J. Indian Chem. Soc.,
Vol. 89, November 2012, pp. 1499-1506

Mechanistic investigation of oxidation of some substituted aromatic acetals with N-bromosuccinimide in acetonitrile medium – A kinetic approach

N. Mathiyalagan

Post Graduate and Research Department of Chemistry, St. Joseph's College (Autonomous), Tiruchirappalli-620 002, Tamilnadu, India

E-mail : sjcmathi@yahoo.co.uk

Manuscript received 13 September 2011, accepted 21 February 2012

Abstract : The oxidation of *meta*- and *para*-substituted aromatic acetals by N-bromosuccinimide (NBS) to the corresponding esters and alkyl bromide, is first-order in [NBS] and [acetal]. The effect of substituents in the aromatic ring of some aromatic acetals [X-$C_6H_4CH(OBu\text{-}n)_2$] {X = H, *p*-OMe, *p*-Me, *p*-Cl, *p*-NO_2, *m*-OMe, *m*-Cl, *m*-NO_2} on the kinetics of above oxidation has been studied in acetonitrile medium at various temperatures by iodometric method. The rate of the reaction increases with the increase in the dielectric constant of the medium. The stoichiometry of the reaction is found to be 1 : 1. A primary kinetic isotopic effect k_H/k_D of 1.8 is observed, which indicates the C-H bond cleavage of the aldehydic carbon in the rate determining step. The Hammett reaction constant (σ) for the reaction is found to be -1.38 and -1.42 at 313 K and 323 K respectively. The Exner plot is found to be linear with the isokinetic temperature 132 K. The kinetic and activation parameters E_a, A, $\Delta H^{\neq}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$ have been calculated. A mechanism involving simultaneous loss of H^+ from the aldehydic carbon and expulsion of bromide ion with the formation of carbonium ion intermediate is proposed.

Keywords : N-Bromosuccinimide, acetals, oxidation, kinetics.

Introduction

Acetals play a vital role in bio-organic research in exploring biological activities[1] (antimalarial, antiviral etc.). The most stable form of glucose in solution is its cyclic hemiacetal and maltose is an acetal made from two glucose units. Acetaldehyde diethyl acetal is an important flavouring compound in distilled beverages. Acetal polymers (polyacetals) are tough and hard plastics used as substitutes for metals. Acetals are sometimes used as protecting group for carbonyl groups in organic synthesis as they are stable with respect to hydrolysis by bases. Acetal molecules are used as an intermediate for the production of polymers, vitamins, carotenoid pigments, dyes, pharmaceuticals, pesticides, corrosion inhibitors and perfumes. The susceptibility of acetals to oxidation[2] and rearrangement[3] is reported earlier. In the recent years, studies of oxidation of various organic compounds by N-halo compounds have attracted considerable attention. It is known that some acetals have been oxidized by chromic oxide[4] and N-bromosuccinimide[5-7].

N-Bromosuccinimide (NBS) is a source of positive halogen and this reagent has been exploited as oxidant[8] for a variety of substrates in both acidic and alkaline medium. The nature of active oxidizing species[9] and the mechanism depends on the nature of the halogen atom, the groups attached to the nitrogen and the reaction condition. The species responsible for such oxidizing character may be different depending on the pH of the medium. The probable reactive species of the oxidant in acid solution are NBS itself, HOBr, $NBSH^+$ or H_2OBr^+ and the reactive species in alkaline solutions are NBS itself, HOBr and OBr^-. The use of NBS as an oxidant is extensive in the determination of number of organic compounds[10-12]. Some kinetic investigations involving NBS oxidation of alcohols[13,14], ketones[15,16], amino acids[17-20], ternary complex of dipicolinate chromium(III) and aspartic acid[21], aspirin[22], 2-hydroxynaphthaldehyde[23], D-mannitol[24], dipeptides[25], aminoalcohols[26], cyclopentanol and cyclohexanol[27], 3-benzoyl propionic acid[28], ethylamine and benzylamine[29], gabapentin[30] and benzyl methyl ethers[31] are reported. A thorough literature survey re-

veals that only few works on the oxidation of acetals have been reported so far. Although the NBS oxidation of a large variety of organic compounds has been studied, there seems to be no systematic kinetic work on the oxidation of aromatic acetals by NBS.

