number of these oxidants such as 4-(dimethylamino)pyridinium chlorochromate [2], tetraethylammonium chlorochromate [3], tetramethylammonium fluorochromate [4], 2,6-dicarboxypyridinium chlorochromate [5], *N*-methyl piperidinium chlorochromate [6], tetramethylammonium fluorochromate(VI) [7], *N*-methylbenzylammonium fluorochromate (VI) [8] and tetrabutylammonium bromochromate [9]. These reagents may all be used for the oxidation of alcohols to corresponding aldehydes and ketones.

Literature survey revealed that the studies on the mechanism of oxidation of benzhydrols by several oxidants such as chloramine-B [10], tributylammonium chlorochromate [11], *N*-bromosuccinimide [12], Tl(III) [13] and *N*-bromophthalimide [14] have been reported. Recently, several researchers reported the oxidation of some organic substrates by Cr(VI) [15-20]. The present communication describes the results of oxidation of 12 mono- and di-substituted benzhydrols by tetrabutylammonium bromochromate.

EXPERIMENTAL

All the employed chemicals and solvents were of analytical grade. Benzhydrols were used with substituents H, *p*-OCH₃,

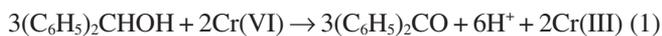
p-OC₂H₅, *p*-CH₃, *p*-F, *p*-Cl and *p*-NO₂. Benzhydrols were prepared by means of the reduction of corresponding benzophenones with sodium borohydride. The purity of benzhydrols was checked by m.p. and elemental analysis. Tetrabutylammonium bromochromate (TBABC) was prepared by a reported method [9] and its purity was checked by the iodometric method. Doubly distilled water was used for all purposes. Acetic acid was purified by standard method and the fraction distilling at 118 °C was collected.

Deuterated (α -C-D) benzhydrols were prepared by the method of Shanker and Suresh [21]. α -D-benzhydrols were prepared by refluxing corresponding benzhydrols (α -C-H) in D₂O for 2-3 h, removing the solvent under a pump and repeating the process three times to ensure complete exchange of protons. PMR analysis was conducted to confirm the deuterated (α -C-D) benzhydrols.

Kinetic measurements: A thermostatic water bath was used to maintain the desired temperature within ± 0.1 °C. The calculated amount of the reactants, *i.e.*, benzhydrol (BH), TBABC, perchloric acid, acetic acid and water taken in a reaction vessel which was kept in a thermostatic water bath. After allowing sufficient time to attain the temperature of the experiment, a requisite amount of solutions were rapidly pipetted out into the spectrophotometric cell. The total volume of the reaction mixture was 5 mL in each case. Progress of the reaction was followed by measuring the decrease in [TBABC] by spectrophotometrically at 362 nm using UV-visible spectrophotometer,

Shimadzu UV-1800 model. The reaction was carried under pseudo first-order conditions, *i.e.*, $[BH] \gg [TBABC]$ in the presence of perchloric acid in 50 % acetic acid – 50 % water medium.

Stoichiometric studies and product analysis: Reaction mixtures, in which $[TBABC]$ was in large excess of $[BH]$, were kept in the presence of perchloric acid 50 % acetic acid – 50 % water medium. Estimation of unreacted TBABC showed the following stoichiometric equation (1):



The oxidation of benzhydrol resulted in the formation of the corresponding benzophenone. The DNP of benzophenone was determined by a reported method [15].

RESULTS AND DISCUSSION

The oxidation of 12 mono- and di-substituted benzhydrols such as *p*-H (S1), *p*-OCH₃ (S2), *p*-OC₂H₅ (S3), *p*-CH₃ (S4), *p*-F (S5), *p*-Cl (S6), *p*-NO₂ (S7), *p*-CH₃, *p*-CH₃ (S8), *p*-OCH₃, *p*-F (S9), *p*-OCH₃, *p*-Cl (S10), *p*-Cl, *p*-Cl (S11) and *p*-CH₃, *p*-NO₂ (S12) by TBABC have been conducted in 50 % acetic acid and 50 % water medium at 303 K, under pseudo first order conditions and the result obtained are discussed in the following paragraphs.

Order of reaction: The values of pseudo first-order rate constants were unaltered with variation in $[TBABC]$, indicating the first-order dependence on $[TBABC]$ (Table-1).

