KINETICS AND MECHANISM OF THE OXIDATION OF ALIPHATIC ALDEHYDES BY SODIUM N-BROMOARYLSULPHONAMIDES IN ACID SOLUTION

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Abstract - The oxidation of aliphatic aldehydes to the corresponding carboxylic acids by sodium N-bromoarylsulphonamides (N-bromoamines) is first order with respect to the oxidant, the aldehyde and hydrogen ions. In the oxidation of acetaldehyde at 298 K, the primary kinetic isotope effect, $k_{\rm H}/k_{\rm p}$ is 4.91 \pm 0.14 and the solvent isotope effect, $k(\rm H_2O)/k(\rm D_2O)$, is 0.43. A ddition of the parent sulphonamide does not affect the rate. The reduction of six substituted N-bromoamines exhibited a reaction constant of 1.22 at 298 K. (ArSO_NH_2Br)' is postulated as the reactive oxidising species. Separate-rate constants for the oxidation of aldehyde hydrate and free aldehyde hydrates correlate well with Taft's substituent constants with negative reaction constants. A mechanism involving hydride transfer from the aldehyde hydrate to the oxidation is proposed.

The kinetics of the oxidation of organic compounds by N-metallo-N-haloarylsulphonamides (N-haloamines) like bromamine-T (BAT), bromamine-B (BAB) have received considerable attention.¹ However, the oxidation of aliphatic aldehydes has not been studied, except for a couple of reports on the oxidation of acetaldehyde by chloramine-T.^{2,3} Moreover, no effort has been made to evaluate the role of hydrate form in the oxidation process. Hence this investigation was undertaken.

EXPERIMENTAL

<u>Materials</u>. Aldehydes were commercial products. The purity of aldehydes was checked by determining the bp/mp except in the case of formaldehyde where the aqueous solutions were standardised by the hypoiodite reagent. The bromoamines were prepared by adding bromine to alkaline suspension of the corresponding sulphonamides. The aqueous solutions of the N-bromoamines were standardized by iodometry and were stored in brown bottles. Perchloric acid (Merck) was used as a source of hydrogen ions. Deuterium oxide (99.4%) was supplied by BARC, Bombay.

Product Analysis. In a typical experiment, acetaldehyde (1.8 g, 0.04 mol) and BAT (0.98 g, 0.003 mol) were made upto 100 ml in aqueous perchloric acid (the total solution was 0.2 M in HC10₄). The mixture was kept in the dark for ca. 10 h to ensure completion of the reaction. The reaction mixtures was then extracted with ether (3×50 ml) and the ether extract was dried over anhydrous MgSO₄. The e ther solution was treated with 5 ml of thionyl chloride. The solvent was removed by evaporation. Dry methanol (3 ml) was then added and the HCl formed was removed in a current of dry air. The residue was dissolved in 100 ml of dry ether and the ester content was determined colorimetrically as ferric hydroximate by the procedure described by Hall and Schaefer. The analysis showed that the yield of acetic acid was 0.17 g (94%; based on the consumption of BAT).

Stoichiometry. The aldehyde (0.01 mol) and the N-bromoamine (0.05 mol) were made upto 100 ml in aqueous perchloric acid (the total solution was 0.03 M in $HC10_{4}$). When the reaction was complete, the residual N-bromoamine was determined iodometrically. Several determinations, with different aldehydes and N-bromoamines, indicated a 1:1 stoichiometry.

Kinetic Measurements. Pseudo-first-order conditions were attained by keeping an excess (10-fold or greater) of the aldehyde over the oxidant. The reactions were followed by determining the unreacted oxidant iodometrically for upto 65-70% of the reaction. The rate constants were computed from the linear productive operation in the linear productive operation. (r 0.99) plots of log [oxidant] against time. Duplicate kinetic runs showed that the rates were reproducible within $\pm 4\%$. The experimental rate constant, k_{ex} , was calculated by the relation $k_{ex} = k_1 / [RCHD]$ [H⁺].