Since acetals have biological activity and engineering properties, the present work constitutes an investigation on the kinetics of oxidation of aromatic acetals by NBS with a view to correlate structure with reactivity and postulate a plausible mechanism for the above oxidation reaction. The effect of substituents in the aromatic ring of some aromatic acetals [X-$C_6H_4CH(OBu\text{-}n)_2$], {X = H, *p*-OMe, *p*-Me, *p*-Cl, *p*-NO_2, *m*-OMe, *m*-Cl, *m*-NO_2} has been studied in acetonitrile medium at various temperatures.

Results and discussion

The rates of the reaction have been measured by following the disappearance of NBS iodometrically in acetonitrile medium at constant ionic strength, under the conditions [NBS] << [acetal]. It is observed that the dependence of [NBS] on the reaction rate is first-order as evidenced by the linear plot of log [NBS] versus time ($r > 0.99$).

The effect of varying initial concentration of acetals (Table 1) shows a first-order dependence of rate on [acetal], as indicated by the linear plot of log k_1 versus log [acetal] with slope unity (1.02 ± 0.008).

Ionic strength of the reaction mixture is varied by adding (Table 2) sodium perchlorate monohydrate (0.1 to 0.4 *M*) and the reaction rate slightly increases with increasing [$NaClO_4.H_2O$]. Addition of the reaction products ester and alkyl bromide has no influence on the rate.

The dielectric constant of the medium is varied by adding different proportions of water (2–10%) to the reaction mixture. The rate increases with increasing proportion of water (Table 3). Addition of reaction mixture to aqueous acrylamide solutions do not initiate polymerization, showing the absence of free radical species.

The effect of one of the products of the reaction on the rate is studied by varying the initial concentrations of succinimide, keeping [acetal] and [NBS] constant (Table 4). The reaction rate shows a retardation effect on increasing the [succinimide].

The oxidation of all the acetals has been studied at different temperatures (308–323 K). The Arrhenius plot of log k_2 vs $1/T$ is linear ($r > 0.99$). From the plot, the Arrhenius and thermodynamic activation parameters are evaluated. The results are shown in Table 5. It is observed that the deuterated acetal, $C_6H_5CD(OBu\text{-}n)_2$ is oxidized 1.8 times slower than the protic compound, showing the breaking of C–H proton in the rate-determining step.

Mechanism :

A mechanism is proposed assuming Br^+ as the oxi-

Table 1. Dependence of rate on [acetal]

[NBS] = 6.0×10^{-3} *M*, Temperature = 323 K, [$NaClO_4$] = 0.1 *M*, Solvent = 100% CH_3CN

[S] × 10^2	X-$C_6H_4CH(OR)_2$ $k_1 \times 10^5$ (s^{-1})							
(*M*)	H (X)	*p*-OMe (X)	*p*-Me (X)	*p*-Cl (X)	*m*-OMe (X)	*p*-NO_2 (X)	*m*-Cl (X)	*m*-NO_2 (X)
2.0	-	18.0	-	-	-	-	-	-
4.0	-	35.6	-	-	-	-	-	-
6.0	18.1	53.6	26.8	14.5	10.1	-	-	-
8.0	24.9	71.3	36.0	19.4	14.2	1.81	6.48	2.64
10.0	31.4	90.1	-	-	-	-	-	-
12.0	37.1	-	54.1	28.8	20.6	2.67	9.85	3.91
16.0	51.1	-	72.1	39.2	27.2	3.60	13.05	5.26
18.0	-	-	81.0	45.0	32.0	-	-	-
20.0	-	-	-	-	-	4.60	16.31	6.56
24.0	-	-	-	-	-	5.52	19.60	7.80

Table 2. Dependence of the rate on $[NaClO_4]$

$[NBS] = 6.0 \times 10^{-3}$ *M*, Temperature = 323 K, Solvent = 100% CH_3CN

		X-$C_6H_4CH(OR)_2$ $k_1 \times 10^5$ (s^{-1})							
$[S] \times 10^2$ (*M*)	$[NaClO_4] \times 10$ (*M*)	H (X)	*p*-OMe (X)	*p*-Me (X)	*p*-Cl (X)	*m*-OMe (X)	*p*-NO_2 (X)	*m*-Cl (X)	*m*-NO_2 (X)
6.0	1.0	18.10	53.60	26.80	14.50	10.10	-	-	-
6.0	2.0	18.71	54.21	27.41	15.11	10.62	-	-	-
6.0	3.0	19.45	54.95	28.15	15.85	11.36	-	-	-
6.0	4.0	20.03	55.53	28.73	16.43	11.91	-	-	-
16.0	1.0	-	-	-	-	-	3.60	13.05	5.26
16.0	2.0	-	-	-	-	-	4.21	13.66	5.87
16.0	3.0	-	-	-	-	-	4.95	14.40	6.61
16.0	4.0	-	-	-	-	-	5.53	14.98	7.19

