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OXIDATION KINETICS AND INFLUENCE OF MEDIA ON SOME α-HYDROXY ACIDS BY 2-PICOLINIUM CHLOROCHROMATE

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ABSTRACT

A few substituted mandelic acids are oxidized by one of the halochromates 2-picolinium chlorochromate (PiCC) under the influence of dimethyl-sulphoxide (DMSO) as a solvent medium, leading to the form of some oxo-acids. It was observed that this reaction is found to be of unit order with oxidant and less than unity with the reactant. It was also observed that the reaction is not proceeding through the free radical mechanism. A considerable kinetic isotope effect was observed in the oxidation of the deuteriated form of mandalic acid (DMA). The solvent isotope effect was also absent in this reaction. The hydrogen ion effect was observed as the rate is increasing with an increase in the acidity of the medium. To ascertain the importance of solvent media, the reaction of the acids is studied in nineteen different solvent media, which was analyzed by the multipara metric LSER model of Taft and solvating power model of Swain. We are proposing the transfer of hydride ions from acid to the oxidant as its mechanism.

Keywords: Correlation Studies, Halochromate, Hydroxy acid, Kinetics, Mechanism, Oxidation.
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INTRODUCTION

Synthetic organic chemistry is known to be the selective oxidation of some organic compounds in non-aqueous solvents.[1-4] 2-picolinium chloro-chromate (PiCC) is also used for the same purpose to oxidize the alcoholic and aldehydic substrates.[5] Our interest is to find out the oxidation kinetics with these types of chromium six compounds, which have already been available in the literature.[6-10] We are unable to find this study in the literature, therefore we are presenting this work on the oxidation kinetics of hydroxy acids with PICC. We also propose to establish and postulate a mechanism for this reaction.

EXPERIMENTAL

Experimental Methods

Acids so used are easily available as common chemicals and are taken to our experiments as supplied. A few mandelic acids are prepared by the method available in the literature.[11] The oxidant used in the investigation is also prepared by the method available in the literature.[5] DMA is also prepared by Kemp and Water's method of preparation.[12] The purity of the DMA is found to be around 94.5%, checked by NMR. PTS is used for the acidity of the medium. A very simple and common method was used to purify the solvent media.[13]

Investigation of Products

We have done the investigation of the product as per our reaction conditions. Means large excess of the substrate over oxidant. A certain amount of substrate and oxidant dissolved in hundred millilitres of solvent and was kept away from light for at least twenty-four hours to complete the reaction. Now, this mixture was treated with a saturated solution of DNP with a certain amount of HCl, two mol dm^{-3} and put in a freezing device for at least twelve hours. Now the precipitated 2-4-DNP so obtained is purified with alcohol after drying and weighing. The products so obtained were found to be the same as checked with their melting and mixed melting points with a valid model of DNP of phenyl glyoxylic acid. All other acids used in the investigation are given the same type of experimental results in a range of 78 to 90 percent receipt of products after being purified by crystallization. The oxidation number of Cr in the last stage of the reaction was found to be ±4.

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Kinetic Calculations

All the reactions are carried out under kinetic conditions. A constant temperature was maintained. The solvent medium was dimethyl sulphoxide. The decrease in the concentration of oxidant was monitored on a spectrophotometer at a lambda max of 361nm and up to four half-lives. The linear least square plots against time are used to calculate the log k_{obs}. All the experiments are done without hydrogen ions except those in which the effect of acidity was studied.

RESULTS AND DISCUSSION

Due to the similar results with all the hydroxy acids under study, only some of the data are presented here.

Stoichiometric Determinations

Hydroxy acids are oxidized as oxo-acids in our reactions, which may be represented as the following overall reaction. The reaction is given below in equation (1).

$$\text{Ar-CH-(OH)-COOH} + O_2CrClO^{-}PicH^{+} \rightarrow$$
$$\text{Ar-CO-COOH} + H2O + OCrClO^{-}PicH^{+} \qquad (1)$$

It has been observed that PiCC showed a change of 2 electrons in its oxidation state. It has already been noticed in the case of similar halochromates like pyridinium chloro-chromate (PCC)[14] and pyridinium fluoro-chromate (PFC).[15] Further, it has also been established that these oxidants are reduced to chromium four state and act as 2 electron oxidizing reagents.

