Kinetics and Mechanism of Oxidation of Some Substituted Benzhydrols by *N*-Bromosuccinimide[1]

B. L. Hiran*, R. K. Malkani*, and N. Rathore**

* Chemical Kinetics Laboratory, Department of Chemistry, College of Science,
M.L. Sukhadia University, Udaipur, 313001 India
** Department of Chemistry, B.N.P.G. College, Udaipur, 313001 India
e-mail: hiranbl@rediffmail.com
Received May 17, 2003

Abstract—*N*-bromosuccinimide (NBS) oxidation of some substituted benzhydrols (4-Cl-, 4-Me-, 4-OMe-, 4-NO^{2-}, 4,4'-dimethyl-, 4,4'-dichloro-, 4,4'-dimethoxy-, and 4-methyl-2-nitro-) yields corresponding benzophenones in the presence of Hg(OAc)$_2$. The reaction is first-order in [NBS], [substrate], and [H$^+$]. A study on the primary kinetic hydrogen isotope effect and solvent isotope effect suggest that C–H and O–H stretching frequencies are affected in the transition state. Activation parameters for the rate-determining step have been evaluated. The results are in accord with the linear free energy relationship (LFER). The linear plot of $\log(k_{obs}/k_0)$ vs. σ^+ ($\rho = -0.69$) and Bunnett plots support the existence of proton-transfer in the rate-determining step. Rate behavior in different solvent compositions suggests dipolar–dipolar interaction in the absence of acid and ion–dipolar interaction in the presence of acid. Two different mechanisms have been suggested: cyclic transition state with unprotonated *N*-bromosuccinimide (NBS) in the absence of acid and noncyclic transition state with protonated NBS in the presence of acid.

INTRODUCTION

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 DDQ/PbO [1], 2,2'-bipyridyl-Cu(II)permanganate [2], V(V) [3], pyridinium chlorochromate [4], chloramine-T [5], photolytic oxidation [6], NBS [7], molecular bromine [8], Tl(III) [9], and many other well-known oxidizing agents. NBS provides for a good yield of the product, benzophenone (85–90%). The mechanism of oxidation by NBS is at present not fully understood. Most investigations into NBS oxidation of organic substances have assumed that the molecular NBS acts only through its positive polar end [10], producing Br$^+$, which is subsequently solvated. Thus, H$_2$OBr$^+$ has been considered an effective oxidizing species of NBS in an acidic medium. In the presence of mercuric acetate, the protonated form of NBS, i.e., N$^+$BSH, has also been considered [11] a reactive species of NBS in an acidic medium. Hypobromide ion as a reactive species in Os(VIII) catalyzed oxidation of allyl alcohol by NBS has also been proposed [12]. It was therefore considered important to investigate oxidation by NBS. For this study, benzhydrol, 4-chloro-, 4-nitro, 4-methyl-, 4-methoxy-, 4,4'-dichloro-, 4,4'-dimethyl-2-nitro-4-methyl-, and 4,4'-dimethoxybenzhydrol were obtained in order to understand the mechanism of oxidation and explain the structure reactivity relationship. The advantages of choosing this class of compounds are the following:

(i) the two benzene rings make it possible to control the variation of electronic requirements at the reaction site;

(ii) complications arising as a consequence of bromination of the oxidation product are ruled out; and

(iii) deuterated analogues can be prepared, enabling one to evaluate the relative importance of C–H bond stretching in the transition state.

This report deals with the oxidation of benzhydrols by NBS.

EXPERIMENTAL

Benzhydrols were prepared by means of the reduction of corresponding benzophenones with sodium borohydride and 4,4'-dimethoxybenzhydrol that was of Fluka (Puriss). The purity of benzhydrols was checked by m.p., IR spectrum, and elemental analysis. Acetic acid was purified by distillation over CrO$_3$ followed by fractionation in the presence of acetic anhydride. Pure acetic acid fraction was collected over 115°C. *N*-bromosuccinimide (BDH), potassium iodide (E. Merck), and sodium thiosulfate (BDH "AnalaR") were used in the present study. All solutions were prepared in double distilled water except benzhydrols. *N*-bromosuccinimide solution was prepared afresh and standardized iodometrically [13]. The required amount of double distilled water and acetic acid was added to a reaction mix-

[1] This article was submitted by the authors in English.

