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Kinetic and mechanistic features of glycolic and lactic acids are selectively oxidized by trichloroisocyanuric acid

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Abstract
Trichloroisocyanuric acid (TCCA) selectively oxidizes α-hydroxy acids, such as lactic and glycolic acids, in a dimethyl sulfoxide (DMSO) medium to create the appropriate oxoacid. For hydroxy acids, a Michaelis-Menten type kinetics was seen, however for TCCA, a unit dependency on rate was noted. The formation constants and decomposition rates of α-hydroxy acid TCCA complexes have been assessed at different temperatures. For the complex's creation and disintegration, respectively, the thermodynamic and activation parameters have been established. As the concentration of protons rises, the oxidation process quickens. The deuterium isotope effect suggests an α-C-H bond fisson in the rate-controlling phase. Glycolic acid oxidation was found to have k_H/k_D = 5.74 at 298 K. 19 organic solvents were used to assess the oxidation rates, and it was found that the cation's solvating capability played a bigger part. A method that suggests a rate-controlling breakdown of the complex to produce the final product through hydride-ion transfer with a cyclic transition state depends on the kinetic parameters, solvent effect analysis, and thermodynamic parameter results.

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

I. Introduction

The oxidation of organic molecules under non-aqueous medium is a significant reaction in synthetic organic chemistry. As a result, several Cr(VI) complexes have been reported [1,2]. A compound of Cr(VI) called trichloroisocyanuric acid (TCCA) was discovered in 1998. Compared to other Cr(VI) derivatives, TCCA is easier to store and more stable because it is neither light-sensitive nor hygroscopic. It is widely known that TCCA may convert allylic alcohols to their corresponding carbonyl compounds with a yield of 75 to 98% [3]. We concentrate on mechanistic studies involving the kinetic features of the oxidation by TCCA, and some research articles from our lab have already been published [4–10]. According to the literature, no research on the oxidation kinetics of lactic and glycolic acids by TCCA has been published. Here, we examine the oxidation kinetics of lactic acid (LA) and glycolic acid (GA) by TCCA in solvent DMSO.

II. Experimental

Materials

Oxidant TCCA was created using the method outlined in process 3, and its immaculateness was assessed using iodometry. The hydroxy acids were used exactly as supplied due to their highest level of cleanliness. Alkalimetry was used to standardize solutions of lactic and glycolic acids. ^{1}H NMR spectra showed that the purity of α,α-dideuterio-glycolic acid ($CD_2OHCOOH$) was 97.7%, and it was produced using the method described in procedure [11]. The methods mentioned [12] were used to determine the purification of solvents. TsOH was used as a source of hydrogen ions since CS_2 is a hazardous and combustible liquid in the presence of solvents. The TsOH solution was standardized using the standard alkali solution.

Product analysis

A positive iodophenine test [13] confirmed that the oxidation of hydroxy acids results in the formation of a matching oxoacid. In order to ensure the completion of the reaction, 100 milliliters of lactic acid (9.0 g, 0.1 mol), TsOH (19.02 g, 0.1 mol) and TCCA (4.54 g, 0.01 mol) in DMSO were combined. The mixture was then left in the dark for a day. After reacting with 200 milliliters of 2,4-dinitrophenylhydrazine (saturated) solution in 2 M hydrochloric acid, the mixture was placed in a chiller for the entire night. The resulting hydrazone was then percolated, dried, weighed, and recrystallized with ethyl alcohol before being weighed once more. The creation of 2,4-dinitrophenylhydrazone DNP, earlier and subse quently recrystallization was 3.63 g (92%) and 3.33 g (83%) correspondingly. It was thought to be

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analogous to a real sample of phenylglyoxylic acid DNP (mixed m.p. and m.p.). A similar experiment was conducted using glycolic acid, and the yield of DNP of the associated oxoacid after recrystallization was approximately 80–89%.

