# Structure-reactivity relation in the oxidation of some aliphatic aldehydes by Tripropylammonium chlorochromate

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***Abstract***

*The oxidation of six aliphatic aldehydes by tripropylammonium chlorochromate (TPACC) in dimethyl sulfoxide (DMSO) leads to the formation of corresponding carboxylic acids. The reaction is of first order each in TPACC. A Michaelis-Menten type of kinetics is observed with respect to the aldehydes. The reaction is catalysed by hydrogen ions. The hydrogen-ion dependence has the form: $k_{obs} = a + b[H^+]$. The oxidation of deuteriated acetaldehyde MeCDO exhibited a substantial primary kinetic isotope effect ($k_H/k_D = 5.75$ at 298 K).*

*The oxidation of acetaldehyde has been studied in nineteen different organic solvents. The solvent effect has been analysed using Taft's and Swain's multiparametric equations. The rate constants correlate well with Taft's $\sigma^*$ values, reaction constants being negative. A mechanism involving transfer of hydride ion has been suggested.*

**Keywords:** Aldehydes, correlation analysis, halochromate, kinetics, mechanism, oxidation.

## Introduction

A large number of halochromates have already been used as mild and selective oxidizing reagents in synthetic organic chemistry[2,4,9,14,24]. Tripropylammonium chlorochromate (TPACC) is also one of such compounds used for the oxidation of primary and secondary alcohols[13]. The kinetic and mechanistic aspects of the oxidation by complexed Cr(VI) species and several studies on halochromates including TPACC have already been reported.[6,21,23,27] In continuation of our earlier work, we report here the kinetics and mechanism of oxidation of six aliphatic aldehydes by TPACC in dimethylsulphoxide (DMSO) as solvent. The mechanistic aspects are also discussed.

## Material and Methods

**Materials**: TPACC was prepared by the reported method[13] and its purity was checked by iodometric determinations. Solutions of formaldehyde were prepared by heating para-formaldehyde and passing its vapours in DMSO. The amount of HCHO in DMSO was determined by chromotropic acid method[22]. Other aldehydes were commercial products and were used as such. p-Toluenesulphonic acid (TsOH) was used as a source of hydrogen ions. Deuteriated acetaldehyde (MeCDO) was obtained from Sigma Chemicals. Solvents were purified by their usual methods[26].

**Product Analysis**: The product analysis was carried out under kinetic conditions. In a typical experiment, acetaldehyde (4.4 g, 0.1mol) and TPACC (2.79 g, 0.01mol) were dissolved in DMSO (100 ml) and the reaction mixture was allowed to stand for *ca*. ≈ 24 to ensure completion of the reaction. It was then rendered alkaline with NaOH, filtered and the filtrate was reduced to dryness under pressure. The residue was acidified with perchloric acid and extracted with diethyl ether (5%, 50 ml). The ether extract was dried ($MgSO_4$) and treated with 10 ml of thionyl chloride. The solvent was allowed to evaporate.

Dry methanol (7 ml) was added and the HCl formed was removed in a current of dry air. The residue was dissolved in diethyl ether (200 ml) and the ester content was determined colorimetrically as Fe (III) hydroxymate by the procedure of Hall and Schaefer[15]. Several determinations indicated a 1:1 stoichiometry. The oxidation state of chromium in a completely reduced reaction mixture determined by iodometric titrations was 3.95 ± 0.1.

**Kinetic Measurements**: Pseudo-first-order conditions were attained by keeping an excess (×15 or greater) of the [aldehyde] over [TPACC]. The solvent was DMSO unless mentioned otherwise. All reactions were carried out in flasks blackened from the outside to prevent any photochemical reactions. The reactions were carried out at constant temperature (±0.1 K) and were followed up to 80% of the extent of reaction by monitoring the decrease in [TPACC] at 375 nm. The pseudo-first-order rate constant $k_{obs}$ was computed from the linear least-squares plot of log [TPACC] versus time. Duplicate runs showed that the rate constants were reproducible to within ±3%. The second order rate constant $k_2$ was calculated from the relation: $k_2 = k_{obs}/[\text{aldehyde}]$.

