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Original Scientific Article

Kinetics and Mechanism of the Oxidation of Aliphatic Aldehydes by Benzimidazolium Dichromate

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Abstract. Kinetic and mechanistic studies of the oxidation of aliphatic aldehydes, (in organic non-aqueous solvents), were discussed with an emphasis of correlation of structure and reactivity. The reactions were of first order with respect to BIDC and hydrogen-ion. However, Michaelis-Menten type kinetics were observed with respect to aldehyde. The deuterium isotope effect for the oxidation of acetaldehyde ($k_H/k_D = 6.36$ at 298 K) indicated an α-C–H bond cleavage in the rate-determining step. Based on kinetic data, analyses of the solvent effect and results of structure-reactivity correlation along with some non-kinetic parameters suggested a mechanism involving rate-determining oxidative decomposition of a aldehyde-BIDC complex *via* a cyclic transition state to give a carbocationic species through hydride-ion transfer from the aldehyde to the oxidant. (doi: 10.5562/cca1694)

Keywords: kinetics, oxidation, aliphatic aldehydes, benzimidazolium dichromate, mechanism

INTRODUCTION

Selective oxidation of organic compounds under non-aqueous conditions is an important transformation in synthetic organic chemistry. For this, a number of different chromium(VI) derivatives have been reported.[1,2] In 1998, Meng *et al.*[3] reported a new Cr(VI) derivative - benzimidazolium dichromate (BIDC). It is neither hygroscopic nor light sensitive, therefore, it is more stable and easily stored as compared to other Cr(VI) reagents. BIDC is reported[3] to convert benzylic and allylic alcohols to corresponding carbonyl compounds in yield ranging from 75 to 98 %. We have been interested in the kinetics and mechanism of the oxidation by newer Cr(VI) derivatives. There seems to be only two reports available on the kinetic and mechanistic aspects of the oxidation by BIDC.[4,5] These are published from our laboratory. In the continuation of our studies, we report here the kinetics of the oxidation of six aliphatic aldehydes *viz.* formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, 2-methylpropionaldehyde and chloroacetaldehyde by BIDC in dimethylsulphoxide (DMSO) as the solvent. The present investigation was undertaken, primarily to discuss the kinetic and mechanistic aspects along with structure-reactivity correlation in the oxidation reaction and secondly to compare the results with that of the oxidation of aliphatic aldehydes by other Cr(VI) complexes.

EXPERIMENTAL

Materials

BIDC was prepared by the reported method[3] and its purity was checked by an iodometric method. All the aldehydes were commercial products and were purified by the methods described earlier.[6,7] Deuteriated acetaldehyde (MeCDO) was obtained from Sigma Chemicals. The solvents were purified by the reported methods.[8] Amongst the solvents, CS_2 is a flammable liquid and is toxic. Toluene p-sulphonic acid (TsOH) was used as a source of hydrogen ions.

Product Analysis

The product analysis was carried out under kinetic conditions. In a typical experiment, acetaldehyde (0.1 mol) and BIDC (0.01 mol) were made up to 100 ml in DMSO in the presence of 1.0 mol dm^{-3} TsOH. It was then kept in the dark for *ca.*15–20 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 sulfate 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

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Table 1. Stoichiometry of the oxidation of propionaldehyde by BIDC

10^3 [BIDC] / mol dm^{-3}	10^3 [Aldehyde] / mol dm^{-3}	10^3 [Residual BIDC] / mol dm^{-3}	[Aldehyde] / [Consumed BIDC]
5.0	1.0	4.35	1.54
5.0	2.0	3.65	1.48
5.0	3.0	3.04	1.53
		Mean = 1.52	

air. The residue was dissolved in ether (200 ml) and the ester content was determined colorimeterically as iron(III) hydroximate by the method of Hall and Schaefer.[9] The yield of acetic acid was 89 %.

Stoichiometry

To determine the stoichiometry, BIDC (0.005 mol dm^{-3}) and aldehyde (0.001 mol dm^{-3}) were made up to 100 ml in DMSO in the presence of 1.0 mol dm^{-3} TsOH. The reaction was allowed to stand for *ca.* 20 h to ensure completion of the reaction. The residual BIDC was determined spectrophotometrically at 364 nm. Several determinations, with different aldehydes using different concentrations showed that the stoichiometry is 3:2 *i.e.* 3 moles of aldehyde are consumed by 2 moles of oxidant. The results with propionaldehyde are presented in Table 1. BIDC thus acts as a 3-electron oxidant and is reduced to Cr(III).