Stoichiometry

Relating oxoacids are created when lactic and glycolic acids oxidize. TCCA (4.54 g, 0.0 mol) and hydroxy acid (0.18 g, 0.002 mol) in DMSO were mixed to 200 ml with 1.0 M TsOH in order to determine stoichiometry. The solution was left unaltered for a day in order to guarantee the reaction's completion. The residual TCCA was determined using spectrophotometry at 364 nm. Three moles of hydroxy acid react with two moles of TCCA at different hydroxy acid concentrations, according to a number of observations. Table 1 displays the results with LA. TCCA is reduced to Cr(III) and acts as a 3-electron oxidant in the process.

Table 1 Stoichiometry data for the oxidation by TCCA 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

Kinetic measurements

By maintaining an excess of hydroxy acid (15 times or more) on TCCA, the pseudo-first order state was carried out for all kinetic runs at a constant temperature (±0.1). Unless otherwise noted, DMSO served as the reaction's solvent. By tracking the consumption of TCCA at 370 nm, the reaction's progress up to 75% was examined. Beer's law applies to this inquiry at all concentrations. The velocity constant (k_{obs}) was derived using a linear graph between log [TCCA] and time with $r^2 > 0.99$, and replicability of ±3% was noted for more than two runs.

Coefficient of determination (R^2 or r^2), Exner's parameter [14] (Ψ) and standard deviation (sd) were included in correlation analysis.

III. Results and discussion

The following general reactions for the oxidation of GA and LA, respectively, were confirmed by the stoichiometric ratios, [substrate]/[TCCA].

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

$$3CH_3CH(OH)COOH + 2Cr_2O_7^{2-} + 22H^+ \rightarrow 3CH_3COCOOH + 2Cr^{6+} + 2Cr^{3+} + 14H2O \quad (2)$$

The graph showed a straight line ($r^2 > 0.996$) between the logarithms of [TCCA] and time in this oxidation reaction since unit dependency was evident as for TCCA. The pseudo-first order velocity constant, or k_{obs}, does not significantly change with TCCA starting concentration (Table 2). The fractional dependency (0 < order < 1) was observed for hydroxy acids (Table 2). A graphic between k_{obs} and [Hydroxy acid] is shown in Fig. 1. The development of a complex is revealed by the curve of the plots that lead to a lower level. Fig. 2 shows a straight line with a positive intercept in the double reciprocal graph between $1/k_{obs}$ and 1/[Hydroxy acid]. Thus, a Michaelis-Menten kind kinetics was seen for each GA and LA. This implies that the following rate rule and mechanism exist:

$$\text{Hydroxy acid} + \text{TCCA} \overset{K^{\#}}{\Leftrightarrow} [\text{Complex}) \quad (3)$$

$$[\text{Complex}] \overset{k_2}{\rightarrow} \text{Product} \quad (4)$$

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

$$\text{or, } 1/(\text{Rate}/[\text{TCCA}]_t) = 1/k_{obs} = 1/k_2 K^{\#} [\text{Hydroxy acid}] + 1/k_2 \quad (6)$$

Here, $[TCCA]_t = [Complex] + [TCCA]$

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Table 2 Rate data at 308 K for hydroxy acid's oxidation by TCCA

10^3 [BIDC] (mol dm^{-3})	[Hydroxy acid] (mol dm^{-3})	10 [H^+] (mol dm–3)	10^3k_{obs} (s^{-1})	
			LA	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

