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Environmental Science & Technology**PG and Research Department of Chemistry, Presidency College (Autonomous),
Chennai-600 005, India**Iron(II) catalysis in perborate oxidation of 5-oxo acids**S. Shree Devi¹, P. Krishnamoorthy² and B. Muthukumaran^{3*}¹Research and Development Centre, Bharathiar University, Coimbatore – 641 046,
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Abstract : Iron(II) catalyzes perborate oxidation of substituted 5-oxo acids in acidic solution. The catalyzed oxidation is first order with respect to the oxidant and catalyst. The rate of iron(II) catalyzed oxidation displays the Michaelis-Menten kinetics on the reductant and is independent of $[H^+]$ of the medium. The rate of oxidation, under identical conditions, in the presence of iron(II) is practically the same as that in the presence of iron(III). Hydrogen peroxide is the reactive species of perborate and the kinetic results reveal formation of iron(III) peroxy species-5-oxo acid complex. Electron-releasing substituents accelerate the reaction rate and electron-withdrawing substituents retard it. The order of reactivity among the studied 5-oxo acids is *p*-methoxy \gg *p*-methyl $>$ *p*-phenyl $>$ -H $>$ *p*-chloro $>$ *p*-bromo $>$ *m*-nitro. Activation parameters are evaluated using Arrhenius and Eyring's plots. A mechanism consistent with the observed kinetic data is proposed and discussed. A suitable rate law is derived based on the mechanism.

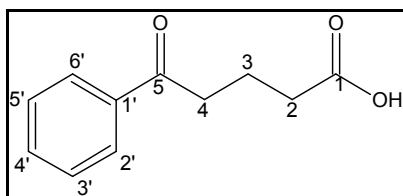
Keywords: Catalysis, Iron(II), Oxidation, 5-Oxo acids, Perborate.

Introduction

Sodium perborate ($NaBO_3 \cdot 4H_2O$) is a cheap, environment friendly large scale industrial chemical used extensively in detergents as a bleaching agent. It is a mild oxidant and search for suitable catalysts for perborate oxidation is of interest. It is a convenient source of hydrogen peroxide¹, commercially, industrially and also in the laboratory. PMR spectral analysis² and X-ray diffraction studies³ conclude perborate as a true peroxy salt with water of crystallisation. It is an effective reagent in organic synthesis and acetic acid is the solvent of choice⁴. Perborate in aqueous solution yields hydrogen peroxide and the kinetic studies in aqueous and partly aqueous acidic media confirm perborate oxidation as hydrogen peroxide oxidation^{5,6}. This stable and easily handled crystalline substance oxidizes organic sulphides⁷, anilines⁸ and indole⁹. This communication reports iron(II) or iron(III) catalysis in perborate oxidation of 5-oxo acids. Vanadium(V) also catalyzes perborate oxidation of 5-oxo acids¹⁰.

5-Oxo acid is an attractive substrate in terms of its enolization. In strong acid medium the substrate undergoes enolization. The reactive species of the substrate is reported in the literature to be the enol form^{11,12}. Studies of the oxidation of various organic compounds by perborate have attracted considerable attention. A

through literature survey reveals that relatively little work on the oxidation of oxo acids have been reported so far^{13,14}. Although the perborate oxidations of organic compounds have been studied, there seems to be no report on a systematic kinetic study of the oxidation of 5-oxo acids by perborate and we report here for the first time the kinetics and mechanism of iron(II) catalysis in perborate oxidation of substituted and unsubstituted 5-oxo acids. The various unsubstituted and substituted 5-oxo acids (**S1-S7**) employed in the present study are listed below.



5-oxo acids (S1-S7): S1: Unsubstituted, S2: 4'-Methoxy, S3: 4'-Methyl, S4: 4'-Phenyl, S5: 4'-Chloro, S6: 4'-Bromo, S7: 3'-Nitro.

