

## Kinetics of Os(VIII)-catalysed Oxidation of Benzaldehyde & Substituted Benzaldehydes by Chloramine-T

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The kinetics of OsO<sub>4</sub>-catalysed oxidation of benzaldehyde and substituted benzaldehydes by chloramine-T in aqueous and aqueous *t*-butanol under alkaline conditions has been investigated. The order with respect to CAT and OsO<sub>4</sub> is one each. The dependence on [OH<sup>-</sup>] is inverse first order. The reactions are zero order in substrate. The complete absence of substituent effect is a novel feature of these oxidations. A suitable mechanism involving a radical intermediate is postulated.

M USHRAN and coworkers<sup>1</sup> have made extensive investigations on chloramine-T (CAT) oxidation of organic molecules. Non-enolizable aldehydes like benzaldehyde are inert to CAT, but reactions are facile in the presence of OsO<sub>4</sub>. Since no work has been done regarding structure and reactivity correlation in benzaldehyde oxidation by CAT, it was thought worthwhile to study the kinetics of OsO<sub>4</sub>-catalysed oxidation of benzaldehyde and substituted benzaldehydes by CAT in aqueous and aqueous *t*-butanol systems under alkaline conditions.

### Materials and Methods

All the aldehydes used were of AR grade and were redistilled or recrystallized before use. CAT and OsO<sub>4</sub> were also of AR grade. Kinetic runs were followed by estimating CAT by standard iodometric method. All the runs were made in duplicate and the results are reproducible within ±3%. Variation of ionic strength by adding salts like KCl did not have any significant effect on the reaction rate.

### Results and Discussion

*Dependence on [substrate]* — Rate constants at varying [substrate] recorded in Table 1 show the zero-order dependence on the substrate.

*Dependence on [CAT]* — The order with respect to CAT is one as seen from the linearity of log [CAT] versus time plots. All the rate constants computed are first order rate constants with respect to CAT.

*Dependence on [OsO<sub>4</sub>]* — The plots of log *k*<sub>1</sub> versus log [OsO<sub>4</sub>] are linear with the slope of unity, confirming first order dependence on [OsO<sub>4</sub>] (Table 2).

*Dependence on [alkali]* — The plots of *k*<sub>1</sub> versus 1/[OH<sup>-</sup>] are linear with the slope of unity, indicating that the reaction has inverse first order dependence on [OH<sup>-</sup>] (Table 3). The rate can be expressed by the relation (1).

$$-d[\text{CAT}]/dt = k[\text{CAT}][\text{OsO}_4][\text{OH}^-]^{-1} \quad \dots(1)$$

*Structure and reactivity* — All the aldehydes with both electron-releasing and electron-withdrawing groups are oxidized essentially at the same rate at

TABLE 1 — EFFECT OF VARYING [SUBSTRATE] ON THE REACTION RATE

{[NaOH] = 0.108M; [OsO<sub>4</sub>] = 1.17 × 10<sup>-3</sup>M; [CAT] = 0.0005M; temp. = 60°}

| [Substrate] 10 <sup>3</sup> M | 10 <sup>3</sup> <i>k</i> <sub>1</sub> (min <sup>-1</sup> ) |
|-------------------------------|--|
| BENZALDEHYDE                  |  |
| 2.0                           | 5.23   |
| 5.0                           | 5.40   |
| 7.0                           | 5.53   |
| <i>o</i> -CHLOROBENZALDEHYDE  |  |
| 1.0                           | 5.00   |
| 2.0                           | 4.70   |
| 3.0                           | 5.20   |
| <i>p</i> -NITROBENZALDEHYDE   |  |
| 0.8                           | 5.20   |
| 1.6                           | 5.42   |
| 2.0                           | 5.34   |

