Indian Journal of Chemistry
Vol. 62, March 2023, pp. 372-379
DOI: 10.56042/ijc.v62i4.410

Kinetics and structure reactivity correlation in the oxidation of some *para*- substituted benzhydrols by benzimidazolium dichromate

Dinesh Panday
Department of Chemistry, M. L. Sukhadia University, Udaipur, Rajasthan 313001, India
E-mail: dpanday26@gmail.com

Received 5 March 2022; accepted (revised) 17 March 2023

The oxidation of some *para*-substituted benzhydrols by benzimidazolium dichromate (BIDC) in dimethyl sulfoxide (DMSO) medium, results in the formation of corresponding diphenyl ketone. The reaction has been investigated on the condition of pseudo-first order. In terms of both BIDC and hydrogen-ion, the reaction is first order. In the case of benzhydrols, however, Michaelis-Menten type kinetics is observed. At different temperatures, the formation constants and rates of breakdown of benzhydrol-BIDC complexes have been determined. Complex formation thermodynamic parameters and activation parameters for complex decomposition have been computed. The kinetic isotope effect found in the oxidation of benzhydrol ((k_H/k_D = 5.93 at 293 K) shows that the rate-determining step involved α-C-H bond fission. For the kinetic analysis of the reaction, nineteen organic solvents have been utilized. The solvent impact have been investigated, and found that cation-solvation plays a significant role. A suitable mechanism is proposed based on the kinetic data, solvent effect analysis, and results of various non-kinetic parameters.

Keywords: Benzhydrols, Kinetics, Mechanism, Oxidation, Correlation, Benzimidazolium dichromate

Cr(VI) as chromate or dichromate is normally insoluble in most organic solvents, but soluble in water and is very poisonous. In spite of these difficulties, many Cr(VI) complexes are utilised to oxidise organic compounds[1]. Selective oxidation of organic molecules under non-aqueous conditions is a beneficial conversion in synthetic organic chemistry. A variety of chromium(VI) compounds have been identified for this purpose[2-4]. In 1998, a Cr(VI) derivative called benzimidazolium dichromate (BIDC) was synthesized[5]. BIDC is more stable and easy to store than other Cr(VI) derivatives because it is neither light sensitive nor hygroscopic. BIDC has been reported to convert benzylic and allylic alcohols[4] to carbonyl compounds with a yield of 75-98%. We have developed an interest in the kinetics and mechanistic investigation of BIDC oxidation, and a few studies have already come out of our laboratory[6-13]. Oxidation of benzohydrols results in benzophenones, which are useful synthones for fullerenes, bioactive oxygen heterocyclics, dyes, and medications[14]. According to a review of the literature, there appears to be no information on the kinetics and mechanism of BIDC oxidation of benzhydrols. The oxidation kinetics of several *para*-substituted benzhydrols by BIDC in dimethyl sulfoxide (DMSO) solvent are described in this work. Mechanistic features are also examined.

Experimental Details

Materials and methods

For performing the oxidation process[4], benzimidazole (LOBA, AR) and chromic acid (LOBA, AR) were used to make BIDC, which was then tested for purity using an iodometric method. For the kinetic investigation, AR grade (Sigma-Aldrich Chemicals) benzhydrol, *p*-methoxybenzhydrol, *p*-methylbenzhydrol, *p*-bromobenzhydrol, and *p*-nitrobenzhydrol (Sigma-Aldrich Chemicals) were chosen. The described methods[15] were used to determine the purity of the solvents (E. Merck, AR). Toluene *p*-sulphonic acid (LOBA, AR) was used as a source of H^+ ions. Titrations against standard alkali were used to standardize toluene *p*-sulphonic acid (TsOH) solutions.

The method described by Ramashanker and Suresh[16] was used to produce deuterated (α-C-D) benzhydrols. α-D-benzhydrols were synthesized by refluxing corresponding benzhydrols (α-C-H) in D_2O for 2-3 h, removing the solvent with a pump, and repeating the process three times to ensure complete

proton exchange. NMR (300 MHz, JEOL) analysis was performed to ensure that the deuterated (α-C-D) benzhydrols were present.

Product analysis

Product analyses were carried out under kinetic conditions, *i.e.*, an excess of benzhydrol over BIDC. In this experiment, benzhydrol (18.4 g, 0.1 mol), TsOH (19.02 g, 0.1 mol), and BIDC (4.54 g, 0.01 mol) in DMSO were combined to make 100 mL, which was then left in the dark for a day to ensure that the reaction was completed. The above solution was then reacted by 200 mL of 2,4-dinitrophenylhydrazine (DNP) (saturated) solution in 2 mol dm^{-3} hydrochloric acid and kept in a chiller for the rest of the night and the obtained hydrazone was percolated, parched, weighed, purified by recrystallization with ethanol, and weighed again. The amount of DNP formed before and after recrystallization was 5.03 g (92%) and 4.59 g (84%), respectively. The product was identical to an authentic sample of DNP of diphenyl ketone (mixed m.p. and m.p.). Similar experiments were carried out with other benzhydrols, with the yield of DNP of the corresponding diphenyl ketone varying from 81 to 87 percent after recrystallization.

