Asian Journal of Chemistry; Vol. 29, No. 4 (2017), 810-816

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2017.20318

Oxidation of Benzhydrol by Tetrabutylammoniumbromochromate in Presence and Absence of Picolinic Acid and 1,10-Phenanthroline: A Kinetic Study

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Received: 28 September 2016; *Accepted*: 27 December 2016; *Published online*: 31 January 2017; AJC-18249

The oxidation of benzhydrol (BH) by tetrabutylammoniumbromochromate (TBABC) was studied in aqueous acetic acid medium. The reaction is first order with respect to tetrabutylammoniumbromochromate, benzhydrol and [H^+] and the reaction is catalyzed by hydrogen ions. The reaction has been studied in the presence of picolinic acid and 1,10-phenanthroline as promoters. The promoters used in this oxidation reaction, picolinic acid and 1,10-phenanthroline are strong chelating ligands which form complexes with most transition metal ions. Among the two promoters oxidation is much faster with 1,10-phenanthroline. The low dielectric constant of the medium assists the complex formation and enhances the reactivity. The reactions were studied at different temperatures at different acetic acid-water composition and various thermodynamic parameters have been determined. The observed experimental results have been explained by plausible mechanisms.

Keywords: Tetrabutylammoniumbromochromate, Benzhydrol, Picolinic acid, 1,10-Phenanthroline.

INTRODUCTION

A variety of compounds containing chromium(VI) have proved to be versatile reagents capable of oxidizing almost every oxidizing functional group [1]. A number of new chromium compounds like pyridinium fluorochromate [2], benzimidazolium fluorochromate [3], tetramethylammonium fluorochromate [4], tributylammonium chlorochromate [5], tripropylammonium fluorochromate [6], tetraethylammonium chlorochromate [7] and tetraheptylammonium bromochromate [8] have been used to study the kinetics and mechanism of oxidation of various organic compounds. Recently tetrabutylammoniumbromochromate (TBABC) has been reported as a new and stronger oxidizing agent [9].

Benzhydrols yield benzophenones upon oxidation, which are useful synthones for fullerenes, bioactive oxygen heterocyclics, dyes and medicines. For this purpose, various oxidizing agents are used, such as chloramine-B [10], *N*-bromosuccinimide [11,12], Tl(III) [13], *N*-bromopthalimide [14] and permanganate [15].

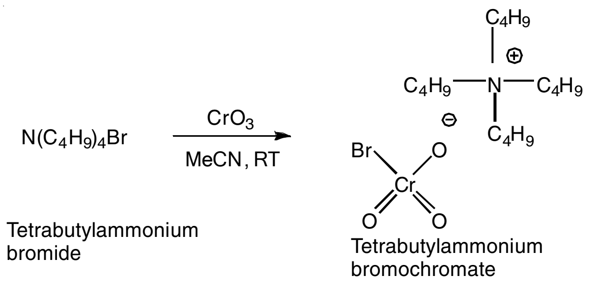
Among the different chelating agents [16-21] that promote Cr(VI) oxidation of different types of organic substrate, picolinic acid and 1,10-phenanthroline are quite important [22-28].

As a part of our continuing investigations of the oxidation of benzhydrol by Cr(VI) [29,30], we report the kinetic features of the oxidation of benzhydrol by TBABC. Literature review reveal that, no detailed kinetic study of oxidation of benzhydrol by TBABC in the absence and presence of promoters such as picolinic acid and 1,10-phenanthroline have so far been attempted. This prompted us to undertake the present investigation. Here we studied the kinetics of oxidation of benzhydrol by TBABC in the absence and presence of picolinic acid and 1,10-phenanthroline and observed that 1,10-phenanthroline is the most suitable promoter of this oxidation. Mechanistic aspects are also discussed.

EXPERIMENTAL

Tetrabutylammonium bromide and chromium trioxide were obtained from Fluka (Buchs, Switzerland). Benzhydrol (SRL,AR), picolinic acid (Aldrich) and 1,10-phenanthroline (Merck, GR) were used after repeated crystallization from methanol. Acetic acid was purified by standard method and the fraction distilling at 118 °C was collected.

Preparation of tetrabutylammoniumbromochromate: Tetrabutylammoniumbromochromate, $[(C_4H_9)_4N][CrO_3Br]$ was prepared by dissolving chromium(VI) oxide (1 g, 10 mmol) in acetonitrile and addition of this solution to a solution of tetrabutylammonium bromide (3.22 g, 10 mmol) in acetonitrile under stirring at room temperature until an orange precipitate was formed. After 2 h stirring, the mixture was filtered. The solid was washed with hexane and dried under vacuum for 1 h. The TBABC salts are somewhat hygroscopic and best stored under a layer of hexane, whereas all of the salts are photosensitive and moisture-sensitive, both in solution and solids. Tetrabutylammoniumbromochromate was recrystallized from methylene chloride by addition of hexane [9].



