Kinetics and mechanism of oxidation of aliphatic aldehydes by N-bromobenzamide

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The oxidation of six aliphatic aldehydes by N-bromobenzamide (NBB) in 1:1 (v/v) acetic acid-water leads to the formation of the corresponding carboxylic acids. The reaction is first order with respect to both NBB and aldehyde and is catalysed by hydrogen ions. The observed hydrogen ion dependence indicates that both NBB and its protonated form are reactive oxidizing species. The oxidation of MeCDO exhibits a substantial kinetic isotope effect. With an increase in the proportion of acetic acid in the solvent mixture of acetic acid and water, the rate decreases. Addition of benzamide has no effect on the rate. The reaction fails to induce the polymerization of acrylonitrile. The role of aldehyde hydrate in the oxidation process is discussed. The rates correlate well with Taft's σ^* substituent constants, with negative reaction constant. A mechanism involving transfer of a hydride ion to the oxidant in the rate determining step has been proposed.

Kinetics of oxidation of aliphatic aldehydes by different oxidizing agents[1-7] have been reported. The role of hydrate form of aldehydes in the chromium(VI) oxidation was studied by Banerji and Goswami and by Rocek and Ng[1]. It was concluded that the oxidation of aldehydes proceed via the hydrate form instead of the free carbonyl form. Similarly oxidations of aldehydes by acid permanganate[2], N-bromoacetamide[3], Os(VIII)[4], pyridinium hydrobromide perbromide[5] and bis(2,2'-bipyridyl)copper (II) permanganate[6] are also reported to involve the hydrate form in the oxidation process. In contrast Agarwal et al.[7] reported free carbonyl form as the reactive oxidizing species in the oxidation of aldehydes by pyridinium fluorochromate. In this note we report the kinetics of oxidation of six aliphatic aldehydes by N-bromobenzamide (NBB) in aqueous acetic acid solution. Attempts have been made to determine the role of the hydrate form in the oxidation process.

Materials and Methods

All the aldehydes were commercial products and were purified by the methods described earlier[8,9]. NBB was prepared by the literature method and its purity was checked by an iodometric method. Deuteriated acetaldehyde (MECDO) was obtained from Sigma Chemicals. Acetic acid was refluxed with chromic oxide and acetic anhydride for

6 h and then fractionated. Perchloric acid was used as a source of hydrogen ions.

The product analysis was carried out under kinetic conditions. In a typical experiment, acetaldehyde (4.4 g, 0.1 mol) and NBB (2.0 g, 0.01 mol) were made upto 100 ml in water in the presence of 0.5 mol dm^{-3} perchloric acid. It was then kept in the dark for ca. 10 h to ensure completion of the reaction. It was rendered alkaline and evaporated to dryness under reduced pressure. The residue was acidified and extracted with ether (3 × 50 ml). The ether extract was dried with anhydrous magnesium sulphate and treated with thionyl chloride (10 ml). The solvent was allowed to evaporate. Dry methanol (7 ml) was added and HCl formed was removed in a current of dry air. The residue was dissolved in ether (200 ml) and the ester content was determined colorimetrically as iron(III) hydroximate by the method of Hall and Schaefer[10]. The yield of acetic acid was 89%.

Stoichiometry was ascertained by treating acetaldehyde (0.44 g, 0.01 mol) with NBB (10.0 g, 0.05 mol) in 1:1 (v/v) acetic acid-water. The residual NBB was determined iodometrically. Several determinations with various aldehydes indicated a 1:1 stoichiometry.

Kinetic measurements

The reactions were studied under pseudo-first order conditions by keeping an excess (× 10

Table 1—Rate constants for the oxidation of acetaldehyde by NBB at 308 K

[Aldehyde] (mol dm^{-3})	10^3[NBB] (mol dm^{-3})	[H$^+$] (mol dm^{-3})	$10^5 k_{obs}$ (s^{-1})
0.01	2.0	0.0	0.97
0.02	2.0	0.0	2.00
0.04	2.0	0.0	3.95
0.06	2.0	0.0	6.18
0.10	2.0	0.0	9.88
0.20	2.0	0.0	20.0
0.30	2.0	0.0	31.1
0.30	2.0	0.0	32.5[a]
0.06	0.3	0.0	5.81
0.06	0.8	0.0	6.48
0.06	1.2	0.0	6.23
0.06	3.5	0.0	5.89
0.06	2.0	0.01	14.5
0.06	2.0	0.02*	23.4
0.06	2.0	0.04*	39.5
0.06	2.0	0.10*	90.7
0.06	2.0	0.20*	175
0.06	2.0	0.40*	342