The rate increases with an increase in $[BH]$ (Table-1). Linear plots of $\log k_1$ vs. $\log [BH]$ (Fig. 1) with the slopes (*p*-H (S1): slope = 1.02; *p*-OCH₃ (S2): slope = 0.99; *p*-OC₂H₅ (S3): slope = 1.05; *p*-CH₃ (S4): slope = 0.99; *p*-F (S5): slope = 0.99; *p*-Cl (S6): slope = 1.04; *p*-NO₂ (S7): slope = 1.01; *p*-CH₃, *p*-CH₃ (S8): slope = 1.07; *p*-OCH₃, *p*-F (S9): slope = 1.05; *p*-OCH₃, *p*-Cl (S10): slope = 1.03; *p*-Cl, *p*-Cl (S11): slope = 1.04; *p*-CH₃, *p*-NO₂ (S12): slope = 1.02) demonstrate first order type kinetics on $[BH]$. Further, a plot of k_1 versus $[BH]$ is a straight line passing through origin (Fig. 2), confirming the first-order dependence on $[BH]$.

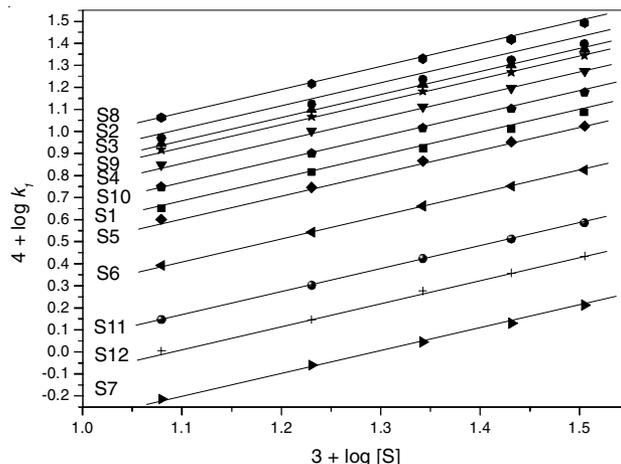


Fig. 1. Order plot for the substrate for the oxidation of benzhydrol (S1), *p*-OCH₃ (S2), *p*-OC₂H₅ (S3), *p*-CH₃ (S4), *p*-F (S5), *p*-Cl (S6), *p*-NO₂ (S7), *p*-CH₃, *p*-CH₃ (S8), *p*-OCH₃, *p*-F (S9), *p*-OCH₃, *p*-Cl (S10), *p*-Cl, *p*-Cl (S11) and *p*-CH₃, *p*-NO₂ (S12) by TBABC at 303 K

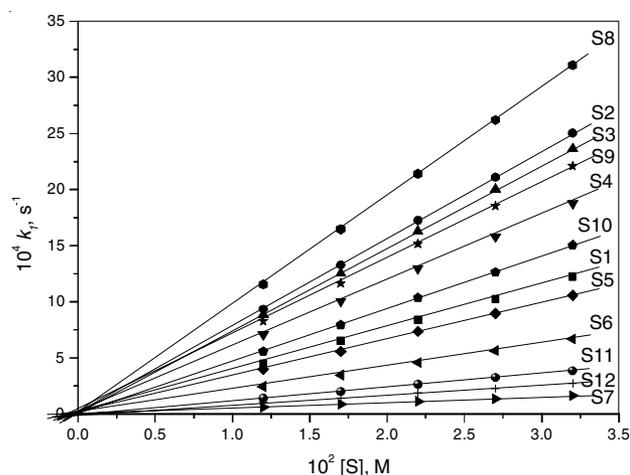


Fig. 2. Direct plot for the substrate for the oxidation of benzhydrol (S1), *p*-OCH₃ (S2), *p*-OC₂H₅ (S3), *p*-CH₃ (S4), *p*-F (S5), *p*-Cl (S6), *p*-NO₂ (S7), *p*-CH₃, *p*-CH₃ (S8), *p*-OCH₃, *p*-F (S9), *p*-OCH₃, *p*-Cl (S10), *p*-Cl, *p*-Cl (S11) and *p*-CH₃, *p*-NO₂ (S12) benzhydrols by TBABC at 303 K

TABLE-1
RATE CONSTANTS FOR THE OXIDATION OF MONO AND DI SUBSTITUTED
BENZHYDROLS BY TBABC IN AQUEOUS ACETIC ACID MEDIUM AT 303 K^a