(1)

Kinetic measurements: The pseudo-first-order conditions were attained by maintaining a large excess (× 15 or more) of benzhydrol over TBABC. The solvent was 50 % acetic acid - 50 % water (v/v), unless specified otherwise. The reactions were followed, at constant temperatures (± 0.01 K), by monitoring the decrease in [TBABC] spectrophotometrically at 364 nm using UV-visible spectrophotometer, Shimadzu UV-1800 model. The pseudo-first-order rate constant k_1, was evaluated from the linear ($r = 0.990$ to 0.999) plots of log [TBABC] against time for up to 80 % reaction. The second order rate constant k_2, was obtained from the relation $k_2 = k_1/[BH]$.

Data analysis: Correlation analyses were carried out using Microcal origin (version 6) computer software. The goodness of the fit was discussed using the correlation coefficient (r in the case of simple linear regression and R in the case of multiple linear regression) and standard deviation (SD).

Product analysis: Product analysis was carried under kinetic conditions. In a typical experiment, benzhyrol (1.8 g, 0.01 mol) and TBABC (8.4 g, 0.02 mol) were made up to 100 mL of the 50 % acetic acid-50 % water mixture and kept in the dark for 24 h to ensure completion of the reaction. The solution was then treated with an excess (200 cm^3) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm^{-3} HCl and kept overnight in a refrigerator. The solvent was removed and the precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered and recrystallized from ethanol. The DNP was found identical (m.p. and mixed m.p.) with DNP of benzophenone. (m.p.: 235-237 °C, lit 237 °C).

Stoichiometric studies: The stoichiomety of the reaction was determined by carrying out several sets of experiments with varying amounts of TBABC largely in excess over benzhydrol. The estimation of unreacted TBABC showed that the following reaction:

$$3(C_6H_5)_2CHOH + 2Cr(VI) \longrightarrow 3(C_6H_5)_2CO + 6H^+ + 2Cr(III) \qquad (2)$$

RESULTS AND DISCUSSION

The oxidation of benzhydrol by TBABC has been conducted in 50 % acetic acid and 50 % water medium at 303 K, under pseudo first order conditions in the absence and presence of picolinic acid and 1,10-phenanthroline.

Effect of varying TBABC concentration: The concentration of TBABC was varied in the range of 0.5 × 10^{-3} to 2.5 × 10^{-3} mol dm^{-1} at constant [BH], [H^+] at 303 K and the rates were measured (Table-1). The near constancy in the value of k_1 irrespective of the concentration confirms the first order dependence on TBABC.

TABLE-1
RATE CONSTANTS FOR THE OXIDATION OF BENZHYDROL BY TBABC IN AQUEOUS ACETIC ACID MEDIUM AT 303 K[a]

10^3 [TBABC] (mol dm^{-3})	10^2 [BH] (mol dm^{-3})	[H^+] (mol dm^{-3})	10^4 k_1[b] (s^{-1})	10^2 k_2[c] (dm^3 mol^{-1} s^{-1})
0.5	2.2	0.28	8.36	3.800
1.0	2.2	0.28	8.40	3.820
1.5	2.2	0.28	8.32	3.780
2.0	2.2	0.28	8.50	3.860
2.5	2.2	0.28	8.46	3.840
1.0	1.2	0.28	4.48	3.730
1.0	1.7	0.28	6.54	3.840
1.0	2.7	0.28	10.24	3.790
1.0	3.2	0.28	12.22	3.820
1.0	2.2	0.12	3.44	0.286
1.0	2.2	0.20	5.92	0.296
1.0	2.2	0.36	10.92	0.303
1.0	2.2	0.44	13.20	0.300
1.0	2.2	0.24	8.46	3.840[d]
1.0	2.2	0.24	7.36	3.340[e]

[a]As determined by a spectrophotometric technique following the disappearance of oxidant 10^2 [BH] = 2.2 mol dm^{-3} ; 10^3 [TBABC] = 1.0 mol dm^{-3}; [H^+] = 0.28 mol dm^{-3}; Solvent composition: 50 % Acetic acid – 50 % Water (v/v); [b]Estimated from pseudo-first order plots over 80 % reaction; [c]Individual k_2 values estimated as k_1/[BH] or k_1/[H^+]; [d]Contained 0.001 mol dm^{-3} acrylonitrile; [e]In the presence of 0.003 mol dm^{-3} Mn(II).