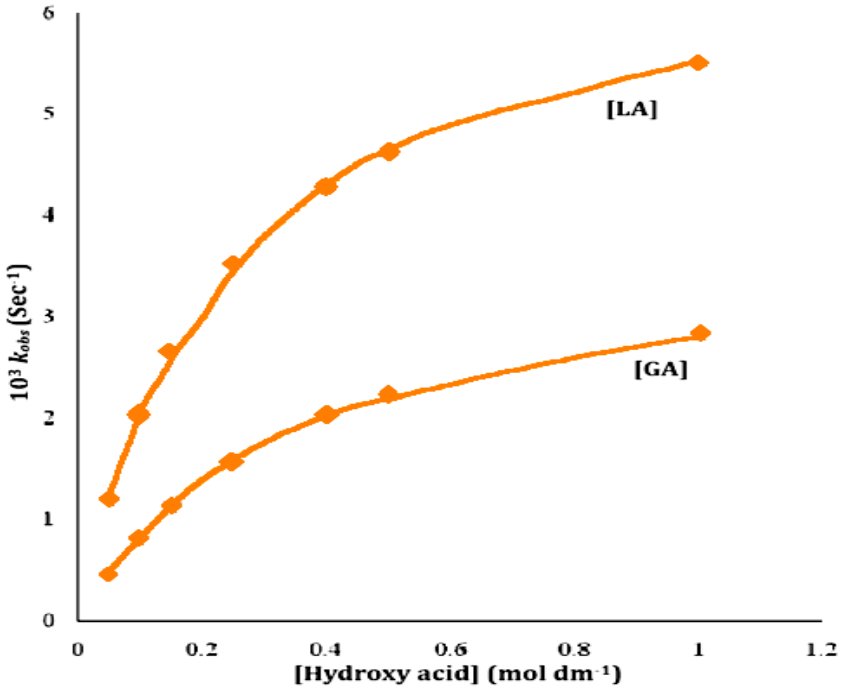

Fig. 1 A graphic of 10^3k_{obs} against [Hydroxy acid] at 308 K [TsOH] = 0.2 mol dm^{-3}; [TCCA] = 0.001 mol dm^{-3}

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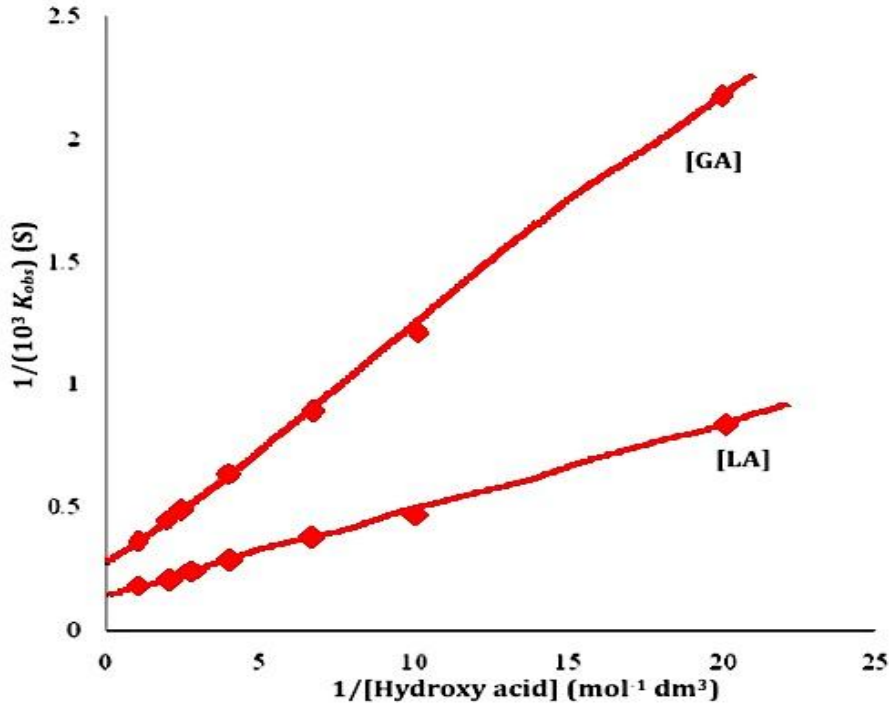

Fig. 2 A graphic of $1/(10^3 k_{obs})$ against 1/[Hydroxy acid] at 308 K [TsOH] = 0.2 mol dm^{-3}; [TCCA] = 0.001 mol dm^{-3}

Equation (6) was used to compute the k_{obs} dependency on both hydroxy acid concentrations at non-identical temperatures, and the double reciprocal graph was used to estimate the k_2 and $K^{\#}$ values. In order to establish the complex, the thermodynamic parameters (Table 3) and their breakdown, the activation parameters (Table 4), were calculated from k_2 and $K^{\#}$ values, respectively, at non-identical temperatures.