## Results and Discussion

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

**Stoichiometry**: The oxidation of aliphatic aldehydes by TPACC leads to the formation of corresponding carboxylic acids. The overall reaction may be written as:

$$R - CHO + CrO_2ClO^-N^+(C_3H_7)_3 \longrightarrow RCOOH + CrOClO^- N^+(C_3H_7)_3 \quad (1)$$

TPACC undergoes two-electron change. This is in accordance with the earlier observations with structurally similar other halochromates also. It has already been shown that both pyridinium chlorochromate (PCC)[7] and pyridinium fluorochromate (PFC)[5] act as two electron oxidants and are reduced to chromium (IV) species by determining the oxidation state of chromium by magnetic susceptibility, ESR and IR studies.

**Rate-Laws**: The reactions are of first order with respect to TPACC. Further, the pseudo-first order rate constant, $k_{obs}$ is independent of the initial concentration of TPACC. The reaction rate increases with increase in the concentration of the aldehydes but not linearly (Table 1). The figure 1 depicts a typical kinetic run. A plot of $1/k_{obs}$ against 1/[aldehyde] is linear ($r > 0.995$) with an intercept on the rate-ordinate. Thus, Michaelis-Menten type kinetics is observed with respect to the aldehydes. This leads to the postulation of following overall mechanism (2) and (3) and rate law (4).

$$\text{Aldehyde} + \text{TPACC} \underset{}{\overset{K}{\leftrightarrows}} [\text{Complex}] \quad (2)$$

$$[\text{Complex}] \xrightarrow{k_2} \text{Products} \quad (3)$$

$$\text{Rate} = k_2 K [\text{Aldehyde}] [\text{TPACC}] / (1 + K [\text{Aldehyde}]) \quad (4)$$

The dependence of reaction rate on the reductant concentration was studied at different temperatures and the values of K and $k_2$ were evaluated from the double reciprocal plots (Figure 2).

The thermodynamic parameters of the complex formation and activation parameters of the decomposition of the complexes were calculated from the values of K and $k_2$ respectively at different temperatures (Tables 2 and 3).

**Induced polymerization of acrylonitrile/ Test for free radicals**: The oxidation of aldehydes in an atmosphere of nitrogen failed to induce polymerisation of acrylonitrile. Further, the addition of acrylonitrile did not affect the rate. This indicates that a one-electron oxidation, giving rise to free radicals is unlikely in the present reaction (Table 1). To further confirm the absence of free radicals in the reaction pathway, the reaction was carried out in the presence of 0.05 mol $dm^{-3}$ of 2,6-di-t-butyl-4-methylphenol (butylated hydroxytoluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively.

**Kinetic Isotope Effect**: 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 3).

**Effect of acidity**: The reaction is catalysed by hydrogen ions (Table 4). The hydrogen- ion dependence has the following form $k_{obs} = a + b[H^+]$. The values of *a* and *b* for acetaldehyde are $12.6 \pm 0.48 \times 10^{-4}$ $s^{-1}$ and $21.8 \pm 0.79 \times 10^{-4}$ $mol^{-1}$ $dm^3$ $s^{-1}$ respectively ($r^2 = 0.9948$).

$$\text{Rate} = k_2 [\text{TPACC}] [\text{Aldehyde}] + k_3 [\text{TPACC}] [\text{Aldehyde}] [\text{TsOH}] \quad (5)$$

**Effect of solvents**: The oxidation of acetaldehyde was studied in 19 different organic solvents. The choice of solvents was limited due to the solubility of TPACC and its reaction with primary and secondary alcohols. There was no reaction with the solvents chosen. The kinetics was similar in all the solvents. The values $k_2$ are recorded in table 5.

