Selective oxidation of glycolic and lactic acids by benzimidazolium dichromate – A kinetic and mechanistic aspects

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Selective oxidation in dimethyl sulfoxide (DMSO) medium by benzimidazolium dichromate (BIDC) of α-hydroxy acid viz. glycolic and lactic acids, produces corresponding oxoacid. A Michaelis-Menten kind kinetics noticed as for hydroxy acids while unit dependency on rate observed as for BIDC. At non-identical temperatures the formation constants and the rates of decomposition of hydroxy acid-BIDC complexes have been evaluated. Thermodynamic parameters and activation parameters for formation of the complex and break down of the complexes have been determined respectively. The oxidation process accelerates with increase in proton concentration. An α-C-H bond fisson in the rate-controlling step suggested by the deuterium isotope effect. For oxidation of glycolic acid, k_H/k_D = 5.74 at 298 K, was observed. The oxidation rates have been evaluated in 19 organic solvents and greater role of solvating power of the cation is observed. Depended on the kinetic parameters, solvent effect analysis and the outcome of thermodynamic parameters, a mechanism in which rate-controlling break down of the complex is suggested, to give the resulting product through hydride-ion transfer with a cyclic transition state.

Keywords: Kinetics, glycolic acid, lactic acid, oxidation, solvent-effect mechanism, BIDC.
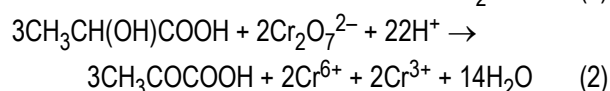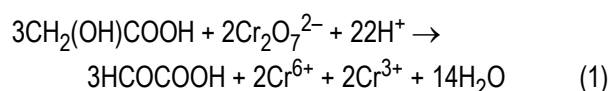
Introduction

In synthetic organic chemistry, under non-aqueous medium particular oxidation of organic compounds is a significant conversion. Due to this reason various Cr(VI) complexes have been documented[1,2]. Benzimidazolium dichromate (BIDC) is a complex of Cr(VI), reported in 1998[3]. Since BIDC is neither light sensitive nor hygroscopic, thus, it is stored easily and more stable rather than other derivatives of Cr(VI). Conversion of allylic and benzylic alcohols by BIDC to their respective carbonyl compounds with 75 to 98% yield is well documented[3]. We get focused on mechanistic investigations with kinetic aspects of the oxidation by BIDC and from our research laboratory some research papers have been published earlier[4–10]. A study of literature appears that there is no work reported on the oxidation kinetics of lactic and glycolic acids by BIDC. Here we investigate the oxidation kinetics of glycolic acid (GA) and lactic acid (LA) by BIDC in solvent DMSO.

Results and discussion

The stoichiometric ratios, Δ[substrate]/Δ[BIDC], confirmed the following overall reactions for the oxidation of GA and LA respectively.

$$3CH_2(OH)COOH + 2Cr_2O_7{}^{2-} + 22H^+ \rightarrow$$
$$3HCOCOOH + 2Cr^{6+} + 2Cr^{3+} + 14H_2O \qquad (1)$$
$$3CH_3CH(OH)COOH + 2Cr_2O_7{}^{2-} + 22H^+ \rightarrow$$
$$3CH_3COCOOH + 2Cr^{6+} + 2Cr^{3+} + 14H_2O \qquad (2)$$

In this oxidation reactions unit dependency exhibited as for BIDC therefore graphic was straight line ($r^2 > 0.996$) between logarithms of [BIDC] and time. The k_{obs} (pseudo-first order velocity constant) do not alter appreciably on BIDC beginning concentration (Table 1). The fractional dependency (0 < order < 1) was observed for hydroxy acids (Table 1). In Fig. 1, a graphic between k_{obs} and [Hydroxy acid] is exhibited. The curvature of the plots leading towards a lower level reveals the development of a complex. Double reciprocal graphic between $1/k_{obs}$ and 1/[Hydroxy acid] was straight line with positive intercept (Fig. 2). Hence, as for each GA and LA, a Michaelis-Menten kind kinetics was noticed. This suggests the existence of following rate law and mechanism:

$$\text{Hydroxy acid} + \text{BIDC} \xrightarrow{K^{\#}} \text{[Complex)} \qquad (3)$$

$$[Complex] \xrightarrow{k_2} Product \tag{4}$$

$$Rate = k_2 K^{\#} [Hydroxy\ acid]\ [BIDC]_t /$$
$$(1 + K^{\#} [Hydroxy\ acid]) \tag{5}$$