Table 3 Hydroxy acid-TCCA complex formation constants and their parameters of thermodynamics

[HA]	$K^{\#}$ (mol^{-1} dm^3)				ΔS (kJ mol^{-1})	ΔH (J mol^{-1} K^{-1})	Δ G (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 4 Hydroxy acid-TCCA complex decomposition constants and their parameters of activation

[HA]	$k_2 \times 10^3$ (s^{-1})				ΔS* (kJ mol^{-1})	ΔH* (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			

When LA and GA were oxidized by TCCA in a nitrogen atmosphere, acrylonitrile-induced polymerization did not occur. In the absence of hydroxy acids, no significant TCCA consumption was seen. The addition of acrylonitrile had no effect on the oxidation rate (Table 2). The reaction was carried out using 0.005 mol dm^{-3} of butylated hydroxytoluene (BHT) to further confirm that there was no single electron oxidation during the process. The BHT was observed almost quantitatively and did not exhibit any significant change.

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The concentration of hydrogen ions catalyzes the oxidation rates of both GA and LA (Table 5). A straight line with a positive slope that is less than one can be shown in a visual between log k_{obs} and log $[H^+]$. This indicates that the relationship between rate and hydrogen-ion concentration is between zero and one. A graphic between $1/k_{obs}$ and $1/[H^+]$ was therefore created, and a straight line with a positive intercept was produced (Fig. 3).

Table 5 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

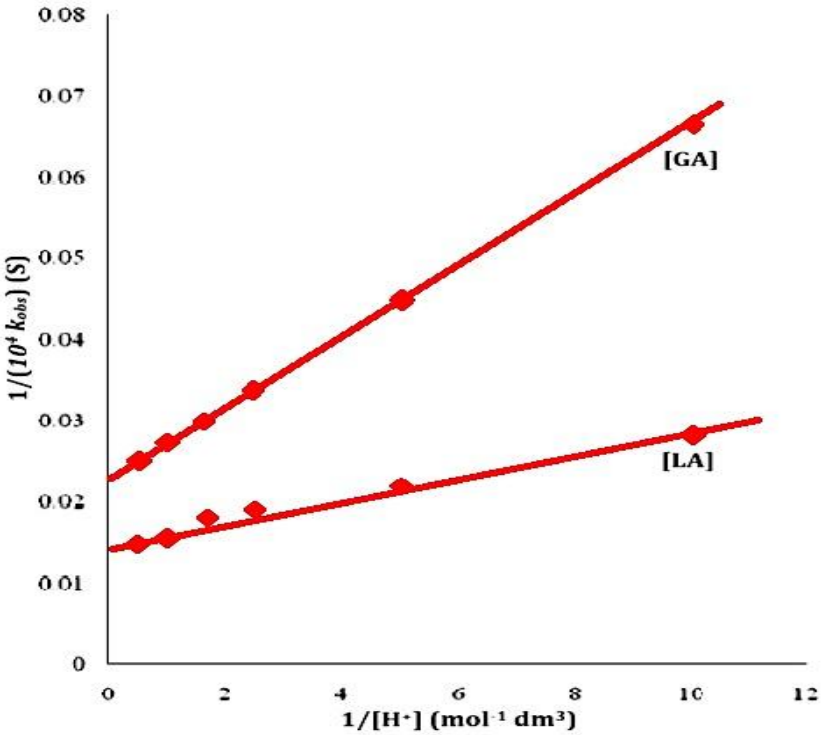

Fig. 3 A graphic of $1/(10^4 k_{obs})$ against $1/[H^+]$ at 308 K [Hydroxy acid] = 0.5 mol dm^{-3}; [TCCA] = 0.001 mol dm^{-3}

Without toluene p-sulphonic acid (TsOH), no specific reaction was seen. With three different acidities, the rate of reaction dependence on GA and LA concentration was examined (Table 6). The value of the formation constant, $K^{\#}$, increases with the acid concentration, while the rate of complex breakdown, k_2, does not change significantly. Similar outcomes have been noted in the oxidation of mandelic acid (MA) by TCCA [9].

