CORRELATION ANALYSIS OF REACTIVITY IN THE OXIDATION OF SUBSTITUTED BENZALDEHYDES BY QUINOLINIUM FLUOROCHROMATE

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Oxidation of thirty six monosubstituted benzaldehydes by quinolinium fluorochromate (QFC) in dimethylsulphoxide (DMSO), leads to the formation of corresponding benzoic acids. The reaction is of first order with respect to QFC. A Michaelis-Menten type kinetics was observed with respect to the reactants. The reaction is promoted by hydrogen ions; the hydrogen-ion dependence has the form k_{obs}=a +b[H$^+$]. The oxidation of [^{2}H]benzaldehyde (PhCDO) exhibited a substantial primary kinetic isotope effect. The reaction was studied in nineteen different organic solvents and the effect of solvent was analysed using Taft's and Swain's multi-parametric equations. The rates of the oxidation of para- and meta-substituted benzaldehydes showed excellent correlation in terms of Charton's triparametric LDR equation, whereas the oxidation of ortho-substituted benzaldehydes were correlated well with tetraperametric LDRS equation. The oxidation of para-substituted benzaldehydes is more susceptible to the delocalized effect than is the oxidation of ortho- and meta-substituted compounds, which display a greater dependence on the field effect. The positive value of η suggests the presence of an electron-deficient reaction centre in the rate-determining step. The reaction is subjected to steric acceleration by the ortho-substituents. A suitable mechanism has been proposed.

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1. Introduction

Halochromates have been used as mild and selective oxidizing reagents in synthetic organic chemistry. [1] Quinolinium fluorochromate(QFC) is also one of such compounds used as mild and selective oxidizing agent in synthetic organic chemistry. [2] We have been interested in kinetics of oxidations by Cr(VI) species and have already published a few reports on oxidation by other pyridinium[3,4] and quinolinium halochromates. [5,6] In continuation of our earlier work, we report in the present article the kinetics of oxidation of some monosubstituted benzaldehydes by QFC in DMSO as solvent. The major objective of this investigation was to study the structure-reactivity correlation for the substrate undergoing oxidation.

2. Experimental Section

2.1 Materials

QFC was prepared by reported method and its purity was checked by iodometric method. The aldehydes were commercial products. The liquid aldehydes were purified through their bisulfite addition compounds and distilling them, under nitrogen, just before use. [7] The solid aldehydes were recrystallized from ethanol. Deuteriated benzaldehyde (PhCDO) was also prepared by the reported method. [8]

Its isotopic purity, as ascertained by its NMR spectrum, was 96±5%. Due to non-aqueous nature of the solvent, toluene-*p*-sulphonic acid (TsOH) was used as a source of hydrogen ions. Solvents were purified by the usual methods.

2.2 Product analysis

The product analysis was carried out under kinetic conditions. In a typical experiment, benzaldehyde (5.25 g, 0.05 mol) and QFC (2.49 g, 0.01 mol) were made up to 50 cm^3 in DMSO and kept in the dark for *ca*. 15 h to ensure completion of the reaction. The solution was then treated with an excess (200 cm^3) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm^{-3} HCl and kept overnight in a refrigerator. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol, and weighed again. The yields of DNP before and after recrystallization were 2.52 g (88%) and 2.32 g (81%) respectively. The DNP was found identical (m.p. and mixed m.p.) with the DNP of benzaldehyde. Similar experiments were performed with other aldehydes also. The oxidation state of chromium in completely reduced reaction mixtures, determined by an iodometric method was 3.90±0.10.

2.3 Kinetic Measurements:

The pseudo-first order conditions were attained by maintaining a large excess (× 15 or more) of the aldehyde over QFC. The solvent was DMSO, unless specified otherwise. The reactions were followed, at constant temperatures (±0.1 K), by monitoring the decrease in [QFC] spectrophotometrically at 354 nm. No other reactant or product has any significant absorption at this wavelength. The pseudo-first order rate constant, k_{obs}, was evaluated from the linear (r^2 =0.990-0.999) plots of log [QFC] against

time for up to 80% reaction. Duplicate kinetic runs showed that the rate constants were reproducible to within ±3%. The second order rate constant, k_2, was obtained from the relation: $k_2 = k_{obs}/[aldehyde]$. All experiments, other than those for studying the effect of hydrogen ions, were carried out in the absence of p-$CH_3C_6H_4SO_3H$ (TsOH).