Experimental

Materials

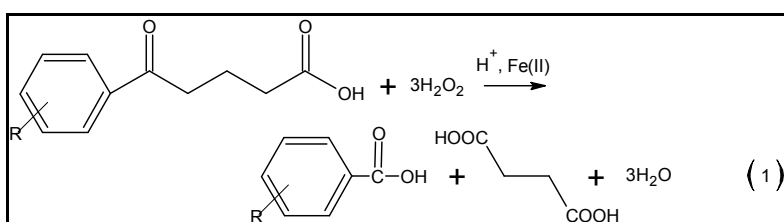
Sodium perborate, $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ (Riedel) and ferrous sulphate (Merck) were used as received. Other chemicals were of AR grade. Analytical grade acetic acid (BDH) was refluxed for 6h over chromium(VI) oxide and distilled through a column. Solutions of perborate were prepared afresh and standardized iodometrically. Kinetics of the oxidation in aqueous sulphuric acid at constant temperature was studied iodometrically under pseudo-first order conditions with a very large excess of 5-oxo acids. Double distilled water (conductivity $< 10 \mu\text{S}\cdot\text{cm}^{-1}$) was employed in all kinetic runs. All the chemicals used were 99.8% pure. The parent 5-oxo acid namely 5-oxo-5-phenylpentanoic acid (**S1**), and the phenyl substituted 5-oxo acids (**S2-S7**) were prepared by Friedel-Crafts acylation of the substituted benzene with glutaric anhydride¹⁵⁻¹⁹. All the 5-oxo acids were crystallized twice from water and their purity was checked by their melting points and UV, IR and NMR spectra. All absorption measurements were made with Shimadzu UV-visible spectrophotometer (MPS-5000) equipped with a temperature controller.

Kinetic measurements

The reaction mixture, containing 5-oxo acid, catalyst 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 iodometrically in aqueous acetic acid at constant temperature under pseudo-first order conditions by keeping the substrate in excess over the oxidant. The pseudo-first order rate constant was calculated from the slope of the linear plot of $\log [\text{perborate}]_t$ against time by the method of least squares. The error quoted in k^* is the 95% confidence limit of a student's *t*-test. The progresses of the oxidations were followed by iodometric determination of the oxidant. Freshly prepared solutions of oxo acids in purified acetic acid were used to avoid any possible side reactions.

Reaction stoichiometry and product analysis

Under the conditions $[\text{5-oxo acid}]_0 \gg [\text{oxidant}]_0 \gg [\text{Fe(II)}]$, the stoichiometry of the catalytic reaction was determined by equilibrating reaction mixture of various $[\text{perborate}]/[\text{5-oxoacid}]$ ratios at 308 K for 12h, keeping all other reagents constant. Estimation of unconsumed perborate (iodometrically) revealed that one mole of 5-oxo acid consumed three moles of perborate (Eq. 1).



The products were extracted with ether, dried and analyzed. Benzoic acid was identified by its melting point (121 °C). Then it was estimated quantitatively using UV-Vis spectrophotometry with a standard curve at

$\lambda_{max} = 235$ nm. Succinic acid was identified by its melting point (185 °C) and also tested with its characteristic spot test²⁰. Identification of the products, namely, benzoic and succinic acids, were also made by comparing the R_f values of the authentic samples.

Results

Effect of concentrations

In acidic medium, iron(II) and Iron(III) catalyzed perborate oxidation of 5-oxo acids whereas cobalt(II), nickel(II), chromium(VI), titanium(IV), cerium(IV), thorium(IV), uranium(VI), copper(II), zinc(II), cadmium(II), mercury(II), aluminum(III), tin(II), lead(II), arsenic(III), antimony(III), bismuth(II), selenium(IV) and tellurium(IV) do not. Iron(II) catalyzes perborate oxidation of substituted 5-oxo acids in acid medium and the oxidation is first order with respect to perborate. Under the conditions $[5\text{-oxo acid}]_0 \gg [\text{oxidant}]_0 \gg [\text{Fe(II)}]$, plot of $\log [\text{perborate}]_t$ versus time is linear at least up to 80 % of the oxidation with correlation coefficient (r) not less than 0.999 and standard error of estimate (sd) not larger than 0.013. The specific rate of oxidation in perborate remains constant when $[\text{perborate}]_0$ is increased by 8-fold (Table 1).

