

Research Article

Perborate Oxidation of Substituted 5-Oxoacids in Aqueous Acetic Acid Medium: A Kinetic and Mechanistic Study

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Kinetics and mechanism of oxidation of substituted 5-oxoacids by sodium perborate in aqueous acetic acid medium have been studied. The reaction exhibits first order both in [perborate] and [5-oxoacid] and second order in $[H^+]$. Variation in ionic strength has no effect on the reaction rate, while the reaction rates are enhanced on lowering the dielectric constant of the reaction medium. Electron releasing substituents in the aromatic ring accelerate the reaction rate and electron withdrawing substituents retard the reaction. The order of reactivity among the studied 5-oxoacids is *p*-methoxy \gg *p*-methyl $>$ *p*-phenyl $>$ -H $>$ *p*-chloro $>$ *p*-bromo $>$ *m*-nitro. The oxidation is faster than H_2O_2 oxidation. The formation of $H_2BO_3^+$ is the reactive species of perborate in the acid medium. Activation parameters have been evaluated using Arrhenius and Eyring's plots. A mechanism consistent with the observed kinetic data has been proposed and discussed. Based on the mechanism a suitable rate law is derived.

1. Introduction

Sodium perborate ($NaBO_3 \cdot 4H_2O$) is a nontoxic cheap large scale industrial chemical primarily used as a source of "active oxygen" in detergents and as a mild antiseptic. This active oxygen has the oxidising properties of hydrogen peroxide. PMR spectral analysis [1] and X-ray diffraction studies [2] conclude that perborate is a true peroxy salt with water of crystallisation. Perborate is a heterocycle and is in a dimeric tetrahedral configuration with dihedral angle of 64° and anionic formula: $B_2(O_2)_2(OH)_4^{2-}$ [3]. Oxidative study suggests perborate as not peroxoborate but borate peroxyhydrate. Hydrogen peroxide acquires stronger electrophilicity by the coordination with borate [4]. It is an effective reagent in organic synthesis and acetic acid is the solvent of choice [5–7]. Perborate in aqueous solution yields hydrogen peroxide and the kinetic studies in aqueous and partly aqueous acidic media confirm that perborate oxidation is hydrogen peroxide oxidation [8–10]. This stable and easily handled crystalline

substance oxidizes organic sulphides [11–13], anilines [14], and indole [15].

5-Oxoacid is an attractive substrate in terms of its enolization. In strong acid medium the substrate undergoes enolization. The reactive species of the substrate has been reported in the literature to be the enol form [16, 17].

In recent years, studies of the oxidation of various organic compounds by perborate have attracted considerable attention. A thorough literature survey reveals that relatively little work on the oxidation of oxoacid has been reported so far [18–21]. Although the perborate oxidation of organic compounds has been studied, there seems to be no report on a systematic kinetic study of the oxidation of 5-oxoacids by perborate and we report here for the first time the kinetics and mechanism of perborate oxidation of substituted and unsubstituted 5-oxoacids. The various unsubstituted and substituted 5-oxoacids (S1–S7) employed in the present study are listed in Figure 1.

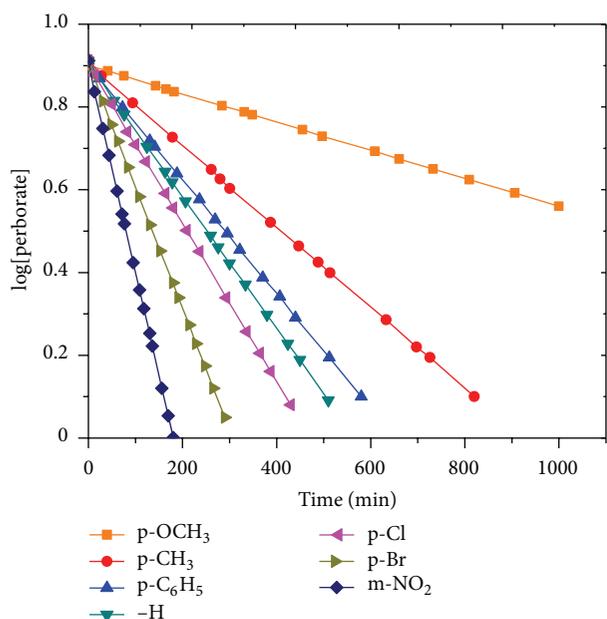


FIGURE 1: S1: unsubstituted, S2: 4'-methoxy, S3: 4'-methyl, S4: 4'-phenyl, S5: 4'-chloro, S6: 4'-bromo, and S7: 3'-nitro.