RESULTS

The oxidation of the aldehydes by N-bromoamines yields the corresponding carboxylic acids. The overall reaction may be written as follows (eq. 1).

RCHO + ArSO₂NBr⁻ + H₂O \rightarrow RCOOH + ArSO₂NH₂ + Br⁻ (1) Since results are similar only representative data are given here.

Rate Laws. The oxidation of the aldehydes by N-bromoamines shows a first-order dependence on the oxidant both as regards time (evidenced by the good fits of log [oxidant] versus time plots) and concentration (evidenced by the first-order-rate coefficient being independent of initial [oxidant]. The reaction is also first order with respect to [aldehyde] and $[H^+]$. The rate date for the oxidation of acetaldehyde by BAT are summarised in Table 1.

Table 1. Rate constants for the oxidation of acetaldehyde by BAT at 298 K.

| [MeCHO] | 10 ³ [BAT] | [H ⁺] | 10 ⁵ k ₁ |
|----------------------|-----------------------|----------------------|--------------------------------|
| mol dm ⁻³ | mol dm ⁻³ | mol dm ⁻³ | s ⁻¹ |
| 0.10 | 2.0 | 0.10 | 1.58 |
| 0.10 | 5.0 | 0.10 | 1.51 |
| 0.10 | 7.5 | 0.10 | 1.53 |
| 0.10 | 10.0 | 0.10 | 1.47 |
| 0.10 | 15.0 | 0.10 | 1.52 |
| 0.20 | 5.0 | 0.10 | 3.07 |
| 0.30 | 5.0 | 0.10 | 4.47 |
| 0.40 | 5.0 | 0.10 | 6.10 |
| 0.50 | 5.0 | 0.10 | 7.42 |
| 0.70 | 5.0 | 0.10 | 10.7 |
| 1.00 | 5.0 | 0.10 | 15.2 |
| 0.20 | 5.0 | 0.05 | 1.53* |
| 0.20 | 5.0 | 0.20 | 6.08* |
| 0.20 | 5.0 | 0.30 | 9.20* |
| 0.20 | 5.0 | 0.40 | 12.1* |
| 0.20 | 5.0 | 0.50 | 15.4* |
| 0.20 | 5.0 | 0.75 | 23.0* |

$*1 = 1.0 \text{ mol dm}^{-3}$

Isotope Effects. To ascertain the importance of the cleavage of the aldehydic C-H bond in the rate determin-ing step, the oxidation $[^{2}H]$ acetaldehyde was studied. The primary kinetic isotope effect, k/k_d, is 4.91 ± 0.14 at 298 K (Table 2). The oxidation of formaldehyde and acetaldehyde by BAT was studied in D₂O. The overall deuterium content of the solvent was 95%, as $HC10_{4}$ was used as a source of hydrogen ions. The soslvent isotope effect, $k(H_2O)/k(d_2O)$, is 0.43 at 298 K (Table 3).

Table 2. Kinetic isotope effect in the oxidation of acetaldehyde by BAT at 298 K.

| [Aldehyde) | Туре | 10 ⁶ k1 | |
|----------------------|---|--------------------|--|
| mol dm ⁻³ | | s ⁻¹ | |
| 0.30 | MeCHO | 44.7 | |
| 0.40 | MeCHO | 61_0 | |
| 0.50 | MeCHO | 74.2 | |
| 0.10 | MeCDO | 3.12 | |
| 0.20 | MeCDO | 6.30 | |
| 0.30 | MeCDO | 9.05 | |
| | $10^4 k_{\rm H} = 15.0 \pm 0.2 {\rm dm}^{-6} {\rm mol}^2 {\rm s}^{-1}$ | | |
| | $10^4 k_{\rm D} = 3.06 \pm 0.09 {\rm dm}^{-6} {\rm mol}^2 {\rm s}^{-1}$ | L | |
| | $k_{\rm H}/k_{\rm D} = 4.91 \pm 0.14$ | | |

| | 10 ⁴ k _{ex} /d | $m^{-6} mol^2 s^{-1}$ | | |
|---------------|------------------------------------|-----------------------|--|--|
| Aldehyde | H ₂ O | D ₂ O | - K(H ₂ O/K(L ₂ O) | |
| HCHO MeCHO | 2.90 15.1 | 6.72 35.1 | 0.43 0.43 | |