(mol dm ⁻³)			10 ⁴ k ₁ (s ⁻¹) ^a											
10 ³ [Ox]	10 ² [BH]	[H ⁺]	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12
0.5	2.2	0.28	8.36	17.32	16.28	12.90	7.41	4.64	1.10	21.36	15.10	10.31	2.63	1.88
1.0	2.2	0.28	8.40	17.25	16.32	12.94	7.35	4.59	1.12	21.40	15.16	10.35	2.65	1.89
1.5	2.2	0.28	8.32	17.18	16.34	12.88	7.38	4.66	1.14	21.48	15.18	10.43	2.67	1.86
2.0	2.2	0.28	8.50	17.20	16.38	12.98	7.29	4.52	1.16	21.44	15.22	10.39	2.68	1.85
2.5	2.2	0.28	8.46	17.28	16.24	12.86	7.30	4.55	1.10	21.47	15.14	10.34	2.64	1.84
1.0	1.2	0.28	4.48	9.34	8.82	7.06	4.00	2.46	0.61	11.56	8.27	5.59	1.40	1.01
1.0	1.7	0.28	6.54	13.28	12.54	10.04	5.58	3.48	0.87	16.48	11.63	7.93	2.00	1.40
1.0	2.7	0.28	10.24	21.10	20.02	15.78	8.96	5.64	1.35	26.19	18.56	12.64	3.25	2.28
1.0	3.2	0.28	12.22	25.04	23.64	18.76	10.58	6.68	1.63	31.08	22.09	15.02	3.85	2.72
1.0	2.2	0.12	3.44	7.44	6.90	5.60	3.11	1.90	0.48	9.22	6.44	4.44	1.11	0.80
1.0	2.2	0.20	5.92	12.40	11.66	9.32	5.18	3.22	0.80	15.36	10.74	7.32	1.86	1.35
1.0	2.2	0.36	10.92	22.12	20.88	16.66	9.42	5.96	1.45	27.46	19.42	13.24	3.43	2.45
1.0	2.2	0.44	13.20	27.06	25.74	20.29	11.51	7.18	1.72	33.63	23.79	16.22	4.14	2.95
1.0	2.2	0.28	6.06 ^b	12.66 ^b	11.86 ^b	9.08 ^b	5.28 ^b	3.42 ^b	0.84 ^b	15.64 ^b	11.24 ^b	7.64 ^b	1.94 ^b	1.26 ^b

^aAs determined by a spectrophotometric technique following the disappearance of oxidant; 10² [BH] = 2.2 mol dm⁻³; 10³ [TBABC] = 1.0 mol dm⁻³; [H⁺] = 0.28 mol dm⁻³; Solvent composition : 50 % Acetic acid – 50 % Water (v/v)

^bIn the presence of 0.003 mol dm⁻³Mn (II).

The increase in $[\text{HClO}_4]$ in the oxidation reaction increases the rate of the reaction and shows a direct first order dependence on $[\text{HClO}_4]$ (Table-1). A plot of $\log k_1$ against $\log [\text{H}^+]$ is linear with the slopes [*p*-H (S1): slope = 1.04; *p*-OCH₃ (S2): slope = 1.01; *p*-OC₂H₅ (S3): slope = 1.03; *p*-CH₃ (S4): slope = 1.06; *p*-F (S5): slope = 1.04; *p*-Cl (S6): slope = 0.99; *p*-NO₂ (S7): slope = 0.99; *p*-CH₃,*p*-CH₃ (S8): slope = 1.03; *p*-OCH₃,*p*-F (S9): slope = 1.06; *p*-OCH₃,*p*-Cl (S10): slope = 0.99; *p*-Cl, *p*-Cl (S11): slope = 1.01; *p*-CH₃, *p*-NO₂ (S12): slope = 0.99] (the plots are not shown). The experimental data confirms the first order dependence on $[\text{H}^+]$. Further, a plot of k_1 versus $[\text{H}^+]$ is a straight line passing through origin (the plot is not shown), confirming the first-order dependence on $[\text{H}^+]$.

Induced polymerization and effect of added MnSO₄:

The oxidation of benzhydrol in a nitrogen atmosphere failed to induce the polymerization of acrylonitrile. Therefore, a one-electron oxidation, giving rise to free radicals, is unlikely. Furthermore, the rate of oxidation decreased with the addition of Mn(II), indicating the involvement of a two-electron reduction of Cr(VI) to Cr(IV) (Table-1).

