



The Oxidative Transformation of Substituted Mandelic acids by Ethylenediammonium Dichromate in AcOH-H₂O medium: (A Kinetic Study)

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ABSTRACT

The oxidation of Mandelic acids to the corresponding oxoacids with ethylenediammonium dichromate (EDDC) in aqueous acetic acid has been studied. The reaction is first order with respect to [EDDC] and less than two order observed for mandelic acids and [H⁺]. The oxidation of α -deuteriomandelic acid shows the presence of a primary kinetic isotope effect ($k_H/k_D=6.01$ at 298K). The reaction has been found to be catalyzed by [H⁺] ions. The various thermodynamic parameters for the oxidation have been reported and discussed along with the validity of the isokinetic relationship. With a negative reaction constant (ρ), the reaction displayed a strong correlation with the Hammett values. All of the chosen Mandelic acids are oxidised by the same process, according to the Exner plot.

Keywords: Mandelic acid, Ethylenediammonium dichromate, Kinetic isotope effect, Isokinetic temperature, Hammett equation.

INTRODUCTION

Chromium (VI) has been approved as a consequential reagent in organic synthesis and has been utilized to oxidize organic compounds in both aqueous and non-aqueous media¹⁻³. It is investigated to be venomous for humans and as well as for plants and it is soluble in water⁴. In organic chemistry, Cr(VI) reagents are often used for hydroxy acid oxidation to oxoacids or ketone. Many different oxidants are being used in various experimental setups to conduct kinetic studies on the oxidation of mandelic acids. In recent years oxidation of α -hydroxy acids by several oxidants, including benzimidazolium dichromate⁵ quinaldinium

fluorochromate⁶, tripropylammonium fluorochromate⁷ pyridinium chlorochromate⁸, morpholinium fluorochromate⁹ and tetrabutylammonium tribromide¹⁰ have been investigated. Recently a new oxidising agent called EDDC has been identified. A literature survey revealed that there is no available reports on the oxidation of mandelic acids by EDDC. Owing to the above arguments, the title reaction has been studied. The objective of this study is to perform a thorough evaluation of the substituent and solvent effects on the oxidation of various para- and meta-substituted mandelic acids in various concentrations of acetic acid-water in order to better understand the mechanism of mandelic acid oxidation.



EXPERIMENTAL

Materials

The current experiment employed only reagent grade chemicals (Merck-Aldrich), and their solutions were created by dissolving the necessary amounts of the samples in double distilled water. The oxidant EDDC was made using the mentioned technique¹¹ and its purity was assessed by iodometric analysis. Mandelic acid was a commercially accessible substance of the greatest purity and was employed as such. Acetic acid was cleaned up according to conventional procedures and the proportion that began to distil at 118°C was gathered.

Product analysis

This study proves that oxoacids were the end result of the oxidation. The 2,4-dinitrophenylhydrazine methodology was used to quantify oxoacids within dynamic environments, i.e. with an abundance of mandelic acid over the oxidant (EDDC). In a common experiment, mandelic acid (0.15 mol, 22.8 g) and EDDC (0.015 mol, 4.17 g) were dissolved in a combination of 50% acetic acid and 50% water with TsOH (0.5 mol dm⁻³). To determine that the reaction had ended, the following solution was left in the dark for 24 hours. The bulk of solvent were eliminated through distillation at a low pressure. The aforementioned solution was combined with 200 mL of a 2,4-dinitrophenylhydrazine (saturated) solution in 2 M hydrochloric acid, and the reaction was then carried out overnight in a refrigerator. After being produced, hydrazone was percolated, dried, and weighed before being re-crystallized with ethyl alcohol and being weighed again. The result (m.p. and combined m.p.) was identical to an actual sample of DNP of benzoylformic acid. Before and after recrystallization, the DNP yields were 4.35 g (88%) and 4.01 g (81%), respectively. After recrystallization, similar tests with additional substituted mandelic acids generated 75-83% of the equivalent oxoacid's DNP yields. The ultimate reduction of Cr(VI) to Cr(III) was shown to occur.

Stoichiometry

Mandelic acid (0.002 mol dm⁻³) and EDDC (0.01 mol dm⁻³) were prepared to a volume of 100 ml in the presence of TsOH (1.0 mol dm⁻³), in order to determine the stoichiometry. In the related rate measurements, the solvent compositions of 50% acetic acid and 50% water (v/v) were maintained. For 24 h, the reaction was allowed to stand in order to ensure that it had finished. According to the findings,

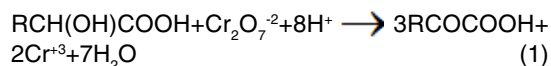
there are 3 moles of mandelic acid for every 1 mole of oxidant, or a 3:1 stoichiometry.