$$or,\ 1/(Rate/[BIDC]_t) = 1/k_{obs} =$$
$$1/k_2 K^{\#} [Hydroxy\ acid] + 1/k_2 \tag{6}$$
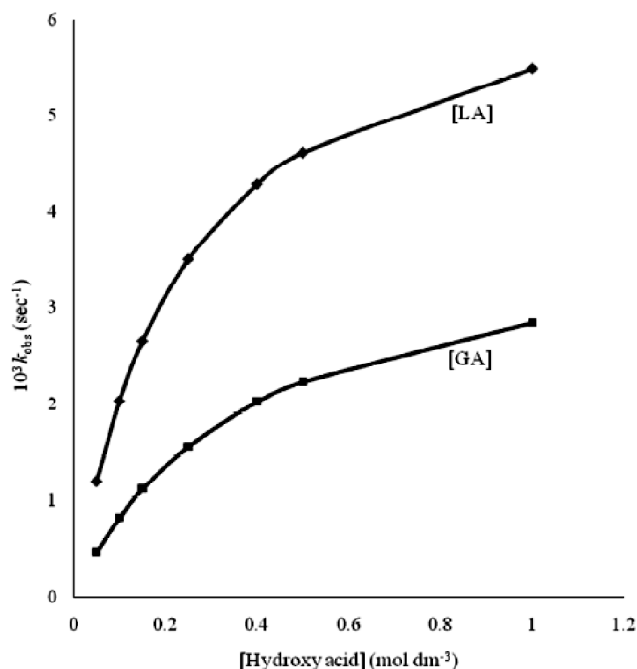
Here, $[BIDC]_t = [Complex] + [BIDC]$

At non-identical temperatures, the k_{obs} dependency on both hydroxy acid concentrations were calculated and using eq. (6), k_2 and $K^{\#}$ values with the help of double reciprocal graphic, were determined. For establishment of complex, the thermodynamic parameters (Table 2) and breaking down of them, the activation parameters (Table 3) were determined at non-identical temperatures, from k_2 and $K^{\#}$ values respectively.

Oxidations of LA and GA by BIDC, under nitrogen ambience, the acrylonitrile induce polymerization was not observed. No considerable BIDC consumption, in absence of hydroxy acids, was noticed. The oxidation rate was unaffected on acrylonitrile addition (Table 1). For additional confirmation of the absence of one electron oxidation during course of the reaction, the reaction was executed with 0.005 mol dm^{-3} of butylated hydroxytoluene (BHT). The BHT did not show any considerable change and observed nearly quantitatively.
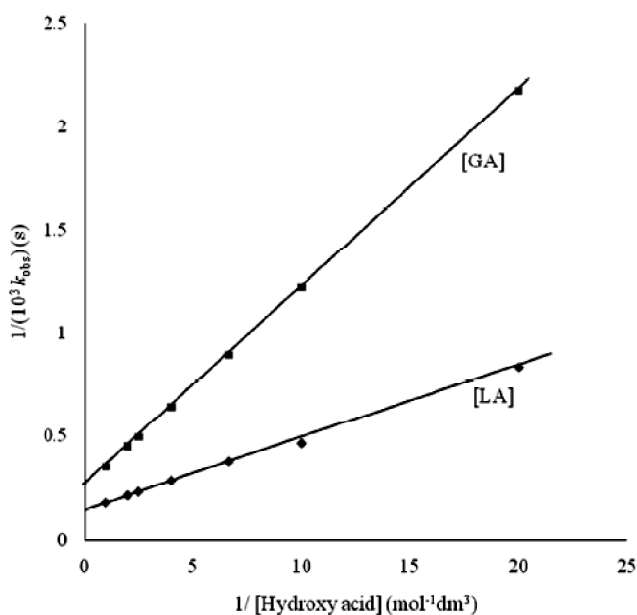

Fig. 1. A graphic of $10^3 k_{obs}$ against [Hydroxy acid] at 308 K [TsOH] = 0.2 mol dm^{-3}; [BIDC] = 0.001 mol dm^{-3}.

Fig. 2. A graphic of $1/(10^3 k_{obs})$ against 1/[Hydroxy acid] at 308 K [TsOH] = 0.2 mol dm^{-3}; [BIDC] = 0.001 mol dm^{-3}.