Table 3. Dependence of the rate on the dielectric constant of the medium

$[X\text{-}C_6H_4CH(OR)_2] = 8.0 \times 10^{-2}$ *M*, Temperature = 323 K, $[NBS] = 6.0 \times 10^{-3}$ *M*, $[NaClO_4] = 0.1$ *M*

		X-$C_6H_4CH(OR)_2$ $k_1 \times 10^5$ (s^{-1})							
H_2O-CH_3CN % (v/v)	*D*	H (X)	*p*-OMe (X)	*p*-Me (X)	*p*-Cl (X)	*m*-OMe (X)	*p*-NO_2 (X)	*m*-Cl (X)	*m*-NO_2 (X)
0–100	37.50	24.90	71.30	36.00	19.40	14.20	1.81	6.48	2.64
2–98	38.35	25.80	72.20	36.81	20.30	14.97	2.58	7.25	3.41
4–96	39.20	26.65	73.05	37.63	21.15	15.82	3.43	8.10	4.26
5–95	39.63	27.05	73.45	38.05	21.55	-	-	-	-
6–94	40.05	-	-	-	-	16.14	3.75	8.42	4.58
8–92	40.90	-	-	-	-	17.27	4.88	9.55	5.71
10–90	41.75	29.15	75.50	40.04	23.64	18.44	6.05	10.72	6.88

Table 4. Dependence of rate on [succinimide]

$[NBS] = 6.0 \times 10^{-3}$ *M*, Temperature = 323 K, $[X\text{-}C_6H_4CH(OR)_2] = 8.0 \times 10^{-2}$ *M*, Solvent = 100% CH_3CN, $[NaClO_4] = 0.1$ *M*

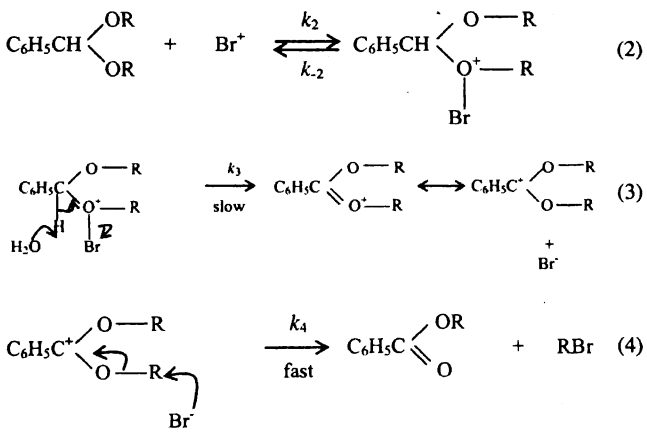
	X-$C_6H_4CH(OR)_2$ $k_1 \times 10^5$ (s^{-1})							
[Succinimide] $\times 10^2$ (*M*)	H (X)	*p*-OMe (X)	*p*-Me (X)	*p*-Cl (X)	*m*-OMe (X)	*p*-NO_2 (X)	*m*-Cl (X)	*m*-NO_2 (X)
0.00	24.90	71.30	36.00	19.40	14.20	1.81	6.48	2.64
2.00	17.15	56.64	29.20	16.74	13.56	1.17	4.22	1.99
4.00	12.51	48.98	20.00	10.71	12.50	0.31	3.30	1.54
6.00	14.70	44.67	21.50	11.70	9.50	0.45	2.18	1.14
8.00	15.10	40.74	25.00	13.52	7.51	0.70	2.71	1.29

dizing species[31]. The oxidizing species (Br^+) formed in the equilibrium step (1) attack the acetal molecule in another equilibrium reaction (2). The abstraction of proton from the aldehydic carbon and expulsion of bromide ion take place in the rate-determining step (3). The carbonium ion formed in step (3) is subsequently transformed to stable products, ester and alkyl bromide in a fast step (4).

$$\rangle NBr + \text{solvent} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \rangle NH + \text{reactive oxidizing species} \quad (1)$$

The solvent consists of a mixture of acetonitrile and water (from $NaClO_4.H_2O$). The reactive oxidizing species

may be Br^+ or solvated Br^+. The reactive species formed in the above equilibrium step attacks the acetal molecule in another equilibrium reaction.