Spectral Studies

UV-VIS spectra of (i) BIDC (0.0003 mol dm^{-3}) alone and (ii) of propionaldehyde (1.35 mol dm^{-3}) + BIDC (0.0003 mol dm^{-3}) were recorded on UV-VIS spectrophotometer (Model UV5704, ECIL). The solvent was DMSO. The concentration of TsOH used was 0.0005 mol dm^{-3} and temperature was 293±1 K. The spectra of the reaction mixture (ii) was also recorded at different times till completion of reaction. For (i) the blank was the solvent and for (ii) the blank was a solution of propionaldehyde (1.35 mol dm^{-3}) in DMSO in the presence of 0.0005 mol dm^{-3} TsOH. The time gap between the preparation of the reaction mixture and recording of spectrum (B) was < 30 s.

Kinetic Measurements

Pseudo-first order conditions were attained by keeping a large excess (10 times or greater) of the aldehyde over the oxidant. The reactions were carried out at constant temperature (± 0.1 K). The solvent was DMSO, unless stated otherwise. The reactions were followed by monitoring the decrease in the concentration of BIDC at 364 nm for up to 80 % of the reaction. The Beer's law is valid for BIDC within the concentration range used in our experiments. The pseudo-first order rate constant, k_{obs}, was evaluated from the linear ($r^2 > 0.995$) plots of log [BIDC] *vs.* time. Duplicate kinetic runs showed that the rate constants were reproducible to within ± 3 %. In correlation analyses, we have used coefficient of determination (R^2 or r^2), standard deviation (SD) and Exner's parameter,[10] Ψ, as the measures of the goodness of fit.

RESULTS

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

The oxidation of aliphatic aldehydes by BIDC resulted in the formation of the corresponding acid. The product analysis and the stoichiometry determination suggested the following overall reaction:

$$3\ \text{RCHO} + 2\ \text{Cr}_2\text{O}_7^{-2} + 22\ \text{H}^+ \rightarrow$$
$$\rightarrow 3\ \text{RCOOH} + 2\ \text{Cr}^{+3} + 11\ \text{H}_2\text{O} + 2\ \text{Cr}^{+6} \quad (1)$$

Test for Free Radicals

The oxidation of an aldehyde by BIDC, in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. In blank experiments, with the substrate absent, no noticeable consumption of BIDC was observed. The addition of acrylonitrile had no effect on the rate of oxidation (Table 2). 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.

Rate Laws

The reactions were found to be of first order with respect to BIDC. In individual kinetic runs, plots of log [BIDC] *vs.* time were linear ($r^2 > 0.995$). Further, the pseudo-first order rate constants do not depend on the initial concentration of BIDC (Table 2). The order with respect to aldehyde was less than one (Table 2). A plot of k_{obs} *vs.* [aldehyde] is shown in Figure 1 (formaldehyde and chloroacetaldehyde were excluded because the rates are not comparable with other aldehydes). The

Table 2. Rate constants for the oxidation of aldehydes (RCHO) by BIDC at 308 K, $[H^+] = 1.0$ mol dm^{-3}

[RCHO]	10^3 [BIDC]	$10^3 \times k_{obs}/s^{-1}$					
mol dm^{-3}	mol dm^{-3}	H	Me	Et	Pr	Pr^i	ClCH$_2$
0.05	1.0	0.672	8.39	13.6	16.1	24.3	0.0300
0.08	1.0	0.973	12.0	19.8	23.4	35.3	0.0435
0.10	1.0	1.12	14.6	23.1	27.3	41.3	0.0514
0.20	1.0	1.79	21.8	36.4	43.5	65.8	0.0793
0.40	1.0	2.38	30.8	49.5	60.0	89.8	0.109
0.60	1.0	2.76	34.8	57.0	68.9	104	0.126
1.00	1.0	3.09	40.0	64.5	78.3	118	0.141
0.10	0.5	1.17	15.0	22.6	27.0	42.0	0.0531
0.10	0.8	1.21	13.9	23.5	26.4	39.9	0.0499
0.10	2.0	1.15	14.5	21.8	28.0	43.1	0.0520
0.10	3.0	1.12	14.9	23.0	26.9	42.9	0.0500
0.10	5.0	1.20	15.3	21.9	25.9	41.0	0.0511
0.05	1.0	0.681(a)	8.47(a)	13.0(a)	15.6(a)	24.5(a)	0.0317(a)
0.08	1.0	0.968(a)	11.8(b)	20.5(b)	23.0(b)	35.0(b)	0.0429(b)

(a) *c*(acrylonitrile) = 0.001 mol dm^{-3}.
(b) *c*(acrylonitrile) = 0.005 mol dm^{-3}.