2. Experimental

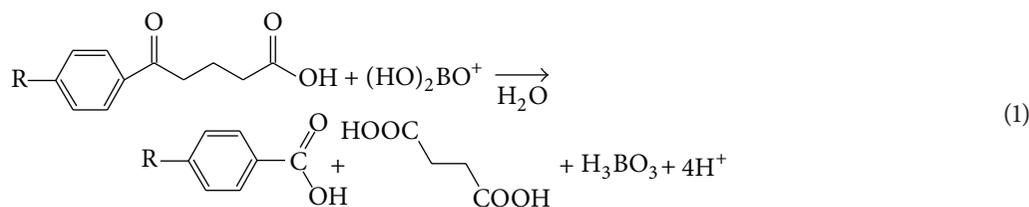
2.1. Materials. Sodium perborate, $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ (Riedel), was used as received. Acetic acid (BDH) was refluxed for 6 h over chromium (VI) oxide and distilled through a column. Aqueous solutions of perborate were prepared as and when required and standardized iodometrically. Sodium metaborate and perchloric acid were prepared in double distilled water. Double distilled water (conductivity $< 10 \mu\text{S}\cdot\text{cm}^{-1}$) has been employed in all kinetic runs. All the chemicals used were 99.8% pure. The parent 5-oxoacid, namely, 5-oxo-5-phenylpentanoic acid (S1), and the phenyl

substituted 5-oxoacids (S2–S7) were prepared by Friedel-Crafts acylation of the substituted benzene with glutaric anhydride [22–26]. All the 5-oxoacids were crystallized twice from water and their purity was checked by their melting points and UV, IR, and NMR spectra. All other chemicals were of analytical grade.

All absorption measurements were made with Shimadzu UV-visible spectrophotometer (MPS-5000) equipped with a temperature controller. Regression analysis of experimental data yielded the regression coefficient (r) and standard deviation (s).

2.2. Kinetic Measurements. The reaction mixture, containing 5-oxoacid and sulphuric acid solutions, was thermally equilibrated and the reaction was initiated by the addition of temperature-equilibrated perborate solution of requisite concentration. The oxidation kinetics was followed in aqueous acetic acid at constant temperature by measuring the concentration of benzoic acid formed iodometrically under pseudo-first order conditions by keeping the substrate in excess over the oxidant. The pseudo-first-order rate constant (k') was calculated from the slope of the linear plot of $\ln [\text{perborate}]$ versus time by the method of least squares. The error quoted in k' is the 95% confidence limit of the Student's t -test. The progress of the oxidation was followed by iodometric determination of the oxidant. Freshly prepared solutions of oxoacids in purified acetic acid were used to avoid any possible side reactions.

2.3. Reaction Stoichiometry and Product Analysis. The stoichiometry of the reaction was determined by equilibrating reaction mixture of various $[\text{perborate}]/[5\text{-oxoacid}]$ ratios at 313 K for 12 h, keeping all other reagents constant. Estimation of unconsumed perborate (iodometrically) revealed that one mole of 5-oxoacid consumed one mole of perborate:



The products were extracted with ether, dried, and analyzed. Benzoic acid was identified by its melting point (121°C). Then it has been estimated quantitatively using UV-Vis spectrophotometry with a standard curve at $\lambda_{\text{max}} = 235 \text{ nm}$. Succinic acid was identified by its melting point (185°C) and also tested with its characteristic spot test [27]. Identification of the products, namely, benzoic and succinic acids, was also made by comparing the R_f values of the authentic samples. Boric acid was identified by adding an alkaline solution of benzoin, resulting in the formation of a yellow-green fluorescent complex.