Table 6 Dependence of substrate variation at different acidities at 308 K by TCCA (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

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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

TCCA was used to examine the oxidation of α,α-dideuterio-glycolic acid (DGA) in order to determine the importance of α-C H bond fission in the rate-controlling pathway. The results (Table 4) showed that GA and DGA's complex formation constants are almost identical, but their decomposition rates (Table 5) showed a deuterium isotope effect (k_H/k_D = 5.74 at 298 K). When MA was oxidized by TCCA [9], the primary kinetic isotope effect value was found to be almost the same. Furthermore, as the temperature drops in the current investigation, the value of k_H/k_D rises.

Solvent effect

The oxidation of glycolic acid by TCCA was investigated with nineteen organic solvents. The solvent's selectivity was limited by the reaction of TCCA with 1º and 2º alcohols and the solubility of the reactant. With the chosen solvents, no response was seen. With these solvents, the kinetics were almost identical. The appropriate $K^{\#}$ and k_2 values are listed in Table 7.

Table 7 Solvent's effect at 308 K on the glycolic acid oxidation of by TCCA

Solvent	$K^{\#}$ (dm^3mol^{-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

It seems that protonated oxidant ($TCCAH^+$) is an ionic compound. Conductivity measurements are used in our reaction environment to determine the nature of TCCA at 308 K. Due to the low conductivity of DMSO and the negligible change in conductivity value caused by the addition

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of TCCA to DMSO, TCCA remains non-ionized in our reaction system because it does not disintegrate into trichloroisocyanuaric acid and dichromate ions. The idea that TCCA stays non-ionized [10] is further supported by the fact that the rate of oxidation does not change when cyanurium ions are added. The crystal structure investigation of TCCA was reported by Meng *et al*., [15] and his research supports the idea that the oxidant exhibits non-ionic characteristics. The dichromate ion and three trichloroisocyanuric acid are joined by hydrogen bonds. TCCA creates several hydrogen bonds in the molecule with the aid of hydrogen acceptor (O) and hydrogen donor (N H), and an uncommon intermolecular hydrogen bridge is generated between two neighboring dichromate ions. Because of these hydrogen bridges, the molecules are joined into endless chains, which restrict the dichromate ions' ability to release energy in our reaction system, making the TCCA act as non-ionic in our reaction.

Following protonation, TCCA (X) is found to create a protonated Cr(VI) species (Y), which is a stronger oxidant and an aggressive electrophile (eq. (7)). Thus, proton concentration affects the oxidation process via TCCA.

$$(TCOH)_2Cr_2O_5 + H^+ \overset{K_1}{\rightleftharpoons} (TCOH)_2O\overset{+}{C}r(OH)OCrO_2 \quad (7)$$

Here, TC represents trichloro. Further, effect of proton concentration on rate could be expressed as:

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

It has previously been proposed that the reactions of other Cr(VI) complexes may result in the generation of a protonated Cr(VI) complex [16,17] increased reactivity brought about by the internal electron transfer from hydroxy acid to TCCA, which is encouraged by TCCA's formation. Additionally, hydrogen ion dependency exhibits rapid equilibrium between (X) and (Y), the value of the equilibrium constant, K_1, is less, and the reaction remains incomplete at higher $[H^+]$ concentrations since no leveling of velocity constants occurs at higher hydrogen ion concentrations. It is advised that just the protonated TCCA (Y) proceeds like an oxidizing species since no remarkable oxidation was observed in the absence of TsOH. Similar hydrogen ion requirement was seen in the oxidation of MA by TCCA [9].