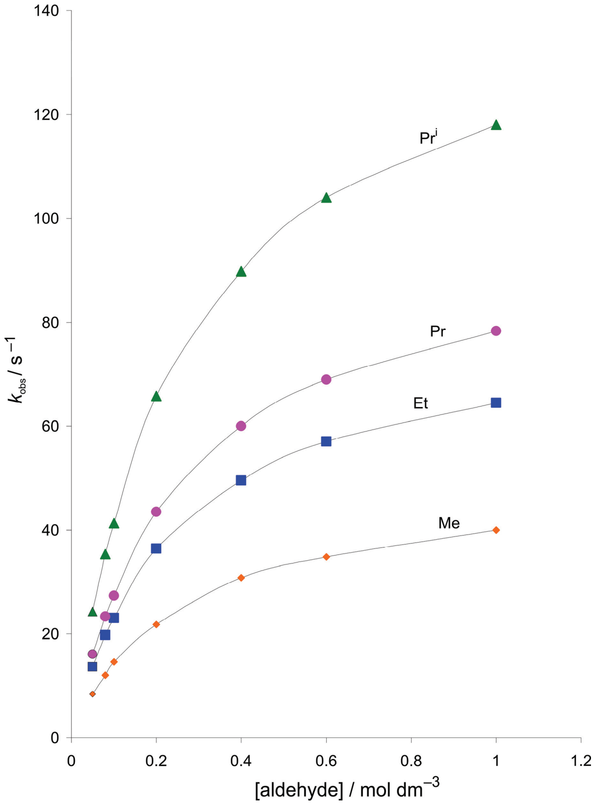


Figure 1. A plot of 10^3 k_{obs} *vs.* [aldehyde]. [BIDC] = 0.001 mol dm^{-3}; $[H^+] = 1.0$ mol dm^{-3}; temperature 308 K.

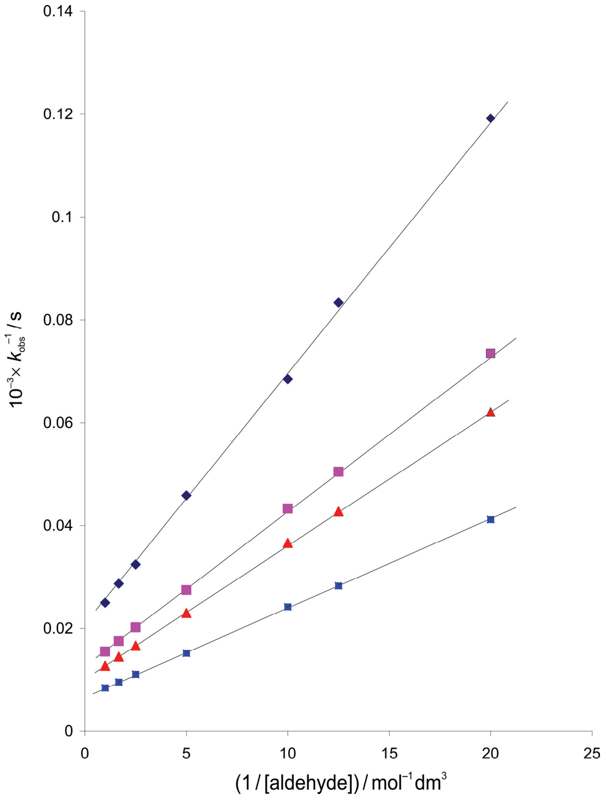


Figure 2. A plot of 10^{-3} $1/k_{obs}$ *vs.* 1/[aldehyde]. [BIDC] = 0.001 mol dm^{-3}; [H+] = 1.0 mol dm^{-3}; temperature 308 K.

downward curvature of the plots suggests the existence of a complex. A plot of $1/k_{obs}$ *vs.* 1/[aldehyde] was linear with an intercept on the rate ordinate (Figure 2). Thus, a Michaelis-Menten type kinetics were observed with respect to aldehyde. This leads to the postulation of following overall mechanism and rate law:

$$\text{Aldehyde} + \text{BIDC} \overset{K}{\rightleftharpoons} [\text{Complex}] \quad (2)$$