Kinetic measurements

Pseudo-first-order conditions were conducted at constant temperature (±0.1K) for all kinetic analyses, keeping a significant excess of benzhydrols (10 times or more) relative to BIDC. The reaction was performed under DMSO solvent, unless otherwise indicated. The progress of the reaction was investigated by monitoring the consumption of BIDC at 370 nm for a maximum of 80% of the reaction. The Beer law holds for all concentrations used in our experiments. Using linear ($r^2 > 0.99$) log[BIDC] plots over time, the rate constant, k_{obs}, was estimated. The observed values were the average of two or more sets (reproducibility 3%). As measures of goodness of adjustment, in correlation analysis, we applied the coefficient of determination (R^2 or r^2), standard deviation (sd), and Exner's parameter (ψ)[17].

Results and Discussion

The oxidation of benzhydrol by BIDC results in the formation of corresponding diphenyl ketone. To determine stoichiometry, BIDC (2.27 g, 0.005 mol) and benzhydrol (0.184 g, 0.001 mol) in DMSO were combined in 200 mL with 1.0 mol dm^{-3} TsOH. The solution was allowed to stand for 24 h to ensure that the reaction was completed. The residual BIDC was assessed by using a UV-visible spectrophotometer (Model UV5704, ECIL) set to 370 nm. Three moles of benzhydrols were observed to react with two moles of BIDC at different concentration of benzhydrol. The results obtained with benzhydrol are shown in Table 1. BIDC was reduced to Cr(III) and was involved in the reaction as a 3-electron oxidant. For the oxidation of benzhydrol, the product analysis and stoichiometric determination showed the following overall reactions.

$$3(C_6H_5)_2CHOH + 2\ Cr_2O_7^{-2} + 8H^+ \longrightarrow 3(C_6H_5)_2CO + 2\ Cr^{+3} + 7\ H_2O \quad \ldots (1)$$

Test for free radicals

The oxidation of benzhydrols by BIDC in a N_2 gas atmosphere failed to produce acrylonitrile polymerization. There was no major BIDC consumption in the absence of benzhydrol. The rate of oxidation was almost unchanged by the addition of acrylonitrile (Table 2). The reaction was performed with 0.005 mol dm^{-3} of butylated hydroxytoluene (BHT) to further validate the absence of free radical oxidation during the reaction. The BHT did not indicate any significant changes and was almost quantitatively observed.

Rate laws

In terms of BIDC, the reactions were determined to be of first order. The graphs of log [BIDC] with time in various kinetic runs were linear ($r^2 > 0.99$). Furthermore, the pseudo first-order rate constants are independent of the initial BIDC concentration (Table 2). In the case of benzhydrol, the order was less than one. Based on the downward curvature of the plots it appears that a complex relationship exists. Plotting $1/k_{obs}$ *versus* 1/[benzhydrol] revealed a linear relationship with an intercept on the rate-ordinate (Fig. 1). In response to benzhydrol and substituted benzhydrol, a Michaelis-Menten reaction kinetics is observed. In conclusion, these overall mechanisms and rate laws are as follows.

Table 1 — Stoichiometry data for the oxidation of benzhydrol by BIDC

10^3[BIDC] (mol dm^{-3})	10^3 [benzhydrol] (mol dm^{-3})	10^3 [Unused BIDC] (mol dm^{-3})	[benzhydrol] / [Used up BIDC]
10.0	2.0	8.65	1.48
10.0	4.0	7.42	1.55
10.0	6.0	6.08	1.53
			Mean = 1.52±0.04

Table 2 — Rate data for *para*-substituted benzhydrols oxidation by BIDC, TsOH= 0.4 mol dm^{-3} at 313 K temperature

10^3[BIDC] (mol dm^{-3})	[benzhydrol] (mol dm^{-3})	10^4 k_{obs} (s^{-1})				
		H	*p*-NO_2	*p*-Br	*p*-CH_3	*p*-OCH_3
1.0	0.05	2.34	0.11	0.94	4.54	7.05
1.0	0.1	4.0	0.18	1.59	7.8	12.0
1.0	0.2	6.2	0.27	2.43	12.2	18.7
1.0	0.3	7.6	0.33	2.96	14.9	23.0
1.0	0.4	8.5	0.37	3.31	17.0	25.9
1.0	0.6	9.7	0.41	3.77	19.5	29.7
1.0	1.0	11.0	0.46	4.23	22.1	33.6
0.5	0.6	9.81	0.36	3.86	20.4	30.3
0.8	0.6	9.73	0.43	3.79	20.1	29.7
1.5	0.6	9.6	0.48	3.73	19.3	29.4
2.0	0.6	9.84	0.39	3.9	19.7	30.1
5.0	0.6	9.69	0.4	3.81	20.0	29.5
1.0	0.1	4.06*	0.16*	1.61*	7.72*	12.2*