The information in Table 7 shows that while the equilibrium constant ($K^{\#}$) is rather insensitive, the rate constant (k_2) varies significantly with changes in solvent. Similar oxidation kinetics were seen in the oxidation of MA by TCCA [9] and hydroxy acids by pyridinium bromochromate [18]. Therefore, in connection to the linear solvation energy relationship (LSER) of Kamlet et al., [19], k_2 for the breakdown of complexes has been connected with 18 solvents (CS_2 has not been explored because the absolute range of solvent parameters are unavailable). Irrelevant correlations were discovered.

In relation to Swain's [20] equation (9), solvent effect data were examined, where A, B, and (A+B) represent the solvating power of anion, solvating power of cation, and polarity of solvent, respectively, and C represents the intercept term.

$$\log k = aA + bB + C \quad (9)$$

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

$$\log k_2 = 0.35\pm0.008\ A + 1.60\pm0.007\ B - 4.26 \quad (10)$$

$R^2 = 0.9999$, sd = 0.0048, $\psi = 0.01$, n = 19

$$\log k_2 = 0.12\pm0.53\ A - 3.016 \quad (11)$$

$r^2 = 0.0032$, sd = 0.43, $\psi = 1.03$, n = 19

$$\log k_2 = 1.57\pm0.06\ B - 4.143 \quad (12)$$

$r^2 = 0.9741$, sd = 0.07, $\psi = 0.17$, n = 19

$$\log k_2 = 1.19\pm0.159\ (A+B) - 4.22 \quad (13)$$

$r^2 = 0.7647$, sd = 0.21, $\psi = 0.50$, n = 19

Swain's equation showed a perfect link between the perceived solvent effect and the solvating power of both cation- and anion-participating. Despite having a larger contribution, the solvating power of cation accounts for 97.4% of the data on its own. 76.4% of the data can be explained by the solvent's polarity (A + B). Since the polarity of the solvent accounts for 76.4% of the

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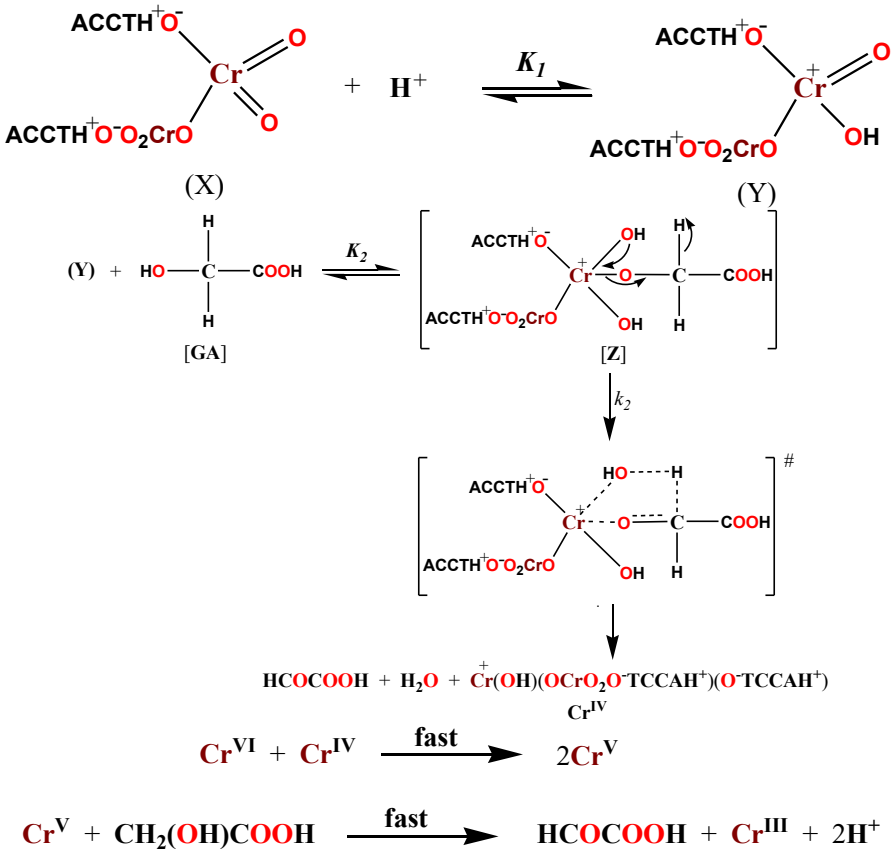
data, the relative permittivities of the solvents were correlated with the data. Plotting log k_2 against 1/D, where D stands for the solvent's relative permittivity, is not linear ($r^2 = 0.4758$). This shown that the solvent's polarity and relative permittivity do not reflect the same solvent properties, as stated by Swain et al., [20].