Method

The pseudo first-order condition were executed for all kinetic runs at constant temperature (0.1), by keeping an excess of mandelic acids (15-fold or greater) over EDDC. The solvent was 50% AcOH- 50% water unless specified otherwise.. Residual IQDC was measured with the help of spectrophotometer (Systronics, model no. 177) at 370nm. The progress of reaction up to 75% was studied by the help of spectrophotometer (Systronics, model no. 177) with monitoring the consumption of EDDC at 356nm. In this investigation for all concentrations Beer's law is applicable. A graphic between log [EDDC] and time was linear with r²>0.99 and rate constant (k_{obs}) was obtained from it and for more than two runs replicability 3% was observed. In correlation analyses coefficient of determination (R² or r²), standard deviation (sd) and Exner's parameter (ψ)¹² was used.

RESULTS

For all of the substituted mandelic acids, the rate laws and further experimental studies were established. The oxidation of mandelic acid and substituted mandelic acids, the equivalent oxoacids are produced by EDDC. A stoichiometric determination indicates the general reaction that follows:



R is a phenyl or a substituted phenyl group in this particular case where substituents are m-Cl, m-Br, m-NO₂, p-OMe, p-Me, p-F, p-Cl, p-Br, p-NO₂.

Induced polymerization of cyanoethylene

Cyanoethylene did not polymerize when mandelic acid was oxidised by EDDC in a nitrogen environment. The rate of oxidation was also unaffected by the addition of cyanoethylene (Table 1). The reaction was performed with the addition of 0.1M butylated hydroxytoluene (BHT) in order to further verify a chemical route without free radicals (BHT). BHT was found to be essentially quantitatively unaltered.

Rate laws

In terms of EDDC, the reaction was observed to be of first order. Plotting log (EDDC)

vs time throughout individual kinetic runs revealed linear behaviour ($r^2 > 0.99$). Additionally, EDDC initial concentration had no impact on the pseudo first-order rate constants (Table 1). Regarding MA, the order ranged from one to two (Table 1).

Table 1: Rate constants for oxidation of mandelic acid by EDDC at 298K

[Mandelic acid] (mol dm ⁻³)	10 ³ [EDDC] (mol dm ⁻³)	[H ⁺] (mol dm ⁻³)	10 ⁴ k _{exp} (sec ⁻¹)
0.05	1.0	0.5	0.53
0.1	1.0	0.5	1.69
0.15	1.0	0.5	4.5
0.25	1.0	0.5	9.6
0.4	1.0	0.5	16.7
0.6	1.0	0.5	23.9
1.0	1.0	0.5	29.3
2.0	1v	0.5	33.5
1.0	1.5	0.5	30.2
1.0	2.5	0.5	28.9
1.0	4.0	0.5	29.8
0.6	1.0	0.5	a22.5
0.6	1.0	0.5	b23.9

Based on the downward curvature of the plots it appears that a complex relationship exists. Plotting $1/k_{exp}$ versus $1/[\text{Mandelic acid}]^2$ revealed a linear relationship with an intercept on the rate-ordinate Figure 1.

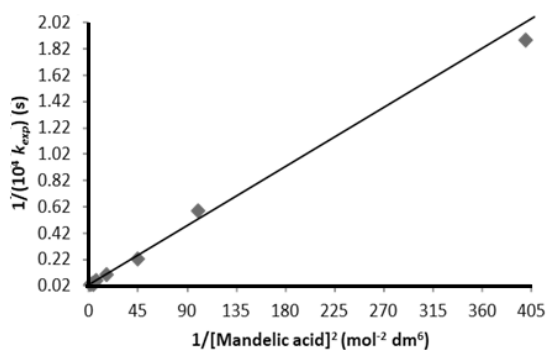
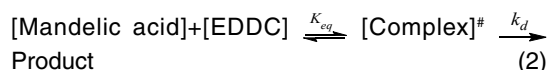


Fig. 1. Plot of $1/(10^4 k_{exp})$ vs $1/[\text{Mandelic acid}]^2$ at 298K [H⁺] = 0.5 mol dm⁻³, 10³[EDDC]=1.0 mol dm⁻³