Effect of varying concentration of benzhydrol: The concentration of benzhydrol varied in the range of 1.2 × 10^{-2} to 3.2 × 10^{-2} mol dm^{-1} at 303 K and keeping all other reactant concentrations as constant and the rates were measured (Table-1). The rate of oxidation increased progressively on increasing the concentration of benzhydrol. The plot of log k_1 *versus* log [BH] gave the slope of 1.02 for benzhydrol (Fig. 1). Under pseudo-first-order conditions, the plot of k_1 *versus* [BH] is linear passing through origin. These results confirm the first-order nature of the reaction with respect to [BH].

Effect of varying perchloric acid concentration: Perchloric acid has been used as a source of H^+ in reaction medium. The concentration of H^+ varied in the range 0.12 to 0.44 mol dm^{-1} keeping all other reactant concentration as constant at 303 K and the rates were measured (Table-1). The acid catalyzed nature of this oxidation is confirmed by an increase in the rate on the addition of H^+. The plot of log k_1 *versus* log [H^+] is a straight line with the slope of 1.04. Therefore, order with respect to H^+ is one for benzhydrol. Tetrabutylammonium-bromochromate may become protonated in the presence of acid and the protonated TBABC may function as an effective oxidant.

Effect of acrylonitrile and $MnSO_4$: The reaction did not promote polymerization of acrylonitrile indicating the absence of free radicals (Table-1). However, the addition of Mn(II)

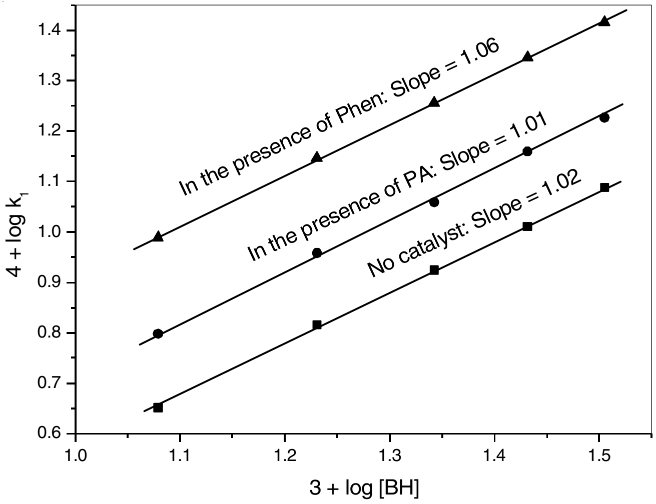


Fig. 1. Showing order plot for the oxidation of oxidation of benzhydrol in the absence and presence of picolinic acid and 1,10-phenanthroline by TBABC

(0.003 mol dm^{-3}),in the form of $MnSO_4$ retards the rate of oxidation. This indicates the involvement of Cr(IV) intermediate in the oxidation of benzhydrol by Cr(VI) reagent and confirms the two electron transfer process in the reaction. Mn(II) ion reduces Cr(IV) formed to Cr(III). In the absence of Mn(II) ion, formed Cr(IV)reduces Cr(VI) to Cr(V) and the oxidation of benzhydrol by Cr(V) is fast [25]. The decrease in the rate of Cr(VI) reduction on the addition of Mn(II) has been attributed to the removal of Cr(IV) by reaction with Mn(II).

Effect of acidity: The reaction is catalyzed by hydrogen ions (Table-1). The acid-catalysis may well be attributed to a protonation of TBABC to give a stronger oxidant and electrophile.

$$O_2CrFO^-NH^+(C_3H_7)_3 + H^+ \rightleftharpoons (OH)OCrFO^-NH^+(C_3H_7)_3 \quad (2)$$

The formation of a protonated Cr(VI) species has earlier been postulated in the reactions of structurally similar PCC [31] and PFC [32].

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 (DBH) was studied. Results showed the presence of a substantial primary kinetic isotope effect (Table-2).

TABLE-2
KINETIC ISOTOPE EFFECT ON THE OXIDATION OF BENZHYDROL BY TBABC

Substrate	$10^4 \times k_1$ (s^{-1})			
	298 K	303 K	308 K	313 K
BH	5.88	8.40	11.54	15.70
DBH	1.10	1.52	2.02	2.66
k_H/k_D	5.34	5.52	5.71	5.90

Solvent composition = 50 % AcOH-50 % H_2O (v/v); 10^2 [BH] = 2.0 mol dm^{-3}; 10^3 [TBABC] = 1.0 mol dm^{-3}; 10 [H^+] = 2.8 mol dm^{-3}

Effect of varying picolinic acid and 1,10-phenanthroline concentration: The concentration of picolinic acid and 1,10-phenanthroline were varied in the range of 0.0 × 10^{-3} to 10.0 × 10^{-3} mol dm^{-1} at constant [TBABC], [BH] and [H^+] at 303 K and the rates were measured (Table-3). We observed that the rate increases linearly with increasing promoter concentration. For 1,10-phenanthroline the rate is much faster than picolinic acid, because of easy decomposition of the ternary complex of the active oxidant in the presence of 1,10-phenanthroline and benzhydrol, because of steric crowding.