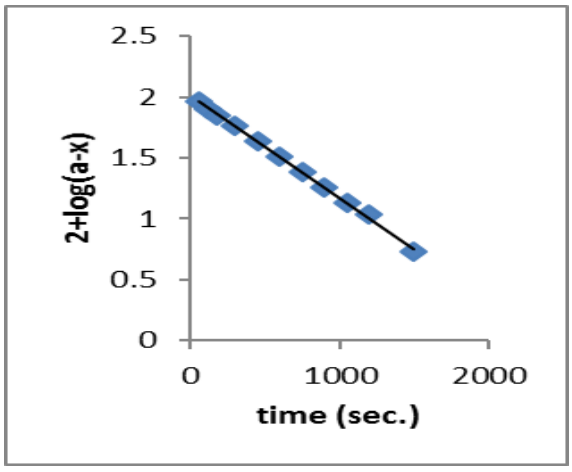



**Figure 1: Oxidation of acetaldehyde by TPACC: A typical kinetic run**

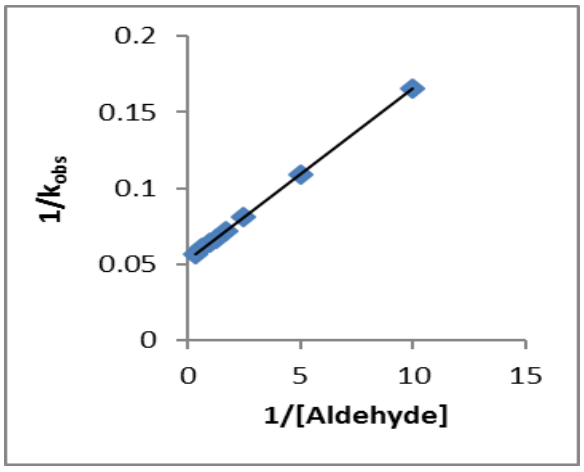



**Figure 2: Oxidation of acetaldehyde by TPACC: A double reciprocal plot**

**Table 1**
**Rate constants for the oxidation of acetaldehyde by TPACC at 288 K**

| $10^3$ [TPACC] / mol dm$^{-3}$ | [Aldehyde] / mol dm$^{-3}$ | $10^4$ $k_{obs}$ / s$^{-1}$ |
|---|---|---|
| 1.00 | 0.10 | 6.03 |
| 1.00 | 0.20 | 9.14 |
| 1.00 | 0.40 | 12.3 |
| 1.00 | 0.60 | 13.9 |
| 1.00 | 0.80 | 14.9 |
| 1.00 | 1.00 | 15.6 |
| 1.00 | 1.50 | 16.5 |
| 1.00 | 3.00 | 17.6 |
| 2.00 | 0.20 | 9.36 |
| 4.00 | 0.20 | 9.09 |
| 6.00 | 0.20 | 9.27 |
| 8.00 | 0.20 | 9.00 |
| 1.00 | 0.40 | 12.6[*] |
| [a] contained 0.001 M acrylonitrile | | |

**Table 2**
**Formation constants and thermodynamic parameters of the aliphatic aldehydes – TPACC complexes.**

| K (dm$^3$ mol$^{-1}$) | | | | | $-\Delta H^*$ | $-\Delta S^*$ | $-\Delta G^*$ |
|---|---|---|---|---|---|---|---|
| Aldehyde | 288 K | 298 K | 308 K | 318 K | (kJ mol$^{-1}$) | (J mol$^{-1}$K$^{-1}$) | (kJ mol$^{-1}$) |
| H | 5.94 | 5.35 | 4.68 | 4.08 | 12.1±0.4 | 19±1 | 6.61±0.3 |
| Me | 6.12 | 5.46 | 4.86 | 4.26 | 11.6±0.3 | 17±1 | 6.69±0.2 |
| Et | 5.85 | 5.25 | 4.59 | 3.99 | 12.3±0.4 | 20±2 | 6.57±0.4 |
| Pr | 6.03 | 5.45 | 4.77 | 4.17 | 11.9±0.4 | 18±1 | 6.66±0.3 |
| Pr$^i$ | 5.58 | 4.93 | 4.32 | 3.71 | 12.8±0.4 | 22±1 | 6.42±0.3 |
| $ClCH_2$ | 5.67 | 5.04 | 4.45 | 3.78 | 12.7±0.5 | 21±2 | 6.48±0.4 |
| MeCDO | 5.76 | 5.15 | 4.50 | 3.90 | 12.4±0.4 | 20±1 | 6.52±0.3 |