Table 2: Formation constants and thermodynamic parameters for [Mandelic acid - EDDC] complexes

Substituents	K _{eq} (mol ⁻² dm ⁶)				ΔH _f (kJmol ⁻¹)	ΔS _f (Jmol ⁻¹ K ⁻¹)	ΔG _f (298K) (kJmol ⁻¹)
	298K	308K	318K	328K			
H	6.33	3.90	2.80	1.6	-38.6±1.8	-106±5.8	-7.10±1.4
m-Cl	6.19	4.03	2.85	1.55	-39.0±2.1	-107±7.7	-7.10±1.8
m-Br	5.92	3.82	2.56	1.49	-39.3±1.5	-109±4.9	-7.00±1.1
m-NO ₂	6.25	3.75	2.62	1.7	-37.1±0.8	-102±2.8	-6.90±0.7
p-OMe	6.45	3.79	2.65	1.69	-38.0±1.1	-105±3.2	-7.06±0.8
p-Me	6.08	3.86	2.64	1.56	-38.6±1.4	-107±4.4	-7.01±1.07
p-F	6.81	3.86	2.89	1.72	-38.3±1.9	-105±6.1	-7.20±1.5
p-Cl	6.59	4.10	2.76	1.51	-41.5±1.9	-116±6.2	-7.24±1.5
p-Br	6.25	3.95	2.70	1.42	-41.6±2.4	-116±7.9	-7.14±1.9
p-NO ₂	6.64	3.96	2.91	1.81	-36.6±1.4	-100±4.5	-7.14±1.1

As a result, the following general mechanism and rate equation are postulated.



$$\text{Rate} = k_d K_{eq} [\text{Mandelic acid}]^2 [\text{EDDC}] / (1 + K_{eq} [\text{Mandelic acid}]^2) \quad (3)$$

$$\text{Or, } (\text{Rate} / [\text{EDDC}]t) - 1 = 1/k_{exp} = 1/k_d K_{eq} [\text{Mandelic acid}]^2 + 1/k_d \text{ Here, } [\text{EDDC}]_t = [\text{Complex}] + [\text{EDDC}] \quad (4)$$

At various temperatures, equation (4) was used to examine the influence of k_{exp} on the concentration of Mandelic acid, the double reciprocal plots were used to compute the values of K_{eq} and k_d . Using the corresponding values of K_{eq} and k_d at various temperatures, the activation components for the complex breakdown and the thermodynamic components for the complex creation were computed. (Tables 2 and 3).

Kinetic isotopic effect

It was investigated that the cleavage of the α-C-H bond had a role in the rate-determining phase during the oxidation of deuterated mandelic acid by EDDC. The findings (Tables 2 and 3) revealed that while the rates of their breakdown had a significant kinetic isotope effect ($k_H/k_D = 6.01$ at 298 K), the formation constants of the complexes of ordinary and deuterated mandelic acids were quite similar. In the mandelic acid oxidation by water based chromic acid, the value of a primary kinetic isotope effect of ca. 6 was found to be substantially comparable¹³. In the current investigation, the kinetic isotope effect's value also dropped as temperature rose.

Table 3: Rate constants for decomposition of [Mandelic acid-EDDC] complexes and their activation parameters

Substituents	103k _d (s ⁻¹)			ΔH* (kJmol ⁻¹)	ΔS* (Jmol ⁻¹ K ⁻¹)	ΔG* (298K) (kJmol ⁻¹)	
	298K308K	318K328K					
H	3.43	7.12	15.6	34.7	60.1±1.4	-91±4.6	87.2±1.10
m-Cl	0.71	1.70	3.80	0.80	65.3±0.7	-87±2.3	91.0±0.56
m-Br	0.65	1.60	3.50	8.20	65.6±0.8	-86±2.7	91.2±0.65
m-NO ₂	0.17	0.42	1.03	2.60	71.2±1.1	-79±3.7	94.6±0.91
p-OMe	10.7	22.1	43.2	94.0	55.8±1.3	-96±4.3	84.3±1.00
p-Me	7.05	15.0	29.7	65.1	57.1±1.2	-95±3.9	85.3±0.96
p-F	2.64	5.60	13.1	28.6	62.4±1.3	-86±4.1	87.8±1.00
p-Cl	1.32	3.10	6.70	15.6	64.0±1.0	-86±3.1	89.5±0.75
p-Br	1.28	2.82	6.40	14.5	63.2±1.1	-89±3.6	89.6±0.87
p-NO ₂	0.12	0.32	0.80	2.10	74.6±1.0	-70±3.1	95.4±0.70
Deuteriated mandelic acid	0.57	1.26	2.93	6.73			
k _H /k _D	6.01	5.72	5.32	5.15			