Table 1 Pseudo-first order rate constant for perborate oxidation of substituted 5-oxo acids in presence of Iron(II) ^a

5-Oxoacid	$10^3 k^* (s^{-1})$				
	$10^3 [\text{Perborate}]_0 (\text{mol dm}^{-3})$				
	0.5	1.0	2.0	3.0	4.0
<i>p</i> -OCH ₃	22.90	24.27	23.29	22.75	25.27
<i>p</i> -CH ₃	11.45	12.14	11.65	11.38	12.64
<i>p</i> -C ₆ H ₅	8.34	8.86	8.50	8.30	9.22
-H	7.53	7.98	7.66	7.48	8.31
<i>p</i> -Cl	2.32	2.46	2.36	2.31	2.57
<i>p</i> -Br	1.19	1.26	1.21	1.18	1.31
<i>m</i> -NO ₂	0.59	0.63	0.60	0.57	0.65

^a $10^2 [5\text{-Oxo acid}]_0 = 4.0 \text{ mol dm}^{-3}$; $10^2 [H^+] = 9.88 \text{ mol dm}^{-3}$; $*10^4 [\text{Fe(II)}] = 1.0 \text{ mol dm}^{-3}$; HOAc-H₂O = 1:1 % (v/v); Temp. = 308 K.

Effect of catalyst

The oxidation is catalyzed by iron(III) as well. The specific rate of oxidation in perborate increases with the increasing $[\text{Fe(II)}]$ or $[\text{Fe(III)}]$ (Table 2). Further, the rate of oxidation, under identical conditions, in the presence of iron(II) is practically the same as that in the presence of iron(III). Plot of k^* , the specific oxidation rate in perborate in the presence of catalyst, versus $[\text{Fe(II)}]$ or $[\text{Fe(III)}]$ is a straight line with a positive y-intercept (Fig. 1; $r = 0.999$, 0.9996 , $sd = 1.35 \times 10^{-4}$, 1.13×10^{-4} , slope = 44.2, $50.6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, intercept = 3.11×10^{-3} , $2.88 \times 10^{-3} \text{ s}^{-1}$ for iron(II) and iron(III), respectively). Hexacyanoferrate(II) and hexacyanoferrate(III) do not catalyze the oxidation.

Table 2 Iron(II) or Iron(III) catalysis of perborate oxidation of substituted 5-oxo acids ^a

5 - Oxoacid	$10^3 k^* (s^{-1})$														
	$10^5 [\text{Catalyst}] (\text{mol dm}^{-3})$														
	Fe(II)							Fe(III)							
	0	2.0	5.0	8.0	10.0	15.0	20.0	0	2.0	5.0	8.0	10.0	15.0	20.0	20.0
<i>p</i> -OCH ₃	8.64	12.44	16.21	20.35	23.29	29.84	35.89	8.79	11.34	16.42	21.35	24.29	32.24	39.23	8.69
<i>p</i> -CH ₃	4.32	6.22	8.11	10.17	11.65	14.92	17.94	4.39	5.67	8.21	10.68	12.14	16.12	19.62	4.35
<i>p</i> -C ₆ H ₅	3.15	4.54	5.92	7.43	8.50	10.89	13.09	3.21	4.14	5.99	7.79	8.86	11.77	14.32	3.18
-H	2.84	4.09	5.33	6.69	7.66	9.81	11.8	2.89	3.73	5.40	7.02	7.98	10.6	12.9	2.86 [#]
<i>p</i> -Cl	0.88	1.26	1.65	2.07	2.36	3.03	3.64	0.89	1.15	1.67	2.17	2.47	3.27	3.98	0.88
<i>p</i> -Br	0.45	0.64	0.84	1.05	1.21	1.54	1.86	0.46	0.59	0.85	1.11	1.26	1.67	2.03	0.45
<i>m</i> -NO ₂	0.22	0.32	0.42	0.52	0.60	0.77	0.92	0.23	0.29	0.42	0.55	0.63	0.83	1.01	0.22

^a $10^3 [\text{Perborate}]_0 = 1.0 \text{ mol dm}^{-3}$; $10^2 [5\text{-Oxo acid}]_0 = 4.0 \text{ mol dm}^{-3}$; $10^2 [H^+] = 9.88 \text{ mol dm}^{-3}$; HOAc-H₂O = 1:1 % (v/v); Temp. = 308 K. [#]Hexacyanoferrate as the catalyst.