TABLE-3
RATE CONSTANTS FOR THE OXIDATION OF BENZHYDROL BY TBABC IN AQUEOUS ACETIC ACID MEDIUM IN THE PRESENCE OF PICOLINIC ACID OR 1,10-PHENANTHROLINE AT 303 K^a

10^3 [TBABC] (mol dm^{-3})	10^2 [BH] (mol dm^{-3})	[H^+] (mol dm^{-3})	10^3 [Cat] (mol dm^{-3})	10^4 k_1^b (s^{-1})	
				PA	Phen
1.0	2.2	0.28	0.0	8.40	8.40
1.0	2.2	0.28	2.0	0.48	11.96
1.0	2.2	0.28	4.0	10.50	16.12
1.0	2.2	0.28	6.0	11.44	18.00
1.0	2.2	0.28	8.0	12.58	23.40
1.0	2.2	0.28	10.0	13.76	29.72
0.5	2.2	0.28	6.0	11.40	18.10
1.5	2.2	0.28	6.0	11.48	18.12
2.0	2.2	0.28	6.0	11.42	18.06
2.5	2.2	0.28	6.0	11.46	18.04
1.0	1.2	0.28	6.0	6.28	9.74
1.0	1.7	0.28	6.0	9.08	14.00
1.0	2.7	0.28	6.0	14.44	22.16
1.0	3.2	0.28	6.0	16.86	26.04

^{a}As determined by a spectrophotometric technique following the disappearance of oxidant; 10^2 [MA] = 2.0 mol dm^{-3} ; 10^3 [TriPAFC] = 1.2 mol dm^{-3}; 10 [H^+] = 2.4 mol dm^{-3}; 10^3 [Cat] = 6.0 mol dm^{-3}; Solvent composition: 50 % Acetic acid – 50 % Water (v/v); ^{b}Estimated from pseudo-first order plots over 80 % reaction

Effect of varying TBABC and benzhydrol concentration in the presence of picolinic acid or 1,10-phenanthroline: The values of k_1 were calculated in the presence of 6.0 × 10^{-3} mol dm^{-1} picolinic acid or 1,10-phenanthroline for different concentrations of TBABC by maintaining other parameters constant. Table-3 shows that the rate constant did not get much altered with increase in [TBABC]. The constancy of k_1 values at different [TBABC] reveals that the reaction follows a first-order kinetics with respect to [TBABC]. Further it reveals that TBABC does not get diminished at our experimental conditions.

Under these experimental conditions, [BH] >> [TBABC], the concentration of benzhydrol is varied in the range of 1.2 × 10^{-2} to 3.2 × 10^{-2} mol dm^{-1} at 303 K in the presence of 6.0 × 10^{-3} mol dm^{-1} picolinic acid or 1,10-phenanthroline and keeping all other reactant concentrations as constant and the rates were measured (Table-3). The rate of oxidation increased progressively on increasing the concentration of benzhydrol. From the plot of k_1 *versus* [BH] it was established that the reaction shows first-order dependence on [BH]. This result, coupled with the nearly unit slope value of the double logarithmic plot between k_1 and [BH] confirms the first-order nature of the reaction with respect to [BH] (Fig. 1).

Effect of solvent polarity on reaction rate: The oxidation of benzhydrol has been studied in the binary mixture of acetic acid and water as the solvent medium. The reaction rate increased remarkably with the increase in the proportion of acetic acid in the solvent medium. These results are presented in Table-4.

The effect from solvent composition on the reaction rate was studied by varying the concentration of acetic acid from

TABLE-4
EFFECT OF VARYING SOLVENT POLARITY ON THE RATE OF REACTION IN THE PRESENCE AND ABSENCE OF PICOLINIC ACID AND 1,10-PHENANTHROLINE AT 303 K

% AcOH-H_2O (v/v)	Dielectric constant	1/D	10^4 k_1 (s^{-1})		
			No promoter	PA	Phen
30-70	72.0	0.0138	6.75	9.06	14.28
40-60	63.3	0.0158	7.48	10.22	15.96
50-50	56.0	0.0178	8.40	11.44	18.00
60-40	45.5	0.0219	10.40	14.16	22.28
70-30	38.5	0.0259	12.88	17.16	27.18

10^2 [BH] = 2.0 mol dm^{-3}; 10^3 [TBABC] = 1.0 mol dm^{-3}; 10 [H^+] = 2.8 mol dm^{-3}; 10^3 [PA] = 6.0 mol dm^{-3}; 10^3 [Phen] = 6.0 mol dm^{-3}