Kinetic Dependence

The reactions are of unit order w.r.t. PICC, and the pseudo-first-order rate constant, are not dependent of the starting concentrations of PICC. The rate of the reaction increases with an increment in concentrations of acids but not in a linear fashion as depicted in Table-1 and Fig.-1. Plot of $1/k_{obs}$ versus 1/[Acid] is linear ($r > 0.995$) with an intercept on rate axis. Thus, fractional order kinetics is observed w.r.t. the alcohol. It can be represented by the following mechanistic steps 2 and 3 and rate law 4.

$$\text{HA} + \text{PiCC} \overset{K}{\underset{k_2}{\leftrightarrows}} [\text{complex}] \qquad (2)$$

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

$$\text{Rate} = k_2 K [\text{HA}] [\text{PiCC}] / (1 + K [\text{HA}]) \qquad (4)$$

Reaction rates are dependent on reactant concentrations, which were studied at four diverse temperatures (288 to 318K). Formation constants K and decomposition constants of the complex k_2 are also calculated. From these K and k_2 various thermodynamic and activation parameters are also evaluated, which are presented in Tables-2 and 3.

Table-1: Values of k_{obs} of Hydroxy Acid (MA) by PiCC at 308 K

10^3 [PiCC] mol dm^{-3}	[HA] mol dm^{-3}	10^4 k_{obs} s^{-1}
1.00	0.10	5.28
1.00	0.20	7.59
1.00	0.40	9.72
1.00	0.60	10.7
1.00	0.80	11.3
1.00	1.00	11.7
1.00	1.50	12.2
1.00	3.00	12.8
2.00	0.20	7.47
4.00	0.20	7.56
6.00	0.20	7.74
8.00	0.20	7.50
1.00	0.40	9.81^{*}

[a] contained 0.001 M acrylonitrile

Table-2: Values of Formation Constants and Thermodynamic Parameters of PiCC–Hydroxy-Acid-Complexes

R	K / (dm^3 mol^{-1})				$-\Delta H^*$	$-\Delta S^*$	$-\Delta G^*$
	288K	298K	308K	318K	(kJ mol^{-1})	(J $mol^{-1}K^{-1}$)	(kJ mol^{-1})
H	6.43	5.60	4.83	4.05	14.2±0.5	25±1	6.74±0.4
p-F	5.94	5.15	4.32	3.53	15.7±0.6	31±2	6.50±0.5
p-Cl	5.85	5.06	4.25	3.42	16.0±0.8	33±2	6.46±0.6
p-Br	6.21	5.43	4.62	3.78	15.0±0.7	29±2	6.64±0.6
p-Me	6.39	5.60	4.77	3.93	18.8±0.7	28±2	6.71±0.5
p-Pr^i	5.67	4.93	4.14	3.34	16.2±0.7	33±2	6.41±0.5
p-OMe	5.58	4.80	3.96	3.17	16.8±0.8	36±3	6.32±0.6
m-Cl	6.03	5.25	4.41	3.62	15.4±0.6	30±2	6.55±0.5
m-NO_2	5.99	5.20	4.38	3.53	15.8±0.8	32±3	6.53±0.6
p-NO_2	5.85	5.02	4.25	3.42	16.0±0.7	32±2	6.45±0.6
GA	5.67	4.88	4.05	3.26	16.5±0.7	35±2	6.36±0.6
LA	5.90	5.04	4.28	3.33	16.1±0.7	33v2	6.47±0.6
MLA	5.72	4.59	4.14	3.3.	16.2±0.8	33±2	6.40±0.6
DMA	5.80	4.99	4.20	3.39	16.0±0.7	33±2	6.43±0.5

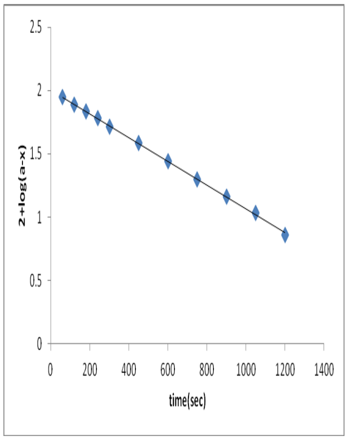


Fig.-1: Oxidation of MA by PiCC: A typical Kinetic graph

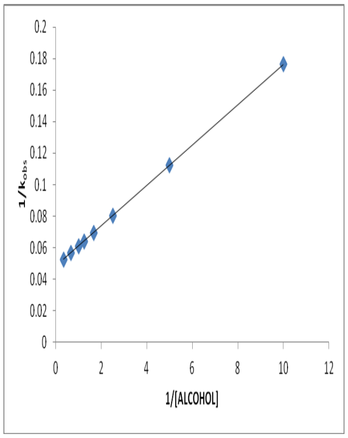


Fig.-2 Oxidation of HAs by PiCC: Plot of 1/k versus 1/acid

Presence of Free Radical Test

Polymerisation by vinyl chloride is done to check the presence of free radical in the reaction. It was done in the inert atmosphere created by nitrogen. The absence of any free radical indicated that no operation of one electron oxidisation process is in operation in this reaction. The experiments with BHT are also not positive in this reaction, is again indicating non-operation of free radical mechanism.