Table 1. Variation of rate with concentration of N-bromo-succinimide

| [N-BS] $\times 10^3$, M	$k_{obs} \times 10^5$, s^{-1} (318 K)	$k_{obs}^* \times 10^5$, s^{-1} (298 K)
0.5	16.4	10.9
1.0	16.5	10.8
2.0	16.6	10.9
3.0	16.4	10.8
4.0	16.2	11.0
5.0	16.6	10.9

Note: [Benzhydrol] = 2×10^{-2} mol/l, solvent = 50% AcOH (v/v), [Hg(OAc)$_2$] = 5×10^{-3} mol/l, [NaOAc] = 3×10^{-1} mol/l.
* [HClO$_4$] = 0.9 mol/l, μ = 2.7 mol/l.

ture containing the appropriate quantities of benzhydrols solution in acetic acid, mercuric(II) acetate, and sodium acetate solutions, so that the total volume of the mixture was 50 ml after adding NBS solution. The mixture and NBS solutions of desired concentration were kept separately at the desired temperature (±0.1 K). The reaction was started by adding NBS. Estimation of the unconsumed NBS iodometrically followed the progress of the reaction. $\log(a - x)$ vs. t yields a straight line for nearly 70 to 80% of the reaction. Pseudo-first-order rate constants were calculated by these graphs.

The D$_2$O (99.8%) was obtained from BARC, Trombay, Mumbai (India). Deuterated (α-D 90 ± 5%) benzhydrol was prepared by the method of Shanker and Suresh [14]. α-H, O–D and α-D, O–D benzhydrols were prepared by refluxing corresponding benzhydrols (α-H and α-D) in D$_2$O for 2–3 h, removing the solvent under the pump, and then repeating the process three times to ensure complete exchange of O–H protons. PMR analysis was conducted at TIFR, Mumbai (India).

Rate laws and other experimental data were obtained for the oxidation of all the benzhydrols by NBS. The stoichiometry corresponds to the reaction

$$(C_6H_5)_2CHOH + Br–N\!<$$

$$\longrightarrow (C_6H_5)C{=}O + HBr + HN\!<$$
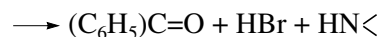
Study of the product was carried out under kinetic conditions. After completion of the reaction, the resultant solution was neutralized with sodium bicarbonate followed by ether extraction. The resulting ether solution was treated with 2,4-dinitrophenylhydrazine solutions. The benzophenones were characterized and estimated as 2,4-dinitrophenylhydrazones (yield 95 ± 3%). No bromination of the aromatic ring was observed.

RESULTS

Oxidation of benzhydrols was carried under pseudo-first-order conditions, i.e., [benzhydrol] $\gg$ [NBS], and in the presence of mercuric acetate, in order to completely suppress the evolution of bromine.

The observed rate constant did not change with variations in the concentration of the oxidant. Table 1 summaries the values of pseudo-first-order rate constants k_{obs} at different [NBS] in the case of the oxidation of benzhydrol. The rate of oxidation of benzhydrols follows first-order rate laws with respect to the substrate.

The rate constant increased with increases in the concentration of the substrate. Table 2 summarizes variations of the pseudo-first-order rate constant at different concentrations of benzhydrols. Ramchandran *et al.* [15] observed a fractional order with respect to benzhydrols in oxidation by chloramine-T.

The rate constants are little affected (practically constant) by the addition of sodium acetate and sodium benzoate (NaOBz) at constant ionic strength, which suggests the absence of a base catalysis or of its participation in the transition state. Representative data for the oxidation of benzhydrol is collected in Table 3.

At constant ionic strength, the rate of oxidation of benzhydrols increased in all cases upon addition of perchloric acid. The plot of $\log k_{obs}$ vs. $\log[H^+]$ yields a straight line with a slope equal to 0.99. Representative data for the oxidation of benzhydrol is given in Table 4.