3. Results and discussion

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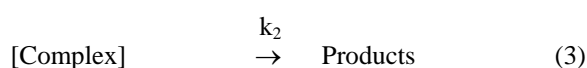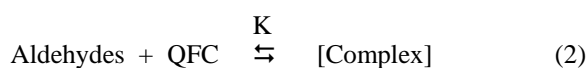
3.1 Stoichiometry:

Oxidation of benzaldehydes by QFC results in the oxidation of corresponding benzaldehydes. Analysis of products and the stoichiometric determinations indicate the following overall reaction (1).

$$ArCHO + CrO_2FOQH + H_2O \longrightarrow ArCOOH +$$

$$(HO)_2CrFOQH \qquad (1)$$
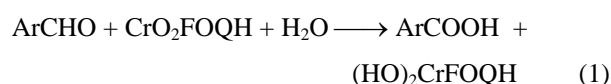
Thus QFC undergoes a two electron change. This is in accord with the earlier observations with other halochromates. It has already been shown that both pyridinium fluorochromate (PFC) [9] and pyridinium chlorochromate (PCC)[10] act as two electron oxidants and are reduced to chromium (IV) species.

3.2 Rate laws

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

$$\text{Aldehydes} + \text{QFC} \overset{K}{\rightleftharpoons} [\text{Complex}] \qquad (2)$$

$$[\text{Complex}] \overset{k_2}{\rightarrow} \text{Products} \qquad (3)$$

$$\text{Rate} = k_2K[\text{Aldehyde}][\text{QFC}]/(1+K[\text{Aldehyde}]) \qquad (4)$$

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. 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 3 and 4).
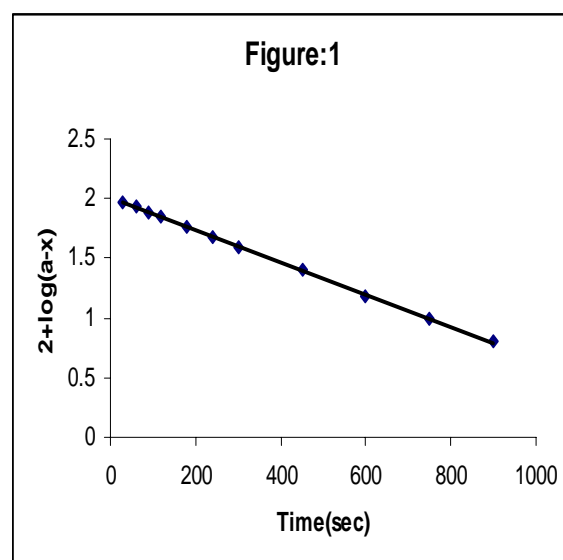

Figure 1. Oxidation of Benzaldehyde by QFC: A typical Kinetic Run

3.3 Test for free radicals

The oxidation of benzaldehyde by QFC, in an atmosphere of nitrogen failed to induce the polymerisation of acrylonitrile. Further, an addition of a radical scavenger, acrylonitrile, had no effect on the rate (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.

Table 1. Rate constants for the oxidation of benzaldehyde by QFC at 298 K

$10^3[QFC]$ (mol dm^{-3})	[Aldehyde] (mol dm^{-3})	[TsOH] (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1})
1.0	0.10	0.0	4.46
1.0	0.20	0.0	6.59
1.0	0.40	0.0	8.66
1.0	0.60	0.0	9.67
1.0	0.80	0.0	10.3
1.0	1.00	0.0	10.7
1.0	1.50	0.0	11.2
1.0	3.00	0.0	11.9
2.0	0.40	0.0	8.82
4.0	0.40	0.0	8.25
6.0	0.40	0.0	9.00
8.0	0.40	0.0	8.46
1.0	0.20	0.0	7.02[*]

[*]contained 0.001 mol dm^{-3} acrylonitrile

Table 2. Dependence of the reaction rate on hydrogen–ion concentration

[TsOH]/ mol dm^{-3}	0.10	0.20	0.40	0.60	0.80	1.00
$10^4 k_{obs}/s^{-1}$	5.22	6.12	7.79	8.64	10.8	12.6

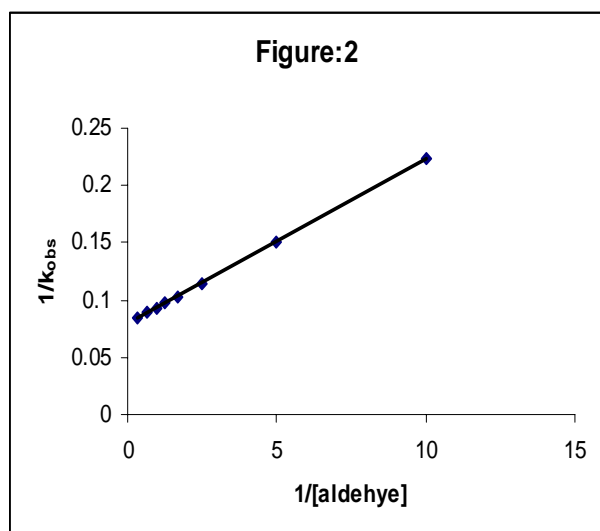[Benzaldehyde] 0.10 mol dm^{-3} ; [QFC] 0.001 mol dm^{-3};T=298 K

Figure 2. Oxidation of Benzaldehydes by QFC: A double reciprocal plot.