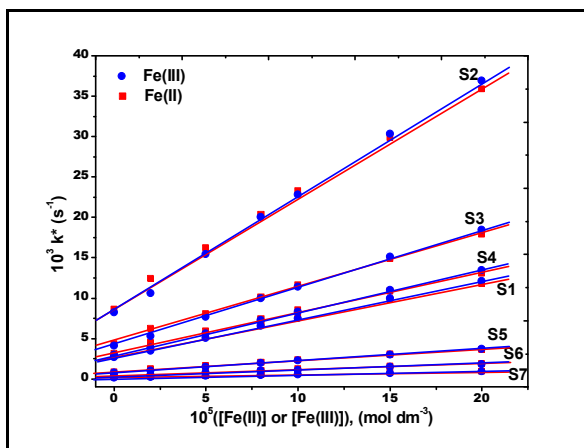


Fig. 1 Linear dependence of k^* on [Catalyst] under the conditions of Table 2.(S1) -H, (S2) 4'-Methoxy, (S3) 4'-Methyl, (S4) 4'-Phenyl, (S5) 4'-Chloro, (S6) 4'-Bromo, (S7) 3'-Nitro.

The oxidation proceeds in the absence of catalysts also and the uncatalyzed oxidation is first order in the oxidant. Plot of $\log [\text{perborate}]_t$ versus time is linear. Also, the pseudo-first order rate constant of the uncatalyzed oxidation (k') remains constant when the $[\text{perborate}]_0$ is varied 8-fold. The y -intercepts of k^* versus $[\text{Fe(II)}]$ or $[\text{Fe(III)}]$ plots are equal to the specific rate of uncatalyzed oxidation. The difference in the specific rate of oxidation in the presence and absence of iron(II) ($k^* - k'$) is the specific rate of iron(II) catalyzed oxidation, and the iron(II) or iron(III) catalyzed oxidation is first order with respect to the catalyst.

At fixed $[\text{perborate}]_0$, $[\text{H}^+]$ and $[\text{Fe(II)}]$, the specific rate of iron(II) catalyzed oxidation increases but less rapidly with the increasing $[\text{5-oxo acid}]_0$ (Table 3).

Table 3 Rate Dependence on $[\text{5-Oxo acid}]_0$ ^a

5-Oxo acid	$10^3 k^* (s^{-1})$						$10^3 (k^* - k') (s^{-1}) 308 \text{ K}$					
	$10^2 [\text{5-Oxo acid}]_0 (\text{mol dm}^{-3}) 308 \text{ K}$											
	2.0	3.0	4.0	6.0	8.0	10.0	2.0	3.0	4.0	6.0	8.0	10.0
<i>p</i> -OCH ₃	14.99 (4.78)	20.47 (7.66)	24.27 (8.64)	31.63 (11.95)	36.19 (16.21)	40.15 (18.86)	10.13	12.80	15.63	19.68	20.10	21.38
<i>p</i> -CH ₃	7.49 (2.39)	10.23 (3.83)	12.14 (4.32)	15.82 (5.98)	18.09 (8.11)	20.07 (9.43)	5.06	6.40	7.82	9.84	10.05	10.69
<i>p</i> -C ₆ H ₅	5.47 (1.74)	7.47 (2.79)	8.86 (3.15)	11.55 (4.36)	13.21 (5.92)	14.65 (6.88)	3.69	4.67	5.71	7.18	7.34	7.80
-H	4.93 (1.57)	6.73 (2.52)	7.98 (2.84)	10.4 (3.93)	11.9 (5.33)	13.2 (6.20)	3.33	4.21	5.14	6.47	6.61	7.03
<i>p</i> -Cl	1.52 (0.49)	2.08 (0.78)	2.46 (0.88)	3.21 (1.21)	3.67 (1.65)	4.07 (1.91)	1.03	1.29	1.59	1.99	2.04	2.17
<i>p</i> -Br	0.78 (0.25)	1.06 (0.39)	1.26 (0.45)	1.64 (0.62)	1.87 (0.84)	2.08 (0.98)	0.52	0.66	0.81	1.02	1.04	1.11
<i>m</i> -NO ₂	0.39 (0.12)	0.53 (0.19)	0.63 (0.22)	0.82 (0.31)	0.93 (0.42)	1.03 (0.49)	0.26	0.33	0.40	0.51	0.52	0.55