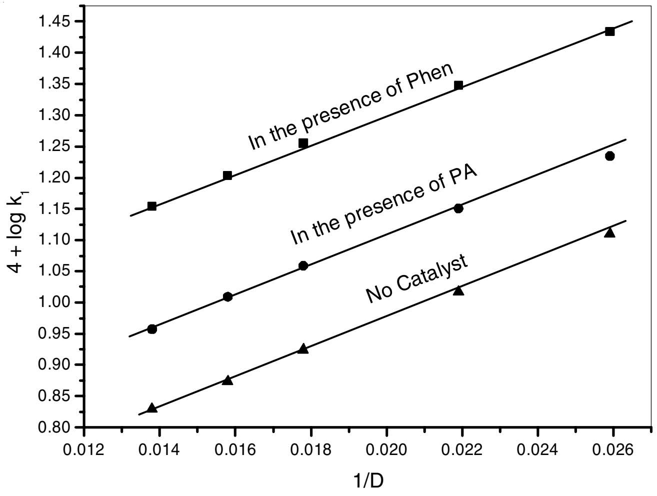


Fig. 2. Plot of 1/D against log k_1 showing effect of solvent polarity for the oxidation of oxidation of benzhydrol by TBABC in the absence and presence of picolinic acid and 1,10-phenanthroline

30 to 70 %. The pseudo-first-order rate constants were estimated for the oxidation of benzhydrol with TBABC in the presence of perchloric acid at a constant ionic strength. The reaction rate is increases markedly with the increase in the proportion of acetic acid in the medium (Table-4). When the acid content increases in the medium, the acidity of the medium is increased whereas the dielectric constant of the medium is decreased. These two effects cause the rate of the oxidation to increase markedly. The enhancement of the reaction rate with an increase in the amount of acetic acid may be generally attributed to two factors, *viz.*, (i) the increase in acidity occurring at constant [H^+] and (ii) the decrease in the dielectric constant with an increase in the acetic acid content.

The plot of log k_1 *versus* 1/D (dielectric constant) is linear with positive slope suggesting the presence of either dipole-dipole or ion-dipole type of interaction between the oxidant and the substrate [33] (Fig. 2). Plot of log k_1 *versus* (D – 1)/(2D + 1) is a curvature indicating the absence of dipole-dipole interaction in the rate determining step. 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.

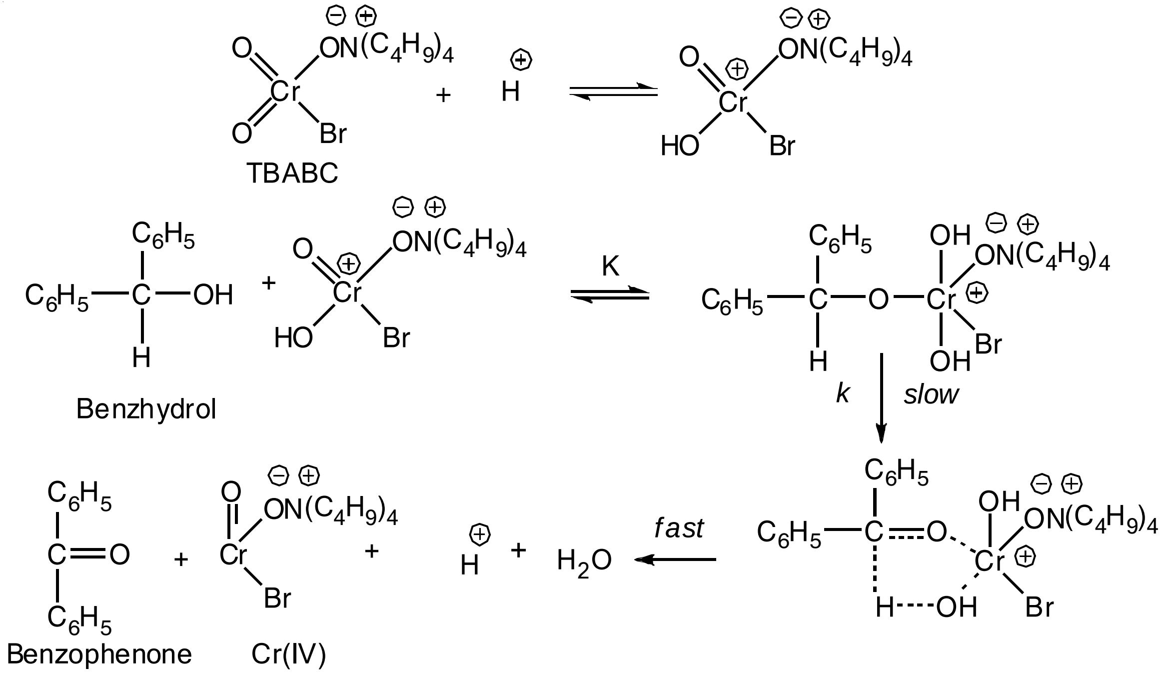
Amis [34] holds the view that in an ion-dipole reaction involving a positive ionic reactant, the rate would decrease with increasing dielectric constant of the medium and if the reactant were to be a negatively charged ion, the rate would increase with the increasing dielectric constant. In this case there is a possibility of a positive ionic reactant, as the rate decreases with the increasing dielectric constant of the medium. Due to the polar nature of the solvent, transition state is stabilized, *i.e.,* the polar solvent molecules surround the transition state and result in less disproportion.