[a]Contained 0.005 mol dm^{-3} acrylonitrile;
*Ionic strength $I = 0.4$ mol dm^{-3}

Table 2—Rate constants for the oxidation of RCHO by NBB at 298 K

Substituent (R)	K_d^a	Rate constants (dm^{3}mol^{-1}s^{-1})		
		$10^5 k_{ex}$	$10^5 k_{HY}$	$10^5 k_A$
H	6.9×10^{-4}	7.5	7.5	15000
Me	0.77	66.6	111	166
Et	1.7	81.9	195	141
Pr	2.6	67.2	210	98.8
Pr^i	2.8	96.0	320	137
ClCH$_2$	0.032	0.34	0.35	13.1

[a]Data from ref. 18

$$RCHO + PhCONHBr \rightarrow RCOOH + PhCONH_2 + HBr \qquad \ldots (1)$$

The reactions were found to be first order with respect to NBB. Further, the first order rate coefficient did not vary with the initial concentration of NBB. The effect of the variation in the concentration of aldehyde showed that the reaction is first order with respect to aldehyde also (Table 1).

The oxidation of acetaldehyde under nitrogen atmosphere, failed to induce polymerization of acrylonitrile. Further, an addition of acrylonitrile had no effect on the rate (Table 1).

Addition of perchloric acid, at constant ionic strength of 0.4 mol dm^{-3}, increases the rate (Table 1) and the hydrogen ion dependence has the form (2).

$$k_{obs} = a + b[H^+] \qquad \ldots (2)$$

The values of a and b are 6.40×10^{-5}s^{-1} and 3.40×10^{-3} dm^{3}mol^{-1}s^{-1} respectively ($r^2 = 0.9998$).

To ascertain the importance of the cleavage of the aldehydic C−H bond in the rate-determining step, the oxidation of MeCDO was studied. The results show the presence of a substantial primary kinetic isotope effect. The value of k_H/k_D is 3.89 at 308 K.

The rate of oxidation of acetaldehyde was obtained in solvent mixtures containing different proportions of acetic acid and water. It was found that the rate decreases with an increase in the amount of acetic acid in the solvent mixture. Under the conditions [NBB] = 2.0×10^{-3} mol dm^{-3}, [MeCHO] = 6.0×10^{-2} mol dm^{-3} and at 308 K, when % AcOH (v/v) was increased from 25 to 72, $10^5 k_{obs}$ decreased from 27.5 to 1.93 s^{-1}.

Addition of benzamide had no effect on the oxidation rate.

The plot of log(rate) at 298 K is linearly related to log(rate) at 313 K (slope = 0.9406 ± 0.0038; $r^2 = 0.9999$). The value of the isokinetic tempera-

or greater) of the substrate over NBB. Mercury(II) acetate (0.01 mol dm^{-3}) was added to each reaction mixture to prevent liberation and further reactions of bromine[11]. All reactions were carried out in flasks blackened from the outside to avoid any photochemical reactions. The reactions were studied at constant temperature (± 0.1 K) and were followed by monitoring the decrease in the concentration of NBB iodometrically up to 80% reaction. The solvent used was 1:1 (v/v) acetic acid-water, unless mentioned otherwise. All experiments, other than those used to study the effect of hydrogen ions, were carried out in the absence of any added perchloric acid. Pseudo-first order rate constants, k_{obs}, were evaluated from linear plots ($r > 0.990$) of log[NBB] against time. Duplicate kinetic runs showed that the rate constants are reproducible to within $\pm 3\%$. Specific rate constant, k_{ex}, was calculated from the relation $k_{ex} = k_{obs}/$[Aldehyde]. Simple and multivariate regression analyses were carried out by the least squares method.
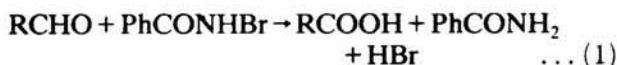
Results and Discussion

The experimental data were obtained for all the aldehydes. Since the results are similar only representative data are reproduced here.