**Table 3**
**Rate constants and activation parameters of the aliphatic aldehydes – TPACC complexes.**

| $10^4$ $k_2$ / ( dm$^3$ mol$^{-1}$ s$^{-1}$ ) | | | | | $\Delta H^*$ | $-\Delta S^*$ | $\Delta G^*$ |
|---|---|---|---|---|---|---|---|
| Aldehyde | 288 K | 298 K | 308 K | 318 K | (kJ mol$^{-1}$) | (J mol$^{-1}$K$^{-1}$) | (kJ mol$^{-1}$) |
| H | 3.60 | 8.28 | 18.9 | 38.7 | 58.0±0.4 | 110±1 | 90.6±0.3 |
| Me | 34.2 | 70.2 | 144 | 270 | 50.1±0.3 | 118±1 | 85.3±0.3 |
| Et | 54.0 | 109 | 216 | 396 | 48.2±0.2 | 121±1 | 84.2±0.2 |
| Pr | 57.6 | 117 | 230 | 423 | 48.2±0.1 | 121±1 | 84.0±0.1 |
| Pr$^i$ | 81.0 | 160 | 315 | 567 | 47.1±0.3 | 122±1 | 83.2±0.3 |
| $ClCH_2$ | 0.27 | 0.27 | 1.80 | 4.32 | 67.8±0.3 | 100±1 | 96.6±0.2 |
| MeCDO | 5.67 | 12.2 | 26.2 | 52.3 | 53.6±0.3 | 121±1 | 89.6±0.2 |
| $k_H/k_D$ | 6.03 | 5.75 | 5.50 | 5.26 | | | |

**Table 4**
**Dependence of the reaction rate on hydrogen–ion concentration**

| **[TPACC] = 0.001 mol dm$^{-3}$; [Aldehydel] = 1.0 mol dm$^{-3}$; Temp. = 288 K** | | | | | | |
|---|---|---|---|---|---|---|
| [H$^+$]/mol dm$^{-3}$ | 0.10 | 0.20 | 0.40 | 0.60 | 0.80 | 1.00 |
| $10^4$ $k_{obs}$/s$^{-1}$ | 6.92 | 8.10 | 9.81 | 11.7 | 13.5 | 16.2 |

**Table 5**
**Effect of solvents on the oxidation of acetaldehyde-TPACC complex at 298 K**

| Solvents | K ($dm^{-3}$ $mol^{-1}$) | $10^4$ $k_{obs}$ ($s^{-1}$) | Solvents | K ($dm^{-3}$ $mol^{-1}$) | $10^4$ $k_{obs}$ ($s^{-1}$) |
|---|---|---|---|---|---|
| Chloroform | 5.85 | 18.2 | Toluene | 5.75 | 5.25 |
| 1,2-Dichloroethane | 5.80 | 22.4 | Acetophenone | 5.92 | 30.9 |
| Dichloromethane | 6.03 | 24.0 | THF | 4.88 | 9.33 |
| DMSO | 5.46 | 70.2 | t-Butylalcohol | 5.67 | 8.51 |
| Acetone | 5.95 | 19.9 | 1,4-Dioxane | 5.99 | 9.77 |
| DMF | 5.85 | 33.9 | 1,2-Dimethoxyethane | 5.55 | 5.75 |
| Butanone | 5.76 | 14.8 | $CS_2$ | 6.12 | 2.82 |
| Nitrobenzene | 5.67 | 27.5 | Acetic Acid | 5.77 | 3.47 |
| Benzene | 5.88 | 6.46 | Ethyl Acetate | 5.69 | 7.94 |
| Cyclohexane | 6.33 | 0.56 | | | |