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

$$\text{Rate} = \frac{k_2 K [\text{Aldehyde}][\text{BIDC}]_t}{1 + K[\text{Aldehyde}]} \quad (4)$$

or,

$$(\text{Rate}/[\text{BIDC}]_t)^{-1} = 1/k_{obs} = \quad (5)$$

$$1/k_2K[\text{Aldehyde}] + 1/k_2$$

Here,

$$[\text{BIDC}]_t = [\text{BIDC}] + [\text{Complex}]$$

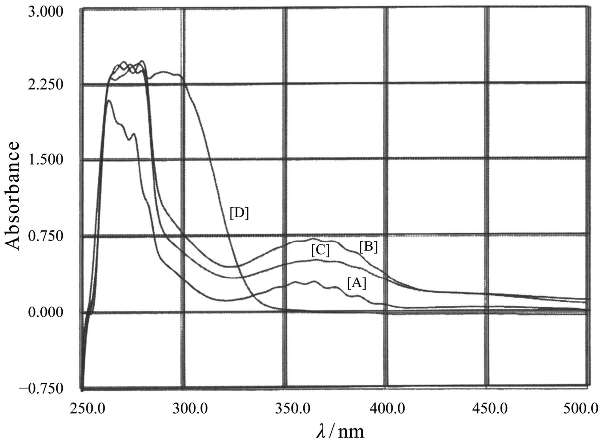


Figure 3. UV-VIS spectra of: (i) [A] – 0.0003 mol dm^{-3} BIDC; (ii) [B] – [A] + 1.35 mol dm^{-3} propionaldehyde; (iii) [C] – [B] after 3600 s; (iv) [D] – [B] on about completion of reactionSolvent – DMSO. T = 293±1 K.

The dependence of k_{obs} on the concentration of aldehyde was studied at different temperatures and the values of K and k_2 were evaluated from the double reciprocal plots using equation (5). The thermodynamic

Table 3. Formation constants and thermodynamic parameters for RCHO-BIDC complexes

Subst. (R)	K/dm^3 mol^{-1}				ΔH	ΔS	ΔG
	298 K	308 K	318 K	328 K	kJ mol^{-1}	J mol^{-1} K^{-1}	kJ mol^{-1}
H	4.89	4.27	3.69	3.31	−13.2 ± 0.2	−23 ± 1	−6.43 ± 0.2
Me	4.71	4.10	3.48	2.99	−14.9 ± 0.3	−29 ± 1	−6.36 ± 0.2
Et	4.78	4.08	3.53	3.13	−14.0 ± 0.2	−26 ± 1	−6.36 ± 0.1
Pr	4.53	3.91	3.42	3.01	−13.6 ± 0.1	−25 ± 1	−6.24 ± 0.2
Pr^i	4.47	3.92	3.45	3.08	−12.6 ± 0.1	−22 ± 1	−6.20 ± 0.2
ClCH$_2$	4.80	4.11	3.50	3.10	−14.5 ± 0.2	−28 ± 1	−6.38 ± 0.2
MeCDO	4.65	4.11	3.53	3.00	−14.4 ± 0.5	−27 ± 2	−6.34 ± 0.4

Table 4. Rates of decomposition and activation parameters for RCHO-BIDC complexes

Subst. (R)	$10^3 k_2$/s^{-1}				ΔH^*	ΔS^*	ΔG^*
	298 K	308 K	318 K	328 K	kJ mol^{-1}	J mol^{-1} K^{-1}	kJ mol^{-1}
H	1.42	3.82	8.69	20.2	68.9 ± 0.7	−69 ± 2	89.2 ± 0.6
Me	21.0	49.2	105	230	62.0 ± 0.5	70 ± 2	88.3 ± 0.4
Et	34.5	80.3	167	365	60.9 ± 0.7	69 ± 2	81.4 ± 0.5
Pr	41.5	98.3	202	438	60.8 ± 0.8	68 ± 2	80.9 ± 0.6
Pr^i	60.0	148	290	622	59.9 ± 1.2	67 ± 4	79.9 ± 1.0
ClCH$_2$	0.062	0.176	0.432	1.14	75.7 ± 0.9	72 ± 3	97.0 ± 0.7
MeCDO	3.30	8.30	18.6	42.5	66.3 ± 0.5	70 ± 2	87.2 ± 0.4
k_H/k_D	6.36	5.93	5.65	5.41			

Table 5. Dependence of reaction rates of aldehydes (RCHO) on the hydrogen-ion concentration[(a)]

$[H^+]$	$10^3\,k_{obs}/s^{-1}$					
mol dm^{-3}	H	Me	Et	Pr	Pr^i	$ClCH_2$
0.1	0.121	1.55	2.24	2.66	4.07	–
0.2	0.230	3.03	4.53	5.55	8.33	0.0110
0.3	0.348	4.50	6.88	8.00	11.8	0.0155
0.4	0.450	5.97	9.27	10.8	16.5	0.0232
0.6	0.647	9.11	13.0	16.0	25.1	0.0309
1.0	1.12	14.8	23.1	27.3	41.3	0.0514

[(a)] [aldehyde] = 0.10 mol dm^{-3}, [BIDC] = 0.001 mol dm^{-3}, T = 308 K.

parameters for the complex formation and the activation parameters for the decomposition of complexes were calculated from the values of K and k_2 respectively, at different temperatures (Tables 3 and 4).