The rates of oxidation of both GA and LA are catalyzed by hydrogen-ion concentration (Table 4). A graphic between log k_{obs} and log [H$^+$] is straight line with positive slope which

Table 1. Rate data at 308 K for hydroxy acid's oxidation by BIDC

10^3 [BIDC] (mol dm^{-3})	[Hydroxy acid] (mol dm^{-3})	10 [H$^+$] (mol dm^{-3})	$10^3 k_{obs}$ (s^{-1}) LA	$10^3 k_{obs}$ (s^{-1}) GA
1.0	0.05	2.0	1.20	0.46
1.0	0.1	2.0	2.03	0.82
1.0	0.15	2.0	2.65	1.12
1.0	0.25	2.0	3.50	1.56
1.0	0.40	2.0	4.28	2.02
1.0	0.50	2.0	4.61	2.23
1.0	1.0	2.0	5.49	2.84
2.0	0.5	2.0	4.64	2.38
4.0	0.5	2.0	4.57	2.20
6.0	0.5	2.0	4.68	2.12
8.0	0.5	2.0	4.52	2.32
1.0	1.0	2.0	5.53[a]	2.89[a]
1.0	1.0	2.0	5.45[b]	2.81[b]

[a,b]Contained 0.001 and 0.005 mol dm^{-3} acrylonitrile.

Table 2. Hydroxy acid-BIDC complex formation constants and their parameters of thermodynamics

[HA]	$K^{\#}$ (mol^{-1} dm^3)				ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔG (kJ mol^{-1})
	298 K	308 K	318 K	328 K			
LA	6.90	4.31	2.83	1.90	−37.36±0.15	−101±0.49	−7.27±0.12
GA	5.11	2.68	2.04	1.22	−40.58±2.12	−115±6.8	−6.45±1.66
DGA	5.16	2.72	2.00	1.20	−40.94±3.0	−116±7	−6.46±1.7

Table 3. Hydroxy acid-BIDC complex decomposition constants and their parameters of activation

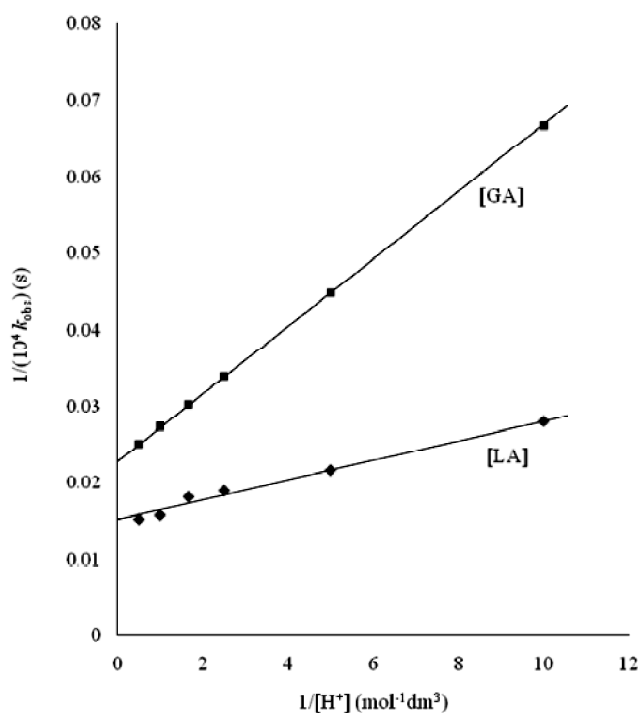| [HA]	$k_2 \times 10^3$ (s^{-1})				ΔH^* (kJ mol^{-1})	ΔS^* (J mol^{-1} K^{-1})	ΔG^* (kJ mol^{-1})
	298 K	308 K	318 K	328 K			
LA	2.98	6.76	15.0	33.4	83±0.69	−26±2.21	70.37±0.54
GA	1.78	3.90	8.50	18.7	61.1±0.9	−36±2.8	71.66±0.68
DGA	0.31	0.73	1.68	3.86	65.69±0.68	−35±2.18	75.98±0.53
k_H/k_D	5.74	5.35	5.06	4.84			

is less than one. This suggests the dependency with hydrogen-ion concentration on rate is between zero to one. Thus, a graphic between $1/k_{obs}$ and $1/[H^+]$ was undertaken and with positive intercept a straight line was obtained (Fig. 3).

No particular reaction was observed without toluene *p*-sulphonic acid (TsOH). The rate of reaction dependency on GA and LA concentration with three distinct acidities was analyzed (Table 5). The rate of decomposition of complex, k_2, does not changes considerably with the acid concentration, however, the value of formation constant, $K^{\#}$, enhances with the acid concentration. In mandelic acid (MA) oxidation by BIDC, similar results have observed[9].