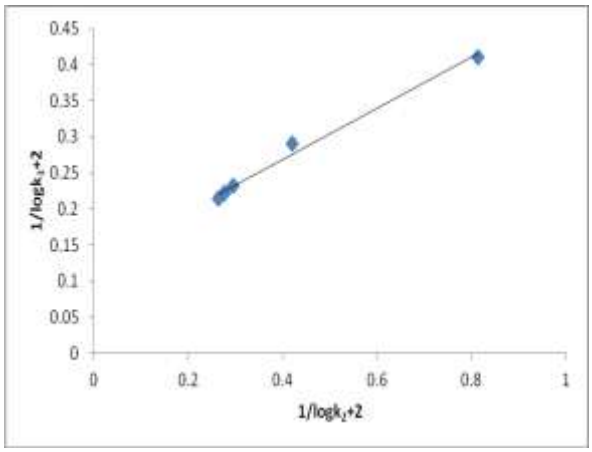



**Figure 3: Exner's Isokinetic Relationship in the oxidation of Aldehydes by TPACC**

A satisfactory correlation (r = 0.9687) between the entropy and enthalpy of activation of the oxidation of six aldehydes indicates the operation of compensation effect in this reaction[20]. The value of isokinetic temperature evaluated[19,25] from this plot is 868±13 K. The correlation was tested and found genuine by Exner's criterion[11]. A correlation between the calculated values of enthalpies and entropies is often vitiated by the experimental errors associated with them. The isokinetic temperature calculated from Exner's plot of log $k_2$ at 288 K versus log $k_2$ at 318 K (r = 0.9998) is 829±21 K (Figure 3). The linear isokinetic correlation suggests that all the aldehydes are oxidized by the same mechanism.

**Solvent effect**: The rate constants $k_2$ in eighteen solvents ($CS_2$ was not considered, as the complete range of solvent parameters was not available) were correlated in terms of the linear solvation energy relationship (6) of Kamlet et al.[16]

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \quad (6)$$

In this equation, $\pi^*$ represents the solvent polarity, β is the hydrogen bond acceptor basicity, α is the hydrogen bond donor acidity and $A_0$ is the intercept term. It may be mentioned here that out of the 18 solvents, 12 have a value of zero for α. The results of correlation analyses in terms of a biparametric equation involving $\pi^*$ and β and separately with $\pi^*$ and β are given in equations 7 to 10:

$$\log k_2 = -4.13 + 1.73\ (\pm 0.20)\ \pi^* + 0.12\ (\pm 0.16)\ \beta + 0.12\ (\pm 0.16)\ \alpha \quad (7)$$
$R^2 = 0.8691$; sd = 0.19; n = 18; $\psi = 0.40$

$$\log k_2 = -4.16 + 1.77\ (\pm 0.19)\ \pi^* + 0.18\ (\pm 0.16)\ \beta \quad (8)$$
$R^2 = 0.8642$; sd = 0.18; n = 18; $\psi = 0.39$

$$\log k_2 = -4.12 + 1.82\ (\pm 0.19)\ \pi^* \quad (9)$$
$r^2 = 0.8528$; sd = 0.19; n = 18; $\psi = 0.41$

$$\log k_2 = -3.12 + 0.49\ (\pm 0.38)\ \beta \quad (10)$$
$r^2 = 0.0935$; sd = 0.46; n = 18; $\psi = 0.98$

Here *n* is the number of data points and ψ is the Exner's statistical parameter[11].

Kamlet et al[16] triparametric equation explains *ca.* 87% of the effect of solvent on the oxidation. However, by Exner's criterion[10] the correlation is not even satisfactory. The major contribution is of solvent polarity. It alone accounted for *ca.* 85% of the data. Both β and α play relatively minor roles.

The data on the solvent effect were analysed in terms of Swain's equation[28] of cation- and anion-solvating concept of

the solvents as in equation (11):

$$\log k_2 = aA + bB + C \quad (11)$$

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

$$\log k_2 = 0.71\ (\pm 0.03)\ A + 1.82\ (\pm 0.02)\ B - 4.31 \quad (12)$$
$R^2 = 0.9969;\ sd = 0.03;\ n = 19;\ \psi = 0.06$

$$\log k_2 = 0.45(\pm 0.60)\ A - 3.09 \quad (13)$$
$r^2 = 0.0326;\ sd = 0.48;\ n = 19;\ \psi = 1.01$

$$\log k_2 = 1.76\ (\pm 0.13)\ B - 4.11 \quad (14)$$
$r^2 = 0.9174;\ sd = 0.14;\ n = 19;\ \psi = 0.29$

$$\log k_2 = 1.45 \pm 0.14\ (A + B) - 4.31 \quad (15)$$
$r^2 = 0.8588;\ sd = 0.18;\ n = 19;\ \psi = 0.31$