3.4 Effect of acidity

The reaction is catalysed by hydrogen ions. The hydrogen-ion dependence taking the form: $k_{obs} = a + b[H^+]$ (Table 2). The values for a and b for benzaldehyde are $4.41 \pm 0.25 \times 10^{-4}$ s^{-1} and $7.97 \pm 0.41 \times 10^{-4}$ mol^{-1} dm^3 s^{-1} respectively ($r^2 = 0.9897$)

3.5 Kinetic isotope effect

To ascertain the importance of the cleavage of the aldehydic C–H bond in the rate–determining step, oxidation of α,α-dideuterio-benzaldehyde (PhCDO) was studied. Results showed the presence of a substantial primary kinetic isotope effect (Table 3).

3.6 Effect of solvents

The oxidation of benzaldehyde was studied in 19 different organic solvents. The choice of solvents was limited by the solubility of QFC and its reaction with primary and secondary alcohols. There was no reaction with the solvents chosen. Kinetics is similar in all the solvents. The values of k_2 are recorded in Table 5.

The correlation between activation enthalpies and entropies of the oxidation of the thirty six benzaldehydes is linear (r^2=0.9428), indicating the operation of a compensation effect [11]. The value of the isokinetic temperature is 583 ± 35 K. However, according to Exner[12], an isokinetic relationship between the calculated values of activation enthalpies and entropies is often vitiated by random experimental errors. Exner suggested an alternative method for establishing the isokinetic relationship. Exner's plot between log k_2 at 288 K and at 318 K was linear (r^2=0.9986; Figure 3). The value of isokinetic temperature evaluated from the Exner's plot is 730 ± 55 K. The linear isokinetic correlation implies that all the alcohols are oxidized by the same mechanism and the changes in the rate are governed by changes in both the enthalpy and entropy of activation.

3.7 Reactivity oxidizing species

The observed hydrogen-ion dependence suggests that the reaction follows two mechanistic pathways, one acid-independent and another acid-dependent. The acid-catalysis may well be attributed to a protonation of QFC as equation (5) to yield a protonated Cr(VI) species which is a stronger oxidant and electrophile. Formation of a protonated Cr(VI) species has earlier been postulated in the reactions of structurally similar pyridinium chlorochromate (PCC).[13]

$$QHOCrO_2F + H^+ \leftrightarrows QHOCr^+(OH)OF \qquad (5)$$

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 linear solvation energy relationship (6) of Kamlet et al.[14]

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

In this equation, π^* represents the solvent polarity, β the hydrogen bond acceptor basicities and α is the hydrogen bond donor acidity. A_0 is the intercept term. It may be mentioned here that out of the 18 solvents, 13 has a value of zero for α. The results of correlation analyses terms of equation (6), a biparametric equation involving π^* and β, and separately with π^* and β are given below (7) - (10).

$$\log k_2 = -3.64 + 1.54(\pm 0.18)\,\pi^* + 0.14\,(\pm 0.15)\,\beta + 0.06\,(\pm 0.14)\,\alpha \qquad (7)$$
$$R^2 = 0.8656;\ sd = 0.17;\ n = 18;\ \psi = 0.40$$

$$\log k_2 = -3.66 + 1.56\,(\pm 0.17)\,\pi^* + 0.12\,(\pm 0.14)\,\beta \qquad (8)$$
$$R^2 = 0.8639;\ sd = 0.16;\ n = 18;\ \psi = 0.39$$

$$\log k_2 = -3.63 + 1.59\,(\pm 0.16)\,\pi^* \qquad (9)$$
$$r^2 = 0.8576;\ sd = 0.16;\ n = 18;\ \psi = 0.39$$

$$\log k_2 = -2.74 + 0.39\,(\pm 0.34)\,\beta \qquad (10)$$
$$r^2 = 0.0784;\ sd = 0.41;\ n = 18;\ \psi = 0.99$$

Here n is the number of data points and ψ is Exner's statistical parameter[15].

