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Kinetics and mechanism of oxidation of aliphatic aldehydes by pyridinium bromochromate

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The oxidation of six aliphatic aldehydes by pyridinium bromochromate (PBC), to the corresponding carboxylic acids, is first order each in PBC and the aldehyde. The reaction is catalysed by H^+; the H^+ dependence has the form, $k_{obs} = a + b[H^+]$. Oxidation of deuterated acetaldehyde (MeCDO) showed the presence of a substantial kinetic isotope effect ($k_H/k_D = 6.40$ at 288 K). Oxidation of acetaldehyde is studied in 19 organic solvents. The solvent effect has been analysed using Taft's and Swain's multiparametric equations. The rate constants correlate well with Taft's σ^* constants; reactions being negative. A mechanism involving transfer of a hydride ion has been suggested.

Pyridinium bromochromate (PBC) is a mild and selective oxidizing agent used in synthetic organic chemistry[1]. Only a few reports about the kinetics and mechanisms of oxidation by PBC are available in literature[2-5]. In continuation of our earlier work, we report here the kinetics and mechanism of oxidation of six aliphatic aldehydes by PBC in dimethyl sulphoxide (DMSO) as solvent. Mechanistic aspects are discussed.

Materials and Methods

PBC was prepared by reported method[1], and its purity was checked by iodometric determinations. Solutions of formaldehyde were prepared by heating paraformaldehyde and passing the vapours in DMSO. The ammount of HCHO in DMSO was determined by chromotropic acid method[6]. The other aldehydes were commercial products and were used as such. *p*-Toluenesulphonic acid (TsOH) was used as a source of hydrogen ions. The solvents were purified by the usual methods[7].

Product analysis

In a typical reaction, acetaldehyde (4.4 g, 0.1 mol) and PBC (2.6 g, 0.01 mol) were dissolved in DMSO (100 ml) and the reaction mixture was allowed to stand for *ca.* 24 h to ensure completion of the reaction. The amount of acetic acid formed was determined by the procedure described earlier[8]. Several determinations indicated a 1 : 1 stoichiometry (Eq. 1).

$$RCHO + CrO_2BrOpyH \rightarrow RCOOH + CrOBrOpyH \quad \ldots (1)$$

Kinetic measurements

Pseudo-first order conditions were attained by keeping an excess ($\times 15$ or more) of [aldehyde] over [PBC]. The solvent was DMSO, unless mentioned otherwise. The reactions were carried out at constnat temperature (± 0.1 K) and were followed upto 80% reaction by monitoring the decrease in [PBC] at 356 nm. The pseudo-first order rate constnats, k_{obs}, were computed from the linear ($r > 0.990$) least squares plots of log [PBC] versus time. Duplicate kinetic runs showed that the rate constants were reproducible within $\pm 3\%$.

Results

The reactions are of first order with respect to [PBC]. Further, the pseudo-first order rate constant, k_{obs}, does not depend on the initial concentration of PBC. The reaction is of first order with respect to aldehydes also (Table 1). The reaction is catalysed by H^+. The H^+ dependence takes the form $k_{obs} = a + b[H^+]$.

The rates of oxidation of the six aldehydes were determined at different temperatures and the activation parameters were calculated (Table 2).

To ascertain the importance of the cleavage of the aldehydic C−H bond in the rate-determining step, the oxidation of deuteriated acetaldehyde (MeCDO) was studied. The oxidation of deuteriated acetaldehyde exhibited a substantial primary kinetic isotope effect (Table 2).

The oxidation of aldehydes by PBC, under a nitrogen atmosphere, failed to induce the polymeriation of acrylonitrile. Further, the addition of a radical scavenger, acrylonitrile had no effect on

the reaction rate (Table 1). Thus a one electron oxidation, giving rise to free radicals is unlikely.

The oxidation of acetaldehyde was studied in 19 different organic solvents. There was no reaction with the solvents chosen. The kinetics was similar in all the solvents. The values of k_2 at 298 K are recorded in Table 3.

Discussion

The entropy and enthalpy of activation of the oxidation of six aldehydes are linearly related ($r=0.9991$). The value of isokinetic temperature evaluated[9,10] from this plot is 1042 ± 21 K. The correlation was tested and found genuine by Exner's criterion[11]. The isokinetic temperature, calculated from Exner's plot of log k_2 at 288 K versus log k_2 at 318 K ($r=0.9999$) is 1037 ± 17 K. The linear isokinetic correlation suggests that all the aldehydes are oxidized by the same mechanism.