The oxidation of α,α-dideuterio-glycolic acid (DGA) was analyzed with BIDC for established the significance of α-C-H bond fission in the rate-controlling pathway. The findings (Table 3) revealed that complex formation constants of GA and DGA are nearly close but decomposition rates of them (Table 4) indicated a deuterium isotope effect (k_H/k_D = 5.74 at 298 K). Primary kinetic isotope effect value was found nearly same in case of MA oxidation by BIDC[9]. Further, in present study, the value of k_H/k_D, increases with decrease in temperature.

Fig. 3. A graphic of $1/(10^4 \, k_{obs})$ against $1/[H^+]$ at 308 K [Hydroxy acid] = 0.5 mol dm^{-3}; [BIDC] = 0.001 mol dm^{-3}.

Solvent effect: Nineteen organic solvents were used to study the oxidation of glycolic acid by BIDC. The reaction of BIDC with 1° and 2° alcohols and reactant's solubility restricted the solvent's selectivity. No reaction was observed with the selected solvents. The kinetics was nearly same with these solvents. In Table 6, corresponding $K^{\#}$ and k_2 values are mentioned.

Table 4. Rate of reaction reliance on concentration of hydrogen-ion

[BIDC] = 0.001 mol dm^{-3}, [Hydroxy acid] = 0.5 mol dm^{-3} at 308 K

| [TsOH] (mol dm^{-3})	0.1	0.2	0.4	0.6	1.0	2.0
$10^4 \, k_{obs}$ (s^{-1}) (GA)	15.0	22.3	29.5	33.1	36.4	39.7
$10^4 \, k_{obs}$ (s^{-1}) (LA)	35.6	46.1	52.82	55.2	63.5	65.8

Table 5. Dependence of substrate variation at different acidities at 308 K by BIDC (0.001 mol dm^{-3})

[Hydroxy acid] (mol dm^{-3})	k_{obs} x 10^4 (s^{-1}) at [H$^+$] (mol dm^{-3})		
	0.2	0.6	1.0
(i) Glycolic acid (GA)			
0.05	4.6	11.3	14.7
0.10	8.2	17.7	21.9
0.25	15.6	26.6	28.7
0.40	20.2	30.5	31.9
0.50	22.3	32.0	33.1
1.00	28.4	35.6	36.4
$K^{\#}$ (dm^3 mol^{-1})	2.68	7.82	12.35
(ii) Lactic acid (LA)			
0.05	12.0	24.7	35.5
0.10	20.3	35.6	47.0
0.25	35.0	48.5	58.4
0.40	42.8	53.4	62.1
0.50	46.1	55.2	63.5
1.00	54.9	59.2	66.4
$K^{\#}$ (dm^3 mol^{-1})	4.31	12.58	20.82
k_2x10^3 (s^{-1})	6.76	6.39	6.96

Protonated oxidant (BIDCH$^+$) appears to be an ionic compound. In our reaction ambience the nature of BIDC is determined at 308 K with conductivity measurements. Low conductivity of DMSO and insignificant variation in conductivity value due to the inclusion of BIDC in DMSO was observed; therefore BIDC does not break up as benzamedazolium and dichromate ions thus BIDC remain non-ionised in our reaction system. The rate of oxidation does not alters on addition of benzimidazolium ion, also favours the postulation that BIDC remain as non-ionised[10]. Meng *et al.*[11] reported the crystal structure study of BIDC, and his study favours that oxidant shows the non-ionic character. Two benzimidazolium rings attached with the dichromate ion via hydrogen bonds. With the help of hydrogen acceptor (O) and hydrogen donor (N-H), BIDC forms a number of hydrogen bonds in the molecule and within two adjacent dichromate ions an intermolecular hydrogen bridge is unusually formed. Hence, the BIDC acts as non-ionic in our reaction, because of these hydrogen bridges the molecules are combined into infinite chains and releasing power of dichromate ions is inhibits by these chains in our reaction system.