Table 2. Variation of rate with concentration of substrate. [NBS] = 2×10^{-3} mol/l, solvent = 50% AcOH (v/v), [Hg(OAc)$_2$] = 2×10^{-3} mol/l, T = 298 K, [NaOAc] = 4.0×10^{-1} mol/l

[Substrate] $\times 10^2$, mol/l	$k_{obs} \times 10^5$, s^{-1}						
	X=H X'=H	4-CH$_3$ H	4-OCH$_3$ H	4-NO$_2$ H	4-Cl 4'-Cl	4-OCH$_3$ 4'-OCH$_3$	4-CH$_3$ 2-NO$_2$
1.0	1.31	2.11	5.81	1.31	0.60	30.4	0.60
2.0	2.72	4.31	11.2	2.42	1.19	56.6	1.08
3.0	3.61	6.53	16.2	3.52	1.70	95.8	1.72
4.0	5.03	8.24	20.8	4.93	2.33	130.4	2.40
5.0	6.24	10.42	26.3	6.20	2.82	165.3	2.90
6.0	7.52	12.52	30.2	7.41	3.41	210.2	3.44

Table 3. Variation of rate with concentration of sodium acetate and sodium benzoate. [Benzhydrol] = 2×10 mol/l, [NBS] = 2×10^{-3} mol/l, solvent = 50% AcOH (v/v), [Hg(OAc)$_2$] = 2×10^{-3} mol/l, T = 313 K

[NaOAc], mol/l	pH	$k_{obs} \times 10^5$, s^{-1}	[NaOBz], mol/l	pH	$k_{obs} \times 10^5$, s^{-1}
0.1	2.8	11.3	0.1	2.9	9.8
0.2	3.0	11.6	0.2	3.0	9.6
0.3	3.2	11.4	0.3	3.1	9.5
0.4	3.4	11.7	0.4	3.2	9.6
0.5	3.6	11.6	0.5	3.3	9.7
0.6	3.8	11.4	0.6	3.5	9.4

Ionic strength was maintained constant by the addition of sodium perchlorate.

The pseudo-first-order rate constant decreased with increases in acetic acid from 30 to 60%. Experiments were carried out at 303 and 318 K. However, at higher percentages (>60% v/v), the rate constant increased with further increases in acetic acid. Table 5 summarizes the variation of rate with solvent composition. The plot of logk_{obs} vs. $(D - 1)/(2D + 1)$ turns out to be linear in the range of 30 to 60% AcA (v/v), where D is the dielectric constant of acetic acid–water (v/v) mixture calculated using the mixture law. This indicates the participation of dipolar–dipolar interaction in the rate-determining step of the uncatalyzed reaction.

Values of k_{C-H}/k_{C-D} for the oxidation of benzhydrol, 4,4'-dichlorobenzhydrol and 4,4'-dimethylbenzhydrol by NBS are collected in Table 6.

Data on the rates of oxidation of Ph$_2$CHOH and Ph$_2$CDOH in 60% AcOH (v/v)–40% H$_2$O (v/v), Ph$_2$CHOD and Ph$_2$CDOD in 60% AcOD (v/v)–40% D$_2$O (v/v) solvent mixtures with NBS are recorded in Table 7. In acid-catalyzed oxidation, D$_2$O enhances the rate of oxidation by NBS (Table 8).

Table 4. Variation of rate with concentration of perchloric acid

[HClO$_4$], mol/l	$k_{obs} \times 10^5$, s^{-1}	$-H_o$	$-\log a_{H_2O}$
0.0	2.6	–	–
0.3	4.6	–	–
0.6	9.2	0.06	0.009
0.9	13.6	0.16	0.016
1.2	18.3	0.36	0.022
1.5	21.7	0.53	0.030
1.8	21.3	0.70	0.038
2.1	31.5	0.83	0.046
2.4	36.3	0.97	0.057
2.7	40.6	1.11	0.068

Note: [Benzhydrol] = 2×10^{-2} mol/l, solvent = 50% AcOH (v/v), [NBS] = 2×10^{-3} mol/l, T = 298 K, [Hg(OAc)$_2$] = 4×10^{-3} mol/l, μ = 3.5 mol/l.

The effect of temperature on rate was studied in the range 293 to 323 K. Thermodynamic parameters for the rate-determining step are summarized in Table 9. Activation parameters for the acid-catalyzed oxidation of benzhydrol by NBS are different from those obtained for the uncatalyzed reaction (Table 9).

No "milky appearance" was observed upon addition of stabilizer-free acrylonitrile (washed with dil NaOH and distilled in water) to the reaction mixture in nitrogen atmosphere,; therefore, the presence of free radical in the reaction is ruled out.