Kinetic isotope effect: To ascertain the importance of the cleavage of the α -C-H bond in the rate-determining step, oxidation of α -deuteriobenzhydrol (α -C-D) was studied. Results showed the presence of a substantial primary kinetic isotope effect (Table-2).

Substrate	$10^4 k_1$ (s ⁻¹)			
	298 K	303 K	308 K	313 K
Benzhydrol	5.92	8.40	11.92	16.94
α -C-D	1.11	1.48	2.05	2.75
k_H/k_D	5.33	5.67	5.82	6.14

$10^2 [\text{S}] = 2.2 \text{ mol dm}^{-3}$; $10^3 [\text{TBABC}] = 1.0 \text{ mol dm}^{-3}$; $10 [\text{H}^+] = 2.8 \text{ mol dm}^{-3}$

Effect of solvent polarity on reaction rate: An increase in solvent polarity accelerates the rates of reactions where a charge is developed in the activated complex from neutral or slightly charged reactant. An increase in solvent polarity decreases the rates of reactions where there is less charge in the activated complex in comparison to the starting materials. The concentration of acetic acid was varied from 30 to 70 % and pseudo-first-order rate constants were estimated for the oxidation of benzhydrols, with TBABC in the presence of perchloric acid at a constant ionic strength. There is increase

in rate constants with varying the concentration of acetic acid (Table-3). The plot of $\log k_1$ versus $1/D$ (dielectric constant) is linear with positive slope suggesting the presence of ion-dipole type of interaction between the oxidant and the substrate [22] (Fig. 3).

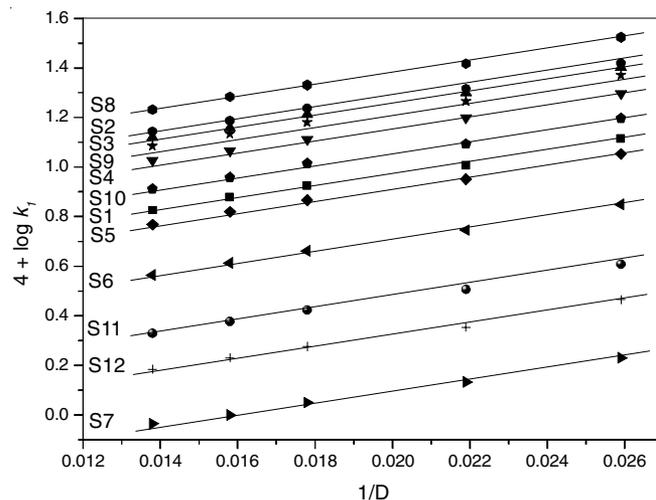


Fig. 3. Plot of $1/D$ against $\log k_1$ showing effect of solvent polarity of benzhydrol (S1), *p*-OCH₃ (S2), *p*-OC₂H₅ (S3), *p*-CH₃ (S4), *p*-F (S5), *p*-Cl (S6), *p*-NO₂ (S7), *p*-CH₃, *p*-CH₃ (S8), *p*-OCH₃, *p*-F (S9), *p*-OCH₃, *p*-Cl (S10), *p*-Cl, *p*-Cl (S11) and *p*-CH₃, *p*-NO₂ (S12) benzhydrols by TBABC at 303 K

Structure reactivity correlation: The effect of structure on reactivity indicates that, the reactivity decreases in the order *p*-OCH₃ > *p*-OC₂H₅ > *p*-CH₃ > *p*-H > *p*-F > *p*-Cl > *p*-NO₂ for the mono *para*-substituents. For di *para*-substituted benzhydrols the reactivity decreases in the following order: *p*-CH₃, *p*-CH₃ > *p*-OCH₃, *p*-F > *p*-OCH₃, *p*-Cl > *p*-Cl, *p*-Cl > *p*-CH₃, *p*-NO₂

The reactivity order is in accordance with the σ -values of the various substituents at *para* position (σ (H) = 0.0; σ (OCH₃) = -0.27; σ (OC₂H₅) = -0.25; σ (CH₃) = -0.17; σ (F) = +0.06; σ (Cl) = +0.23; σ (NO₂) = +0.78). The negative σ values enhances the rate while the positive σ values reduces the rate.