The rates of oxidation of acetaldehyde in different solvents showed an excellent correlation in Swain's equation with the cation-solvating power playing the major role. In fact, the cation-solvation alone accounts for *ca.* 92% of the data. The correlation with the anion-solvating power was very poor. The solvent polarity represented by (A + B) also accounted for *ca.* 86% of the data. In view of the fact that solvent polarity is able to account for *ca.* 89% of the data, an attempt was made to correlate the rate with the relative permittivity of the solvent. However, a plot of $\log k_2$ against the inverse of the relative permittivity is not linear ($r^2 = 0.5185$; sd = 0.34; $\psi = 0.71$).

**Correlation Analysis of Reactivity:** The rates of the oxidation of six aldehydes show an excellent correlation with Taft's $\sigma^*$ substituent constants[29], the reaction constant being negative (Table 6). The negative polar reaction constant indicates an electron-deficient carbon centre in the transition state of the rate-determining step.

**Mechanism:** The observed hydrogen-ion dependence suggests that the reaction follows the two mechanistic pathways, one is acid-independent and the other is acid dependent. The acid-catalysis may well be attributed to a protonation of TPACC to give a stronger oxidant and electrophile as in eq. 16. Both TPACC and $TPACCH^+$ are reactive species with the protonated form being more reactive.

$$CrO_2ClO^-N^+(C_3H_7)_3 + H^+ \leftrightarrows [HOCrOClO^-N^+(C_3H_7)_3]^+ \quad (16)$$

Formation of a protonated Cr(VI) species has earlier been reported in the reactions of structurally similar morpholinium chlorochromate (MCC)[8] and tetraethylammonium chlorochromate (TEACC)[12].

In aqueous solutions, most aliphatic aldehydes exist predominantly in the hydrate form[3] and in many oxidations in aqueous solutions. It has been postulated that the hydrate is the reactive species. However, owing to the non-aqueous nature of the solvent in the present reaction, only the free carbonyl form can be the reactive species.

There is no kinetic evidence for the formation of an intermediate in the present reaction, however, its formation in small amounts cannot be ruled out. The presence of a substantial primary kinetic isotope effect ($k_H/k_D = 5.76$ at 298 K) confirms that the aldehydic C-H bond is cleaved in the rate-determining step.

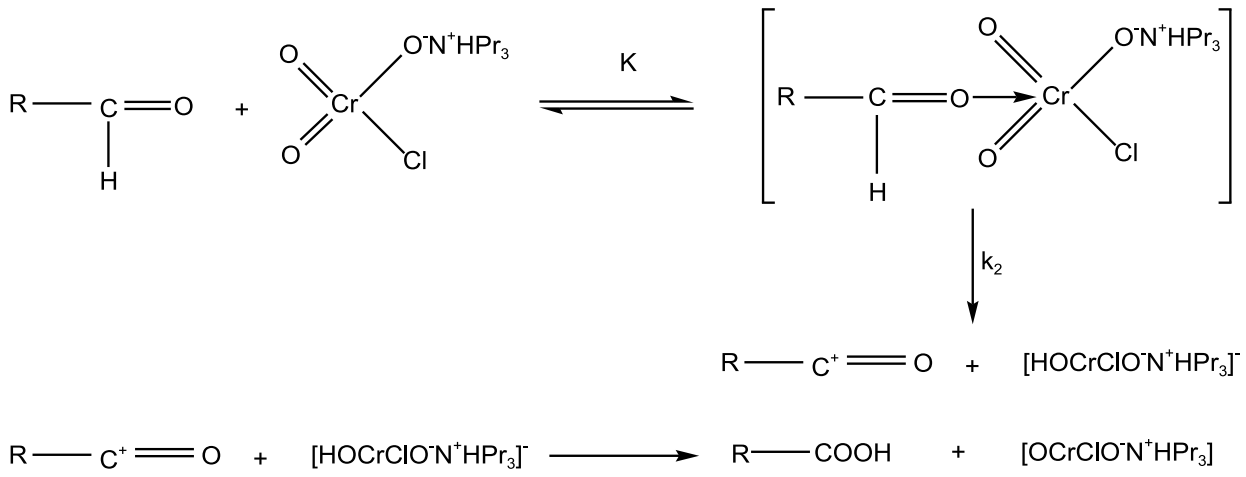
The large negative value of the polar reaction constant together with the substantial deuterium isotope effect indicates that the transition state approaches a carbocation in character. Hence, transfer of a hydride ion from the aldehyde to the oxidant is suggested. The hydride ion transfer mechanism is also supported by major role of cation-solvating power of the solvents (Scheme 1 and 2).