3. Results and Discussion

At fixed concentrations of acid and substrate, the decrease in the concentration of perborate is followed first order kinetics. The first order rate constants (k_1) were calculated from the linear plots ($r \geq 0.98$, $s \leq 0.03$) of $\log [\text{perborate}]$ against time. Such plots are linear for more than three half-lives of the reaction (Figure 2). The k_1 value was independent of initial $[\text{perborate}]$ for all the studied substrates.

The reactions of all the studied 5-oxoacids are first order in the $[\text{substrate}]$ (Table 1) and in $[\text{H}^+]^2$ in the range of

TABLE 1: Effect of varying [substrate] on the rate of perborate oxidation of 5-oxoacids at 313 ± 0.1 K. {[Perborate] = $0.001 \text{ mol dm}^{-3}$; $[\text{H}_2\text{SO}_4]$ = 2.0 mol mol^{-3} ; HOAc- H_2O = 1:1% (v/v)}.

[5-oxo acid] (mol dm^{-3})	$10^5 \times k_{\text{obs}}$ (s^{-1}) ^a						
	<i>p</i> -OCH ₃	<i>p</i> -CH ₃	<i>p</i> -C ₆ H ₅	-H	<i>p</i> -Cl	<i>p</i> -Br	<i>m</i> -NO ₂
0.005	95.91	13.44	9.43	6.36	2.14	1.77	0.77
0.01	191.9	26.85	21.67	12.78	4.25	2.15	1.52
0.015	287.9	40.33	29.98	19.20	6.40	4.43	2.34
0.02	383.7	53.71	36.71	25.59	8.51	5.74	3.05
0.03	575.8	80.59	60.76	38.14	12.78	8.92	4.56
0.04	767.7	107.5	124.91	51.13	17.15	12.53	6.05
0.06	1152	161.3	142.24	76.75	25.59	17.53	9.10

^aMean of duplicate experiments.

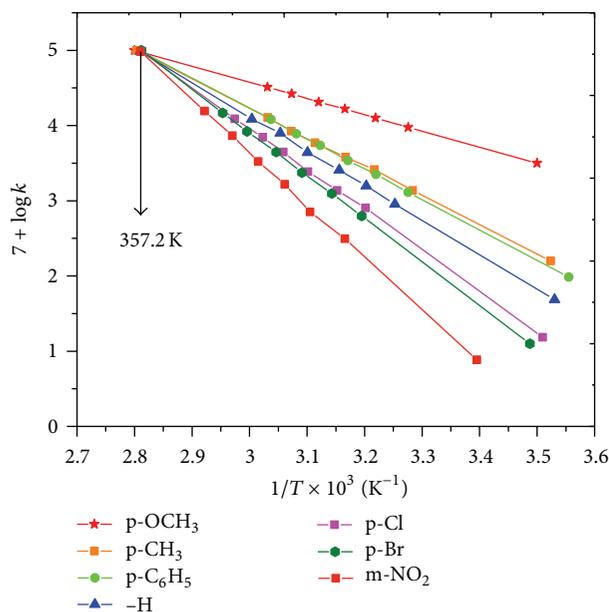


FIGURE 2: Typical first order plots in the perborate oxidation of 5-oxoacids.

0.5–4.0 mol dm^{-3} sulphuric acid (Table 2). From the Zucker-Hammett plots of $\log k$ versus $-\text{H}_o$, the slopes obtained were in the range of 1.0–1.2, indicating the noninvolvement of water molecule in the rate determining step. The H_o values were taken from Long and Paul [28] assuming that the H_o values do not change much in a media containing acetic acid up to 50%.

The effect of dielectric constant (D) on the rate of reaction was studied by varying acetic acid-water content in the reaction mixture. Acetic acid does not react with the oxidants [29], yet the rate of the reaction is enhanced by increasing acetic acid content of the medium (Table 3). Also, $\log k$ against $1/D$ is found linear, suggesting a positive ion-dipole type of interaction [30] in the rate determining step.

There was no induced polymerization of acrylonitrile monomer, ruling out the possibility of free radical formation during the course of the reaction.