Kamlet's triparametric equation explain *ca.* 87% of the effect of solvent on the oxidation. However, by Exner's criterion the correlation is not even satisfactory [cf. (7)]. The major contribution is of solvent polarity. It alone accounted for *ca.* 86 % 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[16] of cation- and anion-solvating concept of the solvents (11).

$$\log k_2 = a A + b B + C \qquad (11)$$

Table 3. Rate constants and activation parameters for the decomposition of QFC-Aldehyde complexes

| Substance	$10^4 k_2$ (dm^3 mol^{-1} s^{-1})				ΔH^*	$-\Delta S^*$	ΔG^*
	288 K	298 K	308 K	318 K	kJ mol^{-1}	J mol^{-1} K^{-1}	kJ mol^{-1}
H	4.86	12.6	31.5	79.2	68.2±0.7	72±2	89.5±0.6
p-Me	10.8	27.0	64.8	153	64.7±0.5	78±1	87.6±0.4
p-OMe	26.1	63.9	150	351	63.3±0.6	75±2	85.5±0.4
p-F	5.67	15.3	38.7	98.1	69.6±0.5	66±2	89.1±0.4
p-Cl	3.33	8.89	23.1	60.3	70.9±0.9	66±3	90.4±0.7
p-NO$_2$	0.21	0.64	1.89	5.35	79.6±0.6	58±2	96.9±0.5
p-CF$_3$	0.63	1.83	5.04	13.6	75.2±0.4	65±1	94.3±0.3
p-COOMe	0.84	2.34	6.48	17.0	74.0±0.6	66±2	93.7±0.5
p-Br	3.21	8.66	22.5	56.9	70.3±0.4	68±1	90.5±0.4
p-NHAc	11.7	29.7	71.1	171	65.4±0.5	75±0	87.4±0.4
p-CN	0.38	1.14	3.24	9.27	78.4±0.7	58±2	95.5±0.6
p-SMe	13.3	35.1	84.6	207	66.9±0.5	68±2	87.0±0.4
p-NMe$_2$	117	270	576	1250	57.3±0.4	83±1	82.0±0.4
m-Me	8.64	21.7	52.2	126	65.3±0.7	77±2	88.2±0.5
m-OMe	8.91	21.6	50.4	117	62.7±0.6	86±2	88.2±0.4
m-Cl	1.48	3.99	10.3	27.0	71.0±0.8	72±3	92.4±0.7
m-Br	1.46	3.92	10.2	26.1	70.6±0.6	74±2	92.4±0.5
m-F	1.86	4.95	12.6	32.4	69.8±0.7	74±2	91.8±0.6
m-NO$_2$	0.15	0.46	1.35	3.96	80.4±0.8	59±2	97.7±0.6
m-CO$_2$Me	0.78	2.20	6.03	16.2	74.4±0.6	59±2	93.8±0.5
m-CF$_3$	0.54	1.53	4.32	11.5	75.2±0.6	66±2	94.7±0.5
m-CN	0.27	0.81	2.34	6.66	78.7±0.7	59±2	96.3±0.6
m-SMe	5.75	14.4	34.2	82.0	64.7±0.6	83±2	89.2±0.5
m-NHAc	5.31	13.5	32.4	78.3	65.6±0.6	80±2	89.4±0.5
o-Me	37.8	85.5	186	405	57.5±0.5	92±2	84.8±0.4
o-OMe	54.9	122	270	585	57.5±0.7	89±2	83.9±0.5
o-NO$_2$	0.46	1.31	3.60	9.81	75.0±0.7	68±2	95.1±0.6
o-COOMe	2.88	7.29	18.0	44.1	66.7±0.7	82±2	90.9±0.6
o-NHAc	61.2	132	280	576	54.4±0.4	99±1	83.7±0.3
o-Cl	11.2	26.1	62.1	137	61.3±0.6	89±2	87.7±0.5
o-Br	14.0	32.4	74.7	165	60.9±0.8	88±3	87.2±0.6
o-I	20.7	47.6	104	225	57.9±0.4	96±1	86.3±0.3
o-CN	0.95	2.61	6.84	18.0	72.0±0.7	72±2	93.4±0.6
o-SMe	62.1	135	283	594	54.7±0.5	98±2	83.7±0.4
o-F	9.02	22.5	54.0	126	64.4±0.4	80±1	88.1±0.3
o-CF$_3$	5.58	13.5	31.5	72.0	62.3±0.4	91±1	89.4±0.3
PhCDO	0.80	2.18	5.73	15.0	71.8±0.7	75±2	93.9±0.5
k_H/k_D	6.08	5.78	5.50	5.28			
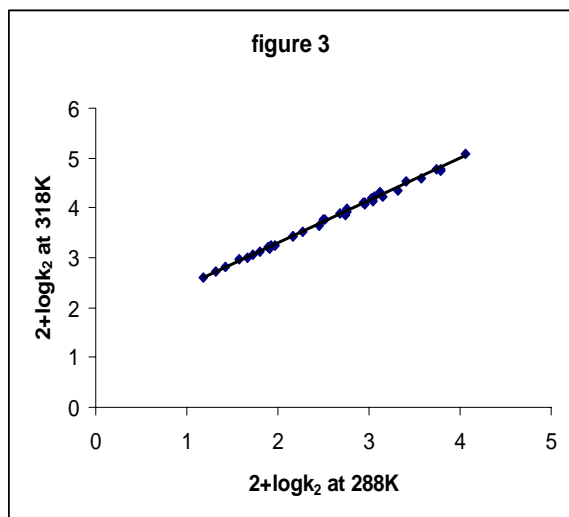
Figure 3. Exner's Isokinetic Relationship in the oxidation of benzaldehydes by QFC