TABLE 2 — EFFECT OF VARYING [OsO<sub>4</sub>] IN THE CAT OXIDATION OF AROMATIC ALDEHYDES

(Substrate: 0.002M; CAT = 0.0005M; NaOH = 0.025M; temp.: 60°C)

| [OsO <sub>4</sub> ] × 10 <sup>5</sup> M | 10 <sup>3</sup> <i>k</i> <sub>1</sub> (min <sup>-1</sup> ) |
|---|--|
| <i>p</i> -NITROBENZALDEHYDE             |  |
| 0.780                                   | 9.2  |
| 0.975                                   | 12.2   |
| 1.170                                   | 18.0   |
| 1.365                                   | 19.0   |
| 1.560                                   | 21.0   |
| <i>m</i> -BROMOBENZALDEHYDE             |  |
| 0.780                                   | 8.6  |
| 0.975                                   | 11.4   |
| 1.170                                   | 17.8   |
| 1.560                                   | 21.0   |
| <i>o</i> -CHLOROBENZALDEHYDE            |  |
| 0.780                                   | 8.4  |
| 0.975                                   | 11.3   |
| 1.170                                   | 18.0   |
| 1.560                                   | 20.0   |

TABLE 3 — DEPENDENCE ON  $[\text{OH}^-]$  IN THE CAT OXIDATION OF AROMATIC ALDEHYDES

$\{[\text{Substrate}] = 0.002M; [\text{CAT}] = 0.0005M; [\text{OsO}_4] = 1.17 \times 10^{-5}M; \text{temp.: } 60^\circ\}$

| $[\text{OH}^-] (M)$          | $10^3 k_1 (\text{min}^{-1})$ | $[\text{OH}^-] (M)$ | $10^3 k_1 (\text{min}^{-1})$ |
|------------------------------|------------------------------|---------------------|------------------------------|
| BENZALDEHYDE                 |                              |                     |                              |
| 0.256                        | 2.8                          | 0.180               | 3.1                          |
| 0.182                        | 3.1                          | 0.108               | 5.2                          |
| 0.108                        | 5.2                          | 0.055               | 8.4                          |
| 0.055                        | 8.3                          |                     |                              |
| <i>p</i> -BROMOBENZALDEHYDE  |                              |                     |                              |
|                              |                              | 0.180               | 3.0                          |
|                              |                              | 0.108               | 5.2                          |
|                              |                              | 0.055               | 8.5                          |
| <i>m</i> -NITROBENZALDEHYDE  |                              |                     |                              |
|                              |                              | 0.180               | 3.0                          |
|                              |                              | 0.108               | 5.2                          |
|                              |                              | 0.055               | 8.5                          |
| <i>m</i> -BROMOBENZALDEHYDE  |                              |                     |                              |
|                              |                              | 0.220               | 3.0                          |
|                              |                              | 0.180               | 3.2                          |
|                              |                              | 0.108               | 5.7                          |
|                              |                              | 0.055               | 8.1                          |
| <i>p</i> -NITROBENZALDEHYDE  |                              |                     |                              |
|                              |                              | 0.180               | 3.1                          |
|                              |                              | 0.108               | 5.3                          |
|                              |                              | 0.055               | 8.3                          |
| <i>p</i> -CHLOROBENZALDEHYDE |                              |                     |                              |
|                              |                              | 0.180               | 3.1                          |
|                              |                              | 0.108               | 5.8                          |
|                              |                              | 0.055               | 8.3                          |
| <i>m</i> -CHLOROBENZALDEHYDE |                              |                     |                              |
|                              |                              | 0.180               | 3.2                          |
|                              |                              | 0.108               | 5.2                          |
|                              |                              | 0.055               | 8.3                          |

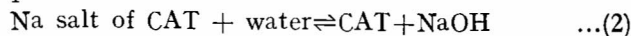
various [substrate]. This shows that it is a perfect zero order reaction with respect to substrate.

**Effect of added EDTA** — Addition of EDTA retards the rate of oxidation of aldehydes up to  $0.001M$  [EDTA]. Above this concentration of EDTA, the oxidation of benzaldehyde is completely inhibited. It seems that at  $[\text{EDTA}] > 0.001M$  the aldehydes form an unreactive complex with EDTA. In the case of *p*-nitrobenzaldehyde, rate constants ( $k_1$ ) are calculated to be  $3.6$  and  $2.8 \times 10^{-3} \text{ min}^{-1}$  respectively at  $[\text{EDTA}] = 0.55$ , and  $0.70 \times 10^{-3}M$ .

**Effect of added salt** — The first order rate constants ( $k_1 \text{ min}^{-1}$ ) without KCl and with KCl ( $0.011$ - $0.02M$ ) for *p*-nitrobenzaldehyde are  $0.0083$ ,  $0.00765$  and  $0.0075$  respectively.