*(acrylonitrile) = 0.005 mol dm^{-3}

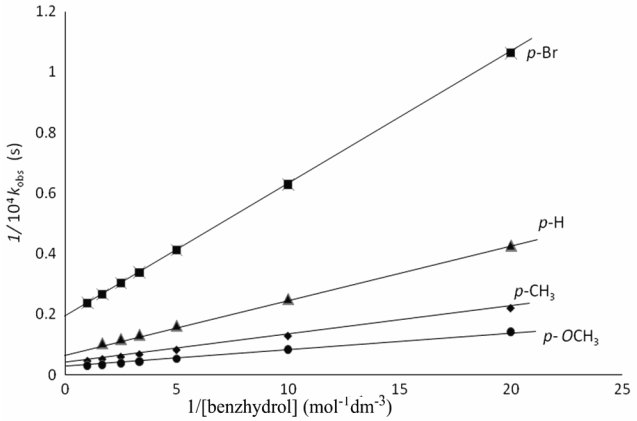


Fig. 1 —Plot of $1/(10^4 k_{obs})$ *versus* 1/ [benzhydrol], TsOH= 0.4 mol dm^{-3}; [BIDC] = 0.001 mol dm^{-3}; in DMSO at 313 K

$$[\text{benzhydrol}] + \text{BIDC} \overset{K^{\#}}{\rightleftharpoons} [\text{complex}] \quad \ldots (2)$$

$$[\text{Complex}] \overset{k_2}{\rightarrow} \text{Product} \quad \ldots (3)$$

$$\text{Rate} = k_2 K^{\#}[\text{benzhydrol}][\text{BIDC}]_t / 1 + K^{\#}[\text{benzhydrol}] \quad \ldots (4)$$

$$\text{or, } (\text{Rate}/[\text{BIDC}]_t)^{-1} = 1/k_{obs} = 1/k_2 K^{\#}[\text{benzhydrol}] + 1/k_2 \quad \ldots (5)$$

Here, $[\text{BIDC}]_t = [\text{complex}] + [\text{BIDC}]$

In this study, k_{obs} was calculated to depend on the concentration of benzhydrols and four *para*-substituted benzhydrols using the double reciprocal plots shown in Eq. (5) for different temperatures, Calculations of the thermodynamic parameters associated with complex establishment and activation parameters for their break-down were based on the values of $K^{\#}$ and k_2, respectively, at non-identical temperatures (Tables 3 and 4).

Spectral analysis

Evaluation of the spectra of BIDC and BIDC + benzhydrol (Fig. 2) showed that there is a definite increase in the absorbance of BIDC on the inclusion of benzhydrol (refer to spectra [A] and [B], respectively). This favours the formation of an intermediate complex. Further, the absorbance decreases with time and minimizes on about completion of reaction (refer to spectra [C] and [D]). This indicates that the complex subsequently decomposes to give the final product

Kinetic isotope effect

The oxidation of α-deuteriobenzhydrol was examined with BIDC to determine the relevance of the cleavage of the α-C-H bond in the rate-controlling pathway. The outcomes (Tables 3 & 4) revealed that the formation constants of normal and deuterated benzhydrol complexes are nearly comparable, but the rates of their decomposition confirmed a primary isotope effect (k_H/k_D = 5.93 at 293 K). The primary kinetic isotope effect was absolutely similar in the oxidation of benzhydrol by benzyltrimethylammonium chlorobromate[18]. Furthermore, the value of the kinetic isotope effect diminishes with increasing temperature in the present investigation.

Effect of acidity

The rate of oxidation is enhanced as acidity rises, and the relationship is of the form: Rate = $k'[H^+]$**.** For all benzhydrols, the order in regard to $[H^+]$, is one (Fig. 3). A graph of log k_{obs} *versus* log $[H^+]$, for benzhydrol, exhibited the slope =1.05 with $r^2 > 0.99$. For the substituted benzhydrols, similar findings were reported. There was no specific reaction in the

Table 3 — Formation constants of benzhydrol-BIDC complexes and their thermodynamic parameters in DMSO

Subst.	$K^{\#}$ (mol^{-1}dm^3)				ΔH	ΔS	ΔG
	293 K	303 K	313 K	323 K	kJ mol^{-1}	Jmol^{-1}K^{-1}	k J mol^{-1}
H	15.1	9.2	4.13	2.96	-47.3±2.9	-131±9.7	-8.5±2.3
p-NO_2	15.75	9.74	4.7	2.98	-49.5±2.0	-128±6.4	-8.71±1.5
p-Br	15.6	9.8	4.4	2.8	-47.3±2.6	-131±8.5	-8.6±2.0
p-CH_3	14.8	9.1	3.98	2.74	-48.8±3.0	-141±9.6	-8.4±2.4
p-O CH_3	14.5	8.9	4.05	2.89	-46.8±2.8	-139±9.3	-8.41±2.2
Benzhydrol-α-D	16.2	10.1	4.8	3.08	-48.1±5	-131±7.1	-8.73±1.7

Table 4 — Decomposition constants of benzhydrol-BIDC complexes and their activation parameters in DMSO

Subst.	10^4 k_2 (s^{-1})				ΔH*	ΔS*	ΔG*
	293 K	303 K	313 K	323 K	kJ mol^{-1}	Jmol^{-1}K^{-1}	k J mol^{-1}
H	1.84	4.92	13.7	38.9	77.5±01.6	-91±5.2	104.4±1.2
p-NO_2	0.06	0.18	0.56	1.67	84.8±1.2	-86.2±3.9	112.8±0.9
p-Br	0.67	1.8	5.2	15.1	79.2±1.8	-87.8±5.8	106.9±1.4
p-CH_3	3.98	10.3	27.8	76.8	75±1.6	-93.1±5.2	85.5±1.3
p-O CH_3	6.2	15.7	41.9	115.4	74.3±1.2	-90.2±5.6	101.5±1.4
benzhydrol-α-D	0.31	0.88	2.58	7.78	81.9±1.67	-93±5.4	91.7±1.3