Table-3: Values of k_{obs} and Activation Parameters for Hydroxy-Acid- PiCC Complexes

R	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	13.5	26.1	50.4	92.7	46.5±0.3	139±1	87.7±0.3
p-F	18.9	36.0	68.4	126	45.7±0.4	139±1	86.9±0.4
p-Cl	8.01	15.3	30.6	56.7	47.4±0.6	140±2	89.0±0.5

p-Br	6.57	13.5	26.1	49.5	48.6±0.1	137±1	89.4±0.1
p-Me	58.5	108	189	333	41.5±0.3	144±1	84.2±0.3
p-Pr^i	51.3	93.6	171	288	41.5±0.3	145±1	84.6±0.2
p-OMe	549	918	1490	2340	34.3±0.1	150±1	78.9±0.1
m-Cl	2.34	4.86	9.90	19.8	51.6±0.4	135±1	91.9±0.4
m-NO_2	0.45	0.99	2.25	4.68	57.2±0.2	130±2	95.8±0.5
p-NO_2	0.33	0.72	1.63	3.42	57.0±0.6	133±2	96.6±0.5
GA	5.94	10.8	18.9	33.3	41.1±0.4	164±1	89.9±0.3
LA	8.64	16.2	31.5	58.5	46.2±0.7	144±1	88.7±0.5
MLA	7.47	14.4	27.9	53.1	47.3±0.6	141±2	89.2±0.5
DMA	2.25	4.59	9.36	18.0	50.4±0.4	140±1	92.0±0.3
k_H/k_D	6.00	5.69	5.38	5.15			

Influence of Hydrogen Ions

Reactions are depending upon the concentration of acid, which is reflected in the rate and the relation is represented in equation 5.

$$k_{obs} = a + b[H^+] \qquad (5)$$

The data of a and b, for p-methyl mandelic acid, are $21.3 \pm 1.06 \times 10^{-4}$ s^{-1} and $37.8 \pm 1.75 \times 10^{-4}$ mol^{-1} dm^3 s^{-1} respectively ($r^2 = 0.9914$).

Table-4: Effect of Acidity on the Rate of Reaction

[PiCC] = 0.001 mol dm^{-3}; [HA] = 1.0 mol dm^{-3}; Temp. = 298 K

$[H^+]$/mol dm^{-3}	0.10	0.20	0.40	0.60	0.80	1.00
10^4 k_{obs}/s^{-1}	5.85	6.75	8.82	9.99	11.7	14.4

Effect of Deuterium Isotope

To find out the involvement of the C-H bond in r.d.s, the oxidation of DMA was oxidized and it was observed that the reaction is having a considerable kinetic isotope effect. Results are summarised in Table three as the value of k_H/k_D is 5.69 at 298 K.

Influence of Solvent Medium on Hydroxy Acids

Nineteen different solvents are used to find out the rate and solvent relationship. It is observed that values of K are not varying much as compared to k_2 values at 308K, which are represented in table five.

Table-5: Influence of Media on the Oxidation of p-methylmandelic Acid by PiCC 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})
$CHCl_3$	6.13	33.9	$C_6H_5CH_3$	4.80	8.13
1,2-$C_2H_4Cl_2$	5.58	41.7	$C_6H_5COCH_3$	4.55	47.9
CH_2Cl_2	6.21	32.4	Tetrahydrofuran	5.49	17.8
DMSO	4.86	108	t-Butylalcohol.	5.55	12.3
CH_3COCH_3	4.55	35.5	1,4 – $C_4H_8O_2$	4.59	18.2
Dimethyl formamide	5.88	51.3	1,2- $C_4H_{10}O_2$	5.66	8.32
C_4H_8O	5.85	25.7	Carbon Disulphiode	4.66	4.27
Nitrobenzene	5.94	38.0	CH_3COOH	4.90	7.41
C_6H_6	6.03	12.0	$C_2H_5COOC_2H_5$	5.77	11.2
C_6H_{12}	6.15	1.23			

All the ten HAs are subjected to isokinetic relationship, which shows a linear relationship ($r^2 = 0.9666$), it shows that reaction is proceeding under a compensation effect.[16] This plot was used to calculate the isokinetic temperature[17,18] its 1168±77 K. as per the exner criterion, correlation is found to be perfect.[19] The temperature, calculated from Exner's plot of log k_2 at two extreme temperatures ($r^2 = 0.9998$), is

1261±104 K. (Fig.-3). This relationship shows that all the HAs are oxidizing by the similar mechanism.