Spectral Analysis

A perusal of spectra of BIDC and BIDC + propionaldehyde showed that there is a distinct increase in the absorbance of BIDC by the addition of aldehyde (refer spectra [A] and [B]). This supports the formation of an intermediate complex. Further, the absorbance decreases with time and minimizes on about completion of reaction (refer spectra [C] and [D]). This indicates that the complex subsequently decomposes to give the ultimate product (Figure 3).

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) by BIDC was studied. The results (Tables 3 and 4) showed that the formation constants of the complexes of ordinary and deuteriated acetaldehyde are almost similar but the rates of their decomposition exhibited a substantial kinetic isotope effect (k_H/k_D = 6.36 at 298 K).

Effect of Acidity

The rate of oxidation increases with an increase in acidity and the dependence is of the form – Rate = k' $[H^+]$ (Table 5). The order with respect to hydrogen ion is one. The log-log plot of k_{obs} *vs.* $[H^+]$, for all the aldehydes, showed that the slope > 0.95 and $r^2 > 0.99$. The dependence of the reaction rate on the concentration of acetaldehyde was studied at three different concentrations of hydrogen-ion *i.e.* $[H^+]$ = 0.2, 0.4 and 1.0 mol dm^{-3}. It was observed that the formation constant, K, does not vary appreciably with the hydrogen-ion concentration, however, the rate of decomposition of complex increases linearly. Similar observations have been made in the oxidation of aldehydes[11,12] and oxyacids of phosphorus[13] by butyltriphenylphosphonium dichromate (BTPPD).

Solvent Effect

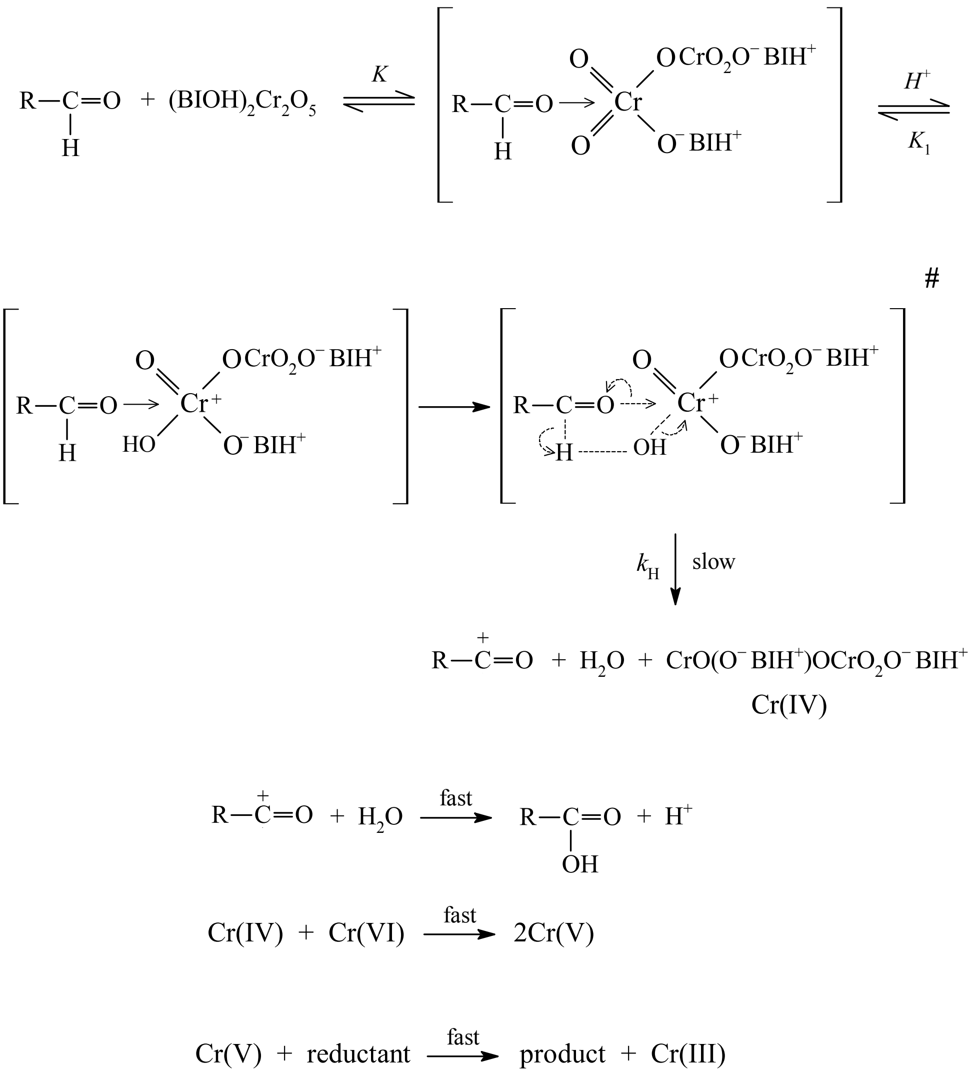
The oxidation of acetaldehyde by BIDC was studied in nineteen organic solvents. The solubility of the reactants and the reaction of BIDC with primary and secondary alcohols limited the choice of solvents. There was no reaction with the chosen solvents. The kinetics were similar in all the solvents. The corresponding values of K and k_2, are recorded in Table 6.