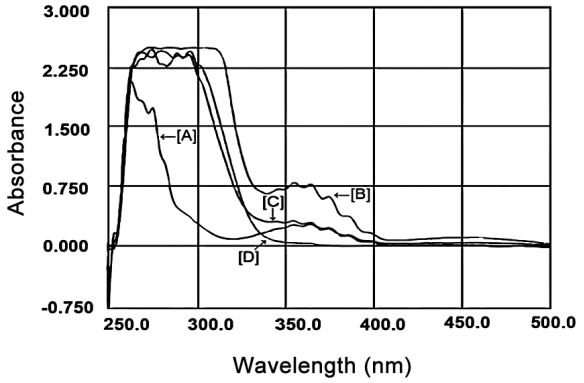


Fig. 2 — UV-visible absorption spectra of [A] 0.0005 mol dm^{-3} BIDC, [B] 0.0005 mol dm^{-3} BIDC + 1.0 mol dm^{-3} benzhydrol, [C] is [B] after 2500 s and [D] is [B] on about completion of reaction. Solvent: DMSO, temperature: 293 ± 1 K

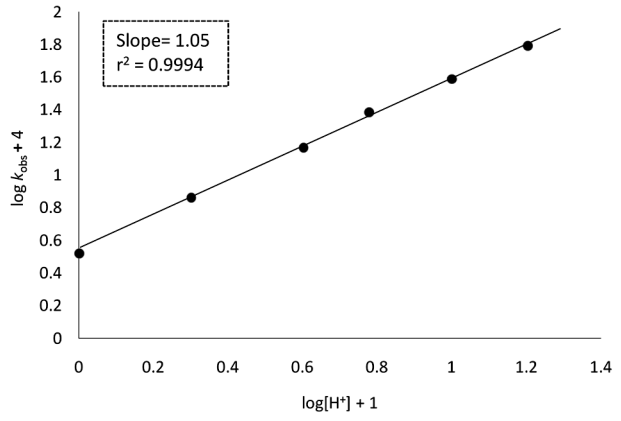


Fig. 3 — A plot of log k_{obs}+ 4 *versus* log [H^+] + 1 [benzhydrol] = 0. 5 mol dm^{-3}; [BIDC] = 0.001 mol dm^{-3} in DMSO at 313 K

absence of TsOH. At various acidities, the reaction rate was studied in relation to the concentration of benzhydrols (Table 5).

Table 5 — Dependence of reaction rate of *para*-substituted benzhydrol on hydrogen- ion concentration [benzhydrol] = 0. 5 mol dm^{-3}; [BIDC] = 0.001 mol dm^{-3}; Temperature 313 K

[TsOH]	10^4 k_{obs} (s^{-1})				
(mol dm^{-3})	H	*p*-NO_2	*p*-Br	*p*-CH_3	*p*-OCH_3
0.1	3.3	1.01	8.32	41.4	61.8
0.2	7.25	1.91	17.2	87.5	121.9
0.4	14.7	3.9	35.7	185	280.5
0.6	24.2	5.7	64.6	286	357.7
1.0	38.7	9.32	93.4	497	590.2
1.6	61.9	14.5	153	826	935.4

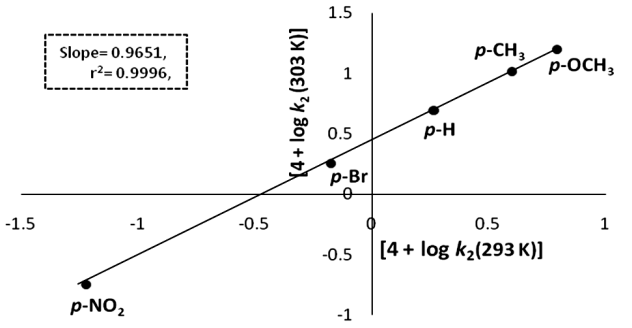


Fig. 4 — Exner's plot of log k_2 (293 K) *versus* log k_2 (303 K) for the oxidation of substituted benzhydrol by BIDC in DMSO

Isokinetic relationship

The activation enthalpies (ΔH*) and entropies (ΔS*) of the oxidation of benzhydrols and four *para*-substituted benzhydrols had a poor correlation (r^2 = 0.8517). Exner's criterion[19] was used to test the correlation, and it was found to be satisfactory. Exner's plot for five benzhydrols in between values of 4+log k_2 (293 K) and 4+log k_2 (303 K) was straight line with slope=0.9651 and r^2= 0.9996 (Fig. 4). Exner's approach yielded a value of 974 K as the isokinetic temperature. The validity of linear free energy relations requires the

existence of a linear isokinetic relationship[19]. This also suggests that all of the reactions which are correlated, follow a common mechanism.