It is observed, after protonation BIDC (X) produce a protonated Cr(VI) species (Y) which is active electrophile and stronger oxidant (eq. (7)). Thus, oxidation process through BIDC depends upon proton concentration.

$$(BIOH)_2Cr_2O_5 + H^+ \xrightarrow[]{K_1} (BIOH)_2O\overset{+}{C}r(OH)OCrO_2 \quad (7)$$
$$(X) \qquad\qquad\qquad (Y)$$
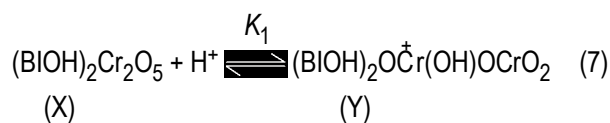
Here, BI represents benzimidazole. Further, effect of proton concentration on rate could be expressed as:

$$k_{obs}^{-1} = a + b \, [H^+]^{-1} \qquad (8)$$

Generation of a protonated Cr(VI) complexes has been before suggested in the reactions of other Cr(VI) complexes[12,13]. Magnified reactivity obtained due to the internal electron transfer from hydroxy acid to BIDC which promotes by the protonation of BIDC. Further, hydrogen ion dependency shows fast equilibrium amid (X) and (Y), magnitude of equilibrium constant, K_1, is less and at higher concentrations of [H$^+$] the reaction remains incomplete because at higher hydrogen ion concentration no leveling of velocity constants occurred. No astounding oxidation noticed without TsOH recommends that just the protonated BIDC (Y) carries on like an oxidizing species. In oxidation of MA by BIDC[9] similar kind of hydrogen-ion dependency observed.

Table 6. Solvent's effect at 308 K on the glycolic acid oxidation of by BIDC

Solvent	$K^{\#}$ (dm^{3}mol^{-1})	10^3 k_2 (s^{-1})
Chloroform	2.32	1.14
1,2-Dichloroethane	2.89	1.44
Dichloromethane	2.09	1.37
DMSO	2.68	3.90
Acetone	2.94	1.34
Dimethylformamide	2.02	2.17
Butanone	2.14	1.02
Nitrobenzene	1.98	1.66
Benzene	1.92	0.55
Cyclohexane	2.78	0.07
Toluene	2.56	0.45
Acetophenone	2.21	1.84
Tetrahydrofurane	2.06	0.75
tert-Butyl alcohol	2.78	0.50
1,4-Dioxane	2.24	0.76
1,2-Dimethoxyethane	2.48	0.41
Ethyl acetate	1.96	0.60
Carbon disulfide	2.18	0.24
Acetic acid	1.96	0.19

The data described in Table 6 represents that with change in solvent the rate constant (k_2), varies considerably though equilibrium constant ($K^{\#}$), is quite insensible. Similar kind of oxidation kinetics observed in hydroxy acids oxidation by pyridinium bromochromate[15] and of MA by BIDC[9]. Hence, k_2 for the breakdown of complexes, in 18 solvents (CS_2 has not been studied because the absolute range of solvent parameters are unavailable), have been associated regarding linear solvation energy relationship (LSER) of Kamlet *et al.*[15]. Irrelevant correlations were observed.

Regarding to the Swain's[16] eq. (9), data of solvent effect had been studied where A, B and (A+B) denotes the solvating power of anion, solvating power of cation and polarity of solvent respectively and intercept term denoted by C.

$$\log k = aA + bB + C \tag{9}$$

In respect of Swain's eq. (9) the conclusion of the correlation studies, separately with A, B and (A + B) are described as:

$$\log k_2 = 0.35\pm0.008\,A + 1.60\pm0.007\,B - 4.26 \tag{10}$$
$$R^2 = 0.9999,\ sd = 0.0048,\ \psi = 0.01,\ n = 19$$

$$\log k_2 = 0.12\pm0.53\,A - 3.016 \tag{11}$$
$$r^2 = 0.0032,\ sd = 0.43,\ \psi = 1.03,\ n = 19$$

$$\log k_2 = 1.57\pm0.06\,B - 4.143 \tag{12}$$
$$r^2 = 0.9741,\ sd = 0.07,\ \psi = 0.17,\ n = 19$$

$$\log k_2 = 1.19\pm0.159\,(A+B) - 4.22 \tag{13}$$
$$r^2 = 0.7647,\ sd = 0.21,\ \psi = 0.50,\ n = 19$$

The observed results of solvent effect revealed a perfect correlation regarding Swain's equation[16] with both solvating power of cation- and anion-participating with perceived effect of solvent. Although, the contribution of solvating power of cation is greater, it alone contributes for 97.4% of the data. (A + B), represents the polarity of the solvent, explains 76.4% of the data. Relative permittivities of the solvents were correlated with the data by considering that 76.4% of the data is contributed by polarity of the solvent. A plot of log k_2 against $1/D$, where D represents relative permittivity of the solvent, though, it is not linear ($r^2 = 0.4758$). This showed that the relative permittivity and polarity of solvent do not represent the same solvent characteristics, defined by Swain *et al.*[16].