Here *A* represents the anion-solvating power of the solvent and *B* the cation-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 equation (8), separately with *A* and *B* and with (*A* + *B*).

$$\log k_2 = 0.70 + (\pm 0.05)\,A + 1.60\,(\pm 0.04)\,B - 3.87 \quad (12)$$

$$R^2 = 0.9911;\ sd = 0.04;\ n = 19;\ \psi = 0.09$$

$$\log k_2 = 0.48\,(\pm 0.53)\,A - 2.77 \quad (13)$$

$$r^2 = 0.0456;\ sd = 0.43;\ n = 19;\ \psi = 1.00$$

$$\log k_2 = 1.55\,(\pm 0.13)\,B - 3.64 \quad (14)$$

$$r^2 = 0.8927;\ sd = 0.14;\ n = 19;\ \psi = 0.36$$

$$\log k_2 = 1.30 \pm 0.12\,(A + B) - 3.84 \quad (15)$$

$$r^2 = 0.8765;\ sd = 0.16;\ n = 19;\ \psi = 0.34$$

The rates of oxidation of benzaldehyde in different solvents showed an excellent correlation in Swain's equation (cf. equation 12) with the cation-solvating power playing the major role. In fact, the cation-solvation alone account for *ca.* 88% of the data. The correlation with the anion-solvating power was very poor. The solvent polarity, represented by (*A* + *B*), also accounted for *ca.* 89% 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 ($r^2 = 0.5521$; sd = 0.29; $\psi = 0.69$).

3.8 Correlation analysis of reactivity

The effect of structure on reactivity has long been correlated in terms of the Hammett equation[17] or with dual substituent-parameter equations.[18,19] In the late 1980s, Charton[20] introduced a triparametric LDR equation for the quantitative description of structural effects on chemical reactivities. This triparametric equation results from the fact that substituent types differ in their mode of electron delocalization.

Here, σ_1 is a localized (field and/or inductive) effect parameter, σ_d is the intrinsic delocalized electrical effect parameter when active site electronic demand is minimal and σ_e represents the sensitivity of the substituent to changes in electronic demand by the active site. The latter two substituent parameters are related by equation (16).

$$\sigma_D = \eta\sigma_e + \sigma_d \quad (16)$$

Here η represents the electronic demand of the reaction site and is given by $\eta = R/D$, and σ_D represents the delocalized electrical parameter of the diparametric LD equation.

For *ortho*-substituted compounds, it is necessary to account for the possibility of steric effects and Charton,[21] therefore, modified the LDR equation to generate the LDRS equation (17).

$$\log k_2 = L\,\sigma_1 + D\,\sigma_d + R\,\sigma_e + S\,\upsilon + h \quad (17)$$

where υ is the well known Charton's steric parameter based on Van der Waals radii.[22]

The rates of oxidation of *ortho-*, *meta-* and *para*-substituted benzaldehydes show an excellent correlation in terms of the LDR/LDRS equations (Table 6). We have used the standard deviation (sd), the coefficient of multiple determination (R^2), and Exner's parameter, ψ, as the measures of goodness of fit.

The comparison of the *L* and *D* values for the substituted benzaldehydes showed that the oxidation of *para*-substituted benzaldehydes is more susceptible to the delocalization effect than to the localized effect. However, the oxidation of *ortho-* and *meta*-substituted compounds exhibited a greater dependence on the field effect. In all cases, the magnitude of the reaction constants decreases with an increase in the temperature, pointing to a decrease in selectivity with an increase in temperature.