(R = *n*-Bu)

The kinetic expression for the reaction can be derived from the concentration of the species involved in the slow step (3).

Applying equilibrium approximation to the intermediate, the following rate law is proposed.

$$\frac{-d[\text{NBS}]}{dt} = \frac{k_3k_2k_1[\text{X-C}_6\text{H}_4\text{CH(OR)}_2]\,[\text{NBS}]}{k_{-2}k_{-1}[\text{succinimide}]}$$

This rate-law is also in agreement with the observed kinetic behavior.

This mechanism with an electron deficient transition state is capable of explaining the enhancement of rate by electron-releasing substituents and retardation of rate by electron-attracting substituents in the aldehydic part of the acetal. A similar phenomenon has been reported by Deno and Potter for the bromine oxidation of ethers[32] and Westheimer for the chromic acid oxidation of alcohols[33]. An increase in the rate with an increase in the dielectric constant and ionic strength of the medium observed is in support of the transition state.

Effect of substituents on reaction rate :

It has been observed that (Table 5) the reaction is facilitated by electron donating groups in the benzaldehyde part of acetal. The rate of oxidation of *meta*- and *para*-substituted benzaldehyde di-*n*-butyl acetals are in the order : *p*-OMe > *p*-Me > H > *p*-Cl > *m*-OMe > *m*-Cl > *m*-NO_2 > *p*-NO_2.

This shows that the presence of the electron withdrawing groups in the aldehyde part of the acetal makes it less reactive by creating a more positive charge on the carbonyl carbon atom of the aldehyde group.

A plot of log k_X/k_H versus Hammett substituents constants (σ) values for the *meta*- and *para*-substituted benzaldehyde di-*n*-butyl acetals is found to be linear (r = 0.99) with reaction constant values ρ of -1.38 and -1.42 at 313 K and 323 K respectively (Table 6, Fig. 1). A good correlation of rates with the Hammett substituent constants (σ) indicates that the reaction site is not directly conjugated with the aromatic ring, but some group is interposed. The negative slope indicates that most probably positively charged activated complex is developed during the course of the reaction.

The genuine nature of isokinetic relationship is verified by the Exner plot[34,35] of log k_2 (323 K) vs log k_2

Table 5. Dependence of the reaction rate on temperature, Arrhenius and thermodynamic activation parameters at 323 K for the oxidation of aromatic acetals by NBS

$[\text{X-C}_6\text{H}_4\text{CH(OR)}_2]$ = 8.0 × 10^{-2} *M*, [NBS] = 6.0 × 10^{-3} *M*, $[NaClO_4]$ = 0.1 *M*, Solvent = 100% CH_3CN, Temperature = 323 K

$[\text{X-C}_6\text{H}_4\text{CH(OR)}_2]$	$k_2 \times 10^4$ ($dm^3\ mol^{-1}\ s^{-1}$)	E_a (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ ($JK^{-1}\ mol^{-1}$)	$\Delta G^{\neq}$ (kJ mol^{-1})	log *A*
X = H	31.1 ± 0.06	66.11 ± 0.34	63.60 ± 0.73	-97.10 ± 1.0	94.55 ± 0.32	8.29 ± 0.1
X = *p*-OMe	89.1 ± 0.44	106.27 ± 0.89	103.76 ± 0.47	36.44 ± 1.2	91.62 ± 0.22	15.2 ± 0.77
X = *p*-Me	45.0 ± 0.16	102.51 ± 0.89	99.51 ± 0.69	17.91 ± 1.7	94.14 ± 0.42	14.2 ± 0.23
X = *p*-Cl	24.5 ± 0.15	80.33 ± 0.90	77.80 ± 0.62	-55.22 ± 1.9	93.30 ± 0.19	10.3 ± 0.28
X = *p*-NO_2	2.25 ± 0.02	88.28 ± 0.75	85.77 ± 0.61	-49.78 ± 1.7	101.61 ± 0.07	10.7 ± 0.25
X = *m*-OMe	17.9 ± 0.01	82.42 ± 0.62	79.99 ± 0.46	-50.05 ± 2.5	96.23 ± 0.02	10.6 ± 0.05
X = *m*-Cl	8.11 ± 0.01	88.71 ± 0.81	86.19 ± 0.53	-37.86 ± 1.2	98.74 ± 0.18	11.2 ± 0.03
X = *m*-NO_2	3.30 ± 0.08	73.61 ± 0.95	70.71 ± 0.82	-92.80 ± 1.0	100.83 ± 0.10	8.41 ± 0.18