Hammett plot: Hammett equation is a linear free energy relationship that studies the effect of substituent changes on reactions [23]. The values of reaction constants (ρ) are determined from the slope of linear Hammetts plot. The reaction constant values (ρ) at different temperatures are: 1.1744 (at 298 K), 1.1099 (at 303 K), 1.0693 (at 308 K) and 1.0172 (at 313 K). The negative ρ values obtained from the Hammett plot is due to decrease in rate by electron withdrawing groups and to increase in rate by electron donating groups. The posi-

% AcOH-H ₂ O (v/v)	D	$10^4 k_1$ (s ⁻¹)											
		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12
30-70	72.0	6.70	13.94	13.19	10.60	5.86	3.66	0.92	17.06	12.14	8.15	2.14	1.53
40-60	63.3	7.56	15.40	14.62	11.60	6.60	4.10	1.01	19.20	13.60	9.08	2.38	1.70
50-50	56.0	8.40	17.25	16.32	12.94	7.35	4.59	1.12	21.40	15.16	10.34	2.65	1.89
60-40	45.5	10.20	20.70	19.90	15.78	8.94	5.56	1.36	26.10	18.44	12.40	3.21	2.26
70-30	38.5	13.00	26.28	25.28	19.80	11.28	7.06	1.70	33.40	23.48	15.70	4.06	2.92

$10^2 [\text{S}] = 2.2 \text{ mol dm}^{-3}$; $10^3 [\text{TBABC}] = 1.0 \text{ mol dm}^{-3}$; $10 [\text{H}^+] = 2.8 \text{ mol dm}^{-3}$

tively charged transition state also due to the negative ρ values obtained from the Hammett plot.

Activation parameters: The substrates mono- and di-substituted benzhydrols were subjected to oxidation kinetics by TBABC at four different temperatures *viz.*, 298, 303, 308 and 313 K in 50 % acetic acid – 50 % water medium in presence of perchloric acid. The pseudo-first order rate constants at four different temperatures are given in the Table-4. The second order rate constants were calculated (Table-5). The Arrhenius plot of $\log k_2$ versus $1/T$ is found to be linear. The enthalpy of activation, entropy of activation and free energy of activation were calculated from k_2 at 298, 303, 308 and 313 K using the Eyring relationship by the method of least square and presented in Table-5.

Substrate	10 ⁴ k ₁ (s ⁻¹)			
	298 K	303 K	308 K	313 K
S1	5.92	8.40	11.92	16.94
S2	12.98	17.25	22.75	30.05
S3	12.10	16.32	21.87	29.08
S4	9.37	12.94	17.82	24.64
S5	5.06	7.35	10.56	15.18
S6	3.17	4.59	6.78	9.72
S7	0.75	1.12	1.72	2.60
S8	16.41	21.40	27.81	36.12
S9	11.13	15.16	20.64	28.03
S10	7.39	10.34	14.47	20.24
S11	1.78	2.65	3.92	5.76
S12	1.25	1.89	2.82	4.22

10² [S] = 2.2 mol dm⁻³; 10³ [TBABC] = 1.0 mol dm⁻³; 10 [H⁺] = 2.8 mol dm⁻³; Solvent composition = 50 % AcOH - 50 % H₂O (v/v)

Isokinetic temperature: Exner suggested a simple method [24] to evaluate the isokinetic relationship. It consisted of plotting the logarithms of rate constants at two temperatures ($T_2 > T_1$) against each other according to the eqn. 2:

$$\log k \text{ (at } T_2) = a + b \log k \text{ (at } T_1) \quad (2)$$

This method is correct in statistics but has the shortcoming that it is only applicable to measurements at two temperatures. Isokinetic temperature obtained is presented in Table-6. At isokinetic temperature all the compounds of the series react equally fast. The linear isokinetic correlation implies that all the mono and di-substituted benzhydrols are oxidized by the same mechanism and the changes in the rate are governed by the changes in both the enthalpy and entropy of activation [25].