Mechanism

Since acrylonitrile has no effect on the reaction rate, it is unlikely that one-electron oxidation is taking place in the current reaction [21]. BHT is an ideal reagent for trapping free radicals. In order to create $TCCAH^+(Y)$, the acid-catalysis is seen as an earlier BIDC protonation. The primary function of the solvating power of It is supported by cation. The Michaelis-Menten type kinetics in the context of hydroxy acid suggest a quick dynamic-equilibrium generation of a 1:1 complex (Z). Complex C is created by the nucleophilic attack of the hydroxy acid's -OH group on $TCCAH^+$ (Y) (Scheme 1).

The methyl group that donates electrons accelerates the oxidation process, which is represented in the power of reactivity. It demonstrates how the availability of electrons in the -OH group increases during complex formation. The complexes of normal and α,α-dideuterioglycolic acid have formation constants that are almost equal, but the rate of breakdown indicates a primary kinetic isotope impact, which implies that the α-C-H bond is broken in the rate-controlling step. The final product (oxoacid) in Scheme 1 formed from the complex (Z) as a result of the hydride-ion shifting from hydroxyl acid to TCCA and the process of this hydride-ion shifting further supports the idea that the cation's solvating power plays a significant role. In the oxidation process, a carbocationic TCCA [9] was found to follow a similar process. However, a few reports on the oxidation of hydroxy acids show the creation of a carbonium ion center in the regulated stage [22,23].



TCCA = trichloroisocyanuric acid

Scheme 1 Oxidation mechanism of glycolic acid (GA) by TCCA

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A chromate ester or an acyclic method can be used to transfer a hydride-ion. Kwart and Nickle [24] developed a technique to investigate the kinetic isotope effect's temperature dependence and found that hydrogen loss is preceded by a coordinated cyclic mechanism. The findings for deuterited and regular glycolic acid have been presented in a well-known way:

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

The final results confirm 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 nearly equal in the current reaction. The difference in activation energy for k_H/k_D is ≈ 4.70 kJ mol^{-1}. It directly agrees with the features of a symmetrical transition state [25,26]. Similar outcomes have previously been observed in the oxidation of alcohol by BTPPD [27].

In addition to the phenomenon of a bimolecular coordinated process of hydrogen shifting that is finished in a single step, Bordwell [28] has provided compelling findings. It is highly advised that the shifting of hydrogen in the current reaction system not follow an acyclic bimolecular pathway. This symmetrical mechanism is actually a sigmatropic reaction that involves the direct transfer of hydrogen and is characterized by a cyclic transition state shifting [29]. The next step in this reaction was the cyclic transfer of two electrons. Six electrons, which are similar to Hückel's (4n+2)π system, are allowed in the oxidation of hydroxy acid by TCCA [30]. Therefore, it is assumed that in LA and GA oxidation by TCCA, hydride-ion transfer takes place via a cyclic transition state. Scheme 1 described mechanism is based on the results of the experiment. The rate law in the proposed mechanism (Scheme 1) could be covered in the section that follows. The equilibrium condition can be used to determine Cr(VI).