Product analysis and stoichiometry determinations indicated the following overall reaction.

Table 3—Temperature dependence of the rate constants and activation parameters of the oxidation of aldehyde hydrates, $RCH(OH)_2$, by NBB

Subst (R)	$10^5 k_{HY}$ $(dm^3 mol^{-1}s^{-1})$				$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}$
	298	303	308	313K	$(kJ mol^{-1})$	$(J mol^{-1}K^{-1})$	$(kJ mol^{-1})$
H	7.5	10.0	14.4	20.0	48.7 ± 1.3	-161 ± 4.2	96.6 ± 1.0
Me	111	139	190	250	40.1 ± 1.4	-168 ± 4.7	90.0 ± 1.1
Et	195	260	345	410	36.5 ± 1.8	-175 ± 6.0	88.4 ± 1.4
Pr	210	270	365	460	38.6 ± 0.9	-167 ± 3.0	88.3 ± 0.7
Pr^i	320	395	515	695	37.6 ± 1.7	-167 ± 5.7	87.3 ± 1.4
$ClCH_2$	0.35	0.5	0.75	1.11	57.4 ± 1.1	-157 ± 3.5	104 ± 0.8

ture by Exner's method[12] is 1649 ± 479 K. A linear isokinetic relationship is a necessary condition for the validity of linear free energy relationships. It also implies that all the compounds so correlated react by the same mechanism.

In aqueous solutions, NBB is likely to hydrolyse and/or disproportionate as shown below (Eqs 3 and 4).

$$PhCONHBr + H_2O \rightleftharpoons PhCONH_2 + HOBr \quad \dots (3)$$

$$2PhCONHBr \rightleftharpoons PhCONH_2 + PhCONBr_2 \quad \dots (4)$$

The probable oxidizing species are, therefore, NBB, HOBr, $PhCONBr_2$ and AcOBr. Since the parent amide does not affect the rate, the participation of HOBr, $PhCONBr_2$, or AcOBr in the oxidation process can be ruled out. This also precludes the formation of a hypobromite ester in a pre-equilibrium step. Thus the reactive oxidizing species is NBB itself. This is in accordance with the earlier observations in the oxidations by NBB[11] and 3,5-dinitro-N-bromobenzamide[13]. However, in the oxidations by N-bromosuccinimide[14] and NBA[15], a retardation of rate on the addition of the parent amide was observed and HOBr was postulated as the reactive species.

The observed dependence on $[H^+]$ indicates that (i) the pre-equilibrium between the protonated and unprotonated forms of the reactant is rapid, (ii) the protonation constant is small and (iii) both the forms are reactive[16]. It is, therefore, suggested that NBB is protonated to give a stronger electophile and oxidant (Eq. 5) and both NBB and $NBBH^+$ are the reactive species.

$$PhCONHBr + H^+ \rightleftharpoons (PhCONH_2Br)^+ \quad \dots (5)$$

Aliphatic aldehydes are known to be hydrated to varying extents in aqueous solution and the equilibrium constant of the following reaction has been reported[17].
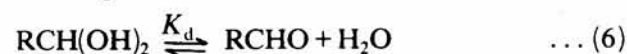
$$RCH(OH)_2 \xrightarrow{K_d} RCHO + H_2O \quad \dots (6)$$

Table 2 records the experimental rate constants, k_{ex}, for the oxidation of six aldehydes. From the values of k_{ex} and K_d, two sets of rate data were computed (Table 2). The values of k_{HY} were obtained by assuming that only the hydrated form participates in the oxidation process and the rate law has the following form (7).

$$Rate = k_{HY} [NBB][RCH(OH)_2] \quad \dots (7)$$

Similarly, the value of k_A were calculated assuming the participation of only the free aldehyde form, according to the rate law (8).

$$Rate = k_A[NBB][RCHO] \quad \dots (8)$$

The values of K_d, k_{ex}, k_{HY} and k_A, at 298 K, are recorded in Table 2. The rate of oxidation of aldehyde hydrates, k_{HY}, correlates very well ($r^2 = 0.9998$) with Taft's σ^* substituent constants[18] with the value of ρ^* being -2.38 at 298 K. On the other hand, no such correlation exists with the rates of oxidation of free aldehyde form. In particular, formaldehyde is found to be much more reactive as compared to other aldehydes. No satisfactory $\log k_A$ versus σ^* correlation was obtained even after neglecting the rate data for the oxidation of formaldehyde ($r^2 = 0.9305$).