Table 3. Solvent isotope effect in the oxidation of aldehydes by BAT at 298 K

 $k_{ex} = k_1 / [aldehyde] [H^+], [HCHO] 0.5 mol dm^{-3},$

 $[MeCHO] 0.2 \text{ mol dm}^{-3}, [H^+] 0.1 \text{ mol dm}^{-3}, [BAT] 0.005 \text{ mol dm}^{-3}$

Effect of Sulphonamide. Addition of the parent sulphonamide does not affect the rate of oxidation (Table 4).

Table 4. Effect of p-toluenesulphonamide on the oxidation of acetaldehyde by BAT.

| 10 ³ [TSA], м | 0.0 | 1.3 | 3.0 | 5.0 | 7.5 | 10.0 | |
|---|------|------|------|------|------|------|--|
| 10^{5} k ₁ , s ⁻¹ | 0.10 | 6.00 | 5.95 | 6.25 | 6.30 | 6.15 | |

[MeCHO] 0.40 mol dm⁻³, [BAT] 0.005 mol dm⁻³, [H⁺] 0.1 mol dm⁻³, temp. = 298 K

<u>Effect of substituents.</u> The rates of reduction of a series of six sodium N-bromoarylsulphonamides by acetaldehyde were obtained (Table 5). The rates exhibited excellent correlation with Hammett's substituent constants (r = 0.9996). The value of the reaction constants is 1.22 at 298 K.

Table 5. Rates of oxidation of acetaldehyde by substituted sodium N-bromosulphonamides at 298 K.

| Substituent | н | p - Me | p - Cl | p-NO2 | m-NO ₂ | p-DMe |
|-------------------------------------|------|--------|--------|-------|-------------------|-------|
| 10 ³ kex s ⁻¹ | 2.53 | 1.51 | 5.12 | 22.0 | 18.8 | 1.20 |

 $k_{ex} = k_1 / [MeCHO] [H^+]$

Effect of Temperature. The rates of the oxidation of the seven aldehydes were obtained at different temperatures between 298 K and 318 K.

DISCUSSION

A knowledge of the possible species of both the oxidant and the substrate under the experimental conditions and the choice of the correct or most probable active species would be helpful in proposing a suitable mechanism.

BAT and other N-bromoamines behave like strong electrolytes in aqueous solution and dissociate into ions (eq.2). The anion picks up a proton in a acid solution to give the free acid, N-bromoarylsulphonamide (3). Although the free acid has not been isolated, there are evidences for its existence. The free acid undergoes disproportionation and hydrolysis eqs. 4-6). Finally hypobromous acid ionises according to reaction (7).

| ArSO ₂ NBrNa | \longrightarrow | ArSO ₂ NBr + Na | (2) |
|--|-------------------|--|-----|
| $ArSO_2NBr^+ + H_3O^+$ | ~` | $ArSO_2NHBr + H_2O$ | (3) |
| 2ArSO ₂ NHBr | <u> </u> | ArSO ₂ NH ₂ + ArSO ₂ NBr ₂ | (4) |
| ArSO ₂ NHBr + H ₂ O | | ArSO ₂ NH ₂ + HOBr | (5) |
| ArSO ₂ NBr ₂ + 2H ₂ O | <u> </u> | ArSO ₂ NH ₂ + 2HOBr | (6) |
| HOBr + H ₂ O | <u> </u> | H_O ⁺ + OBr ⁻ | (7) |

These equilibria have been studied quantitatively in the case of corresponding N-chloro compounds.⁷⁻⁹ The pK_a of the free acid, PhSO₂NHBr is 4.95 at 298 K.