All three regression coefficients, *L*, *D* and *R*, are negative indicating an electron-deficient carbon centre in the activated complex for the rate-determining step. The positive value of η adds a negative increment to σ_d, reflecting the electron-donating power of the substituent and its capacity to stabilise a cationic species. The positive value of *S* indicates that the reaction is subject to steric acceleration by an *ortho*-substituent.

To test the significance of localized, delocalized and steric effects in the ortho-substituted benzaldehydes, multiple regression analyses were carried out with (i) σ_1, σ_d and σ_e (ii) σ_d, σ_e and υ and (iii) σ_1, σ_e and υ. The absence of significant correlations showed that all the four substituent constants are significant.

$$\log k_2 = -1.42\,(\pm 0.36)\,\sigma_1 - 1.95\,(\pm 0.29)\,\sigma_d -$$

$$3.17\,(\pm 1.64)\,\sigma_e - 2.57 \quad (18)$$

$$R^2 = 0.8866;\ sd = 0.25;\ n = 12;\ \psi = 0.39$$

Table 4. Formation constants for the decomposition of QFC–Aldehyde complexes and thermodynamic parameters

Substance	K / (dm³ mol⁻¹)				$-\Delta H$	$-\Delta S$	$-\Delta G$
	288K	298K	308K	318K	(kJ mol⁻¹)	(J mol⁻¹ K⁻¹)	(kJ mol⁻¹)
H	6.21	5.49	4.50	3.69	15.9±0.8	31±3	6.63±0.7
p-Me	5.89	5.17	4.41	3.78	13.8±0.4	25±1	6.53±0.3
p-OMe	5.44	4.72	4.05	3.24	15.4±0.9	31±3	6.30±0.7
p-F	5.81	5.06	4.38	3.69	13.9±0.4	25±1	6.49±0.3
p-Cl	6.15	5.40	4.70	3.99	13.4±0.4	23±1	6.65±0.3
p-NO₂	5.90	5.13	4.47	3.78	13.7±0.4	25±1	6.53±0.3
p-CF₃	5.46	4.77	4.05	3.33	15.0±0.7	30v2	6.32±0.5
p-COOMe	5.32	4.62	3.87	3.15	15.8±0.7	33±2	6.32±0.6
p-Br	5.56	4.86	4.14	3.42	14.8±0.6	29±2	6.37±0.5
p-NHAc	6.13	5.40	4.68	3.96	13.5±0.5	24±1	6.64±0.4
p-CN	5.85	5.13	4.40	3.72	14.0±0.5	26±1	6.51±0.4
p-SMe	6.02	5.49	4.76	4.03	12.7±0.7	21±2	6.65±0.6
p-NMe₂	5.99	5.27	4.59	3.87	13.0±0.5	24±2	6.56±0.4
m-Me	5.45	4.77	4.05	3.33	14.9±0.7	29±2	6.32±0.5
m-OMe	5.73	5.03	4.29	3.57	14.5±0.6	27±2	6.45±0.5
m-Cl	6.20	5.48	4.76	4.05	13.3±0.5	23±1	6.68±0.4
m-Br	6.02	5.31	4.58	3.87	13.6±0.5	24±1	6.57±0.4
m-F	5.66	4.95	4.23	3.51	14.6±0.6	28±2	6.42±0.5
m-NO₂	5.27	4.55	3.83	3.15	15.5±0.6	32±2	6.21±0.5
m-CO₂Me	5.30	4.59	3.87	3.17	15.6±0.7	32±2	6.22±0.5
m-CF₃	5.56	4.86	4.14	3.42	14.8±0.6	29±2	6.37±0.5
m-CN	5.48	4.76	4.05	3.32	15.1±0.6	30±2	6.32±0.5
m-SMe	6.05	5.33	4.61	3.88	13.7±0.5	24±2	6.61±0.4
m-NHAc	5.96	5.24	4.53	3.83	13.7±0.5	24±1	6.57±0.4
o-Me	5.98	5.26	4.54	3.82	13.8±0.5	25±2	6.57±0.4
o-Ome	5.92	5.22	4.50	3.75	14.0±0.6	26±2	6.55±0.5
o-NO₂	6.11	5.39	4.67	3.96	13.5±0.5	23±1	6.64±0.4
o-COOMe	6.18	5.47	4.77	4.03	13.3±0.5	23±2	6.67±0.4
o-NHAc	5.43	4.71	3.95	3.27	14.8±0.7	29±2	6.23±0.6
o-Cl	5.79	5.04	4.32	3.63	14.3±0.4	27±1	6.47±0.4
o-Br	5.36	4.68	3.90	3.20	15.6±0.7	32±2	6.26±0.5
o-I	5.61	4.89	4.17	3.45	14.8±0.6	29±2	6.39±0.5
o-CN	6.15	5.43	4.73	3.96	15.4±0.6	31±2	6.29±0.4
o-SMe	5.82	5.13	4.38	3.96	12.5±0.3	21±1	6.52±0.3
o-F	5.00	4.28	3.55	2.85	16.7±0.7	36±2	6.04±0.6
o-CF₃	5.88	5.16	4.41	3.76	13.9±0.4	25±1	6.52±0.3
PhCDO	6.10	5.40	4.68	3.90	13.8±0.6	24±2	6.63±0.5