In the temperature range of 298–323 K in 2.0 mol dm^{-3} sulphuric acid and acetic acid-water medium (50% v/v)

(Figure 3), the activation energy (E_a) and related thermodynamic parameters (ΔH^\ddagger , ΔG^\ddagger , and ΔS^\ddagger) were evaluated. The plot between ΔH^\ddagger and ΔS^\ddagger is linear (Figure 4, $r \geq 0.98$, $s \leq 0.028$) and the isokinetic temperature (β) obtained is 357 K. The isokinetic relationship in the present study implies that all the 5-oxoacids undergo oxidation by the same mechanism [31].

The effect of substituents on the rate of oxidation was studied using different phenyl substituted 5-oxoacids ($\text{ArCOCH}_2\text{CH}_2\text{CH}_2\text{COOH}$, where Ar = 4'-methoxy, 4'-methyl, 4'-phenyl, 4'-chloro, 4'-bromo, 3'-nitro substituted phenyl) at different temperatures. In all these cases, the reaction orders are the same, namely, first order with respect to [oxidant] and [substrate] and second order with respect to [acid]. Electron releasing substituents in the phenyl ring enhance the rate of oxidation and electron withdrawing substituents decrease it (Table 4). The order of reactivity among the studied 5-oxoacids is *p*-methoxy \gg *p*-methyl $>$ *p*-phenyl $>$ -H $>$ *p*-chloro $>$ *p*-bromo $>$ *m*-nitrophenyl substituted 5-oxoacids. The Hammett plots of $\log k$ versus σ (substituent constant) are smooth curves and concave downward, at all the studied temperatures. However, the Hammett plots are linear with good correlation coefficient at four different temperatures when exalted substituent constant (Brown's σ^+) values are used (Figure 5). The reaction constant (ρ^+) is negative and decreases (in magnitude) from -1.65 to -1.32 with increasing temperature from 303 K to 323 K. The Hammett lines intersect at a point correspondent to a σ_{iso}^+ value of -1.42 and a k_{iso} value of $13.18 \times 10^{-3} \text{ s}^{-1}$ (Figure 5). An oxoacid with a substituent having this σ^+ value (-1.42) will be oxidized by perborate at the same rate at all temperatures. Such insensitivity of the reaction rate to temperature is a pointer to the existence of an isokinetic phenomenon.

A reaction series which exhibits a common point of intersection in the Hammett plot (Figure 5) is expected to have a common point of intersection in the Arrhenius plot as well [32]. From the plots of ΔH^\ddagger against ΔS^\ddagger and ρ against $1/T$, the T_{iso} value is found to be 359 K, which is in good agreement with the value obtained from the slope of Exner's plot.

3.1. Mechanism. In aqueous acetic acid the possible oxidizing species of perborate are perborate anion, perboric acid, peracetic acid, and H_2O_2 . Even though isolation of free

TABLE 2: Effect of varying $[H_2SO_4]$ on the rate of perborate oxidation of 5-oxoacids at 313 ± 0.1 K. $\{[Substrate] = 0.01 \text{ mol dm}^{-3}; [perborate] = 0.001 \text{ mol dm}^{-3}; HOAc-H_2O = 1:1\% (v/v)\}$.

$[H_2SO_4]$ (mol dm ⁻³)	$10^5 \times k$ (s ⁻¹) ^a							
	-H _o	<i>p</i> -OCH ₃	<i>p</i> -CH ₃	<i>p</i> -C ₆ H ₅	-H	<i>p</i> -Cl	<i>p</i> -Br	<i>m</i> -NO ₂
0.51	-0.13	11.89	2.31	1.87	1.58	—	—	—
0.75	0.07	29.93	4.38	3.28	2.88	—	—	—
1.01	0.26	47.98	7.68	5.19	4.52	1.27	1.21	1.18
1.49	0.56	95.96	15.98	12.67	8.84	2.32	1.98	1.26
2.01	0.84	191.9	26.87	19.28	12.78	4.26	3.09	1.52
2.49	1.12	287.9	47.98	38.69	25.59	7.19	5.16	2.57
3.00	1.38	479.8	134.3	79.81	34.85	12.79	7.28	3.97
4.01	1.85	1151	287.8	140.63	57.58	25.58	16.89	7.69
S ^b		2.01	2.01	2.0	2.00	2.01	2.0	2.00
n ^c		1.3	1.0	1.0	1.0	1.1	1.1	1.0

^aMean of duplicate experiments; ^bslopes of log k versus log $[H_2SO_4]$; ^cslopes of the Zucker-Hammett plots.