Effect of acidity

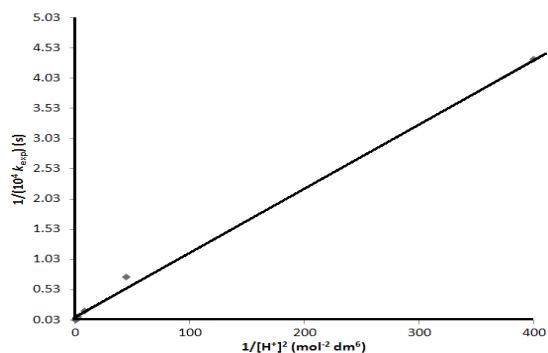
On increasing acidity, the rate of oxidation is also increasing (Table 4). log-log plot between k_{exp} against [H⁺] has a slope of 1.62±0.02 and r²>0.99, indicating that it is linear. It shown that the order in relation to [H⁺] is less than two.

As a result, a plot of k_{exp}⁻¹ vs [H⁺]² was made, and it was discovered to be linear with a clear intercept (Fig. 2). In the absence of TsOH, there was no noticeable effect.

Table 4: Dependence of reaction rate of mandelic acid on hydrogen-ion concentration

[H ⁺](mol dm ⁻³)	0.05	0.15	0.35	0.6	0.75	1.0
104k _{exp} (s ⁻¹)	0.23	1.35	5.4	13.2	20.1	29.3

[Mandelic acid]=1.0 mol dm⁻³, 10³[EDDC]=1.0 mol dm⁻³, temperature=298K

**Fig. 2. Plot of 1/(10⁴k_{exp}) vs 1/[H⁺]² at 298K [Mandelic acid]=1.0 mol dm⁻³, 10³[EDDC]=1.0 mol dm⁻³****Polarity of the solvent and reaction rate**

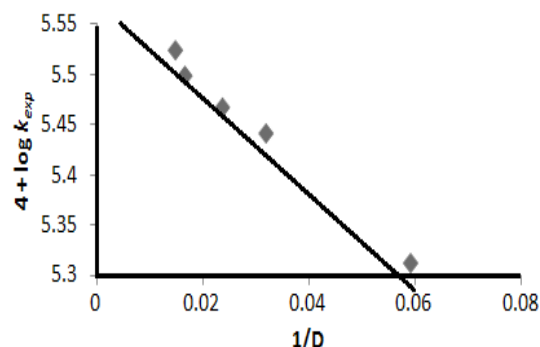
Acetic acid's content is increased from 30% to 70%, investigations were conducted to determine how the solvent content affected the reaction rate

(Table 5). The plot of logk_d vs 1/D [Dielectric constant (D)] is linear and has a positive slope, which suggests that the oxidant and substrate have a dipole-dipole or ion-dipole interaction (Fig. 3). The curvature in the log(k_d) vs (D-1)/(2D+1) picture reveals the lack of dipole-dipole interaction in the rate regulating step¹⁴. Similar kind of solvent polarity effect on rate observed for oxidation of diols by IQDC¹⁵.

Table 5: Effect of solvent polarity on the rate of reaction at 298K

%AcOH-H ₂ O(v/v)	D	1/D	10 ⁴ k _{exp} (s ⁻¹)
15-85	67.46	0.0148	33.4
25-75	60.23	0.0166	31.5
50-50	42.17	0.0237	29.3
65-35	31.33	0.0319	27.6
85-15	16.88	0.0592	20.5

[Mandelic acid]=1.0 mol dm⁻³, [H⁺]=0.5 mol dm⁻³, 10³[EDDC]=1.0 mol dm⁻³

**Fig. 3. Plot of logk_{exp} vs 1/D, showing the effect of solvent polarity for the oxidation of mandelic acid****Isokinetic temperature**

The entropies and enthalpies of activation of the oxidation of mandelic acid and substituted

mandelic acid demonstrated a satisfactory correlation ($r^2=0.9716$). Exner's criteria¹⁶ was used to test the correlation and determine its authenticity. Exner's plot of $\log k_d$ values at 298K and 328K for the substituted mandelic acid was linear ($r^2= 0.9997$). The isokinetic temperature value based on Exner's method, was 825 ± 74 K. The validity of the free energy linear relationship is dependent on the existence of a linear isokinetic relationship¹⁶. This suggests that there is a common mechanism shared by all such correlated reactions.