Table 5. Solvent effect on the oxidation of benzaldehyde by QFC at 298 K

Solvents	K (dm^{-3}mol^{-1})	$10^4 k_2$ (s^{-1})
Chloroform	5.77	41.7
Toluene	5.41	11.7
1,2-Dichloroethane	4.65	49.0
Acetophenone	6.15	50.1
Dichloromethane	4.68	45.7
THF	4.78	22.9
DMSO	5.49	126
t-Butylalcohol	4.46	18.6
Acetone	5.35	38.1
1,4-Dioxane	4.30	16.6
DMF	4.82	72.4
1,2-Dimethoxyethane	5.45	12.9
Butanone	5.89	28.2
CS$_2$	4.88	6.46
Nitrobenzene	4.45	56.2
Acetic acid	5.82	9.33
Benzene	6.03	14.5
Ethyl acetate	5.35	14.8
Cyclohexane	5.29	1.91

$$\log k_2 = -2.04\ (\pm 0.42)\ \sigma_d - 1.78\ (\pm 2.58)\ \sigma_e +$$
$$0.72\ (\pm 0.48)\ \upsilon - 3.40 \qquad (19)$$

$R^2 = 0.7562$; sd = 0.37; $n = 12$; $\psi = 0.57$

$$\log k_2 = -1.91\ (\pm 0.80)\ \sigma_l - 0.28\ (\pm 3.85)\ \sigma_e +$$
$$1.15\ (\pm 0.72)\ \upsilon - 2.22 \qquad (20)$$

$R^2 = 0.4551$; sd = 0.58; n = 12; $\psi = 0.85$

Similarly in the cases of the oxidation of para- and meta-subsituted benzaldehydes, multiple regression analyses indicated that both localization and delocalization effects are significant. There is no significant collinearity between the various substituents constants for the three series.

The percent contribution[23] of the delocalized effect, P_D, is given by following equation (21).

$$P_D = (|D| \times 100) / (|L| + |D|) \qquad (21)$$

Similarly, the percent contribution of the steric parameter[24] to the total effect of the substituent, P_S, was determined by using equation (21).

$$P_S = (|S| \times 100) / (|L| + |D| + |S|) \qquad (22)$$

The values of P_D and P_S are also recorded in Table 6. The value of P_D for the oxidation of *para*-substituted benzaldehydes is *ca.* 42% whereas the corresponding values for the *meta*- and *ortho*-sobstituted aldehydes are *ca.* 34 and 38% respectively. This shows that the balance of localization and delocalization effects is different for differently substituted benzaldehydes. The less pronounced resonance effect from the *ortho*-position than from the *para*-position may be due to the twisting away ofthe alcoholic group from the plane of the benzene ring.

The magnitude of the P_S value shows that the steric effect is significant in this reaction.

The positive value of S showed a steric acceleration of the reaction. This may be explained on the basis high ground state energy of the sterically crowded alcohols. Since the crowding is relieved in the in the product aldehyde as well as the transition state leading to it, the transition state energy of the crowded and uncrowded alcohols do not differ much and steric acceleration, therefore results.

4. Mechanisms

A hydrogen abstraction mechanism leading to the formation of the free radicals is unlikely in view of the failure to induce polymerization of acrylonitrile and no effect of the radical scavenger on the reaction rate. The presence of a substantial kinetic isotope effect confirms the cleavage of a aldehydic C-H bond in the rate-determining step. The negative values of the localization and delocalization electrical effects i.e. of L, D and R points to an electron-deficient reaction centre in the rate-determining step. It is further supported by the positive value of η, which indicates that the substituent is better able to stabilize a cationic or electron- deficient reactive site. Therefore, a hydride-ion transfer in the rate-determining step is suggested. The hydride-ion transfer mechanism is also supported by the major role of cation-solvating power of the solvents.