TABLE 3: Effect of varying solvent composition on the rate of perborate oxidation of 5-oxoacids at 313 ± 0.1 K. $\{[Substrate] = 0.01 \text{ mol dm}^{-3}; [perborate] = 0.001 \text{ mol dm}^{-3}; [H_2SO_4] = 2.0 \text{ mol mol}^{-3}\}$.

ACOH-H ₂ O (v/v, %)	$10^5 \times k$ (s ⁻¹) ^b						
	<i>p</i> -OCH ₃	<i>p</i> -CH ₃	<i>p</i> -C ₆ H ₅	-H	<i>p</i> -Cl	<i>p</i> -Br	<i>m</i> -NO ₂
30 : 70 (53.18)	63.8	9.50	8.67	7.60	2.38	1.97	1.18
40 : 60 (46.48)	115.2	13.10	11.86	9.60	3.10	2.12	1.29
50 : 50 (39.78)	191.8	26.87	18.73	12.80	4.27	3.62	1.50
60 : 40 (33.08)	586	44.70	31.01	15.90	7.20	4.89	1.75
70 : 30 (26.38)	1751	162.9	71.23	38.30	12.80	7.61	2.69

^aValues of dielectric constant of the media are given in parentheses; ^bmean of duplicate experiments.

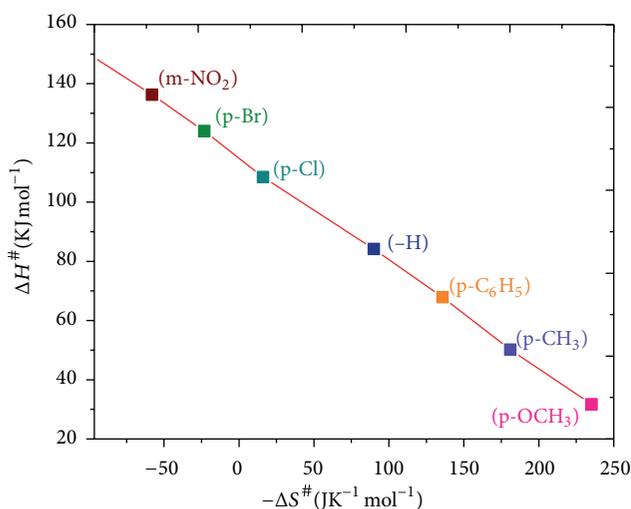


FIGURE 3: Arrhenius plots of log k against $1/T$ showing the isokinetic temperature.

perboric acid has been proved exceedingly difficult, it has demonstrable existence in solution [33]. Perborate is reported to exist in a dimeric tetrahedral configuration with the anionic formula: $B_2(O_2)_2(OH)_4^{2-}$. The oxidation has been carried out in aqueous acetic acid, and from the ionization constant of perboric acid, reported as $(0.6-1.6) \times 10^{-8}$, it

TABLE 4: Effect of substituent on the rate of oxidation of 5-oxoacids by perborate at 313 ± 0.1 K. $\{[Substrate] = 0.01 \text{ mol dm}^{-3}; [perborate] = 0.001 \text{ mol dm}^{-3}; [H_2SO_4] = 2.0 \text{ mol mol}^{-3}; HOAc-H_2O = 1:1\% (v/v)\}$.