DISCUSSION

The entropies and enthalpies of activation of the oxidation of six aliphatic aldehydes do not exhibit satisfactory correlation (r^2 = 0.6511). The correlation was tested and

Table 6. Effect of solvent on the oxidation of acetaldehyde by BIDC at 318 K

Solvent	K / $dm^3\,mol^{-1}$	$10^3\,k_2$ / s^{-1}
Chloroform	3.61	30.3
1,2-Dichloroethane	3.20	37.3
Dichloromethane	3.33	35.0
DMSO	3.48	105
Acetone	2.93	33.7
Dimethylformamide	3.01	55.5
Butanone	3.63	25.2
Nitrobenzene	2.89	42.0
Benzene	3.60	12.7
Cyclohexane	3.52	1.40
Toluene	2.91	10.5
Acetophenone	3.77	45.5
Tetrahydrofurane	3.86	18.0
Tert-Butyl alcohol	3.28	13.0
Dioxane	3.15	18.5
1,2-Dimethoxyethane	3.01	9.48
Acetic acid	2.87	5.51
Ethyl acetate	3.72	13.4
Carbon disulfide	3.81	5.30



BI = benzimidazole

Scheme 1.

found genuine by applying Exner's criterion.[14] The Exner's plot between the values of log k_2 at 298 K and at 328 K, for the six aldehydes, is linear (r^2 = 0.9998). The value of isokinetic temperature, determined by Exner's method, is 5821 ± 317 K. A linear isokinetic relationship is a necessary condition for the validity of linear free energy relationships.[14] It also implies that all the reactions, so correlated, follow a similar mechanism.

BIDC seems to be an ionic compound as a result of proton transfer. To find out the state of BIDC in our reaction conditions, conductivity measurements have been carried out. It was observed that DMSO has very low conductivity and the addition of BIDC in DMSO shows negligible change in the conductivity value. Therefore, BIDC can be considered to be remained as non-ionised under our reaction conditions and does not dissociate as dichromate and benzimidazolium ions. No effect of added benzimidazolium ion on the rate of oxidation also supports the postulation that BIDC remain as nonionised.[5] The crystal structure study of BIDC, reported by Meng *et al.*[15] supports the non-ionic nature of the oxidant in the reaction system. The dichromate ion connects two benzimidazolium rings *via.* hydrogen bonds. With the effective hydrogen donor (N–H) and hydrogen acceptor (O) in the molecule, BIDC forms a number of hydrogen bonds. Furthermore, an intermolecular hydrogen bridge is remarkably formed between two neighboured dichromate ions. The molecules are then linked into infinite chains by these hydrogen bridges which controlled the releasing process of dichromate ions to reaction system and thus the compound behaves as non-ionic in our reaction system.[15]

Solvent Effect

The data recorded in Table 6 indicate that the equilibrium constant, K, is fairly insensitive to the change in solvent, however, k_2, varies appreciably. Therefore, the values of the rate constant of the decomposition of complexes, k_2, in eighteen solvents (CS_2 was not considered as the complete range of the solvent parameters are not available), were correlated in terms of linear solvation energy relationship (LSER) of Kamlet *et al.*[16] But the correlations were insignificant.

The data on solvent effect were then analysed in terms of Swain's[17] equation (6), where A represents the anion-solvating power of the solvent and B the cation-solvating power; C is the intercept term, and (A + B) is postulated to represent the solvent polarity.

$$\log k = a\mathrm{A} + b\mathrm{B} + \mathrm{C} \tag{6}$$

The results of the correlation analyses in terms of Swain's equation, individually with A and B, and with (A + B) are given below.