Acid-independent Path
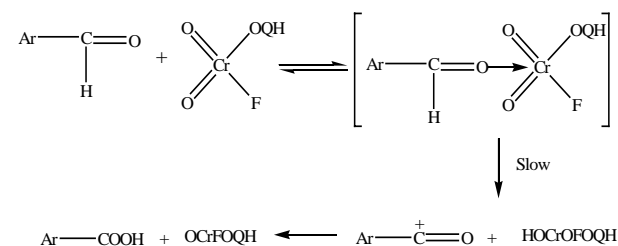
Scheme - 1

The hydride ion transfer may take place either by a cyclic process via an ester intermediate or by an acyclic one-step bimolecular process. Kwart and Nickle have shown that a dependence of kinetic isotope effect on temperature can be gainfully employed to determine whether the loss of hydrogen proceeds through a concerted cyclic process or by an acyclic one.

Acid-dependent Path
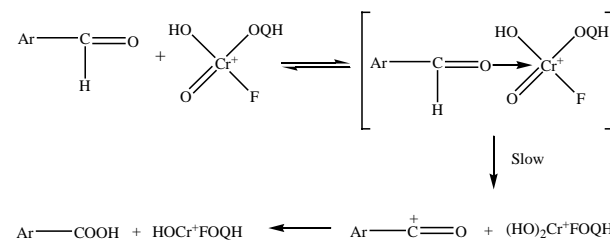
Scheme - 2

The data for protio- and deuterio-benzyl alcohols, fitted to the familiar expression: $k_H/k_D = A_H/A_D(-\Delta H^*/RT)$[21,25] show a direct correspondence of a symmetrical transition state in which activation energy difference for protio- and deuteriocompounds is equal to the difference in the

zero-point energy for the respective C–H and C–D bonds (≈ 4.5 kJ mol^{-1}) and the entropies of activation of the respective reactions are almost equal. Bordwell has documented a very cogent evidence against the occurrence of concerted one-step bimolecular processes by hydrogen transfer and it is evident that in the present studies also the hydrogen transfer does not occur by an acyclic biomolecular process. It is well-established that intrinsically concerted sigmatropic reactions, characterized by transfer of hydrogen in a cyclic transition state, are the only truly symmetrical processes involving a linear hydrogen transfer[26].

Litller[27] has also shown that a cyclic hydride transfer, in the oxidation of alcohols by Cr(VI), involves six electrons and, being a Hueckel-type system, is an allowed process. Thus, a transition state having a planar, cyclic and symmetrical structure can be envisaged for the decomposition of the ester intermediate. Hence, the overall mechanism is proposed to involve the formation of a chromate ester in a fast pre-equilibrium step and then a decomposition of the ester in a subsequent slow step via a cyclic concerted symmetrical transition state leading to the product (Schemes 1 and 2).

Table 6. Temperature dependence for the reaction constants for the oxidation of substituted benzaldehydes by QFC

T/K	$-L$	$-D$	$-R$	S	η	R^2	sd	ψ	P_D	P_S
Para-substituted										
288	1.62	2.07	1.19	-	0.57	0.9999	0.007	0.01	42.4	-
298	1.53	1.99	1.15	-	0.58	0.9998	0.001	0.02	42.6	-
308	1.44	1.89	1.07	-	0.57	0.9989	0.001	0.04	42.9	-
318	1.35	1.82	0.99	-	0.54	0.9999	0.008	0.01	43.6	-
Meta-substituted										
288	1.98	1.44	0.95	-	0.66	0.9998	0.004	0.01	33.0	-
298	1.89	1.36	0.89	-	0.65	0.9997	0.004	0.02	32.9	-
308	1.80	1.26	0.78	-	0.62	0.9989	0.003	0.04	32.8	-
318	1.71	1.17	0.69	-	0.59	0.9998	0.008	0.02	32.8	-
Ortho-substituted										
288	1.71	1.99	1.34	1.08	0.67	0.9999	0.003	0.01	39.5	19.4
298	1.62	1.89	1.26	0.99	0.67	0.9998	0.004	0.02	39.6	17.2
308	1.53	1.80	1.17	0.90	0.65	0.9999	0.002	0.01	40.0	16.7
318	1.46	1.70	1.17	0.81	0.69	0.9989	0.005	0.04	39.3	15.8

The observed negative value of entropy of activation also supports the proposed mechanism. As the charge separation takes place in the transition state, the charged ends become highly solvated. This results in an immobilization of a large number of solvent molecules, reflected in the loss of entropy[28].

5. Conclusion

The reaction is proposed to proceed through a hydride-ion transfer from aldehyde to the oxidant in the rate-determining step. It has also been observed that an α-C-H bond is cleaved in the rate-determining step. Both deprotonated and protonated forms of QCC are the reactive oxidising species.

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