Substituent	σ	σ^+	$10^5 \times k$ (s ⁻¹)	$5 + \log k$
<i>p</i> -OCH ₃	-0.27	-0.78	191.8	2.2829
<i>p</i> -CH ₃	-0.17	-0.31	26.9	1.4293
<i>p</i> -C ₆ H ₅	-0.11	-0.22	18.8	1.2623
-H	0.00	0.00	12.8	1.1070
<i>p</i> -Cl	0.23	0.11	4.3	0.6299
<i>p</i> -Br	0.43	0.38	2.7	0.3470
<i>m</i> -NO ₂	0.71	0.67	1.5	0.1802

may be concluded that perborate exists mainly as perboric acid in aqueous acetic acid, at very low pH maintained with sulphuric acid and hence is unlikely to be the oxidant. The rate of perborate oxidation in aqueous acetic acid compares with that in aqueous ethanol, and hence the oxidation is not through peracetic acid. H_2O_2 is less likely to be the oxidant as the rate of H_2O_2 oxidation is about one-fifth of that of perborate oxidation. The enhancement of reaction rate with an increase in the amount of acetic acid and linear plots of log k versus $1/D$ with positive slopes indicate an interaction between a positive ion and a dipole molecule in the slow step. This supports the postulation of $H_2BO_3^+$ as the reactive

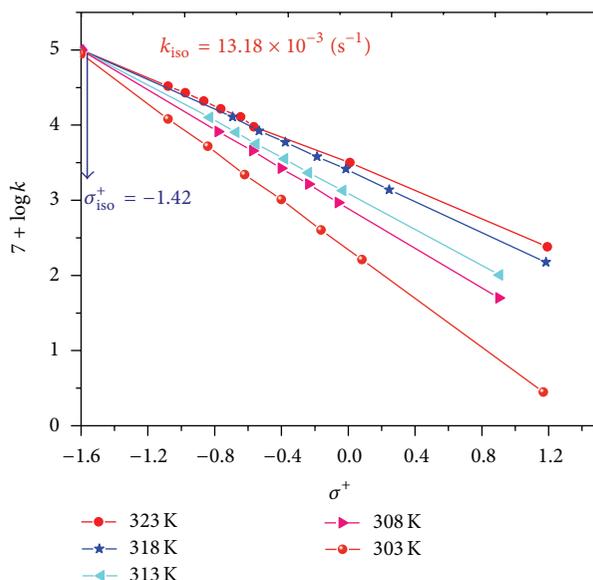


FIGURE 4: Plot of ΔH^\ddagger against $-\Delta S^\ddagger$ showing the isokinetic relationship.

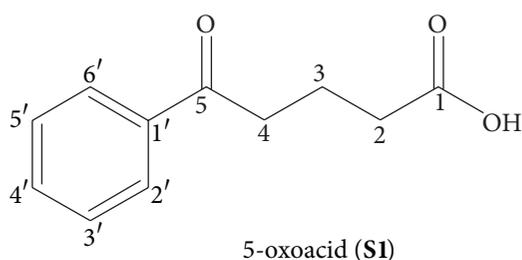
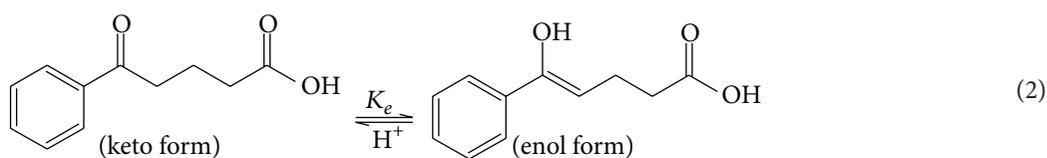


FIGURE 5: Hammett plots of $\log k$ against σ_+ at different temperatures.

species of perborate in the acid medium. The rate acceleration with an increase in [acid] and second order dependence of rate on [acid] in the range studied also confirm that H_2BO_3^+ is the reactive species of perborate taking part in the oxidation of 5-oxoacids.