Mechanism: Considering about the non attendance of any impact of acrylonitrile the reaction rate it is unfavoured that oxidation by one-electron is operative in the present reaction[17]. BHT is a perfect trapping reagent for free radicals. The acid-catalysis is considered as earlier BIDC protonation to produce BIDCH$^+$**(Y)**. The major role of solvating power of cation supports it. In a fast dynamic-equilibrium development of a 1:1 complex **(Z)** recommended by the Michaelis-Menten kind kinetics in the context of hydroxy acid. Nucleophilic attack of -OH group of hydroxy acid on BIDCH$^+$ **(Y)** results in the origination of the complex **C** (Scheme 1). The process of oxidation increases by the electron-donating methyl group and this is reflected by the reactivity increasing power. It shows that in the formation of complex the availability of electron in -OH group expands. It is noticed that the complexes of normal and α,α-dideuterio-glycolic acid have formation constants which are nearly equal, however a primary kinetic isotope impact indicated by the rate of decomposition and it suggests that in the rate controlling step the α-C-H bond is broken. The end product (oxoacid) in Scheme 1 obtained from the complex **(Z)**, due to the hydride-ion shifting from hydroxyl acid to BIDC and mechanism of shifting of this hydride-ion further supports that solvating power of cation have major role. A carbocationic nature accessed by a polar transition status is postulated in oxidation process. It was noticed that the oxidation of MA by BIDC[9] is also followed the similar mechanism. However, the generation of a centre of carbonium ion is suggested in the controlled step in few reports on hydroxy acid's oxidation[18,19].

Transfer of a hydride-ion may occur either by an acyclic process or via a chromate ester. Kwart and Nickle[20] developed a method to study of the temperature reliance of the kinetic isotope effect, revealed that a concerted cyclic mechanism proceeds loss of hydrogen. The results for ordinary and deuterited-glycolic acid have been expressed in a familiar manner:

$$(k_H/k_D) = (A_H/A_D)\exp(-\Delta E_a/RT) \tag{14}$$

The difference of activation energy for k_H/k_D is *ca.* 4.70 kJ mol^{-1} which concluded by final results agrees that the activation entropy (ΔS^*) and zero-point energy gap for both C–D and C-H bonds (*ca.* 4.60 kJ mol^{-1}) are almost same in the present reaction. It is directly agrees with a symmetrical transition state properties[21,22]. Previously, similar kind of results has been noticed in alcohol's oxidation by BTPPD[23].
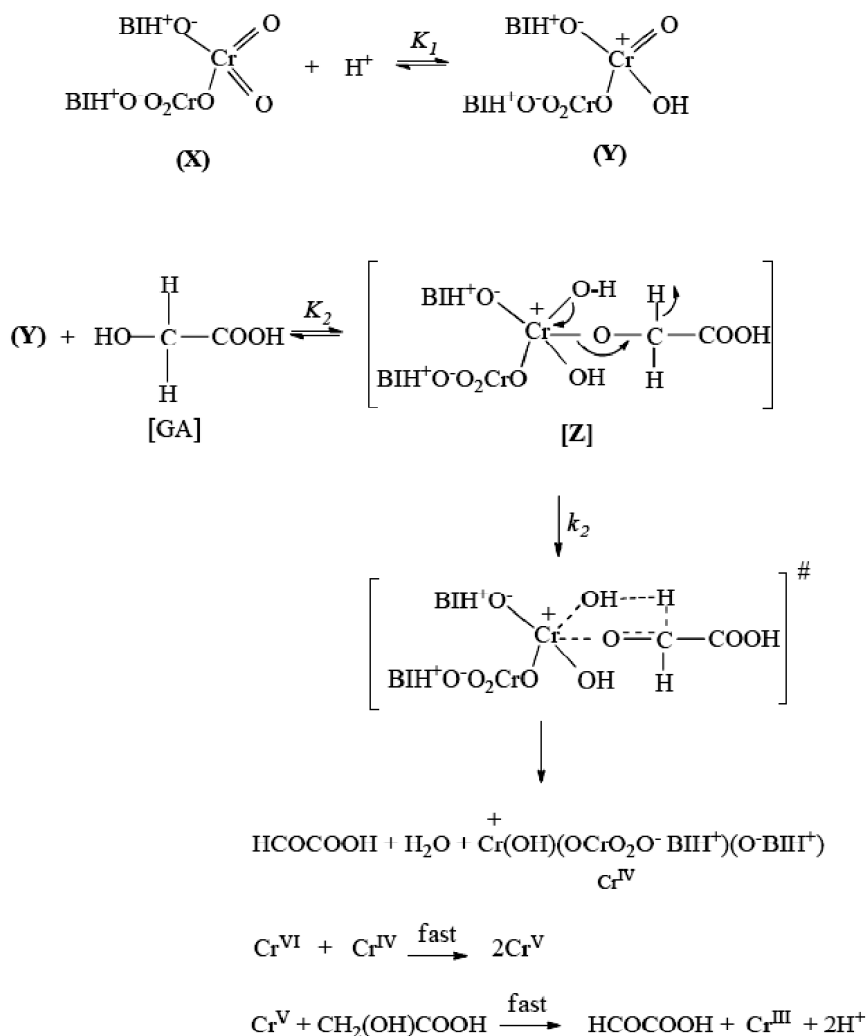
Scheme 1. Oxidation mechanism of glycolic acid (GA) by BIDC.