If one assumes that the aldehydes react via the hydrate form [Eq. (6)], the rate of oxidation of formaldehyde compares favourably with the reactivities of other aldehydes. If the oxidation of free aldehydes [Eq. (7)] is assumed then formaldehyde is nearly 90 times more reactive than other aldehydes. This makes a direct hydrogen transfer between the free aldehyde and the oxidant highly unlikely. The existence of good structure-reactivity correlation in the oxidation of aldehyde hydrates further confirms that the aldehyde hydrate is involved in the oxidation process. Also, most aliphatic aldehydes exist predominantly in the hydrate form in aqueous solution.

From the rate constants, k_{HY}, at different temperature and the equilibrium constants, K_d, at different temperatures[17], activation parameters were calculated (Table 3).

The reaction constant, ρ^*, for the oxidation of aldehyde hydrates at different temperatures were evaluated (Table 4). The magnitude of reaction constant decreases with an increase in temperature, indicating a decrease in the selectivity with an increase in temperature.
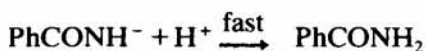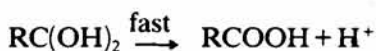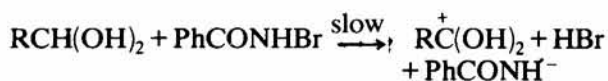
The increase in the rate with an increase in the polarity of the medium suggests that the transition state of the rate-determining step is more polar than the reactants. The solvent effect was analysed using Grunwald-Winstein[19] Eq. (9).

$$\log k = \log k_0 + m Y \qquad \ldots (9)$$

The plot of $\log k$ against Y was linear ($r^2 = 0.9886$) with $m = 0.66 \pm 0.04$. The value of m points to a transition state which is more polar than the reactant.

The value of primary kinetic isotope effect ($k_H / k_D = 3.89$ at 308 K) compares favourably with the values of 3.29 and 4.07 obtained in the oxidation by pyridinium hydrobromide perbromide[5] and pyridinium fluorochromate[7] respectively at 298 K. This confirmed that the aldehydic C—H bond is cleaved in the rate-determining step.
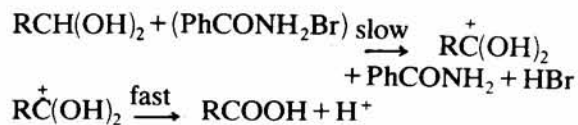
A hydrogen abstraction mechanism leading to the formation of free radicals may be discounted in view of the failure to induce polymerization of acrylonitrile. The negative reaction constant points to an electron-deficient carbon centre in the transition state. The large negative reaction constant and a substantial kinetic isotope effect suggest a considerable carbocation character in the transition state. Considerable charge separation in the transition state is supported by the observed value of m also. Therefore, the following mechanisms involving transfer of a hydride ion in the rate determining step from the aldehyde hydrate to the oxidant are suggested.

$$RCH(OH)_2 + PhCONHBr \xrightarrow{slow} R\overset{+}{C}(OH)_2 + HBr + PhCONH^-$$

$$RC(OH)_2 \xrightarrow{fast} RCOOH + H^+$$

$$PhCONH^- + H^+ \xrightarrow{fast} PhCONH_2$$

Scheme 1

Table 4—Temperature dependence of the reaction constant

Temp/K	298	303	308	313
ρ^*	-2.38 ± 0.02	-2.34 ± 0.02	-2.29 ± 0.03	-2.24 ± 0.03
r^2	0.9998	0.9997	0.9996	0.9998
sd	0.02	0.03	0.03	0.03

$$RCH(OH)_2 + (PhCONH_2Br) \xrightarrow{slow} R\overset{+}{C}(OH)_2 + PhCONH_2 + HBr$$

$$R\overset{+}{C}(OH)_2 \xrightarrow{fast} RCOOH + H^+$$

Scheme 2

The above mechanisms are supported by the observed negative entropy of activation. As the charge separation takes place in the transition state, the two charged ends become highly solvated. This results in an immobilization of a large number of solvent molecules, reflected in the loss of entropy.

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