The oxoacid is a weak acid ($pK_a = 5.77$ at 40°C in aqueous solution) [34], and the undissociated form of the substrate can be taken as the only form in acidic media. In acid solutions, 5-oxoacid undergoes keto enol tautomerism (2):

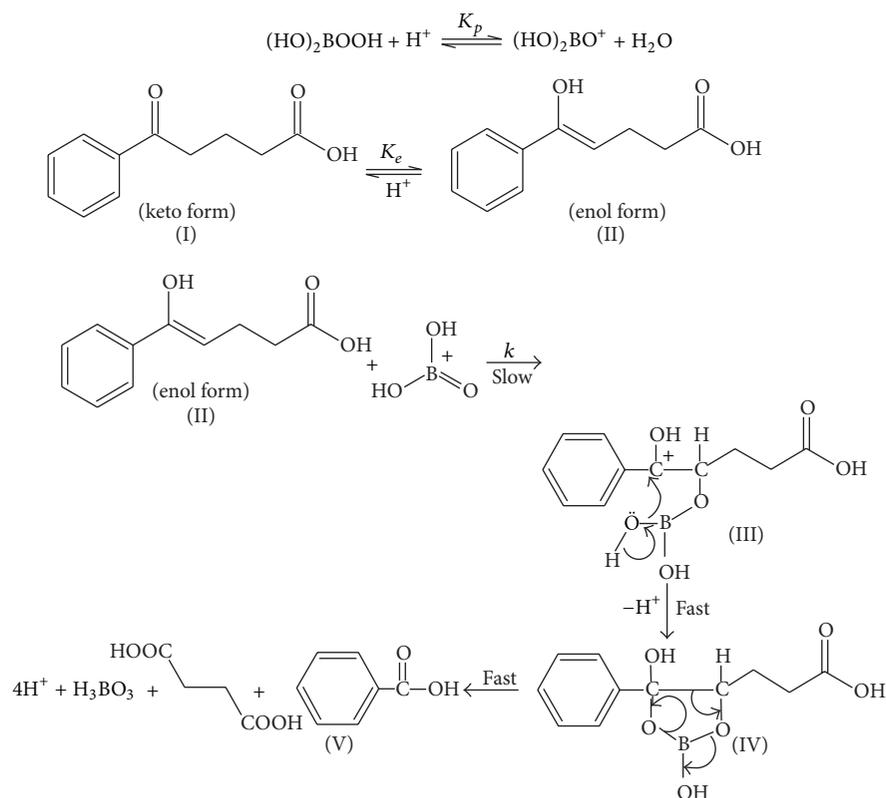


In oxidation reactions, the keto group of the substrate can react either directly or through the enol form. Oxidation rates faster than the rates of enolization have been observed with ceric ion [35], manganic ion [36], cobaltic vanadate ions [37], mercuric perchlorate [38], and alkaline diperiodate argenate(III) [39] as oxidants, indicating that the keto group of the substrate reacts directly. All of these oxidants undergo one-electron reduction, and the reactions proceeded via a free radical mechanism [35–39].

The rates of oxidation and enolization were found to be equal in the oxidation reactions by manganic pyrophosphate [40], thallium triacetate [41], and by diperiodatonickelate (IV) [42]. These reactions were zero order in [oxidant], indicating the enol formation as the rate determining step.

In the present study, the rate of enolization (measured by the bromination method [43]) is greater than the rate of oxidation by a factor of ~ 13 – 15 and the enolization step can be visualized as proceeding via the enol form of the keto group of 5-oxoacid. Hence, the step involving enol formation can be assumed to be a fast step and thus is not the rate determining step of the reaction. The most plausible mechanism therefore seems to be shown in Scheme 1. The proposed mechanism is also in accordance with the observed stoichiometry. The rate equation in consonance with the mechanism proposed is as given in the following equation:

$$\frac{-d[\text{perborate}]}{dt} = K_p K_e k [\text{H}^+]^2 [\text{5-oxoacid}] [\text{perborate}]. \quad (3)$$



SCHEME 1: Formations of benzoic acid and succinic acid were the final products of oxidation.

The obtained rate law could explain the second order in $[\text{H}^+]$ and first order both in $[\text{perborate}]$ and $[\text{5-oxoacid}]$.

4. Conclusions

The above study shows that the H_2BO_3^+ reacts with the enol form of 5-oxoacid in the rate determining step, giving the cyclic boronate ester. Decomposition of the boronate ester results in the cleavage of the carbon-carbon bond, yielding carboxylic acids. This experimental protocol suggests that this reaction could find utility as a regioselective route for the synthesis of carboxylic acids, specially succinic and benzoic acids.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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