Bordwell[24] has specified strong facts beside the phenomenon of bimolecular concerted process of hydrogen shifting completed in one-step. In the present reaction system this is strongly recommended that the shifting of hydrogen does not undergo through an acyclic bimolecular course of action. This symmetrical process is really sigmatropic a reaction in which direct transfer of hydrogen is involved in which a cyclic transition state shifting is specified[25]. Afterwards, two electrons transfer in a cyclic scheme was the next in this reaction. In the oxidation of hydroxy acid by BIDC concerned with six electrons which resembles with Hückel's $(4n+2)\pi$

system, is a permitted process[26]. Hence, it is presumed that hydride-ion transfer occurring through a cyclic transition state in LA and GA oxidation by BIDC.

Described mechanism in Scheme1 is based on the experimental findings. In suggested mechanism (Scheme 1) the rate law could be discussed below. Cr(VI) can be determined on applying the equilibrium condition,

$$-d[Cr(VI)]/dt = k_2 [Z] = k_2 K_1 K_2 [HA] [H^+] [Cr(VI)] \qquad (15)$$

$$\text{or, } -d[Cr(VI)]/dt = \frac{k_2 K_1 K_2 [Cr(VI)]_t [H^+] [HA]}{1 + K_1 K_2 [H^+] [HA]}$$

or, $k_{obs} = \dfrac{k_2 K_1 K_2 \, [H^+] \, [HA]}{1 + K_1 K_2 \, [H^+] \, [HA]}$ (16)

Here, $[Cr(VI)]_t = [Cr(VI)] + [Z]$, here K_1 is low and produced [Y] which get react with HA.

or, $1/k_{obs} = 1/k_2 K_1 K_2 \, [H^+] \, [HA] + 1/k_2$ (17)

The reaction system is well characterized by eqs. (16) or (17).

With the help of eqs. (6) and (17), we have $K^\# = K_1 K_2 [H^+]$.

The observed loss of $(-\Delta S)$ of activation favors proposed mechanism. In the transition state, two ends become extremely solvated when the charge segregation occurs and this leads to stabilization of large number of solvent molecules, which appears as entropy loss. The effect of solvent also accounts by loss of entropy.

In the beginning oxidation state of chromium metal reduced from Cr(VI) to Cr(IV) and expected to react with another Cr(VI) to produced Cr(V). In a fast step this Cr(V) species ultimately produces Cr(III) species. This pattern of reactions in oxidations by Cr(VI) is markedly established[27].

This is interesting to compare the findings of the existing reaction with the results of oxidation of hydroxy acids by other Cr(VI) complexes. The oxidation by butyltriphenylphosphonium dichromate (BTPPD)[28] are observed to be of second order as for both the hydroxy acid and $[H^+]$, however, the order as for BTPPD is one. In the reaction deuterium isotope effect was noticed and protonated dimetallic Cr(VI) species as an active oxidizing species was suggested. In the mechanism hydrogen as an anion shifts through the hydroxy acid to BTPPD by means of a chromate ester, is proposed in rate-controlling path. The kinetics of oxidation by quinolium dichromate (QDC)[29] in M/2 $HClO_4$ of the α-hydroxy acids showed unit dependency as for the hydroxy acid, oxidant and proton concentration. It was observed that ketoacid was product of oxidation and in product formation, C-H bond breaking includes in slowest path. Subsequent aldehyde was final product in the oxidation of HAs by QDC[30] in 30% (v/v) AcOH-H_2O medium. Unit dependency exhibited as for LA and QDC. The reaction rate is directly proportional to acid concentration and inversely proportional to relative permittivity of the solvent. In oxidation process breaking of bond between carbon-carbon is proposed in associated