DISCUSSION

Venkatasubramanian and Thiaggrajan [7] have demonstrated that oxidation of alcohol by NBS is composed of two stages: (a) initial slow reaction with NBS followed by (b) faster Br$_2$ oxidation. The second stage is suppressed by the added mercuric acetate. The function of added mercuric (II) acetate is only to fix up Br$^-$ formed in the course of the reaction as HgBr$_2$ or HgBr$_4^{2-}$, since the effect of mercuric acetate was found to be negligible in the rates of oxidation. On the basis of the value of reaction constant ρ = –2.56 and by analogy with bromine oxidation, a concerted cyclic hydride transfer has been proposed by Venkatasubramanian and Thiaggrajan [7]. The results of this paper do not agree with these authors.

In the absence of perchloric acid, k_{obs} does not change significantly in the pH range 2.8–3.8 (Table 3), which suggests that the reaction species is unprotonated NBS in this pH range, not its protonated form. Here, it resembles the oxidation of alcohols by aqueous bromine in a pH range up to 4. In the presence of perchloric acid, the rate is first-order in [H$^+$] (Table 4). This suggests that $>$NBrH$^+$ is the sole reactive species in high acidity and that $>$NBr is making an insignificant contribution to the overall rate. This is consistent with the observed solvent isotope effect (Table 8) and the solvent effect >60% AcOH–water (v/v) (Table 5). This confirms that, at high acidity, protonated NBS is the reactive species, while, at low acidity, it is the unprotonated NBS that is reactive. This was also proved by lin-

ear plot $\log k_{obs}$ vs. $(D - 1)/(2D + 1)$, with $R^2 = 0.9475$ and 0.9735, respectively, at 303 and 318 K in the range 30 to 60% AcOH, suggesting dipolar–dipolar interaction in rds. The results at low acidity are consistent with the observations of Saroja and Kandliker [16], who suggested that unprotonated NBS is the active species in weak acidic and alkaline media in the oxidation of primary aliphatic amines.

In the present case, the solvent isotope effect k_{D_2O}/k_{H_2O} is nearly equal to 1.37. This supports the acid catalysis of the reaction. D_3O^+ is a stronger acid than H_3O^+, and, hence, the concentration of $>NBrD^+$ increases when D_2O is substituted for H_2O as a solvent. Since $>NBrD^+$ is the active reacting species, an increase in its concentration enhances the rate of oxidation.

The reaction does not follow Zucker–Hammett function H_0. The Bunnett plot $\log k_{obs} + H_0$ vs. $\log a_{H_2O}$ is linear with ω (the Bunnett function) = +9.4 (>3.3), which suggests that the reaction should fall in the third category of Bunnett classification; the latter indicating that the water molecule acts as a proton abstracting agent in the rate-determining step. The kinetic isotope effect (k_{C-H}/k_{C-D}) of 2.32, 3.12, and 1.31 (Table 6) has been observed in the oxidation of benzhydrol, 4,4'-dimethylbenzhydrol and 4,4'-dichlorobenzhydrol, respectively. This suggests that C–H stretching frequency is affected in the rate-limiting step and points to the fact that an electron-donating group such as methyl causes the C–H bond to become relatively more stretched than a bond affected by an electron withdrawing group such as Cl. This follows from the fact that the maximum theoretical value of the isotope effect is observed when the bond is symmetrically stretched in the TS ($>C\ldots\ldots H\ldots\ldots O$), while low values of the kinetic isotope effect point to asymmetrical stretching of the C–H bond, and TS may be a reactant or a product, e.g.,

$$>C\ldots H\ldots\ldots O \quad \text{or} \quad >C\ldots\ldots H\ldots O$$
$$\text{reactant-like} \qquad\qquad \text{product-like}$$
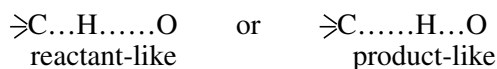
The experimental results show that the rate-limiting step involves the participation of C–H and O–H bonds (Tables 6 and 7, respectively).