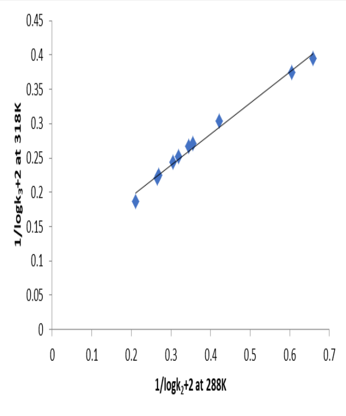


Fig.-3: Graph of Hydroxyacids-PiCC-complexes by Exner Method of Isokinetic Relationship

Influence of Solvents

Kamlet and Taft[20] model of solvent effect is applied to correlate the rate with the LSER method. Carbon disulfide is not taken into the study as the whole series of solvent data are not available.

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

In this equation,
π^* denotes solvent polarity,
β Denotes the hydrogen bond acceptor basicities
α Denotes is the hydrogen bond donor acidity.
A_0 is the intercept term.

As a whole 12 solvents are having a value of alpha is zero. The results, so obtained are summarised below as equations 7 to 10.

$$\log k_2 = -3.92 + (1.63 \pm 0.21)\,\pi^* + (0.15 \pm 0.17)\,\beta - (0.05 \pm 0.16)\,\alpha \qquad (7)$$
$$R^2 = 0.8423; \quad sd = 0.19; \quad n = 18; \quad \Psi = 0.44$$
$$\log k_2 = -3.84 + (1.65 \pm 0.19)\,\pi^* + (0.13 \pm 0.16)\,\beta \qquad (8)$$
$$R^2 = 0.8412; \quad sd = 0.19; \quad n = 18; \quad \Psi = 0.42$$
$$\log k_2 = -3.89 + (1.68 \pm 0.19)\,\pi^* \qquad (9)$$
$$r^2 = 0.8345; \quad sd = 0.18; \quad n = 18; \quad \Psi = 0.42$$
$$\log k_2 = -2.87 + (0.42 \pm 0.36)\,\beta \qquad (10)$$
$$r^2 = 0.0783; \quad sd = 0.44; \quad n = 18; \quad \Psi = 0.99$$

In these equations n represents the data points and ψ is the Exner's mathematical value.[21]
Here 84% of data is explained by the tri-parametric equation of Kamlet[20], where as per the Exner[17] this correlation is not good the mail role is played by solvent polarity, which explains almost 83% of the data point. Alpha and Beeta are not playing any significant role in it.
Therefore, the results are subjected to analyses by another model of cation and anion solvating concept given by Swain's(eqn.-11).[22]

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

In this equation
A is represented by anion-solvating power of the solvent
B the cation-solvating power.
C is the intercept term.
(A + B) is represented the solvent polarity.

As per the relation above, rates of oxidation are subjected to analyses with A, B separately and with A+B also.

$\log k_2 = (0.75 \pm 0.05)\ A + (1.71 \pm 0.04)\ B - 4.06$ (12)
$R^2 = 0.9928;\ sd = 0.04;\ n = 19;\ \Psi = 0.09$
$\log k_2 = 0.50(\pm 0.56)\ A - 2.89$ (13)
$r^2 = 0.0446;\ sd = 0.46;\ n = 19;\ \Psi = 1.00$
$\log k_2 = 1.65\ (\pm 0.14)\ B - 3.92$ (14)
$r^2 = 0.8957;\ sd = 0.15;\ n = 19;\ \Psi = 0.33$
$\log k_2 = 1.39 \pm 0.13\ (A + B) - 4.03$ (15)
$r^2 = 0.8763;\ sd = 0.16;\ n = 19;\ \Psi = 0.36$

Oxidation rates of MA show a very good correlation with Swain's model of solvent effect. Actually, the cation solvating effect alone is explaining 99% of its results, which indicates that a major role is played by the cation solvating effect. The cation solvating effect is showing negligible influence. Solvent polarity is also playing its role and explains 87% of the results. Because of this speciality of solvent polarity, it was correlated with the relative permittivity of the medium. Though the graph plotted between rate and permittivity is non-linear. ($r^2 = 0.5016$; sd = 0.72; $\psi = 0.93$).