^a $10^3 [\text{Perborate}]_0 = 1.0 \text{ mol dm}^{-3}$; $10^2 [\text{H}^+] = 9.88 \text{ mol dm}^{-3}$; $10^4 [\text{Fe(II)}] = 1.0 \text{ mol dm}^{-3}$; HOAc-H₂O = 1:1 % (v/v). Parentheses values indicate the rate constant (k' , s^{-1}) of uncatalyzed reactions.

The rate of iron(II) catalyzed oxidation is independent of $[\text{H}^+]$ of the medium. At fixed $[\text{perborate}]_0$, $[\text{5-oxo acid}]_0$ and $[\text{Fe(II)}]$, $(k^* - k')$ remains constant when $[\text{H}^+]$ is varied twenty-fold.

Effect of hydrogen peroxide

Under identical conditions, the rates of iron(II) catalyzed oxidation of 5-oxo acids by perborate and hydrogen peroxide are almost the same (Table 4).

Table 4 Iron(II) catalyzed oxidation of hydrogen peroxide ^a

10^3 [Oxidant] ₀ (mol dm ⁻³)	10^2 [H ⁺] (mol dm ⁻³)	$10^3 k^*$ (s ⁻¹)									
		Perborate					Hydrogen peroxide				
		<i>p</i> -OCH ₃	-H	<i>p</i> -Cl	<i>p</i> -Br	<i>m</i> -NO ₂	<i>p</i> -OCH ₃	-H	<i>p</i> -Cl	<i>p</i> -Br	<i>m</i> -NO ₂
1.0	9.88	24.27	7.98	2.46	1.26	0.63	25.06	8.24	2.54	1.29	0.65
2.0	9.88	23.29	7.66	2.36	1.21	0.60	23.39	7.69	2.37	1.21	0.60
1.0	14.9	27.34	8.99	2.78	1.42	0.70	27.16	8.93	2.76	1.41	0.69

^a 10^2 [5-Oxo acid]₀ = 4.0 mol dm⁻³; 10^4 [Fe(II)] = 1.0 mol dm⁻³; HOAc-H₂O = 1:1 % (v/v); Temp. = 308 K.

Effect of temperature

The oxidation reactions were studied in the temperature range of 298–318 K. Activation energy (E_a) of the reactions was calculated from the least-square slopes of linear Arrhenius plots (Fig. 2; $r \geq 0.96$; $s \leq 0.02$) of $\log k$ versus $1/T$. The related thermodynamic parameters viz. enthalpy of activation (ΔH^\ddagger), entropy of activation (ΔS^\ddagger) and Gibbs free-energy of activation (ΔG^\ddagger) calculated using appropriate equations are presented in Table 5.