Table 6. Hammett substituent constants (σ) and rate constants (k_2) at 313 K and 323 K for *meta*- and *para*-substituted acetals

$[X\text{-}C_6H_5CH(OC_4H_9)_2]$	σ	$k_2 \times 10^4$ ($dm^3\ mol^{-1}\ s^{-1}$)	$k_2 \times 10^4$ ($dm^3\ mol^{-1}\ s^{-1}$)	k_X/k_H at 313 K	k_X/k_H at 323 K
X = H	0.00	14.19	31.10	1.00	1.00
X = *p*-OMe	-0.27	25.11	89.10	1.77	2.85
X = *p*-Me	-0.17	16.18	45.00	1.14	1.44
X = *p*-Cl	0.23	9.39	24.50	0.66	0.78
X = *m*-OMe	0.12	6.53	17.90	0.46	0.57
X = *m*-Cl	0.37	2.80	8.11	0.20	0.26
X = *m*-NO_2	0.71	1.37	3.30	0.09	0.11
X = *p*-NO_2	0.78	0.79	2.27	0.06	0.07

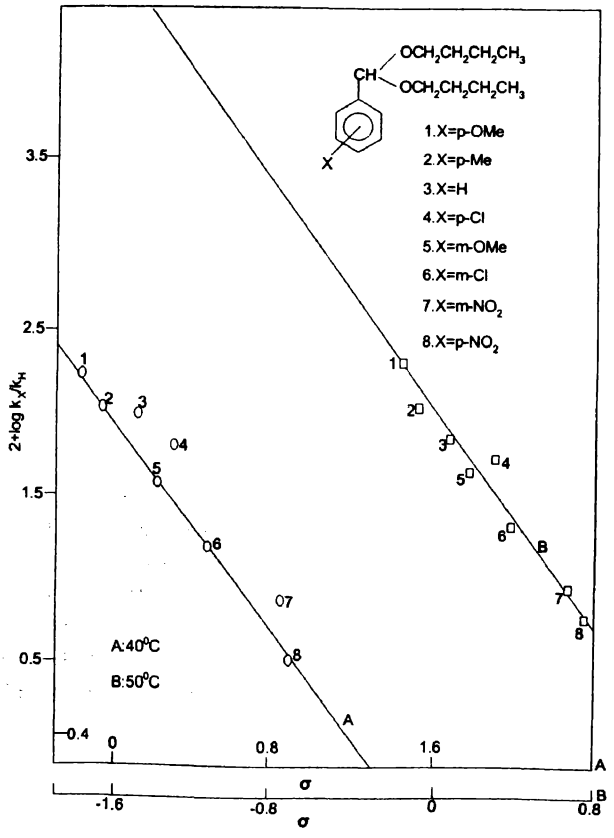


Fig. 1. Hammett correlation : Plot of log k_X/k_H vs σ the Hammett substituent constant.

(313 K) with slope 1.05. This linearity of Exner plot is suggestive of a unified mechanism for the NBS oxidation of different acetals (Table 6, Fig. 2). From the slope of the Exner plot, isokinetic temperature (β) is calculated using the following equation[36].

$$\beta = \frac{T_1 T_2 (b - 1)}{bT_2 - T_1}$$

The slope *b* is greater than 1 and β (132 K) is less than T_1, which indicates an increasing selectivity with increase in temperature and the reaction series is characterized by compensation effect between $\Delta H^{\#}$ and $\Delta S^{\#}$. Since β is well below the experimental temperature (308–328 K) the observed effect of substituents is real and justifies the application of the Hammett equation to the present investigation.

Experimental

Acetals are *gem*-dialkoxy compounds, which are formed by the nucleophilic addition of the alcohol to the carbonyl group of an aldehyde producing a hemiacetal, which reacts further with another molecule of alcohol to give the acetal in the presence of an acid catalyst. Acetals were prepared by the method described in the literature[37,38]. Anhydrous calcium chloride was used as catalyst for the preparation of the aromatic acetals [X-$C_6H_4CH(OBu\text{-}n)_2$] {X = *p*-OMe, *p*-Me, *p*-Cl, *m*-OMe, *m*-Cl}. *p*-Toluene sulphonic acid was used as a catalyst for the preparation of the aromatic acetals [X-$C_6H_4CH(OBu\text{-}n)_2$] {X = *p*-NO_2, *m*-NO_2}. The IR spectra of acetals showed characteristic absorptions in the region 1020–1200 cm^{-1}. NMR spectra showed a characteristic peak at δ 5.2 to 5.8 ppm for aldehydic proton in acetal.