The low value of $\rho = -0.69$ and the kinetic isotope effect k_{D_2O}/k_{H_2O} supports the above proposal. Venkatasubramanian and Thiaggrajan [7] did not demonstrate the participation of the O–H bond. They observed a large negative value of ρ (=–2.56) and hydride ion removal, as shown below, was suggested. Thus,
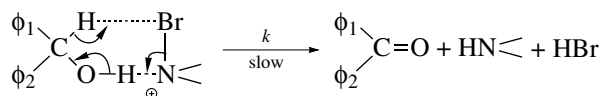
Table 5. Variation of rate with solvent composition

(v/v)	303 K		318 K	
	D	$k_{obs} \times 10^5$, s^{-1}	D	$k_{obs} \times 10^5$, s^{-1}
30	68.82	5.61	52.2	20.82
40	65.50	5.02	45.4	18.30
50	60.50	4.40	39.0	16.4
60	54.92	4.03	32.4	12.02
70	47.72	4.64	26.1	14.45
80	38.34	5.05	–	–

Note: [Benzhydrol] = 2×10^{-2} mol/l, [NBS] = 2×10^{-3} mol/l, [Hg(OAc)$_2$] = 2×10^{-3} mol/l, [NaOAc] = 4×10^{-1} mol/l.

Table 6. Kinetic isotope effect

Substrate	k_{C-H}/k_{C-D}
Benzhydrol	2.32
4,4'-Dimethylbenzhydrol	3.12
4,4'-Dichlorobenzhydrol	1.31

Note: [Substrate] = 4×10^{-2} mol/l, [NBS] = 2.26×10^{-3} mol/l, solvent = 60% AcOH (v/v), [Hg(OAc)$_2$] = 2.26×10^{-3} mol/l, $T = 313$ K, [NaOAc] = 4×10^{-3} mol/l.

Table 7. Kinetic solvent isotope effect

Substrate	$k_{obs} \times 10^4$, s^{-1}	k_{H_2O}/k_{D_2O}
(Ph)$_2$CHOH*	1.8	1.28
(Ph)$_2$CHOD**	1.4	
(Ph)$_2$CDOH*	0.8	1.33
(Ph)$_2$CDOD**	0.6	

Note: Substrate] = 4×10^{-2} mol/l, [NBS] = 2.26×10^{-3} mol/l, [Hg(OAc)$_2$] = 2.26×10^{-3} mol/l, [NaOAc] = 0.4 mol/l, $T = 313$ K.
  * Solvent = 60% AcOH (v/v)–40% H$_2$O (v/v).
  ** Solvent = 60% AcOH (v/v)–40% D$_2$O (v/v).

Table 8. Kinetic solvent isotope effect for acid-catalyzed oxidation

[HClO$_4$], mol/l	$k_{obs} \times 10^5$, s^{-1}	k_{D_2O}/k_{H_2O}
0.3*	4.60	1.35
0.3**	6.20	
0.9*	13.60	1.37
0.9**	18.62	

Note: [(Ph)$_2$CHOH] = 2.0×10^{-2} mol/l, [NBS] = 2.0×10^{-3} mol/l, [Hg(OAc)$_2$] = 2.0×10^{-3} mol/l, $\mu = 2.7$ mol/l, $T = 298$ K.
  * Solvent = 50% AcOH (v/v)–50% H$_2$O (v/v).
 ** Solvent = 50% AcOD (v/v)–50% D$_2$O (v/v).

Table 9. Variation of rate with temperature and activation parameters. [Substrate] = 4×10^{-2} mol/l, [NBS] = 2.26×10^{-3} mol/l, solvent = 40% AcOH (v/v), [Hg(OAc)$_2$] = 2.26×10^{-3} mol/l, [NaOAc] = 4×10^{-1} mol/l