Temp. (K)	Correlation coefficient (r)	Slope (b)	Isokinetic temperature (β)
303 & 298	0.992	0.944	422 K
308 & 298	0.991	0.894	429 K
313 & 298	0.998	0.857	448 K
308 & 303	0.990	0.948	440 K
313 & 303	0.988	0.900	445 K
313 & 308	0.997	0.948	444 K

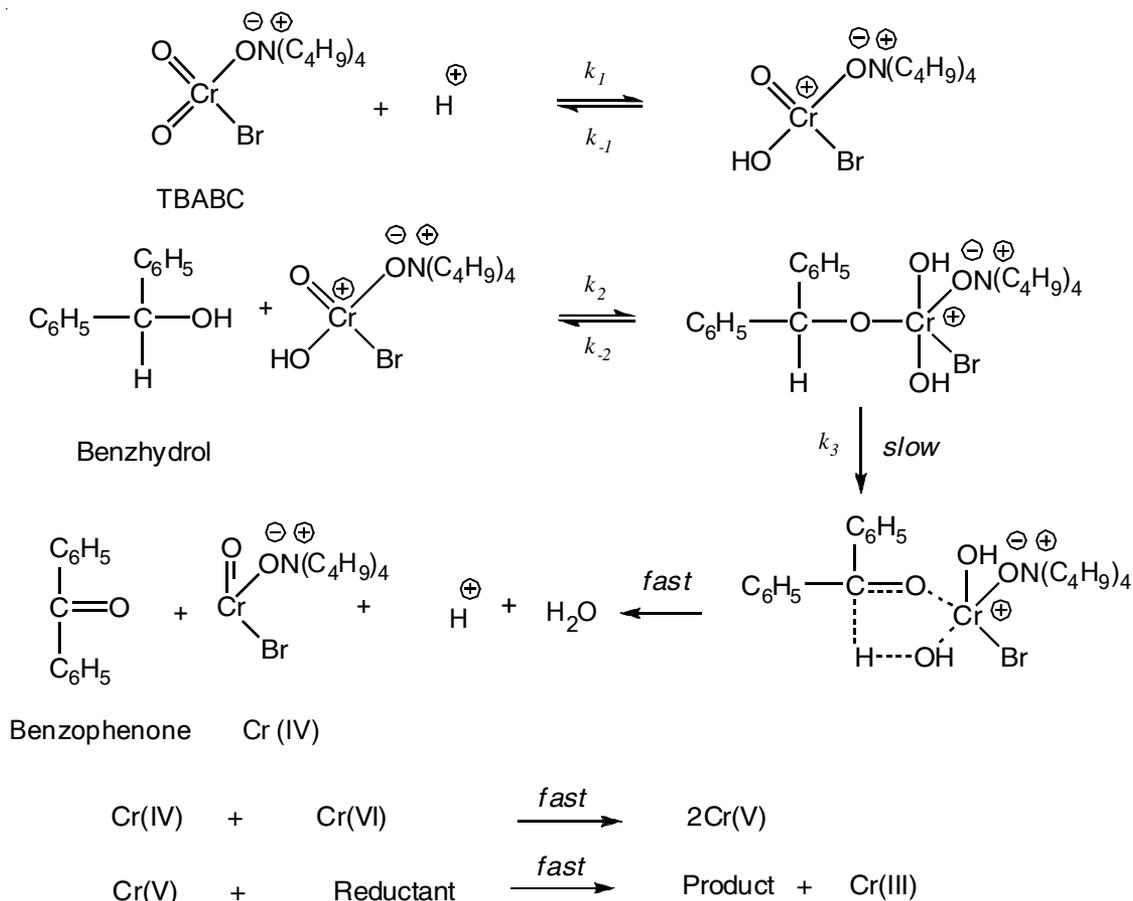
10² [S] = 2.2 mol dm⁻³; 10³ [TBABC] = 1.0 mol dm⁻³; 10 [H⁺] = 2.8 mol dm⁻³; Solvent composition = 50 % AcOH - 50 % H₂O (v/v)

Mechanism of oxidation: A hydride-ion transfer in the rate determining step is suggested from the presence of a substantial kinetic isotope effect. The possibility of a one-electron oxidation, leading to the formation of free radicals is ruled out due to the absence of any effect of added acrylonitrile on the reaction. Product analysis confirmed the formation of dinitro phenyl hydrazone (DNP) suggesting the oxidation of benzhydrol to benzophenone. Negative reaction constants have been used by Banerji as supporting evidence for oxidation mechanisms involving a hydride-ion transfer in the rate determining step [26].