Thermodynamic parameters: The kinetics of oxidation of benzhydrol was studied at four different temperatures *viz.*, 298, 303, 308 and 313 K at various percentage of acetic acid-water medium. The kinetics of oxidation of benzhydrol was also studied in the presence of picolinic acid and 1,10-phenanthroline. 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,

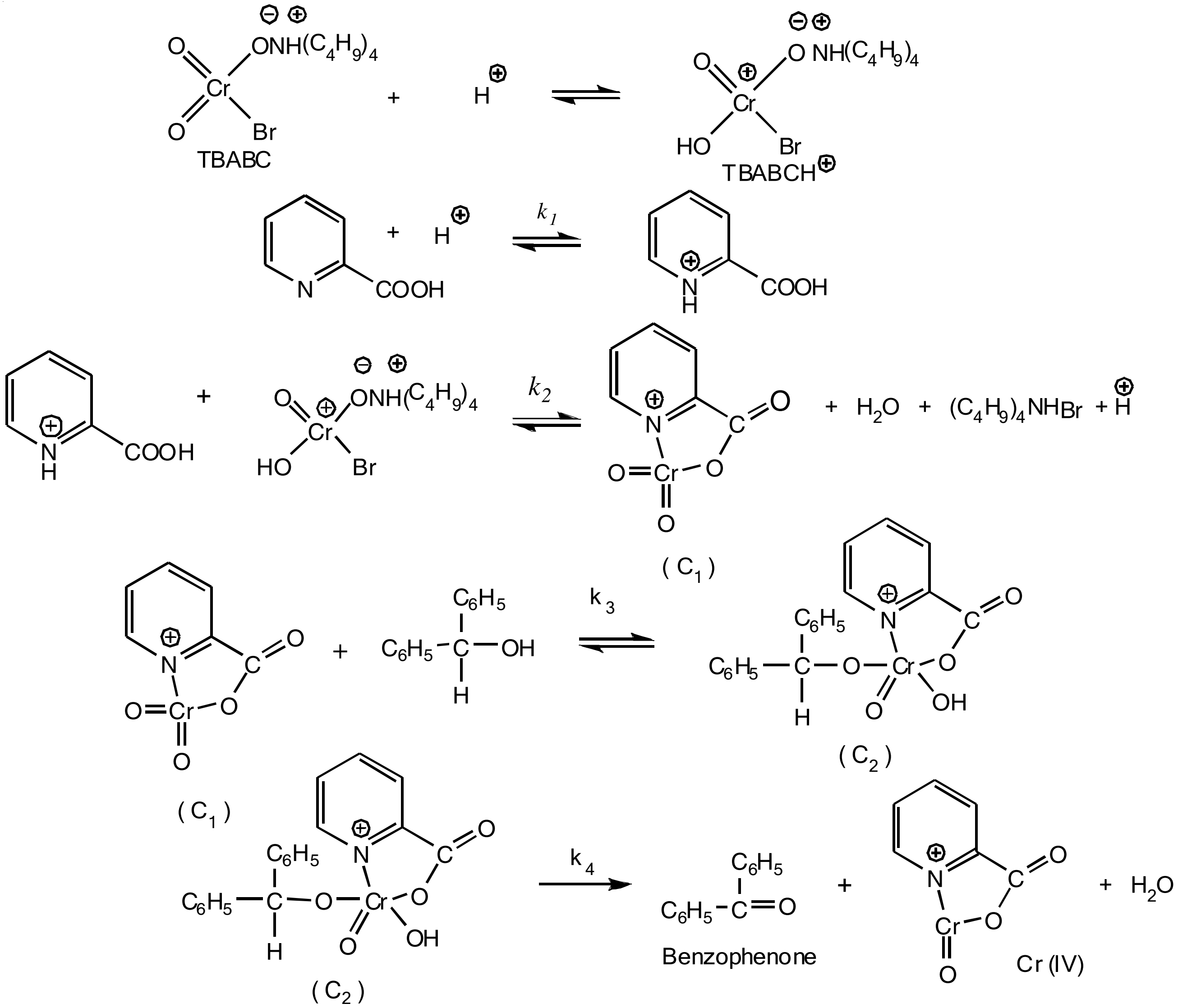
TABLE-5
SECOND ORDER RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE OXIDATION OF BENZHYDROL BY TBABC AT VARIOUS PERCENTAGE OF ACETIC ACID-WATER MEDIUM IN THE PRESENCE AND ABSENCE OF PICOLINIC ACID AND 1,10 PHENANTHROLINE