All the reagents used for the kinetic study were of highest purity available. Acetonitrile (E. Merck) was purified by standard procedure[39]. Aldehydes and alcohols (BDH or Fluka) were purified before use in the preparation of acetals. NBS (Merck) was used as such.

The acetals prepared were screened for antibacterial and antifungal activities against certain pathogenic bacteria by disc diffusion method at concentration 10 μg/mL in DMSO using Gram-positive *Staphylococcus aureus, Staphylococcus farcalis,* Gram-negative *Escherichia coli,*

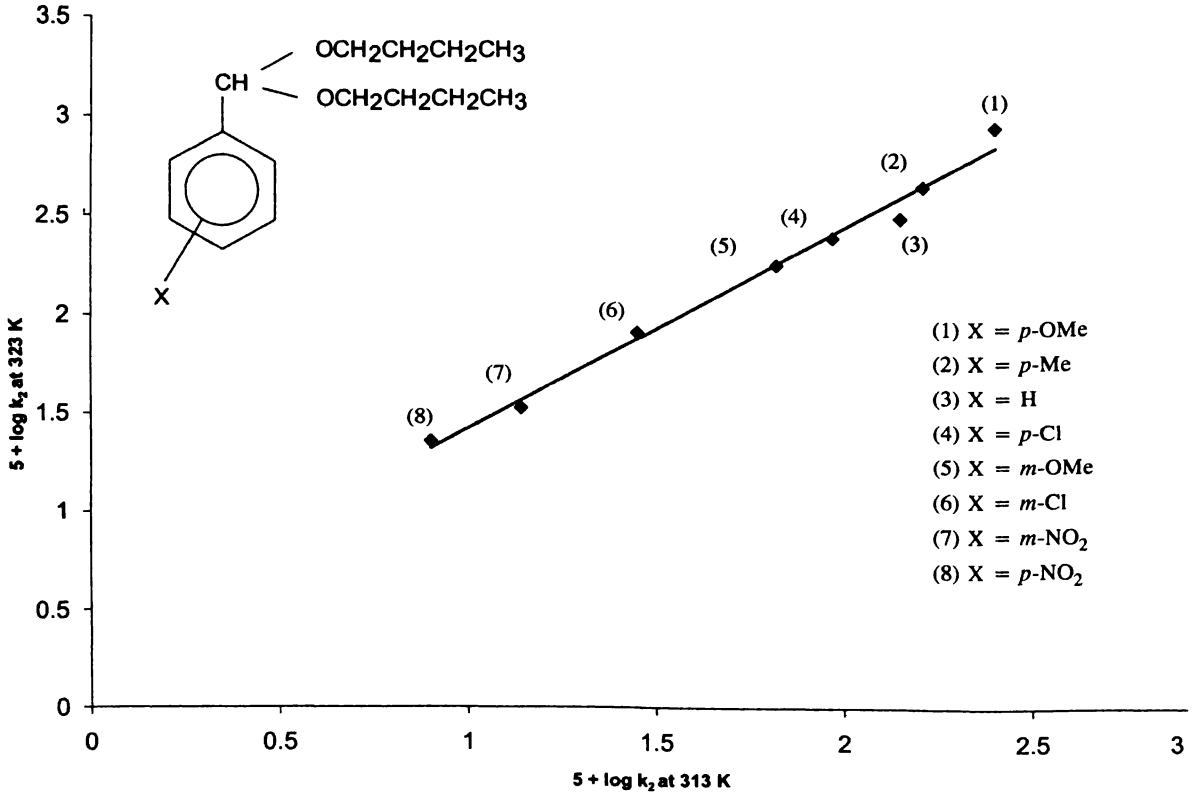


Fig. 2. Exner plot.

Pseudomonas and antifungal activity against *Candida albicans* and *Aspergilles niger*. The zone of inhibition had been measured in mm and activities were compared with ciprofloxacin 5 μg/disc for bacteria and fluconazole 100 μg/disc for fungi as standard drugs. The acetals had maximum inhibition against the entire selected organisms, when compared with the standard (Table 7).