$$\log k_2 = 0.52\pm0.01\ \mathrm{A} + 1.67\pm0.01\ \mathrm{B} - 2.96 \tag{7}$$

$R^2 = 0.9998$, sd = 0.01, $n = 19$, $\Psi = 0.01$

$$\log k_2 = 0.28\pm0.55\ \mathrm{A} - 1.81 \tag{8}$$

$r^2 = 0.0153$, sd = 0.44, $n = 19$, $\Psi = 1.02$

$$\log k_2 = 1.63\pm0.09\ \mathrm{B} - 2.79 \tag{9}$$

$r^2 = 0.9486$, sd = 0.10, $n = 19$, $\Psi = 0.23$

$$\log k_2 = 1.29\pm0.15\ (\mathrm{A} + \mathrm{B}) - 2.93 \tag{10}$$

$r^2 = 0.8190$, sd = 0.19, $n = 19$, $\Psi = 0.44$

The data on solvent effect showed an excellent correlation in terms of Swain's equation with both anion- and cation-solvating powers contributing to the observed solvent effect. However, the role of cation-solvation is major. It alone accounts for *ca.* 95 % of the data. The solvent polarity, represented by (A + B) accounted for *ca.* 82 % of the data. In view of the fact *ca.* 82 % of the data is accounted for by (A + B), an attempt was made to correlate the data with relative permittivity of the solvents. A plot of log k against the inverse of the relative permittivity, however, is not linear ($r^2 = 0.5023$).

Correlation Analysis of Reactivity

The rates of oxidation of the six aldehydes show an excellent correlation with Taft's σ^* substituent constant,[18] the reaction constant being negative.

$$\log k_2 = \rho^* \sigma^* + \log k_0 \tag{11}$$

Here, ρ^* measures the susceptibility of the reaction towards polar effects and k_0 is the rate constant for acetaldehyde. The negative polar reaction constant indicates an electron-deficient carbon centre in the transition state of the rate-determining step. The reaction constant, ρ^*, for the oxidation of aldehydes were calculated at different temperatures (Table 7). The magnitude of the reaction constant decreases with an increase in temperature, indicating a decrease in the selectivity with an increase in temperature.

Mechanism

A one-electron oxidation, giving rise to free radicals, is unlikely in view of the failure to induce polymerisation of acrylonitrile. BHT is an excellent trap for free radicals.[19] The fact that BHT was recovered unchanged also goes against the occurrence of a one-electron oxidation. The formation constants of the complexes of ordinary and deuterated acetaldehyde are almost similar, however, the rates of their decomposition exhibited a substantial kinetic isotope effect. This indicates that the aldehydic C–H bond is cleaved in the rate-determining step. The negative values of the polar reaction constants point to an electron-deficient reaction centre in the transition state of the rate-determining step. This postulation is supported by the analyses of the solvent effect indicating much more contribution of the cation-solvation on the rate of decomposition of the complex. The order of reactivity also supports it. Therefore, the removal of hydrogen as hydride-ion resulting in an electron-deficient species in the rate-determining step, is indicated. However, the observed Michaelis-Menten type kinetics with respect to the aldehyde led us to suggest the formation of 1:1 complex by a nucleophilic attack of aldehydic oxygen on chromium in a rapid pre-equilibrium. The nature of the complex suggested is similar to that reported in the oxidation of aromatic aldehydes by PFC.[20] The observed order of reactivity indicated that the electron-releasing groups accelerated the oxidation process. This is accounted in terms of an increase in the electron-availability at the oxygen of the aldehydic group resulting in the facilitation of the complex formation. The observed acid-dependence of the reaction points to a rapid reversible protonation of the intermediate complex prior to its disproportionation. A mechanism depicted in Scheme 1 accounts for the experimental results. The rate law based on the mechanism (Scheme 1) proposed can be written as-

$$\mathrm{Rate} = \frac{k_{\mathrm{H}} K_1 K [\mathrm{BIDC}]_t [\mathrm{Aldehyde}][\mathrm{H}^+]}{1 + K[\mathrm{Aldehyde}]} \tag{12}$$

Comparing equations (4) and (12), we get $k_2 = k_{\mathrm{H}}\ K_1[\mathrm{H}^+]$

An analysis of the temperature dependence of the kinetic isotope effect by the method of Kwart and Nickle[21] showed that the loss of hydrogen proceeds through a concerted cyclic process. The data for protio- and deuterio-acetaldehyde were fitted to the familiar expression