It is of interest to compare here the mode of oxidation of aliphatic aldehydes by PFC[1], PBC[17], QFC[18] and TPACC. The oxidation by QFC, PFC and TPACC presented a similar kinetic picture i.e. Michaelis-Menten type kinetics with respect to the reductants while by the PBC,[28] reactions are of first order with respect to the reductants.

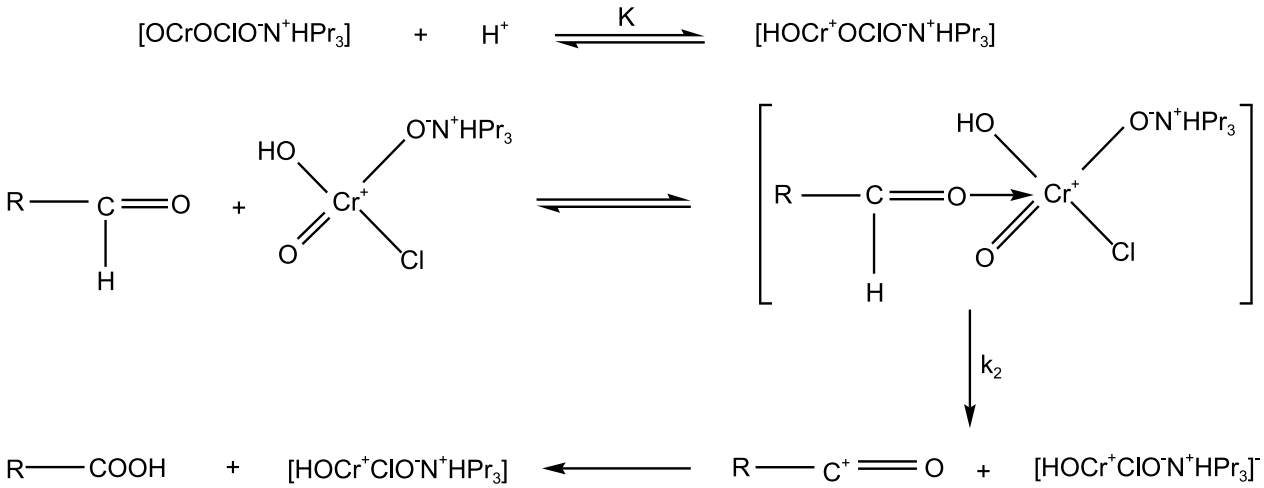
It seems that the values of the formation constants for the intermediates are very small in case of PBC. This resulted in the favour of second-order kinetics. Kinetic isotope effects, solvent effects and the dependence of the hydrogen ions are of similar nature in all these reactions for which essentially similar mechanisms have been proposed.

**Table 6**
**Temperature dependence of the reaction constant**

| Temp./ K | $-\rho^*$ | $r^2$ | Sd | $\psi$ |
|---|---|---|---|---|
| 288 | 2.00±0.01 | 0.9998 | 0.003 | 0.02 |
| 298 | 1.89±0.02 | 0.9989 | 0.002 | 0.04 |
| 308 | 1.81±0.02 | 0.9998 | 0.004 | 0.02 |
| 318 | 1.71±0.02 | 0.9999 | 0.002 | 0.01 |



**Scheme 1: Acid independent path**



**Scheme 2: Acid dependent path**

## Conclusion

The reaction is proposed to proceed through a hydride-ion transfer from aldehyde to the oxidant. The hydride ion transfer mechanism is also supported by major role of cation-solvating power of the solvents. Both deprotonated and protonated forms of TPACC are the reactive oxidising species. An aldehydic C–H bond is cleaved in the rate-determining step.