Reactive oxidising species

Following proton transfer, it appears that EDDC is an ionic molecule. Conductivity measurements were taken at 298K to assess the state of EDDC under our reaction parameters. The observed proton concentration relationship suggests that [EDDC] is protonated, resulting in $\text{enH}_2[\text{Cr}_2\text{O}_7\text{H}_2]^{+2}$ species (Q) that is more effective oxidising agent and active electrophile [eqn (6)].

Further, The following is how the rate relates to $[\text{H}^+]$:

$$k_{\text{exp}} = \alpha[\text{H}]^2 / 1 + \beta[\text{H}]^2 \quad (6)$$

Similar kind of $[\text{H}^+]$ dependency on rate observed for oxidation of amino acids by BDC¹⁷.

DISCUSSION

Correlation analysis of reactivity

A review of the values in Table 2 and 3 indicates that the formation constants, K_{eq} , of the substituted Mandelic acid-EDDC complexes are not very responsive to substitution in the aromatic ring. Similar findings have already been reported in the oxidation processes of various Cr(VI) complexes^{18,19}. However, the complex rates of decomposition, k_d , vary significantly with the substitution. Hammett values were correlated with the mandelic acid and substituted mandelic acid k_d values²⁰.

$$\log k_d = \log k_0 + \rho\sigma \quad (7)$$

Here, the reaction constant is ρ , the substituent constant is σ , the rate constant for mandelic acid is k_0 , and the rate constant for substituted mandelic acid is k_d .

$\log(k_d)$ vs (σ) is linearly plotted (Fig. 4). The analysis revealed excellent correlations with negative reaction constants (Table 6). When the temperature rises, the value of the ' ρ ' falls. This states that when the temperature rises, the reaction's specificity reduces.

Table 6. Temperature dependence of the reaction constants in the oxidation of mandelic acids by EDDC

T(K)	ρ	R^2	sd	ψ	Data points
298	-1.85 ± 0.006	0.9998	0.006	0.015	10
308	-1.74 ± 0.012	0.9995	0.014	0.023	10
318	-1.66 ± 0.001	0.9997	0.0093	0.018	10
328	-1.59 ± 0.006	0.9992	0.0091	0.029	10

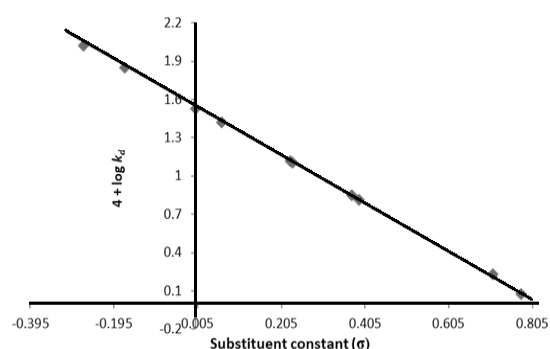


Fig. 4. Aplot of ($4+\log k_d$) vs Hammett values, for the substituted mandelic acid oxidation by EDDC at 298K

Mechanism

Since cyanoethylene has so little influence on the reaction rate, oxidation via single electron resulting to free radicals is unlikely in this process²¹. BHT works well as a free radical trap. The fact that BHT was retrieved intact further opposes the presence of a single-electron oxidation. In the reaction the great magnitude obtained of reaction constant that validates the absence of single-electron oxidation. The majority of hydrogen abstraction processes have relatively tiny reaction constant values²². Prior protonation of EDDC to produce $\text{enH}_2[\text{Cr}_2\text{O}_7\text{H}_2]^{+2}$ was made possible by acid catalysis (Q). The solvent's significant cation-solvating capacity serves as evidence for this. This type of kinetics led us to suggest the formation of 2:1 complex (R) in a rapid pre-equilibrium. A nucleophilic attack of hydroxyl oxygen on $\text{enH}_2[\text{Cr}_2\text{O}_5(\text{OH})_2]^{+2}$ results in the complex (R) is postulated. According to the observed sequence of reactivity, the oxidation process was accelerated by electron-releasing groups. This is accounted for by a rise in the oxygen's hydroxyl oxygen's electron availability, which promotes complex formation.