mechanism. The α-hydroxy acids oxidation under non-aqueous methyl cyanide medium by imidazolium dichromate (IDC) is described to be of unit dependency as for IDC; though, less than one order have been observed as for substrate[31]. The noticed rate is almost unaffected with acid concentration. The formation of corresponding ketoacid was product of oxidation. Under rate controlling step, between substrate and IDC, development of a cyclic complex is postulated. Though, the oxidation reaction by IDC of MA in 50% (v/v) AcOH-H_2O medium, with $HClO_4$, observed same dependency as for each the MA and IDC as above[31], but partial dependency as for acid[32]. Development of an intermediate complex between $IDCH^+$ and MA is involved in the slowest step. Therefore, the oxidation process relies on state of the reaction and character of the oxidant.

Experimental

Materials: From the described procedure[3] oxidant BIDC was composed and its immaculateness was checked iodometrically. The hydroxy acids were utilized as supplied because of its furthest extent of immaculateness. Lactic and glycolic acids solutions were standardized by alkalimetry. α,α-dideuterio-glycolic acid ($CD_2OHCOOH$) was formed by the described procedure[33] and its purity was 97.7% which is determined by ^1H NMR spectra. Purification of solvents was determined by the described methods[34]. CS_2 is a combustible and toxic liquid in the midst of solvents, and as resource of hydrogen ions TsOH was utilized. The standard alkali solution was used for standardization of TsOH solution .

Product analysis: Hydroxy acids oxidation leads to formation of corresponding oxoacid which was confirmed by positive iodophenine test[35]. In this experiment, lactic acid (9.0 g, 0.1 mol), TsOH (19.02 g, 0.1 mol), and BIDC (4.54 g, 0.01 mol) in DMSO were compose to 100 ml and it was then left in absence of light for a day to make sure the reaction accomplishment. The solution with 200 ml of 2,4-dinitrophenylhydrazine (saturated) solution in 2 *M* hydrochloric acid was then reacted by above solution and kept in a chiller for whole night, and obtained product corresponding hydrazone was percolated, parched, weighed and with ethyl alcohol recrystallized it and again weighed. The formation of 2,4-dinitrophenylhydrazone DNP, previously and subsequently recrystallization was 3.63 g (92%) and 3.33 g (83%) correspondingly. It was perceived analogus identical (mixed

m.p. and m.p.) to an authentic sample of DNP of phenylglyoxylic acid. Similar experiment was repeated with glycolic acid the yield of DNP of the related oxoacid later recrystallization was around 80–89%.

Stoichiometry: The oxidation of glycolic and lactic acids prompts the development of relating oxoacid. For stoichiometry determination, BIDC (4.54 g, 0.0 mol) and hydroxy acid (0.18 g, 0.002 mol) in DMSO were composed to 200 ml with 1.0 M TsOH. To ensure the completion of the reaction the solution was kept as it is for a day. Spectrophotometrically at 364 nm the residual BIDC was measured. Various observations indicate that three moles of hydroxy acid react with two moles of BIDC at non-identical hydroxy acid concentrations. The outcomes with LA are shown in Table 7. BIDC is reduced to Cr(III) and participating in the reaction as a 3-electron oxidant.

Table 7. Stoichiometry data for the oxidation by BIDC of lactic acid

10^3 [BIDC] (mol dm^{-3})	10^3 [Hydroxy acid] (mol dm^{-3})	10^3 [Unused BIDC] (mol dm^{-3})	[Hydroxy acid] [Used up BIDC]
10.0	2.0	8.68	1.43
10.0	4.0	7.24	1.46
10.0	6.0	6.14	1.55
			Mean = 1.48

Kinetic measurements: The pseudo-first order state were executed for all kinetic runs at constant temperature (±0.1), by sustaining over abundance of hydroxy acid (15 fold or greater) on BIDC. DMSO was used as solvent in the reaction, unless specified. The progress of reaction up to 75% was studied by monitoring the consumption of BIDC at 370 nm. In this investigation for all concentrations Beer's law is applicable. A graph between log [BIDC] and time was linear with $r^2 > 0.99$ and velocity constant (k_{obs}) was obtained from it and for more than two runs replicability ±3% was observed. In correlation analyses coefficient of determination (R^2 or r^2), Exner's parameter[36] (ψ) and standard deviation (sd) was used.

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