**Solvent effect** — Addition of *t*-butanol to aqueous system in these reactions perceptibly retards the oxidation (Table 4). This seems to be quite in consonance with dipole-dipole reactions. The plots of  $\log k_1$  versus  $1/D$  are linear.

**Mechanism** — The inverse dependence on alkali has been rationalized earlier<sup>2</sup> on the finding that it is not the sodium salt of CAT but CAT itself that takes part in the reaction. Hence, reaction (2) was postulated



to account for the inverse dependence on  $[\text{OH}^-]$ . But we feel that a more rational explanation would be that  $\text{OsO}_4$  molecules probably are able to form complex with CAT acquiring octahedral geometry whereas the species like  $[\text{OsO}_4(\text{OH})(\text{H}_2\text{O})]^{1-}$  or  $[\text{OsO}_4(\text{OH}_2)]^{2-}$  (equilibria 3 and 4) possessing already octahedral geometry may not be able to form complex effectively with CAT. Perhaps it is more realistic to postulate  $\text{OsO}_4$  as the active species

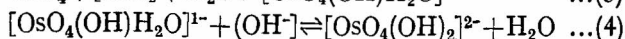
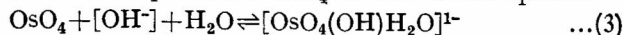
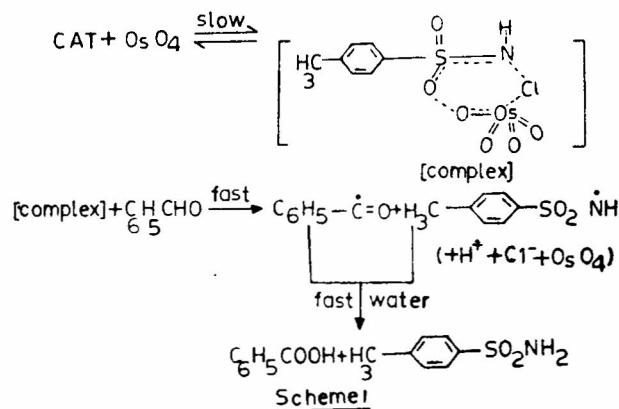


TABLE 4 — SOLVENT EFFECT ON CAT OXIDATION OF AROMATIC ALDEHYDES

$\{[\text{Substrate}] = 0.002M; [\text{CAT}] = 0.0005M; [\text{NaOH}] = 0.05M; [\text{OsO}_4] = 1.17 \times 10^{-5}M; \text{temp.: } 60^\circ\}$

| <i>t</i> -Butanol (% v/v)    | $10^3 k_1 (\text{min}^{-1})$ |
|------------------------------|------------------------------|
| <i>o</i> -CHLOROBENZALDEHYDE |                              |
| 0                            | 8.4                          |
| 20                           | 5.0                          |
| 30                           | 3.7                          |
| <i>m</i> -CHLOROBENZALDEHYDE |                              |
| 20                           | 4.9                          |
| 30                           | 3.6                          |
| <i>m</i> -BROMOBENZALDEHYDE  |                              |
| 20                           | 4.9                          |
| 30                           | 3.6                          |



The concentration of free  $\text{OsO}_4$  which is postulated to be the reacting species decreases with increasing  $[\text{OH}^-]$ . Hence the inverse first order dependence with respect to  $[\text{OH}^-]$ .

The reaction sequence as shown in Scheme 1 is envisaged on analogy with the work of Mushran and coworkers on aliphatic aldehydes<sup>2</sup>.

Though we are in general agreement with the Scheme 1 it is doubtful whether the loss of the hydrogen as  $\text{H}^-$  is plausible, since loss of  $\text{H}^-$  should have been reflected in the substituent effect in the present oxidation process, for the reason that benzaldehyde and *p*-nitrobenzaldehyde have different capacity for liberating a  $\text{H}^-$  even though it is taken up in a fast step. In the oxidation of aldehydes by  $\text{Cr(VI)}$ <sup>3</sup> and  $\text{Mn(VII)}$ <sup>4</sup>, there is first order dependence on [substrate], and  $\text{H}^-$  loss has been invoked which appears likely. However, the complete absence of substituent effect in the present oxidation reactions indicates that the loss of hydrogen as  $\text{H}^-$  by a single electron transfer rather than as  $\text{H}^-$  in the transition state is more likely. The products are the corresponding carboxylic acids.

## References

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