Complexes of regular and deuterated mandelic acid have essentially comparable formation constants. However, there was a noticeable kinetic isotope effect on the rates of their decay. In other words, the α -C-H bond is broken at the rate-determining phase. The emergence of a polar transition state with characteristics that are close to carbocationic is indicated by the minimum negative reaction constant value and the isotope effect. In order to produce the corresponding oxoacid, the complex (R) then goes through a rate-determining hydride-ion transfer from substrate to oxidant (Scheme 1). The cation-solvating ability of the solvents, which plays a significant role, further promotes the hydride-ion transfer process. But in some reports on the oxidation of substituted mandelic acid, the slow step-by-step formation of a carbonium centre is hypothesized^{23,24}.

To transfer hydride ions, one may employ either by a chromate ester or an acyclic procedure. The loss of hydrogen happens by a coordinated cyclic process, according to a Kwart and Nickle method²⁵ analysis of the kinetic isotope effect that occurs temperature dependence. The known equation was employed to analyze the information for mandelic acid and deuterated mandelic acid.

$$k_H/k_D = A_H/A_D e^{-(\Delta E_a/RT)} \quad (8)$$

The findings show that the entropy of activation of the various processes is strikingly comparable and that the activation energy difference for k_H/k_D is 4.36 kJ mol⁻¹, which is in line with the respective C-H and C-D bond's zero-point energy differences. (approximately 4.50 kJ mol⁻¹). This closely resembles a symmetrical transition state's characteristic^{26,27}. When secondary alcohols are oxidised by BDC, similar results has previously been noted²⁸. Bordwell has vehemently rejected the existence of a concerted one-step bimolecular hydrogen transfer process²⁹. It is obvious that the current reaction does not transfer hydrogen through an acyclic bimolecular mechanism.

Only genuinely concerted sigmatropic reactions with a cyclic transition state are fully symmetrical processes requiring linear hydrogen transfer³⁰. As a result, it is safe to conclude that the hydride-ion transfer happens via a cyclic transition state during the oxidation of mandelic acid by EDDC. The experimental findings are explained by a

mechanism shown in Scheme 1. The technique suggested in Scheme 1 may be used to get the rate law, which is shown below:

The equilibrium treatment may be used to calculate EDDC:

$$-d[\text{EDDC}]/dt = k_d[R] = k_d K_{eq} [\text{Mandelic acid}]^2 [Q] \quad (9)$$

$$= k_d K_p K_q [\text{Mandelic acid}]^2 [\text{EDDC}] [\text{H}^+]^2 \quad (10)$$

$$-d[\text{EDDC}]/dt = \frac{k_d K_p K_q [\text{Mandelic acid}]^2 [\text{EDDC}]_t [\text{H}^+]^2}{1 + k_d K_p K_q [\text{Mandelic acid}]^2 [\text{H}^+]^2} \quad (11)$$

$$-d[\text{EDDC}]/dt = \frac{k_d K_p K_q [\text{Mandelic acid}]^2 [\text{H}^+]^2}{[\text{EDDC}]_t + K_p K_q [\text{Mandelic acid}]^2 [\text{H}^+]^2} \quad (12)$$

Here, $[\text{EDDC}]_t = [\text{EDDC}] + [\text{Complex}]$, where K_p is small and $[Q]$ formed will undergo reaction with mandelic acid.

$$\text{Or, } 1/k_{\text{exp}} = 1/k_d K_p K_q [\text{Mandelic acid}]^2 [\text{H}^+]^2 + 1/k_d \quad (13)$$

The reaction system is well described by equations (11) or (12). Comparing eq. (4) with (13), we get

$$K_{eq} = K_p K_q [\text{H}^+]^2 \quad (14)$$

The observed negative entropy ($-\Delta S$) of activation provides additional evidence for the proposed mechanism. As charge separation occurs in the transition state, the two ends extensively solvate. As a result, multiple molecules of solvent are immobilised, which is depicted by the entropy loss. The solvent effect is further explained by the $-\Delta S$ value. First, Cr(VI) is transformed into Cr(IV). This is intended to combine with another Cr(VI) to generate Cr(V), which will then be promptly reduced to the final product Cr(III). It is generally accepted that these steps take place during Cr(VI) oxidations in this manner³¹.