The observed H^+ dependence suggests that the reaction follows two mechanistic pathways, one acid-independent and the other acid-dependent. The acid catalysis can be attributed to a protonation of PBC to give a stronger oxidant and electrophile (2).

$$\text{pyHOCrO}_2\text{Br} + \text{H}^+ \rightleftarrows \text{pyHO}\overset{+}{\text{C}}\text{r(OH)OBr} \quad \ldots (2)$$

The rate constants of oxidation, k_2, is eighteen solvents (CS_2 was not considered as the complete range of solvent parameters are not available) were correlated in terms of linear solvation energy relationship (Eq. 3) of Kamlet *et al.*[12].

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \quad \ldots (3)$$

In the equation, π^* represents the solvent polarity, β the hydrogen bond acceptor basicities and α is the hydrogen bond donor acidity. A_0 is

Table 1—Rate constant for oxidation of acetaldehyde by PBC at 298 K

10^3 [PBC] (mol dm^{-3})	[MeCHO] (mol dm^{-3})	[TsOH] (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1})
1.0	0.10	0.0	7.12
1.0	0.20	0.0	14.3
1.0	0.40	0.0	29.0
1.0	0.60	0.0	42.8
1.0	0.80	0.0	57.1
1.0	1.00	0.0	71.0
2.0	0.40	0.0	28.3
4.0	0.40	0.0	29.0
8.0	0.40	0.0	29.8
1.0	0.40	0.0*	29.4
1.0	0.10	0.1	11.4
1.0	0.10	0.2	16.0
1.0	0.10	0.3	20.2
1.0	0.10	0.5	28.2
1.0	0.10	0.8	41.5
1.0	0.10	1.0	51.0

*contained 0.001 mol dm^{-3} acrylonitrile

Table 3—Effect of solvents on the oxidation of acetaldehyde by PBC at 298 K

Solvent	$10^4 k_2$ (dm^{-3} mol^{-1} s^{-1})	Solvent	$10^4 k_2$ (dm^{-3} mol^{-1} s^{-1})
Chloroform	15.2	Toluene	6.31
1,2-Dichloroethane	25.1	Acetophenone	28.2
Dichloromethane	22.4	Tetrahydrofuran	10.0
DMSO	71.3	-Butyl alcohol	6.46
Acetone	20.0	Dioxane	10.2
Dimethylformamide	40.7	1,2-Dimethoxyethane	5.62
Butanone	14.1	Ethyl acetate	7.94
Nitrobenzene	28.2	Carbon disulphide	3.62
Benzene	7.41	Acetic acid	2.24
Cyclohexane	0.71		

Table 2—Rate constants at different temperatures and the activation parameters of the oxidation of aldehydes by PBC

Subst.	$10^4 K$ (dm^{-3} mol^{-1} s^{-1})				$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})
	288 K	298 K	308 K	318 K			
H	2.00	4.70	11.1	25.3	62.0 ± 0.7	−101 ± 2	91.9 ± 0.5
Me	34.6	71.3	149	305	52.8 ± 0.7	−109 ± 2	85.2 ± 0.6
Et	61.8	124	250	504	50.7 ± 0.8	−112 ± 3	83.8 ± 0.6
Pr	67.9	137	277	542	50.2 ± 0.5	−112 ± 2	83.6 ± 0.6
Pr^i	106	208	410	805	48.9 ± 0.7	−113 ± 2	82.6 ± 0.6
$ClCH_2$	0.075	0.21	0.57	1.47	73.0 ± 0.4	−90 ± 1	99.7 ± 0.3
MeCDO	5.41	12.5	27.2	57.8	57.5 ± 0.4	−108 ± 1	89.6 ± 0.3
k_H/k_D	6.40	5.70	5.48	5.28			

Table 4—Temperature dependence of the reaction constant

Temp./K	288	298	308	318
ρ^*	-2.54 ± 0.01	-2.41 ± 0.02	-2.30 ± 0.01	-2.21 ± 0.01
r^2	0.9999	0.9999	0.9999	0.9999
sd	0.01	0.03	0.03	0.02

the intercept term. The results of correlation analyses terms of Eq. (3), a biparametric equation involving π^* and β, and separately with π^* and β are given below [Eqs (4)-(7)].