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## References

1. Agarwal A., Choudhary K. and Banerji K.K., *J. Chem. Res.*, **S**, 86 **(1990)**

2. Balasubramanian K. and Prathiba V., *Indian J. Chem*., **25B**, 326 **(1986)**

3. Bell R.P., *Adv. Phys. Org. Chem.*, **4**, 1 **(1966)**

4. Bhattacharjee M.N., Choudhuri M.K., Dasgupta H.S., Roy N. and Khathing D.T., *Synthesis*, **7**, 588 **(1982)**

5. Bhattacharjee M.N., Choudhuri M.K. and Purakayastha S., *Tetrahedron*, **43**, 5389 **(1987)**

6. Bishnoi V., Prakash O. and Sharma P.K., *Rasayan J. Chem.*, **14(4),** 2478 **(2021)**

7. Brown H.C., Rao G.C. and Kulkarni S.U., *J. Org. Chem.*, **44**, 2809 **(1979)**

8. Choudhary A., Malani N., Agarwal S., Sharma M. and Sharma V., *J. Indian Chem. Soc.*, **86**, 927 **(2009)**

9. Corey E.J. and Suggs W.J., *Tetrahedron Lett*., **IX,** 2647 **(1975)**

10. Exner O., *Collect Chem. Czech. Commun.*, **31**, 3222 **(1966)**

11. Exner O., *Collect Chem. Czech. Commun.*, **38**, 411 **(1977)**

12. Gehlot M., Prasadrao P.T.S.R.K. and Sharma V., *Asian J. Chem.*, **23(3)**, 1173 **(2011)**

13. Ghammamy S., Shrifnezhad Z., Aghbolagh Z.S. and Sahebalzamani H., *Adv. Appl. Sci. Res.*, **1(2)**, 119 **(2010)**

14. Guziec F.S. and Luzio F.A., *Synthesis*, **VII,** 691 **(1980)**

15. Hall R.T. and Schaefer W.E., *Organic Analysis*, Interscience, New York, 55 **(1954)**

16. Kamlet M.J., Abboud J.L.M., Abraham M.H. and Taft R.W., *J. Org. Chem.*, **48,** 2877 **(1983)**

17. Khanchandani R., Sharma P.K. and Banerji K.K., *Indian J. Chem.*, **35A**, 576 **(1996)**

18. Khurana M., Sharma P.K. and Banerji K.K., *React. Kinet. Catal. Lett.*, **67**, 341 **(1999)**

19. Leffler J.E., *J. Org. Chem.*, **20**, 1202 **(1955)**

20. Liu L. and Guo W.E., *Chem. Review*, **101**, 673 **(2001)**

21. Mathur L., Choudhary A., Prakash O. and Sharma P.K., *Asian J. Chem.*, **26(9)**, 2597 **(2014)**

22. Mitchell J. Jr., Organic Analysis, Interscience, New York, 273 **(1954)**

23. Panchariya P., Purohit T., Swami P., Malani N., Prakash O., Kotai L. and Sharma P.K., *Int. J. Chem. Sci.*, **10(1)**, 557 **(2012)**

24. Pandurangan A., Murugesan V. and Palamichamy P., *J. Indian Chem. Soc.*, **72**, 479 **(1995)**

25. Patterson R.C., *J. Org. Chem.*, **29**, 3133 **(1964)**

26. Perrin D.D., Armarego W.L. and Perrin D.R., Purification of organic Compounds, Pergamon Press, Oxford **(1966)**

27. Prakash O. and Sharma P.K., *J. Indian Chem. Soc.*, **81**, 467 **(2004)**

28. Swain C.G., Swain M.S., Pqwel A.L. and Alunni S., *J. Am. Chem. Soc.*, **105**, 502 **(1983)**

29. Taft R.W., Steric effects in organic chemistry, eds., Newman M.S., Wiley, New York, 43 **(1956)**.

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