CONCLUSION

The oxidation of mandelic acids by EDDC in acetic acid (50%)-water (50%) resulted in the production of the corresponding oxoacid. The reaction has first order kinetics according

to EDDC, while for mandelic acids order is less than two. The reactive oxidizing species is the doubly protonated EDDC, and hydrogen ions are used to catalyze the reactions. Cleavage of the α -C-H bond is observed during the rate-determining phase. It is suggested that the complex goes through rate-determining oxidative breakdown by the transfer of hydride ions from substrate to oxidant, producing the corresponding oxoacid as a product.

ACKNOWLEDGEMENT

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Conflict of interest

No known financial or personal conflict of interest that might have affected the study's conclusion has been found.

REFERENCES

1. Dipti; Tomar, A.; Kumar, A., Kinetic and Mechanistic Studies of the Oxidation of Crotonaldehyde by Tetraethylammonium Chlorochromate in Aqueous Acetic Acid Medium, *Oxid. Commun.* **2012**, *35*, 569-575 <https://scibulcom.net/en/article/itGeZ0pMCM6fY4dGRYX0>.
2. Krishnamoorthy, G.S.; Periyasamy, S.K. *Int. Lett. Chem. Phys. Astron.* **2012**, *5*, 8-19 <https://doi.org/10.18052/www.scipress.com/ILCPA.5.8>.
3. Bhupendra, A. M. B.; Hiran, B. L., kinetics and mechanism of oxidation of benzaldehyde and 4-nitrobenzaldehyde by pyridinium dichromate in aquo-acetic acid medium, *Oxid. Commun.*, **2012**, *35*, 560-568. <https://scibulcom.net/en/article/8RjnUTmOPAhOHOTrrkJg>.
4. Sharma P.; Singh S.P.; Parakh S. K.; Tong Y. W., Health hazards of hexavalent Cr(VI) and its microbial reduction, *Bio engineered.*, **2022**, *13*, 4923-4938. doi: 10.1080/21655979.2022.2037273.
5. Panday, D.; Kachawa, T.; Kothari, S., Kinetics and correlation analysis of reactivity in the oxidation of some α hydroxy acids by benzimidazolium dichromate, *Prog. React. Kinet. Mech.*, **2018**, *43*, 300-314 <https://doi.org/10.3184/146867818X15319903829236>
6. Anbarasu K.; Vasandra D.V., Reactivity of α -hydroxy acids towards quinaldinium fluorochromate, *J appl Sci comput.*, **2019**, *6*, 528-537. DOI:16.10089.JASC.2019.V6I6.453459.1500101562.
7. Shanthi,S.;Asghar, B. H. Mansoor, S. S.,The Kinetics of Tripropylammonium Fluorochromate Oxidation of Mandelic Acids, *Iran. J. Chem. Chem. Eng.*, **2018**, *37*, 97-105 doi: 10.30492/IJCCE.2018.34157.
8. Jain, S.; Hiran, B. L.; Bhatt, C.V., Kinetics and Mechanism of the Oxidation of Lactic Acid and Mandelic Acid by Pyridinium Chlorochromate in Aqueous Acidic Medium, *E-Journal of Chemistry.*, **2009**, *6*, 273-280 <https://downloads.hindawi.com/journals/chem/2009/786890.pdf>.
9. Purohit, V.; Mishra, P., Different α -hydroxy acids oxidation by morpholinium fluorochromate: a kinetic and mechanistic study, *Int. J. Innov. Res. Rev.*, **2018**, *6*, 27-37. <https://www.cibtech.org/J-Innovative-Research-Review/Publications/2018/VOL-NO-1/04-JIRR-005-PALLAVI-HYDROXY-MORPHOLINIUM.pdf>.
10. Baghmar, M.; Sharma, P. K., Kinetics and mechanism of the oxidation of α -hydroxy acids by tetrabutylammonium tribromide, *Indian J. Chem.*, **2001**, *40A*, 311-315 <http://nopr.niscpr.res.in/handle/123456789/18474>.
11. Srinivasan, B.R.; Dhuri, S.N.; Nather, C.; Bensch, W., Synthesis, spectroscopic and X-ray structure characterization of ethylenediammonium chromate and ethylenediammonium dichromate, *Indian J. Chem.*, **2003**, *42A*, 2735-2741. <http://nopr.niscpr.res.in/handle/123456789/20784>.
12. Exner O.; *Collect. Czech. Chem. Commun.*, **1966**, *31*, 3222-3251. <https://doi.org/10.1135/cccc19663222>.
13. Kemp, T. J.; Waters, W.A., The Catalysis by Manganous Ions of Oxidations by Aqueous Chromic Acid, *J. Chem. Soc.*, **1964**, *3193*. <https://doi.org/10.1039/JR9640003193>
14. Amis, E. S., Solvent Effects on Reaction Rates and Mechanisms, Academic Press, New York **1967**, 42.
15. Kalal R.; Panday D., Kinetics and mechanistic study of the oxidation of some diols by isoquinolinium dichromate in aqueous acetic acid medium, *Oxid Commun.*, **2021**, *44*, 513-522.