The probable oxidising species in an acidified solution of a N-Bromoamine are $ArSO_2NHBr$. HOBr, $ArSO_2NBr$, and $ArSO_2NBr_2$. The dibromamine species can be ruled out as an oxidising species in view of the strict first order dependence of the reaction rate on the N-bromoamine. The absence of any effect of the sulphonamide on the rate also precludes both HOBr and the dibromamine species. This leaves $ArSO_2NHBr$ and its anion as the probable oxidising species. However, $ArSO_2NHBr$ is a weak acid¹ and in the acidity range used, almost all of it will be in the form of the free acid. Gunasekaran and Venkatasubramanian¹ in the oxidations by bromamine-T, concluded that the neutral N-bromosulphonamide is the reactive species. They explained the observed first order dependence on acidity on the basis of the protonation of the anion (eq. 8).

$$\operatorname{ArSO}_2\operatorname{NBr}^- + \operatorname{H}_3O^+ \longrightarrow \operatorname{ArSO}_2\operatorname{NHBr} + \operatorname{H}_2O$$
 (8)

However, as mentioned above, under our reaction conditions almost all of the N-bromoamine will exist in the form of thefree acid and a further increase in the acidity will not cause any further increase in the concentration of ArSO₂NHBr. Thus the assumption of the earlier workers¹¹ that the neutral N-halosulphonamide is the reactive species is in error. The linear dependence of the reaction rate on acidity can be explained by assuming a further protonation of ArSO₂NHBr (9).

$$ArSO_2NHBr + H_3O^+ \qquad \longrightarrow \qquad ArSO_2NH_2Br + H_2O \qquad (9)$$

Recently, evidence has been found for the formation of such protonated species by radiochemical method.

Aliphatic aldehydes are extensively hydrated in aqueous solutions and many oxidation reactions proceed via the hydrate form.

Table 6 records the experimental rate constants, k_{d} , for the oxidation of the aldehydes by BAT. The aldehyde hydrate dissociation constant, K_{d} , pertaining to reaction (10), are also given.

From the values of k_{ex} and K_{d} , two sets of rate constants were computed. The value of k_{Hy} was obtained by assuming that only the hydrate form will appear in the rate law (11)

RCHO+H2O

Rate =
$$k_{H_1}$$
 [BAT] [RCH(OH)₂] [H⁺]

≥

Similarly, the values of k_A were calculated using the concentration of free aldehydes according to the rate law (12)

Rate =
$$k_{A}$$
 [BAT] [RCHO] [H⁺]

RCH(OH),

 $k_{\rm Hy}$ and $k_{\rm A}$ represent the specific rate constants for the oxidation of the aldehyde hydrate and the free aldehyde respectively.

| Table 6. Rate constants for the oxid | lation of aliphatic | aldehydes by BAT | at 298 K. |
|--------------------------------------|---------------------|------------------|-----------|
|--------------------------------------|---------------------|------------------|-----------|

| Aldehyde | κa | Rate const | 1 | |
|----------|----------------------|---------------------------------|---------------------------------|--------------------------------|
| | a | 10 ⁸ k _{ex} | 10 ⁸ k _{Hy} | 10 ⁴ k _A |
| НСНО | 5.5×10 ⁻⁴ | 29000 | 29000 | 5800 |
| MeCHO | 0.67 | 151000 | 252000 | 37.8 |
| EtCHO | 1.4 | 161000 | 384000 | 27.8 |
| PrCHO | 2.1 | 134000 | 418000 | 19.7 |
| Pri CHO | 2.3 | 133000 | 444000 | 19.0 |
| CICH_CHO | 0.027 | 2410 | 2470 | 9.21 |
| сі ссно | 3.6x10 ⁻² | 2.35 | 2.35 | 6.52 |

The rates of oxidation of the aldehyde hydrates correlate very well in Taft's equation, 16^{16} with negative reaction constants (Table 7). On the other hand, no such correlation exists between log k and . In particular, formaldehyde is found to be much more reactive as compared to other aldehydes. No satisfacto ry correlation was obtained in Taft's equation even if the rate data of formaldehyde were not considered.