$$-d[Cr(VI)]/dt = k_2 [Z] = k_2K_1K_2 [HA] [H^+] [Cr(VI)] \quad (15)$$

$$\text{or, } -d[Cr(VI)]/dt = \frac{k_2K_1K_2[Cr(VI)]_t[H^+][HA]}{1+K_1K_2[H^+][HA]}$$

$$\text{or, } k_{obs} = \frac{k_2K_1K_2[H^+][HA]}{1+K_1K_2[H^+][HA]} \quad (16)$$

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

$$\text{or, } 1/k_{obs} = 1/k_2K_1K_2 [H^+] [HA] + 1/k_2 \quad (17)$$

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 suggested mechanism is supported by the observed loss of (–ΔS) of activation. When charge segregation takes place in the transition state, two ends become extremely solvated, which stabilizes a large number of solvent molecules and manifests as entropy loss. Loss of entropy is another way that the solvent's action is explained.

Chromium metal's initial oxidation state was reduced from Cr(VI) to Cr(IV), and it was anticipated that this would react with another Cr(VI) to form Cr(V). This Cr(V) species eventually gives rise to Cr(III) species in a quick step. This sequence of reactions in Cr(VI) oxidations is well-established [31].

Comparing the results of the current reaction with those of previous Cr(VI) complexes oxidizing hydroxy acids is intriguing. For both the hydroxy acid and $[H^+]$, the oxidation by butyltriphenylphosphonium dichromate (BTPPD) [32] is found to be of second order; however, the order for BTPPD is one. Protonated dimetallic Cr(VI) species were proposed as an active oxidizing species in the reaction after the deuterium isotope effect was seen. The mechanism proposes a rate-controlling channel for hydrogen as an anion to move through the hydroxy acid to BTPPD via a chromate ester. As for the hydroxy acid, oxidant, and proton concentration, the kinetics of oxidation by quinolium dichromate (QDC) [33] in M/2 $HClO_4$ of the α-hydroxy acids demonstrated unit dependency. Ketoacid was shown to be an oxidation product, and the slowest process of product synthesis included the breaking of C-H bonds. The ultimate product of QDC [34] oxidation of HAs in a 30% (v/v) AcOH-H_2O medium was subsequent aldehyde. Similar to LA and QDC, unit dependency was demonstrated. The reaction rate is inversely correlated with the solvent's relative permittivity and directly correlated with the concentration of acid. The breakage of the carbon-carbon bond during the oxidation process is suggested by a related mechanism.

Although less than one order has been seen as for substrate [35] the oxidation of -hydroxy acids under non-aqueous methyl cyanide medium by imidazolium dichromate (IDC) is stated as being of

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unit dependency. Acid concentration has very little effect on the observed pace. The result of oxidation was the production of a matching ketoacid. The formation of a cyclic complex between substrate and IDC is hypothesized under the rate-controlling stage. However, the oxidation reaction of MA by IDC in 50% (v/v) AcOH-H_2O medium with HClO4 showed partial dependence as for acid [36] but the same dependency as for both MA and IDC as above.

IV. Conclusion

In a dimethyl sulfoxide (DMSO) medium, trichloroisocyanuric acid (TCCA) preferentially oxidizes α-hydroxy acids, including lactic and glycolic acids, to produce the proper oxoacid. A Michaelis-Menten type kinetics was observed for hydroxy acids, however a unit dependency on rate was observed for TCCA. At various temperatures, the formation constants and breakdown rates of α-hydroxy acid TCCA complexes have been evaluated. The thermodynamic and activation parameters have been determined for the formation and disintegration of the complex, respectively. The oxidation process accelerates as the proton concentration increases. An α-C-H bond fisson in the rate-controlling phase is suggested by the deuterium isotope effect. At 298 K, glycolic acid oxidation was reported to have k_H/k_D = 5.74. The oxidation rates were evaluated using 19 organic solvents, and it was discovered that the solvating ability of the cation was more important. The kinetic parameters, solvent effect analysis, and thermodynamic parameter results determine a technique that proposes a rate-controlling breakdown of the complex to yield the final product through hydride-ion transfer with a cyclic transition state.

Conflict of Interest

There is no conflict of interest

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