Kinetic procedure :

In each kinetic run, the reaction was carried out in a glass stoppered pyrex bottle whose outer surface was coated black to eliminate photochemical effects. All experiments were carried out under pseudo-first order conditions with acetal concentration in large excess. The pseudo-first order rate constants (k_1) were obtained graphi-

Table 7. Antimicrobial activities of acetals

[X-$C_6H_4CH(OR)_2$]	Diameter zone of inhibition (mm)					
	Gram-positive		Gram-negative		Fungi	
	Staphylococcus aureus	*Staphylococcus farcalis*	*Escherichia coli*	*Psedomonas*	*Aspergillus niger*	*Candida albican*
X = H	12	33	26	16	28	30
X = *p*-OMe	15	22	20	36	32	37
X = *p*-Me	16	20	18	32	23	32
X = *p*-Cl	17	31	16	30	25	38
X = *p*-NO_2	34	36	30	22	37	38
X = *m*-OMe	14	30	22	32	34	36
X = *m*-Cl	16	33	17	28	31	35
X = *m*-NO_2	33	35	31	20	38	39
Standard	35	38	38	42	30	36

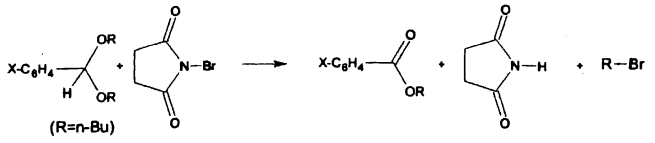
cally by plotting log [oxidant] versus time. The second order rate constants (k_2) were evaluated by dividing (k_1) with the initial concentration of substrate. Appropriate amounts of acetal, sodium perchlorate and acetonitrile were placed in the reagent bottle and thermostated for about 30 min for thermal equilibrium. The reaction was initiated by rapidly adding required amount of thermostated NBS solution to the mixture. The progress of the reaction was monitored for at least two half lives by iodometric determination of unreacted oxidant. The kinetics of the reaction was followed by pipetting out measured aliquots of the reaction mixture at various intervals of time and anlaysing the oxidant concentration by quenching the solution in a mixture containing 50 ml of iodate free KI-$NaHCO_3$ mixture (5% solution) and 2 ml of 6 *N* H_2SO_4 and titrating the liberated iodine with a standard thiosulphate solution (0.002 *N*) to a starch end point.

Oxidation products :

In a typical experiment, a mixture of 0.02 *M* (10 ml) solution of NBS in acetonitrile and 40 ml of 0.04 *M* solution of aromatic acetal in acetonitrile was thermostated for about 1 h. Then the solution was diluted with water and excess NBS was removed with sodium thiosulphate solution. The resulting aqueous solution was extracted with ether and the extract was washed with water and dried over anhydrous sodium sulphate. The solvent ether was removed at reduced pressure. The identity of the products, ester and alkyl bromide, were confirmed by HPLC. The authentic ester and alkyl bromide samples and the product of oxidation gave the same retention time. The products were further confirmed by IR and PMR spectral data.

Stoichiometry :

A known excess of NBS (0.05 *M*) over acetal (0.01 *M*) in acetonitrile medium was equilibrated at 313 K for 24 h. The unchanged NBS concentration in the reaction mixture was determined by iodometric estimation. Similar stoichiometry study was carried out for all other acetals. In all cases the analysis showed that one mole of acetal reacted with one mole of NBS. The observed reaction stoichiometry was 1 : 1.



X = H, *p*-OMe, *p*-Me, *p*-Cl, *p*-NO_2, *m*-OMe, *m*-Cl, *m*-NO_2

Acknowledgement

The author acknowledges with gratitude the support of the St. Joseph's College management and UGC for providing financial assistance.