$$\log k_2 = -4.05 + 1.66\,(\pm 0.20)\,\pi^* + 0.20\,(\pm 0.16)\,\beta - 0.33\,(\pm 0.15)\,\alpha \quad \ldots (4)$$

$R^2 = 0.8782$; sd = 0.18; n = 18; $\psi = 0.27$

$$\log k_2 = -4.13 + 1.78\,(\pm 0.21)\,\pi^* + 0.09\,(\pm 0.17)\,\beta \quad \ldots (5)$$

$R^2 = 0.8398$; sd = 0.20; n = 18; $\psi = 0.31$

$$\log k_2 = -4.11 + 1.80\,(\pm 0.20\ \pi^* \quad \ldots (6)$$

$r^2 = 0.8368$; sd = 0.20; n = 18; $\psi = 0.30$

$$\log k_2 - 3.09 + 0.41\,(\pm 0.39)\,\beta \quad \ldots (7)$$

$r^2 = 0.0639$; sd = 0.47; n = 18; $\psi = 0.89$

Here n is the number of data points and ψ is the Exner's statistical parameter[13].

Kamlet's[12] triparametric equation explain *ca.* 88% of the effect of solvent on the oxidation. However, by Exner's criterion[13] the correlation is poor (cf. Eq. 4). The major contribution is of solvent polarity. It is alone accounted for *ca.* 83% of the data. Both β and α play relatively minor roles.

The data on the solvent effect were also analysed in terms of Swain's equation[14] of cation- and anion-solvating concept of the solvents (Eq. 8).

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

Here A represents the anion-solvating power of the solvent and B the catijon-solvating power. C is the intercept term. (A+B) is postulated to represent the solvent polarity. The rates in different solvents were analysed in terms of Eq. (8), separately with A and B and with (A+B).

$$\log k_2 = 0.38\,(\pm 0.05)\,A + 1.82\,(\pm 0.03)\,B - 4.25 \quad \ldots (9)$$

$R^2 = 0.9948$; sd = 0.04; n = 19; $\psi = 0.05$

$$\log k_2 = 0.12\,(\pm 0.60)\,A - 3.00 \quad \ldots (10)$$

$r^2 = 0.0443$; sd = 0.38; n = 19; $\psi = 0.91$

$$\log k_2 = 1.76\,(\pm 0.08)\,B - 4.12 \quad \ldots (11)$$

$r^2 = 0.9662$; sd = 0.09; n = 19; $\psi = 0.13$

$$\log k_2 = 1.31 \pm 0.19\,(A+B) - 4.19 \quad \ldots (12)$$

$r^2 = 0.7454$; sd = 0.24; n = 19; $\psi = 0.38$

The rates of oxidation of acetaldehyde in different solvents show a very good correlation in Swain's equation (Eq. 9) with the cation-solvating power playing the major role. In fact, the cation solvation alone accounts for *ca.* 97% of the data. The solvent polarity, repersented by (A+B), also accounted for *ca.* 75% of the data.

The rates of the oxidation of the six aldehydes show excellent correlation with Taft's σ^* substituent constants[15], the reaction constant being negative (Table 4). The negative polar reaction constant indicates an electron deficient carbon centre in the transition state of the rate-determining step.

There is no kinetic evidence for the formation of an intermediate complex in the present reaction, however, its formation in small ammounts cannot be ruled out. The presence of a substantial primary kinetic isotope effect ($k_H/k_D = 6.40$ at 288 K), confirms that the aldehydic C−H bond is cleaved in the rate determining step. The large negative value of the polar reaction constant together with the substantial deuterium isotope effect indicates that the transition state approaches a carbocation in character. Hence, transfer of a hydride ion from the aldehyde to the oxidant is suggested. The hydride ion transfer mechanism is also supported by the major role of cation-solvating power of the solvents. The mechanism shown in Scheme 1 accounts for all the observed data.

$$R-\overset{O}{\overset{\|}{C}}-H + OCrOBrOpyH \xrightarrow{\text{slow}} R-\overset{+}{C}=O + (HOCrOBrOpyH)^-$$

$$R-\overset{+}{C}=O + (HOCrOBrOpyH)^- \xrightarrow{\text{fast}} RCOOH + OCrBrOpyH$$

Scheme 1

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