Reactive species

At 313 K, conductivity measurements were taken to determine the state of BIDC in the present reaction conditions. It was reported that DMSO has a very low conductivity value, and that adding BIDC to DMSO results in a negligible change in the conductivity value. As a result, BIDC is non-ionised under our reaction conditions and does not break up into benzimidazolium and dichromate ions. The fact that the rate of oxidation does not change when the benzimidazolium ion is added supports the idea that BIDC stays non-ionised[11]. The non-ionic character of the oxidant in the reaction system is supported by the reported crystal structure analysis of BIDC[20]. Following protonation, BIDC (P) creates a protonated Cr[VI] species (Q), which is a more active electrophile and oxidant (Eq. 6)

$$\underset{(P)}{(BIOH)_2Cr_2O_5} + H^+ \overset{K_1}{\rightleftharpoons} \underset{(Q)}{(BIOH)_2O\overset{+}{C}r(OH)OCrO_2} \quad \ldots (6)$$

BI stands for benzimidazole in this case.

As a result, proton concentration affects the oxidation process *via* BIDC. Internal electron transfer from benzhydrol to BIDC, which is aided by BIDC protonation, results in increased reactivity. Furthermore, the hydrogen ion dependency exhibits a rapid equilibrium between (P) and (Q), with a smaller magnitude of the equilibrium constant, K_1. Without TsOH, no oxidation occurs, implying that only the protonated BIDC (Q) acts as an oxidizing species. Similar hydrogen-ion dependency was reported in the BIDC oxidation of aliphatic aldehyde[10].

Correlation analysis of reactivity

The formation constants, $K^{\#}$ (Table 3) of benzhydrol-BIDC complexes are completely stable by aromatic ring substitution. The rates of breakdown of the complexes, k_2 (Table 4), however, exhibit wide variation with the substitution. Hammett[20] values were correlated with k_2 values for benzhydrol and four monosubstituted benzhydrols. [Eq. (7)].

$$\log k_2 = \rho\,\sigma + \log k_0 \quad \ldots (7)$$

Here, k_2 is the rate constant for substituted benzhydrol, k_0 is the rate constant for benzhydrol, σ is the substituent constant and ρ is reaction constant. A graph of log k_2 *versus* σ is linear, (Fig. 5) where r^2 = 0.999, *sd* = 0.2 with ρ = -1.79 at 313 K temperature. The correlations were excellent, with the reaction constants being negative, based on the present analysis (Table 6). As the temperature rises, the magnitude of the reaction constant falls. The rate of these oxidation reactions is slowed by electron withdrawing groups and sped up by electron donating groups. The following is the reactivity order:

p-NO_2 < *p*-Br < *p*-H < *p*-CH_3 < *p*-OCH_3.

Solvent effect

The oxidation of benzhydrol by BIDC was investigated using 19 organic solvents. Table 7

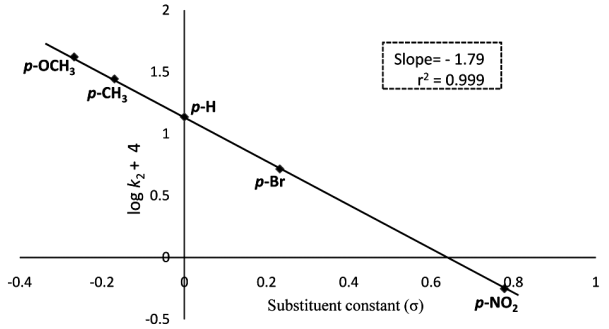


Fig. 5 — Plot of log k_2 + 4 *versus* Hammett σ values for the oxidation of substituted benzhydrol by BIDC in DMSO at 313 K

Table 6 — Correlation of the rates of oxidation of benzhydrols in terms of Hammet equation

T (K)	ρ	r^2	*sd*	ψ	*n*
293	-1.92+0.06	0.996	0.05	0.04	5
303	-1.85+0.08	0.997	0.04	0.03	5
313	-1.79+0.04	0.999	0.02	0.01	5
323	-1.75+0.03	0.995	0.07	0.06	5

n = number of data points

Table 7 — Effect of solvent on the oxidation of benzhydrol by BIDC at 313 K

Solvent	$K^{\#}$ ($mol^{-1}dm^3$)	$10^4 k_2$ (s^{-1})
Chloroform	4.2	3.84
Carbon disulfide	4.08	0.64
1,2-Dichloroethane	3.96	4.64
Dichloromethane	4.26	4.58
DMSO	4.13	13.7
Acetone	4.41	4.18
DMF	3.83	7.21
Butanone	4.0	3.02
Nitrobenzene	4.25	5.39
Benzene	4.72	1.52
Cyclohexane	3.7	0.16
Toluene	3.91	1.18
Ethyl acetate	3.69	1.69
Acetophenone	4.35	5.68
Tetrahydrofurane	4.55	2.17
tert-Butyl alcohol	3.85	1.73
1,4-Dioxane	3.71	2.21
1,2-Dimethoxy ethane	4.81	1.13
Acetic acid	4.25	0.76

demonstrates that variations in the equilibrium constant, $K^{\#}$, are generally unaffected by changes in the solvent, whereas k_2 varies markedly. As a result, the rate constant of complex decomposition, k_2, was connected in terms of the linear solvation energy relationship (LSER) of Kamlet *et al.*[22], which described about 86 percent of the effect of solvent on oxidation. However, according to Exner's criterion, the correlations were insignificant[17].