It is well-established that intrinsically concerted sigmatropic reactions, characterized by transfer of hydrogen in a cyclic transition state, are the only truly symmetrical processes involving

Substrate	10 ² k ₂ (dm ³ mol ⁻¹ s ⁻¹)				E _a (kJ mol ⁻¹)	ΔH [#] (kJ mol ⁻¹)	ΔS [#] (J K ⁻¹ mol ⁻¹)	ΔG [#] (kJ mol ⁻¹)
	298 K	303 K	308 K	313 K				
S1	2.69	3.82	5.42	7.70	54.6	51.9 ± 0.2	100.3 ± 0.6	82.3 ± 0.4
S2	5.90	7.84	10.34	13.66	43.5	41.0 ± 0.6	130.9 ± 1.8	80.7 ± 1.2
S3	5.50	7.42	9.94	13.32	45.6	43.3 ± 0.4	123.7 ± 1.2	80.8 ± 0.8
S4	4.26	5.88	8.10	11.20	50.2	47.5 ± 0.4	111.6 ± 1.2	81.3 ± 0.8
S5	2.30	3.34	4.80	6.90	56.8	54.4 ± 0.6	093.8 ± 1.8	82.8 ± 1.2
S6	1.44	2.09	3.0	84.42	58.4	55.7 ± 0.2	092.8 ± 0.6	83.8 ± 0.4
S7	0.34	0.51	0.78	1.18	64.7	62.0 ± 0.4	083.6 ± 1.2	87.3 ± 0.8
S8	7.46	9.72	12.64	16.42	41.0	38.3 ± 0.4	137.8 ± 1.2	80.1 ± 0.8
S9	5.06	6.89	9.38	12.74	47.8	45.2 ± 0.6	117.5 ± 1.8	80.8 ± 1.2
S10	3.36	4.70	6.58	9.20	52.3	49.6 ± 0.2	106.4 ± 0.6	81.8 ± 0.4
S11	0.81	1.20	1.78	2.62	60.9	58.4 ± 0.3	089.0 ± 0.9	85.4 ± 0.6
S12	0.57	0.86	1.28	1.92	63.0	60.3 ± 0.2	085.4 ± 0.6	86.2 ± 0.4

10² [S] = 2.2 mol dm⁻³; 10³ [TBABC] = 1.0 mol dm⁻³; 10 [H⁺] = 2.8 mol dm⁻³; Solvent composition = 50 % AcOH - 50 % H₂O (v/v)



Scheme-I: Mechanism of oxidation of benzhydrol by tetrabutylammonium bromochromate (TBABC)

a linear hydrogen transfer [27]. From the above experimental facts the product is formed *via* a cyclic concerted symmetrical transition state which involve the formation of a chromate ester in a fast pre-equilibrium step and then a decomposition of the ester in a subsequent slow step [28].

Positive slope of $\log k_1$ *versus* $1/D$ plot indicates that the reaction involves a cation dipole type of interaction in the rate determining step. The negative entropy of activation in conjunction with other experimental data supports the mechanism outlined in **Scheme-I**. The rate law can be given as:

$$-d [\text{TBABC}]/dt = k_1 k_2 k_3 [\text{BH}] [\text{TBABC}] [\text{H}^+]$$

Conclusion

In this paper, the detailed kinetic study for the oxidation of 12 mono- and di-substituted benzhydrols by TBABC in 50 % acetic acid – 50 % water medium in the presence of perchloric acid is reported. The reaction is first order each in $[\text{S}]$, $[\text{TBABC}]$ and $[\text{H}^+]$. The oxidation of benzhydrols yield the corresponding benzophenones. The linear isokinetic correlation implies that all the mono and di-substituted benzhydrols are oxidized by the same mechanism.

ACKNOWLEDGEMENTS

One of the authors, S. Hemalatha expresses her gratitude to the Research and Development Centre, Bharathiar University, Coimbatore, India, for the facilities and support. Another author, S. Sheik Mansoor is thankful to the Management of C. Abdul Hakeem College, Melvisharam, India for the support.