Table 7. Temperature dependence of the reaction constant of the oxidation of RCH(OH)2 by BAT

| Temp. / K | 298 | 303 | 308 | 303 | 318 |
|-------------------------------|--------|--------|--------|--------|--------|
| ρ | - 1.89 | - 1.82 | - 1.77 | - 1.73 | - 1.67 |
| Coefficient of correlation(r) | 0.9998 | 0.9997 | 0.9979 | 0.9985 | 0.9991 |

(11)

(12)

(10)

If one assumes that the aldehydes react via their hydrate form (eq. 11) the rate of oxidation of formaldehyde compares favourably with the reactivities of other aldehydes. If the oxidation of free aldehydes is assumed (eq. 12), then formaldehyde is nearly 300 times more reactive than the other aldehydes. This makes a direct hydrogen transfer between the free aldehyde and the oxident highly unlikely. The existence of a good structure reactivity correlation further confirms that the aldehyde hydrate is involved in the oxidation process. The rate of oxidation of the aldehyde hydrates at different temperatures was calculated and the activation parameters were evaluated (Table 8). The average errors in the values of ΔH^2 , ΔS^2 and ΔG^2 (at 298 K) are \pm 1.5 kJ mol⁻¹, \pm 3 J mol⁻¹ K⁻¹ and \pm 2 kJ mol⁻¹ respectively.

Table 8. Rate constants and activation parameters of the oxidation of aldehyde hydrates, RCH(OH), by BAT

| R | 10 ⁸ k | Hy ^{/dm⁻⁶} | mol ² s ⁻¹ | l | ∆ н [*] | ∆ S* | ∆ G* |
|-------------------|-------------------|--------------------------------|----------------------------------|---------|-------------------------|-------------------------------------|----------------------|
| K | 303K | 308K | 313K | 318K | kJ mol ⁻¹ | J mol ⁻¹ K ⁻¹ | kJ mol ⁻¹ |
| н | 46600 | 66500 | 99800 | 145000 | 60.0 | -110 | 92.9 |
| Me | 36400 | 512000 | 694000 | 938000 | 49.9 | -129 | 87.6 |
| Et | 563000 | 753000 | 1070000 | 1360000 | 47.3 | -131 | 86.6 |
| Pr. | 606000 | 810000 | 1110000 | 1450000 | 46.0 | -135 | 86.3 |
| Pr | 629000 | 836000 | 1150000 | 1580000 | 46.8 | -132 | 86.3 |
| CICI | H_ 4350 | 6440 | 10600 | 16200 | 75.0 | -95 | 98.9 |
| сı ₃ с | 4.96 | 9.38 | 16.8 | 31.6 | 98.2 | -59 | 116 |

The presence of a substantial deuterium isotope effect shows that the aldehydic C-H bond is cleaved in the rate-determining step.

 D_3O^+ is a stronger acid than H_3O^+ ,¹⁷ and the rate of an acid-catalysed reaction, involving a protonation pre-equilibrium is expected to be faster in D_2O than in H_2O . Labile hydrogens like those present in hydroxyl groups are rapidly exchanged in D_2O and if the -OH group is involved in the rate-determining steps, O-H/D-D isotope effect comes into play. This may cancel the rate-enhancement due to D_2O or even results in a slower rate in D_2O . The value of observed solvent isotope effect indicates that the hydroxyl group is not involved in the rate-determining step.