The solvent impact data were then analysed using Swain's[23] eq. (8), where A signifies the solvent's anion-solvating power, B denotes the cation-solvating power, and solvent polarity is denoted by the term (A+ B), with C being the intercept term.

$$\log k_2 = aA + B + C \quad \ldots (8)$$

The following is the outcome of the correlation analysis for Swain's eq. (9), separately with A and B, and with (A + B):

$$\log k_2 = 0.62\pm0.02\ A + 1.7\pm0.01\ B - 4.91 \quad \ldots (9)$$

$R^2 = 0.9996$, $sd = 0.0091$, n = 19, $\psi = 0.02$, T = 313 K

$$\log k_2 = 0.38\pm0.56\ A - 3. \quad \ldots (10)$$

$r^2 = 0.0263$, $sd = 0.452$, n = 19, $\psi = 1.01$, T = 313 K

$$\log k_2 = 1.65\pm0.12\ B - 4.71 \quad \ldots (11)$$

$r^2 = 0.9299$, $sd = 0.1214$, n = 19, $\psi = 0.27$, T = 313 K

$$\log k_2 = 1.34\pm0.14\ (A + B) - 4. \quad \ldots (12)$$

$r^2 = 0.8478$, $sd = 0.1788$, n = 19, $\psi = 0.40$, T = 313 K

The observed solvent effect demonstrated a perfect correlation with Swain's equation (8), with both cation- and anion-solvating powers contributing to the solvent effect. Despite the fact that cation-solvation makes up a larger portion of the data, it only accounts for about 93 percent of it. The solvent polarity (A + B) explains approximately 85% of the data. Because (A+B) contributes approximately 85 percent of the data, relative permittivity of the solvents was connected with the data. However, a plot of log k_2 versus 1/D, where D denotes the solvent's relative permittivity, is not linear ($r^2 = 0.5271$).

Suggested mechanism

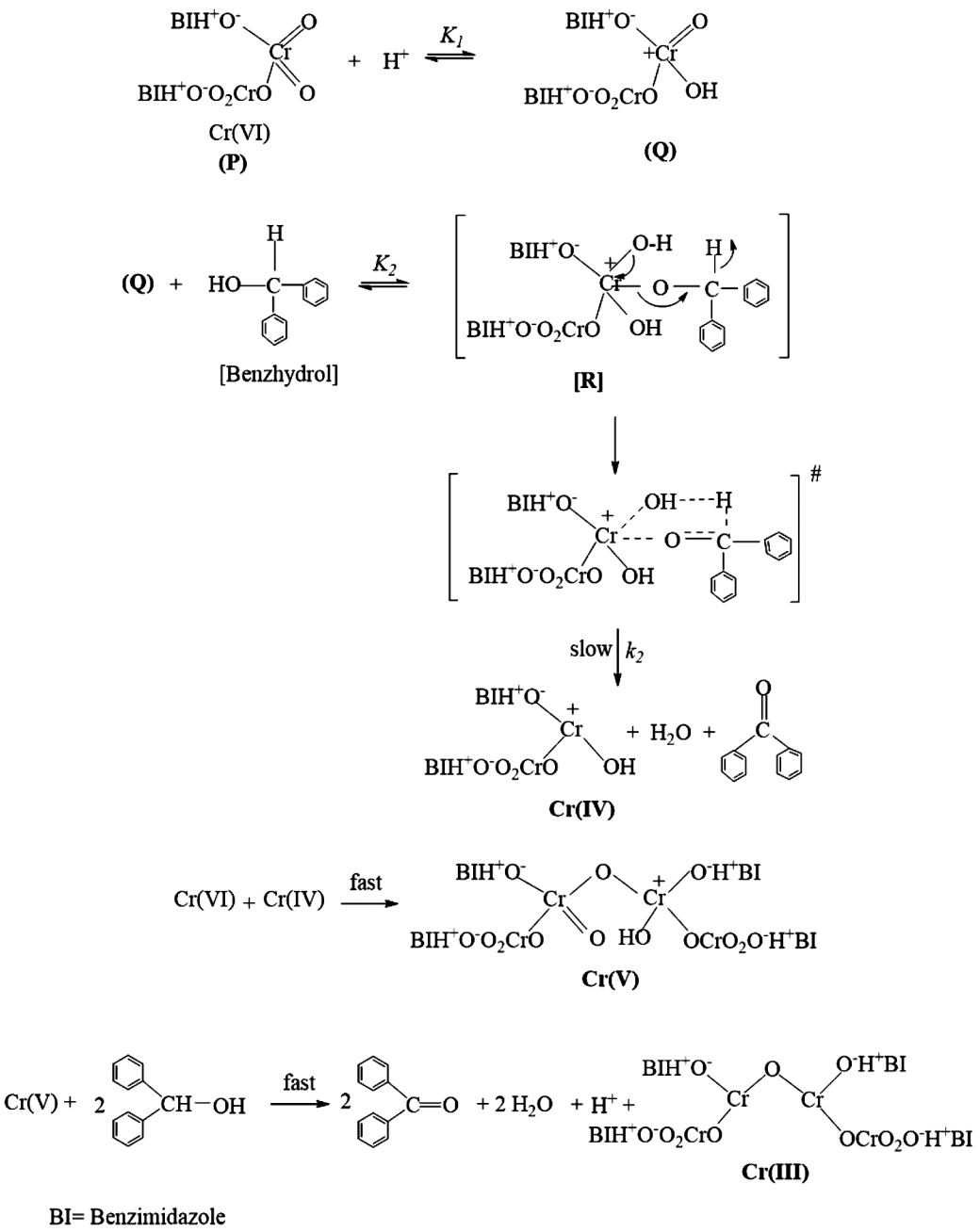
Given the lack of influence of acrylonitrile on reaction rate, it is more likely that free radical oxidation is not present in this reaction and that the radical scavenger has no effect on reaction rate. The acid-catalysis is thought to be a precursor to the BIDC protonation that produces $BIDCH^+$ (Q). It is supported by the cation's solvating power. In the case of benzhydrols, the Michaelis-Menten type kinetics propose a quick dynamic-equilibrium evolution of a 1:1 complex (R). The complex (R) is formed by the nucleophilic attack of the -OH group of benzhydrol on $BIDCH^+$ (Q) (Scheme 1). The electron-donating groups at the *p*-position of the phenyl ring speed up the oxidation process, as seen by the rising reactivity (Table 2). It reveals that when the concentration of electrons at hydroxyl oxygen increases, complex building becomes easier. Although the formation constants of benzhydrol and α-deuteriobenzhydrol are approximately comparable, a major kinetic isotope effect is detected with the rate of breakdown of the complexes. It implies that the α-C-H bond is broken during the rate-controlling phase. The presence of a primary kinetic isotope effect and a negative reaction constant (ρ) indicate that the origination of polar transition states is carbocationic in nature. The end product (diphenyl ketone) in Scheme 1 obtained from the complex (R), due to the hydride-ion shifting from benzhydrol to BIDC and the mechanism of this hydride-shifting ion's supports the idea that the cation's solvating ability is significant. The formation of a carbonium center in the controlled step is proposed in a few papers on the oxidation of benzhydrol[14,24].