% AcOH-H_2O (v/v)	10^2 k_2 (dm^3 mol^{-1} s^{-1})				E_a (kJ mol^{-1})	-$\Delta S^\#$ (JK^{-1} mol^{-1})	$\Delta H^\#$ (kJ mol^{-1})	$\Delta G^\#$ (kJ mol^{-1}) (at 303 K)
	298 K	303 K	308 K	313 K				
				No catalyst				
30-70	2.14	3.07	4.20	5.77	51.12	113.52 ± 1.8	48.64 ± 0.6	83.04 ± 1.2
40-60	2.39	3.40	4.66	6.36	50.54	114.66 ± 2.4	48.06 ± 0.8	84.24 ± 1.6
50-50	2.67	3.82	5.25	7.14	50.92	112.75 ± 2.4	48.44 ± 0.8	83.96 ± 1.6
60-40	3.35	4.73	6.53	8.69	49.58	114.47 ± 1.2	47.28 ± 0.4	83.29 ± 0.8
70-30	4.41	5.85	8.24	11.54	49.40	113.52 ± 1.5	46.90 ± 0.5	82.29 ± 1.0
				Picolinic acid				
30-70	3.09	4.12	5.52	7.32	44.80	132.09 ± 1.5	42.32 ± 0.5	82.34 ± 1.0
40-60	3.46	4.65	6.21	8.32	45.56	128.84 ± 2.7	42.88 ± 0.9	81.92 ± 1.8
50-50	3.82	5.20	7.07	9.18	45.95	127.12 ± 1.5	43.27 ± 0.5	81.78 ± 1.0
60-40	4.74	6.44	8.69	11.36	45.38	126.16 ± 1.2	43.12 ± 0.4	81.34 ± 0.8
70-30	5.82	7.80	10.51	14.32	46.72	120.60 ± 0.6	44.04 ± 0.2	80.58 ± 0.4
				1,10-Phenanthroline				
30-70	4.99	6.49	8.33	10.89	40.40	143.20 ± 1.5	37.91 ± 0.5	81.10 ± 1.0
40-60	5.63	7.25	9.43	12.22	40.21	142.42 ± 1.8	37.91 ± 0.6	81.06 ± 1.2
50-50	6.29	8.18	10.64	13.83	40.97	139.38 ± 3.0	38.28 ± 1.0	80.51 ± 2.0
60-40	7.67	10.13	13.36	17.47	42.70	131.52 ± 2.4	38.48 ± 0.8	78.33 ± 1.6
70-30	9.43	12.35	16.18	21.35	42.30	131.14 ± 1.5	39.82 ± 0.5	79.56 ± 1.0

10^2 [BH] = 2.0 mol dm^{-3}; 10^3 [TBABC] = 1.0 mol dm^{-3}; 10 [H^+] = 2.8 mol dm^{-3}; 10^3 [PA] = 6.0 mol dm^{-3}; 10^3 [Phen] = 6.0 mol dm^{-3}