REFERENCES

- W.B. Wiberg, *Oxidation in Organic Chemistry*, Academic Press, New York (1995).
- G. Rajarajan, N. Jayachandramani, S. Manivarman, J. Jayabharathi and V. Thanikachalam, *Transition Met. Chem.*, **33**, 393 (2008); <https://doi.org/10.1007/s11243-008-9055-1>.
- P. Swami, D. Yajurvedi, P. Mishra and P.K. Sharma, *Int. J. Chem. Kinet.*, **42**, 50 (2010); <https://doi.org/10.1002/kin.20466>.
- B. Sadeghy and S. Ghammami, *Russ. J. Gen. Chem.*, **75**, 1886 (2005); <https://doi.org/10.1007/s11176-006-0008-0>.
- M. Tajbakhsh, R. Hosseinzadeh and M. Yazdani-Niaki, *J. Chem. Res. (S)*, 508 (2002).
- M. Tajbakhsh, M.M. Heravi, F. Mohanzadeh, M. Ghassemzadeh and S. Sarabi, *Monatsh. Chem.*, **132**, 1229 (2001); <https://doi.org/10.1007/s007060170038>.
- A.R. Mahjoub, S. Ghammami and M.Z. Kassaee, *Tetrahedron Lett.*, **44**, 4555 (2003); [https://doi.org/10.1016/S0040-4039\(03\)00989-4](https://doi.org/10.1016/S0040-4039(03)00989-4).
- M.Z. Kassaee, S.Z. Sayyed-Alangi and H. Sajjadi-Ghotbabadi, *Molecules*, **9**, 825 (2004); <https://doi.org/10.3390/91000825>.
- G. Ghammami and K. Mehrani, *Afr. J. Pure Appl. Chem.*, **1**, 8 (2007).
- K.S. Rangappa, H. Ramachandra and D.S. Mahadevappa, *J. Phys. Org. Chem.*, **10**, 159 (1997); [https://doi.org/10.1002/\(SICI\)1099-1395\(199703\)10:3<159::AID-POC867>3.0.CO;2-V](https://doi.org/10.1002/(SICI)1099-1395(199703)10:3<159::AID-POC867>3.0.CO;2-V).
- S.S. Mansoor and S.S. Shafi, *React. Kinet. Mech. Catal.*, **100**, 21 (2010); <https://doi.org/10.1007/s11144-010-0148-4>.
- B.L. Hiran, R.K. Malkani and N. Rathore, *Kinet. Catal.*, **46**, 334 (2005); <https://doi.org/10.1007/s10975-005-0081-0>.
- V.S. Srinivasan and N. Venkatasubramanian, *Proc. Indian Acad. Sci.*, **87A**, 219 (1978).

14. B. Jagdeesh, C. Archana, M. Balaji and C. Fulchand, *J. Indian Chem. Soc.*, **86**, 481 (2009).
15. S.S. Mansoor and B.H. Asghar, *J. Indian Chem. Soc.*, **90**, 1395 (2013).
16. S.S. Mansoor and S.S. Shafi, *J. Mol. Liq.*, **155**, 85 (2010); <https://doi.org/10.1016/j.molliq.2010.05.012>.
17. S. Patel and B.K. Mishra, *Int. J. Chem. Kinet.*, **38**, 651 (2006); <https://doi.org/10.1002/kin.20198>.
18. S.S. Mansoor and S.S. Shafi, *Arab. J. Chem.*, **8**, 480 (2015); <https://doi.org/10.1016/j.arabjc.2011.01.031>.
19. A.K. Durgannavar, M.D. Meti, S.T. Nandibewoor and S.A. Chimatadar, *Cogent Chem.*, **Article: 1115210** (2015); <http://dx.doi.org/10.1080/23312009.2015.1115210>.
20. S.S. Mansoor, S.S. Shafi and S.Z. Ahmed, *Arab. J. Chem.*, **9**, S557 (2016); <https://doi.org/10.1016/j.arabjc.2011.06.026>.
21. R. Shanker and K.S. Suresh, *Curr. Sci.*, **139**, 65 (1970).
22. E.S. Amis, *Solvent Effects on Reaction Rates and Mechanisms*, Academic Press, New York, p. 42 (1967).
23. L.P. Hammett, *Physical Organic Chemistry*, McGraw-Hill, New York, edn 1 (1940).
24. O. Exner, J.R. Streitwiser and R.W. Talt, *Progress in Physical Organic Chemistry*, John Wiley, New York, p. 41 (1973).
25. L. Liu and Q.X. Guo, *Chem. Rev.*, **101**, 673 (2001); <https://doi.org/10.1021/cr990416z>.
26. K.K. Banerji, *J. Org. Chem.*, **53**, 2154 (1988); <https://doi.org/10.1021/jo00245a004>.
27. R.B. Woodward and R. Hoffmann, *Angew. Chem. Int. Ed. Engl.*, **8**, 781 (1969); <https://doi.org/10.1002/anie.196907811>.
28. J.S. Littler, *Tetrahedron*, **27**, 81 (1971); [https://doi.org/10.1016/S0040-4020\(01\)92399-3](https://doi.org/10.1016/S0040-4020(01)92399-3).