A chromate ester or an acyclic approach can be used to transfer a hydride ion. Kwart and Nickle[25] established a method for studying the temperature dependence of the kinetic isotope effect, which demonstrated that hydrogen loss is caused by a concerted cyclic mechanism. The data for protio- and deuteriated-benzhydrols were presented as:

$$(k_H/k_D) = (A_H/A_D) \exp(-\Delta E_a/RT) \quad \ldots (13)$$

The activation energy difference for k_H/k_D is approximately 4.43 kJ mol^{-1}, indicating that the activation entropy (ΔS*) and zero-point energy gap for both C-D and C-H bonds (approximately 4.40 kJ mol^{-1}) are quite similar in present reaction. It is directly agreeing with a symmetrical transition state property[26,27].

Bordwell[28] has provided substantial evidence in addition to the phenomena of a bimolecular concerted hydrogen shifting process that is accomplished in a single step. It is suggested that the hydrogen shifting mechanism in the present reaction system does not involve an acyclic bimolecular process. This symmetrical mechanism is actually a sigmatropic reaction in which direct hydrogen transfer occurs and a cyclic transition state shifting is indicated[29]. The next step in this reaction was the transfer of two



Scheme 1 — Mechanism of oxidation of benzhydrol by BIDC

electrons in a cyclic structure. A permissible process is the oxidation of benzhydrol by BIDC, which is concerned with six electrons and resembles Hückel's (4n+2) system[30]. As a result, it is expected that in the oxidation of benzhydrol by BIDC, hydride-ion transfer occurs via a cyclic transition state.

The experimental results are explained through the mechanism. Rate law can be stated as follows using the proposed mechanism:

$$\text{Rate} = \frac{k_a K_1 K^{\#}[BIDC]_t[Benzhydrol][H]^+}{1+ K^{\#}[Benzhydrol]} \quad \ldots (14)$$

Using Eqs (4) and (14) together, we get

$$k_2 = k_a K_1[H^+] \quad \ldots (15)$$

The measured activation entropy loss supports the postulated mechanism. When charge dispersion occurs in the transition state, two ends become strongly solvated, resulting in the stabilization of a

large number of solvent molecules, which reflects as entropy loss. The influence of the solvent is also accounted for by entropy loss.

Negative entropy (-ΔS) for complex establishment indicates that there is a decrease in the randomness accounted by the formation of an activated complex involving loss in degree of freedom. The negative value of ΔG indicate spontaneity of the complex formation while positive value of ΔG for complex break-down is nonspontaneous stage *i.e.* additional energy must be input for the break-down of the complex.

The oxidation state of Chromium metal was reduced from Cr^{VI} to Cr^{IV} at first, and it was predicted to react with another Cr^{VI} to generate Cr^{V}, which was then quickly reduced to produce Cr^{III}. In Cr^{VI} oxidations, such a pattern of reactions is well documented[31]. In this case, comparing the kinetics of benzhydrol oxidation by other oxidants is interesting. Ti(III)[32], 2,2'-bipyridyl-Cu(II) permanganate[33], tributylammonium chlorochromate[34], imidazolium fluorochromate[35] and *N*-Bromosuccinimide[14] oxidants all exhibit first order dependence with respect to benzhydrol. However, N-bromopthalimide[36] and chloramine (T)[37] oxidants show fractional order dependence with respect to benzhydrol. Thus, it is concluded that the oxidation kinetics of benzhydrol depends on nature of the oxidant.