The large negative value of the reaction constant suggests that in the transition state positive charge is localized on the carbon atom bearing the substituents. It thus approaches a carbocation in character. The observed results thus indicate a hydride ion transfer from the aldehyde hydrate molecule to (ArSO₂NH₂Br) in the rate-determining step.

$$R - C - H + Br - NH_2 SO_2 Ar \longrightarrow RC^+(OH)_2 + HBr$$

$$i + ArSO_2 NH_2$$
(13)

RC+(OH), $RCOOH + H^+$ (14)

The positive reaction constant obtained in the reduction of substituted N-bromoamines also supports the above mechanism. The magnitude of the reaction constant is low. This is because the observed reaction constant is a composite value of the effect of substituents on reactions (9) and (13). The electronic requirements of the protonation and the hydride ion acceptance are in opposite direction. In the oxidation of sulphides by substituted N_{12} chloroamines, in buffered solutions where $ArSO_{2}NHCl$ is the reactive species, the reaction constant is 1.76.

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REFERENCES

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REFERENCES

- 1.
- 2.
- 3.
- 4.
- 5.
- K.K. Banerji, D.S. Mahadevappa and B. Jayaram, <u>J.Scient.Ind. Res.</u>, <u>46</u>, 65 (1987).
 D.S. Mahadevappa and N.B. Jadav and H.M.K. Naidu, <u>J. Indian Chem. Soc.</u>, <u>58</u>, 454 (1981).
 M.C. Agarwal and S.P. Mushran, <u>Z. Naturforsch</u>, <u>27B</u>, 401 (1972).
 J. Mitchell Jr., <u>Organic Analysis</u>, Vol 1, p. 269. Interscience, New York, 1953.
 F.E. Hardy, <u>J.Chem. Soc.</u> (8), 1899 (1971): Petromek and H. Veera, <u>Chem. Listy</u>, <u>72</u>, 1729 (1958).
 R.T. Hall and W.E. Schaefer, <u>Organic Analysis</u> (Edited by Mitchell), Vol. II, p. 55, Interscience, New York, 1954. 6. New York, 1954.
- 7. J.C. Morris, J.A. Salazar and M.A. Wineman, J.Am.Chem. Soc., 70, 2036 (1948).

- 8.
- 9.
- F.C. Soper, <u>J. Chem. Soc.</u>, 1899 (1924). E. Bishop and V.J. Jennings, <u>Talanta</u>, <u>1</u>, 97 (1958). F.E. Hardy and V.J. Johnston, <u>J. Chem. Soc. Perkin Trans. II</u>, 742 (1973). 10.
- F.E. Hardy and V.J. Johnston, J. Chem. Soc. Perkin Trans. II, 742 (1973).
 S. Gunasekeran and N. Venkatasubramanian, J. Chem. Soc. Perkin Trans. II, 949 (1983); Indian J. Chem. Sec. A, 22, 211 (1983).
 S.S. Narayanna and V.R.S. Rao. Radiochem. Acta. 32, 211 (1983).
 A.L. Jain and K.K. Banerji, J.Chem. Rev. (51, 60 (1983). (M), 678 (1983).
 J. Rocek and C.S. Ng, J. Org. Chem., 38, 3345 (1973).
 R.P. Bell, Adv. Phys. Org. Chem., 4, 1 (1966).
 K.B. Wiberg, Physical Organic Chemistry, p. 415, Wiley New York, 1964.
 E.K. Thornton and E.R. Thornton, Isotope Effects in Chemical Reactions (Edited by Colline and Bowman). p. 267, Nostrand, New York, 1970.
 F. Puff and A. Kursman, J. Chem. Soc. Perkin Trans. II, 509 (1975). 11.
- 12.
- 13.
- 14.
- 15.
- 16.
- 17.
- 18. F. Ruff and A. Kucsman, J. Chem. Soc. Perkin Trans. II, 509 (1975).