16. Exner, O., The Enthalpy-Entropy Relationship, *Prog. Phys. Org. Chem.*, **1973**, *10*, 411-482 <http://doi.org/10.1002/9780470171899.ch6>
17. Kachawa T.; Kalal R.; Pandey D.; and Kothari S. Mechanistic studies of oxidation of some alpha amino acids by benzimidazolium dichromate. *Oxid Commun.*, **2019**, *42*, 307-317.
18. Panday, D.; Kothari, S., Kinetics and correlation analysis of reactivity in the oxidation of aromatic aldehydes by butyltriphenylphosphonium dichromate, *Prog. React. Kinet. Mech.*, **2008**, *33*, 293-311 <https://doi.org/10.3184/146867808X340546>
19. Banerji, K.K., Oxidation of Substituted Benzyl Alcohols by Pyridinium Fluorochromate: A Kinetic Study, *J. Org. Chem.*, **1988**, *53*, 2154-2159 <https://doi.org/10.1021/jo00245a004>
20. Johnson, C.D., The Hammett equation, Cambridge University Press, Cambridge, **1973**, 1-67.
21. Mohajer, D.; Tangetaninejad, S., Efficient Olefin Epoxidation with Tetrabutylammonium Periodate Catalyzed by Manganese Porphyrin in the Presence of Imidazole, *Tetrahedron Lett.*, **1994**, *35*, 945-948. [https://doi.org/10.1016/S0040-4039\(00\)76007-2](https://doi.org/10.1016/S0040-4039(00)76007-2)
22. Wiberg, K. B. Physical organic chemistry, Wiley, New York., **1963**.
23. Vyas, V.K.; Kothari, S.; Banerji, K.K., Kinetics and mechanism of oxidation of aliphatic aldehydes by N-bromobenzamide, *Indian J. Chem. Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.*, **1996**, *35*, 112-115 <http://nopr.niscpr.res.in/handle/123456789/41264>.
24. Goyal, A.; Kothari, S., Kinetics and Mechanism of the Oxidation of Some -Hydroxy Acids by Benzyltrimethylammonium Dichloroiodate, *Bull. Chem. Soc. Jpn.*, **2003**, *76*, 2335-2339 <https://doi.org/10.1246/bcsj.76.2335>.
25. Kwart, H.; Nickle, J.H., Transition States in Chromium(VI) Oxidation of Alcohols, *J. Am. Chem. Soc.*, **1973**, *95*, 3394-3396 <https://doi.org/10.1021/ja00791a059>.
26. Kwart, H.; Latimore, M.C., The Kinetic Deuterium Isotope Criterion for Concertedness, *J. Am. Chem. Soc.* **1971**, *93*, 3770-3771 <https://doi.org/10.1021/ja00744a038>.
27. Kwart, H.; Slutsky, J., Transition-state Structure in Thermal *trans*-Elimination of Esters, *J. Chem. Soc. Chem. Commun.*, **1972**, *21*, 1182-1183 <https://doi.org/10.1039/C39720001182>.
28. Kumar, R.; Panday, D.; Kothari, S., Kinetics and mechanism of the oxidation of some secondary alcohols by benzimidazolium dichromate, *Prog. React. Kinet. Mech.*, **2011**, *36*, 1-17 [doi:10.3184/146867810X12894108189440](https://doi.org/10.3184/146867810X12894108189440).
29. Bordwell, F.G., How Common Are Base-Initiated, Concerted 1,2 Eliminations?, *Acc. Chem. Res.*, **1972**, *5*, 374-381. <https://doi.org/10.1021/ar50059a003>.
30. Woodward, R.B.; Hoffmann, R., The Conservation of Orbital Symmetry, *Angew. Chem.*, **1969**, *8*, 781-853 <https://doi.org/10.1002/anie.196907811>.
31. Milazzo, G.; Caroli, S.; Sharma, V.K., Tables of Standard Electrode Potentials. New York: *Wiley and Sons.*, **1978**, *82*, 1114. <https://doi.org/10.1002/bbpc.19780821020>.