References

1. G. H. Posner, H. Dowd, P. Ploypradith, J. N. Cumming, Xies and T. A. Shapiro, *J. Med. Chem.*, 1998, **41**, 2164.
2. S. J. Angyal and K. James, *Aust. J. Chem.*, 1974, **24**, 1219.
3. N. Xavier and S. J. Arulraj, *Tetrahedron Lett.*, 1985, **41**, 2875.
4. S. G. Angyal and K. James, *Chem. Commun.*, 1969, 617; *Aust. J. Chem.*, 1970, **23**, 1209.
5. J. B. Wright, *J. Am. Chem. Soc.*, 1955, **77**, 4883.
6. E. N. Marvel and M. Joncich, *J. Am. Chem. Soc.*, 1951, **73**, 973.
7. D. G. Markees, *J. Org Chem.*, 1958, **23**, 1490.
8. R. Filler, *Chem. Rev.*, 1963, **63**, 21.
9. N. A. Farook, *J. Iran. Chem. Soc.*, 2006, **3**, 378.
10. K. Basavaiah, U. R. Anil Kumar and V. Ramakrishna, *Indian J. Chem. Technol.*, 2007, **14**, 313.
11. K. Basavaiah and U. R. Anil Kumar, *Bull. Chem. Soc. Ethiopia*, 2008, **22**, 135.
12. K. Basavaiah and U. R. Anil Kumar, *Proc. Natl. Acad. Sci. India*, 2007, **77A**, 301.
13. N. Venkatasubramanian and V. Thiagarajan, *Can. J. Chem.*, 1969, **47**, 964.
14. V. Thiyagarajan and N. Venkatasubramanian, *Tetrahedron Lett.*, 1967, 3349.
15. Bharat Singh, L. Pandey and J. Sharma, *Tetrahedron*, 1982, **38**, 169.
16. K. Singh, J. N. Tiwari and S. P. Mushran, *Int. J. Chem. Kinet.*, 1978, **10**, 995.
17. G. Gopalakrishnan and John L. Hogg, *J. Org. Chem.*, 1985, **50**, 1206.
18. L. Donald Heywood and Benjamin Phillips, *J. Org. Chem.*, 1960, **25**, 1699.
19. A. K. Singh, *Asian J. Chem.*, 2003, **15**, 1313.
20. Neelu Kambo, Neeti Grover and Santosh K. Upadhyay, *J. Indian Chem. Soc.*, 2002, **79**, 939.
21. Hassan A. Ewais, Ahmed E. Ahmed and Ahmed A. Abdel-Khalek, *Int. J. Chem. Kinet.*, 2004, **36**, 394.
22. R. Ramachandrappa, Puttaswamy, S. M. Mayanna and N. M. Nade Gowda, *Int. J. Chem. Kinet.*, 1998, **30**, 407.
23. Govindaraj T. Naik, Mohantesh A. Angadi and Abdulazizkhan L. Harihar, *J. Indian Chem. Soc.*, 2009, **86**, 209.
24. Sheila Srivastava, and Vandana Gupta, *J. Indian Chem. Soc.*, 2006, **83**, 1103.

25. N. S. Linge Gowda, M. N. Kumara, D. Channe Gowda and K. S. Rangappa, *Int. J. Chem. Kinet.*, 2006, **38**, 376.

26. S. Pandey, N. Kambo and S. K. Upadhyay, *Oxid. Commun.*, 2004, **27**, 821.

27. Sheila Srivastava and Vandana Gupta, *Oxid. Commun.*, 2004, **27**, 813.

28. N. A. Mohamed Farook, *Asian J. Chem.*, 2000, **12**, 1113.

29. R. V. Nadh, B. Sundar and P. S. Radhakrishnamurthy, *Oxid. Commun.*, 2005, **28**, 81.

30. P. M. Ramdas Bhandarkar and K. M. Mohana, *Indian J. Chem., Sect. A*, 2009, **48**, 1107.

31. S. Sivakamasundari and R. Ganesan, *Int. J. Chem. Kinet.*, 1980, **12**, 837.

32. N. C. Deno and Neil H. Potter, *J. Am. Chem. Soc.*, 1967, **89**, 3550.

33. F. Westhemier, *J. Am. Chem. Soc.*, 1960, **82**, 406.

34. O. Exner, *Nature*, 1964, **201**, 488.

35. O. Exner, *Coll. Czech. Chem. Commun.*, 1964, **29**, 1094.

36. J. F. Bunnett, "Investigation of Rates and Mechanism of Reactions - Techniques of Chemistry", 6th ed., John Wiley, New York.

37. H. Adkins and Nissen, "Organic Synthesis", John Wiley, New York, 1944, Vol. I, p. 1.

38. J. M. Sayer and W. P. Jencks, *J. Am. Chem. Soc.*, 1977, **99**, 465.

39. Cooper and William A. Waters, *J. Chem. Soc.*, 1964, 1538.