$$k_H/k_D = A_H/A_D \exp(-\Delta E_a/RT)$$

or,

$$\log(k_H/k_D) = \log(A_H/A_D) - \Delta E_a/RT \qquad (13)$$

The results showed that the activation energy difference for k_H/k_D is 4.36 kJ which agrees well with the zero-point energy difference for the respective C–H and C–D bonds (*ca.*4.30 kJ mol^{-1}) and the entropy of activation of the respective reactions are equal. This directly corresponds to the properties of a symmetrical transition state.[22,23] Similar phenomenon have been observed earlier in the oxidation of alcohols by BTPPD.[24] Bordwell[25] has given cogent evidence against the occurrence of concerted one-step bimolecular process of hydrogen transfer and it is clear that in the present reaction also, the hydrogen transfer does not occur by an acyclic bimolecular process. The only truly symmetrical processes involving linear transfer of hydrogen are intrinsically concerted sigmatropic reactions characterized by transfer with a cyclic transition state.[26] The second step of the reaction was the transfer of two electrons in a cyclic system. This electrocyclic mechanism for the oxidation of aldehyde by BIDC involved six electrons, being a Hückel type system, is an allowed process.[27] Therefore, one can safely conclude that in the oxidation of aldehyde by BIDC, the hydride-ion transfer occurs *via* a cyclic transition state. The manner of electron transfer has to be established. The first step involved the nucleophilic attack of aldehydic-oxygen electrons on electron-deficient chromium atom to form an intermediate complex. This complex then undergoes unimolecular decomposition in the slow step. The transition state involves the bonding of hydrogen atom to both the aldehydic-carbon and the OH group attached to chromium. The electron flow in a cyclic transition state has been considered assuming that the hydrogen atom is removed as hydride-ion. Thus, the process of electron transfer takes place through the carbon-hydrogen-oxygen-chromium bond. This would facilitate the formation of a carbocationic species by reverting back the nucleophilic attack of aldehydic oxygen. The similar type of mechanism is reported for the oxidation of oxyacids by BTPPD.[13]

The proposed mechanism is, however, supported by the observed negative entropy of activation. As the charge separation takes place in the transition state, the two ends become highly solvated. This results in an immobilization of a large number of solvent molecules, reflected in the loss of entropy. The negative activation entropy additionally accounts for the influence of solvent.

Table 7. Temperature dependence of the reaction constant

Temperature / K	ρ^*	$r^2(n)^{(a)}$	sd	Ψ
298	2.40 ± 0.02	0.9998(6)	0.016	0.015
308	2.34 ± 0.02	0.9996(6)	0.026	0.022
318	2.27 ± 0.02	0.9996(6)	0.022	0.022
328	2.20 ± 0.02	0.9998(6)	0.017	0.015

(a) n = number of data points.

Initially Cr(VI) is reduced to Cr(IV). It is likely to react with another Cr(VI) to generate Cr(V) which is then reduced in a fast step to the ultimate product Cr(III). Such a sequence of reactions in Cr(VI) oxidations is well known.[28]

It is of interest to compare here the results of present reaction with the oxidation of aliphatic aldehydes by other Cr(VI) complexes *viz.* BTPPD,[11] benzyltriethyl-ammonium chlorochromate (BTEACC),[29] pyridinium fluorochromate (PFC),[6] pyridinium bromochromate (PBC),[30] quinolinium fluorochromate (QFC),[31] quinolinium dichromate (QDC),[14] pyridinium chlorochromate (PCC),[32] morpholinium chlorochromate (MCC)[33] and 2,2'-bipyridinium chlorochromate (BPCC).[34] It is observed that all the above oxidation reactions are of first order with respect to Cr(VI) species, however, they differ in the order with respect to aldehyde. The dependence of rate on the aldehyde concentration in the case of QDC, PBC, PCC, QFC, BTEACC, MCC and BPCC is first order, it is less than one in the case of PFC and BIDC, whereas it is more than one but less than two for the oxidation by BTPPD. Thus, a Michaelis-Menten type kinetics were observed in the oxidation by BIDC, PFC and BTPPD. All the reactions are catalysed by hydrogen-ion but the dependence is not same all through. In the oxidation by PBC, MCC, QFC, BPCC and BTEACC the dependence is of form: Rate = $a + b[H^+]$, the oxidation by QDC and BIDC involves first order dependence on $[H^+]$. However, it is of form: Rate = $k[H^+]^2$ in the oxidation by BTPPD. The effect of $[H^+]$ on rate in the case of PFC was not studied. All the reactions exhibited a substantial kinetic isotope effect. The results of solvent effect are of similar nature in all these reactions. The rate constants correlate well with Taft's σ^* values in all the reactions, the reaction constants being negative. A similar kind of mechanisms involving a formation of protonated intermediate complex in a rapid pre-equilibrium which undergoes unimolecular decomposition in slow step *via.* hydride-ion transfer to give either carbocationic species or the final product is postulated. The nature of complex is not same in all the oxidation reactions. In the oxidation by QDC, the reactive reducing species is aldehyde hydrate. Also, in the oxidation reactions of PBC, MCC, QFC, BPCC and BTEACC an acid-independent path is also operative in addition to acid-dependant path. Thus, it is observed that the kinetics and mechanism of the oxidation of aliphatic aldehydes depend on the nature of oxidant.

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