T, K	$k_{obs} \times 10^5$, s^{-1}								
	X=H* X'=H	H** H	H*** H	4-NO$_2$ H	4-OCH$_3$ 4'-OCH$_3$	4-OCH$_3$ H	4-Cl 4'-Cl	4-CH$_3$ H	4-CH$_3$ 2-NO$_2$
293	1.56	2.24	4.82	1.42	29.85	7.81	0.64	2.42	0.40
298	2.80	4.10	10.80	2.31	56.6	11.21	1.21	4.41	1.08
303	4.30	6.50	21.02	2.82	71.12	17.24	1.96	7.04	2.11
308	7.11	8.95	41.82	4.02	106.41	25.82	3.02	14.26	4.02
313	11.20	19.54	83.45	5.52	170.30	52.04	5.91	21.92	8.00
318	16.20	32.20	162.61	7.62	226.22	69.62	8.35	34.34	12.51
323	29.00	52.20	–	10.50	354.82	–	14.25	–	25.22
$\Delta H^{\neq}$, kJ/mol	74 ± 3	82 ± 3	108 ± 4	51 ± 2	62 ± 3	69 ± 2	80 ± 3	83 ± 3	105 ± 4
$\Delta S^{\neq}$, J/(mol K)	–87 ± 3	–56 ± 2	+40 ± 1	–162 ± 5	–103 ± 4	–90 ± 3	–73 ± 2	–52 ± 1	+9 ± 1
$\Delta G^{\neq}_{30}$, kJ/mol	101 ± 4	99 ± 3	95 ± 3	101 ± 4	93 ± 3	97 ± 3	103 ± 4	99 ± 4	102 ± 4

   * At 0.00 mol/l HClO$_4$.

   ** At 3.0×10^{-1} mol/l HClO$_4$.

   *** At 9.0×10^{-1} mol/l HClO$_4$.

If so, the creation of a positive charge on the carbinol carbon atom should be energetically more favorable in 4-methyl benzhydrol than in 4-NO$_2$ benzhydrol, which is contrary to the present observation. We therefore propose the following alternative cyclic transition state, which is consistent with all these observations. Thus,

$$\cdots \xrightarrow{\text{slow}} \text{products.}$$
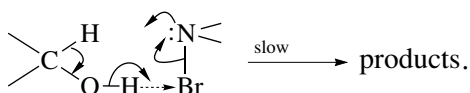
The plot of $\log k_{obs}/k_0$ vs. σ turns out to be a curve, while $\log k_{obs}/k_0$ vs. σ^+ values [17] is a fairly straight line

$$y = -0.6903x + 1.0854$$
$$R^2 = 0.9218$$
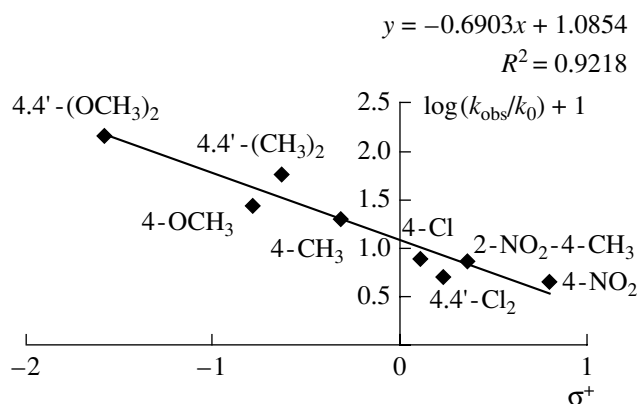
Effect of substituents on the rate of oxidation of benzhydrols by NBS.

(correlation coefficient $R = 0.964$ for eight points) having slope ρ (the reaction constant) = –0.69 (figure). The rate correlates satisfactorily with the Hammett relationship. A similar observation has been made by Rangappa *et al.* [5, 14] for the oxidation of benzhydrols by chloramine-T. The small negative value of ρ (=–0.69) can be explained if it is assumed that the H of C–H is lost as a proton with a concomitant removal of electrons from oxygen to the oxidant. Removal of electrons from the oxygen orbital would affect the O–H bond stretching in the transition state and would account for the low isotope effect observed in the present case. This bears an analogy to the proposal of Lee and Srinivasan [18], who also observed a $\rho = -0.95$ in the reaction of benzyl dimethyl amine by bromine.

The acid-catalyzed reaction involving acyclic structure can then be considered as follows:

$$\xrightarrow{\text{slow}} \overset{\phi_1}{\underset{\phi_2}{\diagup}}C=O + HBr + H_3O^+ + HN{<}$$
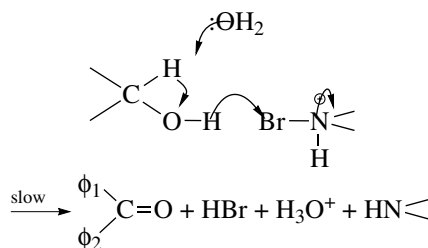
Although the reaction is catalyzed by H$^+$, the activation energies are greater than those for uncatalyzed reactions. The catalyzed reaction seems to be entropy controlled. Protonation of the N atom does not favor hydrogen bond formation in the transition state, permit-

ting the solvent (H_2O) molecule to demonstrate its specificity. This is also confirmed by different values of $\Delta H^{\#}$ and $\Delta S^{\#}$ for 4-methyl-2-nitrobenzhydrol, which is intramolecularly hydrogen-bonded as shown below:
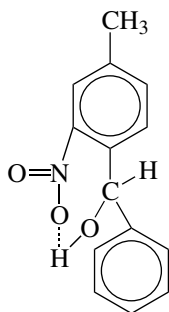
ACKNOWLEDGMENTS