Conclusion

When BIDC oxidized certain *para*-substituted benzhydrol in DMSO, the corresponding diphenyl ketone was formed. In terms of hydrogen-ion and BIDC, the reaction had first-order kinetics. In the case of benzhydrols, Michaelis-Menten kinetics were reported in the rate-controlling stage, α-C-H bond breaking is noted. The rate constants and Hammett σ-values have a strong correlation, with the reaction constant being negative. A rate-controlling oxidative breakdown of complex *via* hydride-ion transfer from benzhydrol to oxidant to yield end product has been proposed.

Acknowledgement

Prof. Seema Kothari, Department of Chemistry, J.N.V. University, Jodhpur, was really helpful with her ideas.

References

1 Viamajala S, Peyton B M, Sani R K, Apel W A & Petersen J N, *Biotechnology Progress*, 20 (2008) 87.
2 (a) Corey E J & Suggs W J, *Tetrahedron Lett*, 16 (1975) 2647; (b) Bhattacharjee M N, Chaudhuri M K, Dasgupta H S, Roy N & Kathing D T, *Synthesis*, 07 (1982) 588.
3 (a) Li M & Johnson M E, *Synth. Commun*, 25 (1995) 533; (b) Firouzabadi H & Sharifi A, *Synthesis*, 10 (1992) 999.
4 (a) Baltroke I M, Sadeghi M M, Mahmoodi N & Kharmesh B, *Indian J Chem,* 36B (1997) 438; (b) Srinivasan R, Akila S, Caroline J & Balasubramanium K, *Synth Commun*, 28 (1998) 2245.
5 Meng Q H, Feng J C, Bian N S, Leu B & Li C C, *Synth Commun*, 28 (1998) 1097.
6 Kalal R, Kachawa T & Panday D, *J Indian Chem Soc*, 97 (2020) 2195.
7 Kumar R, Panday D & Kothari S, *Prog Reac Kinet Mech*, 36 (2011) 352.
8 Kachawa T, Kalal R, Panday D & Kothari S, *Oxid Commun*, 42 (2019) 307.
9 Panday D, Kachawa T & Kothari S, *Prog React Kinet Mech*, 43 (2018) 300.
10 Kumar P, Panday D & Kothari S, *Croat Chem Acta*, 84 (2011) 53.
11 Pandey D & Kothari S, *Bull Chem Soc Jpn,* 87 (2014) 1224.
12 Kumar R, Pandey D & Kothari S, *Oxid Commun*, 37 (2014) 424.
13 Kumar P, Panday D & Kothari S, *J Indian Chem Soc*, 95 (2018) 1207.
14 Hiran B L, Malkani R K & Rathore N, *Kinetics and Catalysis*, 46 (2005) 334.
15 Perrin D D, Armarego W L & D. R. Perrin, *Purification of Laboratory Chemicals*, 2nd edition, (Pergamon, Oxford) 1981, p. 74.
16 Ramashankar & Suresh K S, *Curr Sci*, 39 (1970) 65.
17 Exner O, *Collect Czech Chem Commun*, 31 (1966) 3222.
18 Sharma P K, *Asian J Chem*, 26 (2014) 2702.
19 Exner O, *Prog Phys Org Chem*, 10 (1973) 411.
20 Meng Q, Yan W, Xu S & Huang D, *J Chem Crystallog*, 34 (2004) 333.
21 Johnson C D, *The Hammett Equation*, (Cambridge University Press Cambridge), 1973.
22 Kamlet M J, Abboud J L M, Abraham M H & Taft R W, *J Org Chem*, 48 (1983) 2877.
23 Swain C G, Swain M S, Powell A L & Alunni S, *J Am Chem Soc*, 105 (1983) 502.
24 Mansoor S S & Shafi S S, *Arabian J Chem,* 100 (2010) 2131.
25 Kwart H & Nickle J H, *J Am Chem Soc,* 95 (1973) 3394.
26 Kwart H & Latimore M C, *J Am Chem Soc*, 93 (1971) 3770.
27 Kwart H & Slutsky J, *J Chem Soc Chem Commun,* 21 (1972) 1182.
28 Bordwell F G, *Accounts Chem Res*, 5 (1972) 374.
29 Woodward R W & Hoffmann R, *Angew. Chem Int Ed Engl*, 8 (1969) 781.
30 Littler J S, *Tetrahedron*, 27 (1971) 81.
31 Wiberg K B, *Oxidation in organic chemistry*, Part A, Ch 2, (Academic Press, New York), 1965.
32 Hiran B L, Malkani R K, Nalwaya N, Chand K & Rathore N, *Oxid Commun*, 27 (2004) 98.
33 Grover A, Varshney S & Banerji K K, *Indian J Chem,* 35B (1996) 171.
34 Mansoor S S & Shafi S S, *Reac Kinet Mech Cat*, 100 (2010) 21.
35 Asghar B H, Mansoor S S & Malik V S, *Eur Chem Bull,* 2 (2013) 538.
36 Jagdeesh B, Archana C, Balaji M, Fulchand C, Mazahar F & Milind U, *J Indian Chem Soc*, 86 (2009) 481.
37 Ramachandra H, Mahadevappa D S, Rangappa K S & Made Gowda N M*, Int J Chem Kinet*, 29 (1997) 773.