Scheme-I: Mechanism of oxidation of benzhydrol by TBABC



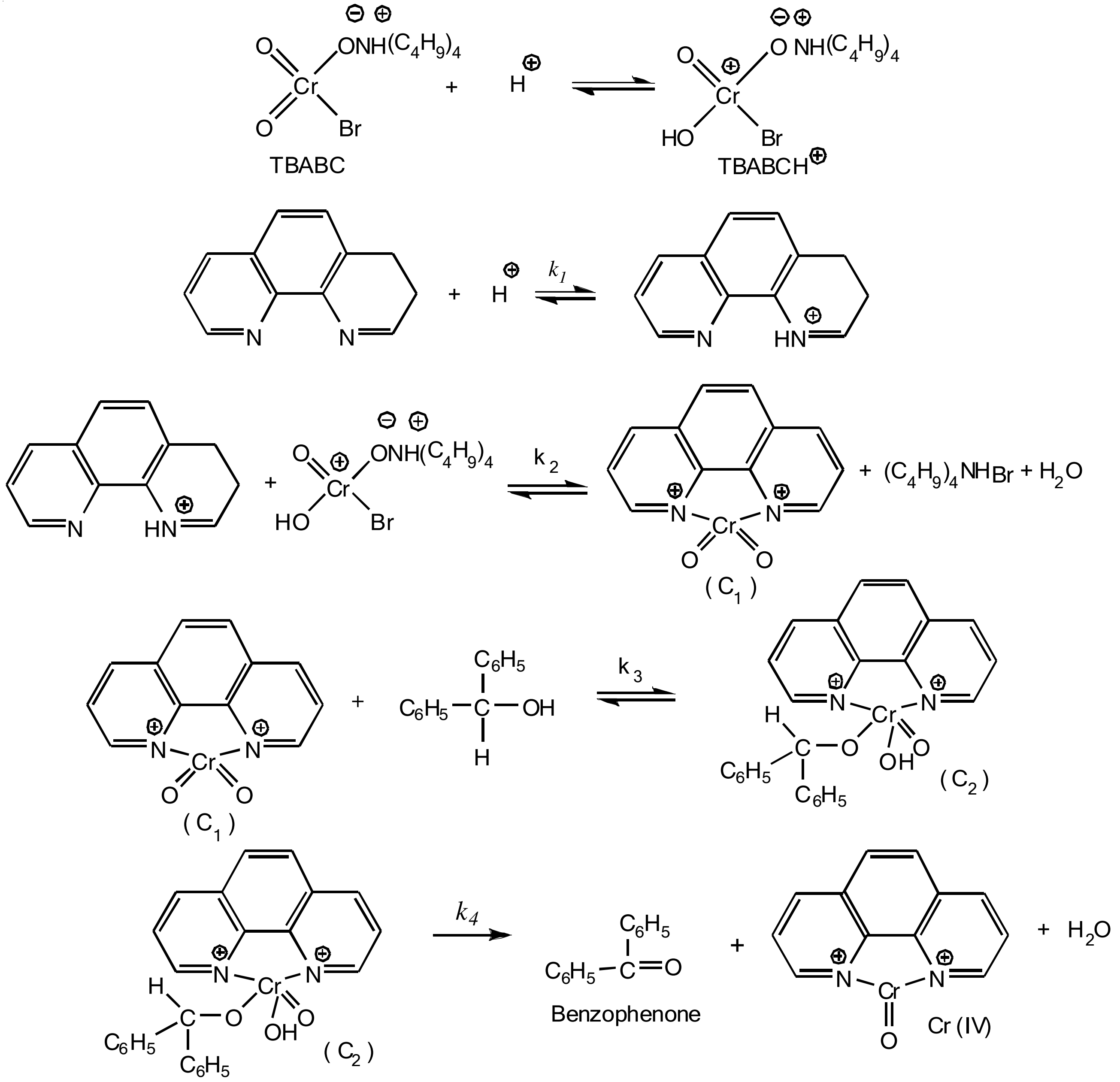
Scheme-II: Mechanism of oxidation of benzhydrol by TBABC in the presence of picolinic acid

308 and 313 K using the Eyring relationship by the method of least square and presented in Table-5. The entropy of activation is negative for benzhydrol in the absence and presence of picolinic acid and 1,10-phenanthroline.

Mechanism of oxidation

Reaction mechanism for TBABC oxidation of benzhydrol in the absence of a promoter: From the product analysis, 2,4-dinitrophenylhydrazine was confirmed. Hence, it shows that under the experimental conditions employed in the present study, benzhydrol is oxidized to benzophenone. Based on the above kinetic observations the following mechanism is proposed for the reaction. 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 presence of a substantial kinetic isotope effect in the oxidation of α-deuterobenzhydrol confirms the cleavage of the α-C-H bond in the rate-determining step. Therefore, a hydride-ion transfer in the rate determining step is suggested. 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**.

Reaction mechanism of the oxidation of benzhydrol by TBABC in the presence of a promoter: The findings with promoter can be explained by considering the reaction mechanism outlined in **Schemes II** and **III**. Picolinic acid (**Scheme-II**) and 1,10-phenanthroline (**Scheme-III**) readily form complexes (C_1) with Cr(VI) which are active oxidants [35-38]. In the next step, the complex reacts with the substrate to form a ternary complex (C_2). This ternary complex (C_2) undergoes redox decom-position by two electron transfer within the cyclic transition state in a rate-determining step involving simultaneous rupture of C–C and C–H bonds to give a benzophenone and the Cr(IV)-promoter complexes.



Scheme-III: Mechanism of oxidation of benzhydrol by TBABC in the presence of 1,10-phenanthroline

Conclusion

The kinetics of oxidation of benzhydrol by TBABC has been investigated in aqueous acetic acid medium by spectrophotometrically at 303 K in the absence and presence of promoters like picolinic acid and 1,10-phenanthroline. The oxidation of benzhydrol by TBABC is first order each with respect to the benzhydrol, TBABC and hydrogen ion. The oxidation is catalyzed by perchloric acid. The lowering of dielectric constant of reaction medium increases the reaction rate significantly. The reaction does not show the polymerization, which indicates the absence of free radical intermediate in the oxidation. The reaction becomes faster with each of the promoters.

ACKNOWLEDGEMENTS

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

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