REFERENCES

1. Kalena, G.P., Jadhav, S.M., and Banerjee, A., *Molecule*, 2000, vol. 5, p. 240.

2. Grover, A., Varshney, S., and Banerji, K.K., *Indian J. Chem., Sect. B*, 1996, vol. 35, p. 206.

3. Saxena, B.B., Babel, D.K., and Shanker, R., *Indian J. Chem., Sect. A.* 1982, vol. 21, p. 171.

4. Venkatasubramanian, N., *Indian J. Chem., Sect. B*, 1978, vol. 16, p. 84.

5. Rangappa, K.S., Ramachandran, H., and Mahadevappa, D.S., *J. Phys. Org. Chem.*, 1997, vol. 10, p. 159.

6. Sharma, K.S., Shardakumar, and Goel, V.K., *J. Indian Chem. Soc.*, 1993, vol. 70, p. 811.

7. Venkatasubramanian, N. and Thiaggrajan, V., *Can. J. Chem.*, 1969, vol. 47, p. 694.

8. Ameta, R.C., Suresh, K.S., and Shanker, R., *Z. Phys. Chem.*, 1986, vol. 267, p. 122.

9. Hiran, B.L., Malkani, R.K., Niranjan Nalwaya, Kailash Chand, and Neeru Rathore, *Oxid. Commun.*, 2004, vol. 27, no. 1, p. 98.

10. Kruse, P.F., Grist, K.L., and McCoy, T.A., *Anal. Chem.*, 1954, vol. 26, p. 1319; Lecomte, J. and Gault, H.C.R.H., *Seances. Acad. Sci.*, 1952, vol. 234, p. 1887; Venkatasubramanian, N. and Thiagarajan, V., *Can. J. Chem.*, 1969, vol. 47, p. 694.

11. Shukla, A. and Upadhyay, S.K., *J. Indian Chem. Soc.*, 1992, vol. 69, p. 745; Reddy, P.G., Ramesh, Y., and Kandlikar, S., *Oxid. Commun.*, 1984, vol. 7, p. 89; Sharma, J.P., Singh, R.N.P., Singh, A.K., and Singh, B., *Tetrahedron*, 1986, vol. 42, p. 2739; Singh, A.K., Ramanai, B., Singh, V.K., Gupta, V., Kesarwani, K., and Singh, B., *Indian J. Chem., Sect. A*, 2001, vol. 40, p. 519; Singh, A.K., Gupta, T., Kumar, V., Kesarwani, D., and Singh B, *Oxid. Commun.*, 2000, vol. 23, p. 617.

12. Chaugle, R.B., Kamble, D.L., and Nandibewoor, S.T., *Pol. J. Chem.*, 1997, vol. 71, p. 986.

13. Mathur, N.K. and Narang, C.K., *The Determination of Organic Compounds with N-Bromosuccinimide*, New York: Academic, 1975.

14. Shanker, R. and Suresh, K.S., *Curr. Sci.*, 1970, vol. 39, p. 65.

15. Ramchandran, H., Mahadevappa, D.S., Rangappa, K.K., and Modegowda, N.M., *Int. J. Chem. Kinet.*, 1998, vol. 30, p. 7.

16. Saroja, P. and Kandliker, S., *J. Indian Chem. Soc.*, 1990, vol. 67, p. 878.

17. Hine, J., *Physical Organic Chemistry*, New York: McGraw-Hill, 1962, p. 87; Leffler, J.E. and Groundwald, E., *Rates and Equilibria in Organic Reactions*, New York: Wiley, 1963, p. 204.

18. Lee, D.G. and Srinivasan, R., *Can. J. Chem.*, 1973, vol. 51, p. 2546.