Reactivity and Correlation Analysis

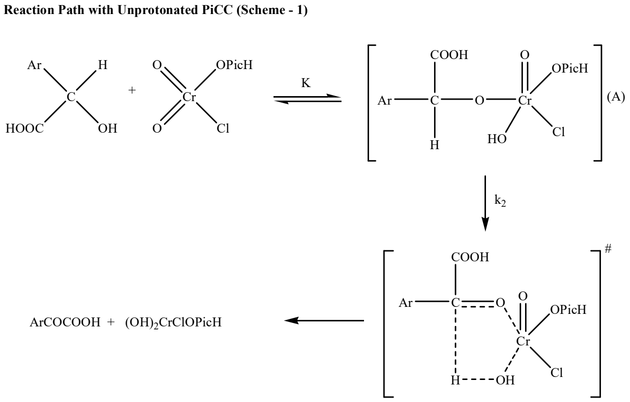
Reaction rates of HAs are subject to correlation on the model of Hammett's using σ values. It did not show a good correlation. But it is observed that rates of HA oxidation are giving an excellent correlation with values of Brown's σ^+.[23] The reactions constants are found to be negative (Table-6). Transition state is carbocationic in nature, has been proved by high negative values of reaction constants in correlation with σ^+ values.

Table-6: Dependence of the Reaction Constant on Temperature

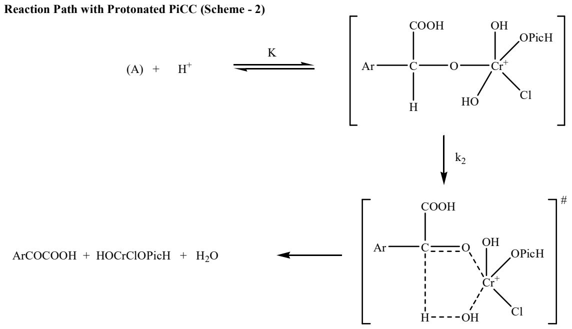
Temp./ K	$-\rho^*$	r^2	Sd	ψ
288	2.07±0.01	0.9999	0.004	0.011
298	1.99±0.01	0.9998	0.008	0.015
308	1.89±0.02	0.9989	0.005	0.035
318	1.81±0.02	0.9999	0.009	0.011

Mechanism

A considerable amount of primary kinetic isotope effect indicates the breaking of alpha C – H bond in the r.d.s. Substantial negative reaction constant (-1.99 at 298 K) along with large primary kinetic isotope influence, is the signal of having a carbon centre move towards to positive in nature. Therefore, a transfer of hydride ion mechanistic path way controlled by cation solvating powers of medium is postulated. It has been observed that –ve reaction constant along with in good correlation with the with Brown's σ^+ values[23] indicating a carbo-cation centre in the transition state. This carbo-cationic nature is also supported by cation solvating power of the solvent media. On the basis of these observation we are of the opinion that a hydride ion transfer mechanism may be involved through a chromate ester. These reactions can continue either of the two path ways. One a reaction which is bimolecular but acyclic in nature. The second may engage a chromate ester transition state but cyclic in nature. Kwart and Nickle[24] resolved this problem by studying a dependence of isotope influence on the temperature of the reaction. The results so observed for protio and duterio secondary alcohols fit into the formula $k_H/k_D = A_H/A_D \exp(E_a/RT$, which shows the corresponding property for transition state[25,26] which is symmetrical in nature, here the difference in activation energies kH over kD is zero energy difference for C-H and C-D bonds, which is almost equal to 4.5 kJ/mol, and these reactions are having almost the same frequency energy disparity in activation entropies. It has already been reported by Boardwell[27] that no one step bimolecular process is not there in these reactions which having hydrogen transfer. Its obvious in this reaction also that hydrogen transfer through acyclic is not taking place. The involvement of a linear hydrogen transfer[28] mechanism is significantly evidenced in concerted sigmatropic reactions. Similar evidence is provided by Littler[29] also, where the oxidation of alcohols by chromium six species is involving six electrons and forms a Huckel-like structure which is evidenced which is permitted one process. Therefore, we propose that the ester intermediate is forming in the fast reaction step which is going to decompose in the rate-determining step through a symmetrical cyclic and planner transition state going to provide the product. On the basis of these mechanistic steps, we propose the following schemes 1 and 2. The proposed mechanism is also supported by the presence of –ve data values activation of entropies. The transition sate is highly charged because of the transfer and the ends are hugely solvated. Therefore a high quantity of solvent molecules are immobilised is resulting into a decrease in the entropy[30] values.



Scheme-1



Scheme-2

CONCLUSION

In the present article, we are going to project that this reaction is subjected to proceed via a hydride ion transfer hydroxy acid to the oxidizing agent way through a chromate ester in the r.d.s. An alpha C - H bond is broken in a slow step. The reactive oxidizing species is PICC (both protonated and unprotonated).

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