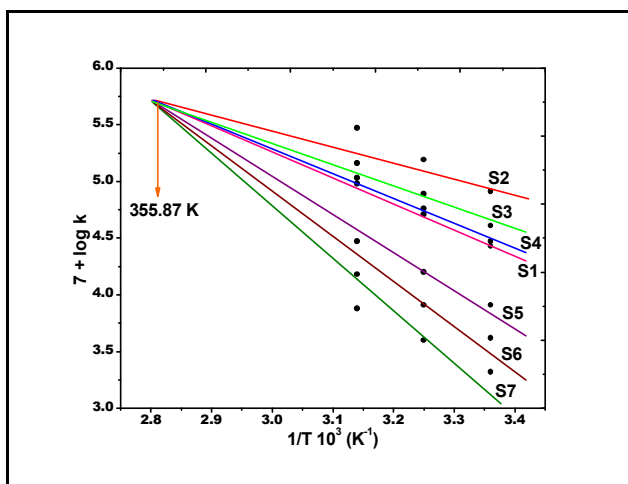


Fig. 3 Arrhenius plots between $\log k$ and $1/T$ showing the isokinetic temperature under the conditions of Table 5. (S1) -H, (S2) 4'-Methoxy, (S3) 4'-Methyl, (S4) 4'-Phenyl, (S5) 4'-Chloro, (S6) 4'-Bromo, (S7) 3'-Nitro.

Table 5 Values of rate constant at different temperatures and activation parameters ^a

5-Oxoacid	$10^3 (k^* - k')$ (s ⁻¹)			ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (J K ⁻¹ mol ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)
	298 K	308 K	318 K			
<i>p</i> -OCH ₃	8.12	15.63	29.23	47.29	-93.03	287.00
<i>p</i> -CH ₃	4.06	7.82	14.61	40.97	-98.97	305.24
<i>p</i> -C ₆ H ₅	2.96	5.71	10.67	38.68	-101.08	311.71
-H	2.67	5.14	9.61	36.19	-102.42	315.81
<i>p</i> -Cl	0.82	1.59	2.97	25.27	-111.99	345.18
<i>p</i> -Br	0.42	0.81	1.51	21.06	-117.54	362.23
<i>m</i> -NO ₂	0.21	0.40	0.75	13.59	-123.48	380.45

^a 10^3 [Perborate]₀ = 1.0 mol dm⁻³; 10^2 [5-Oxo acid]₀ = 4.0 mol dm⁻³; 10^2 [H⁺] = 9.88 mol dm⁻³;

* 10^4 [Fe(II)] = 1.0 mol dm⁻³; HOAc-H₂O = 1:1 % (v/v).

Isokinetic relationships

The plot between ΔH^\ddagger and ΔS^\ddagger is linear (Fig. 4; $r \geq 0.97$, $s \leq 0.029$) and the isokinetic temperature (β) obtained is 355.9 K. The β calculated from the Exner's plot (Fig. 5; $r \geq 0.987$; $s \leq 0.04$) of $\log k_{318K}$ against $\log k_{308K}$ is 353.7 K, which is in good agreement with the value obtained from the ΔH^\ddagger , against ΔS^\ddagger plot. The

isokinetic relationship in the present study implies that all the 5-oxo acids undergo oxidation by the same mechanism²¹.

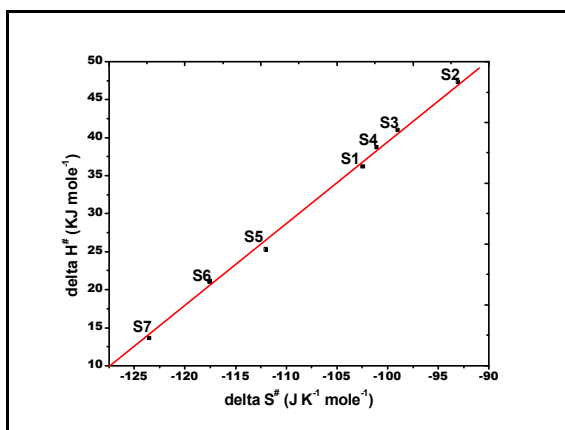


Fig. 4 Plot between ΔH^\ddagger and ΔS^\ddagger : isokinetic relationship under the conditions of Table 5. (S1) -H, (S2) 4'-Methoxy, (S3) 4'-Methyl, (S4) 4'-Phenyl, (S5) 4'-Chloro, (S6) 4'-Bromo, (S7) 3'-Nitro.

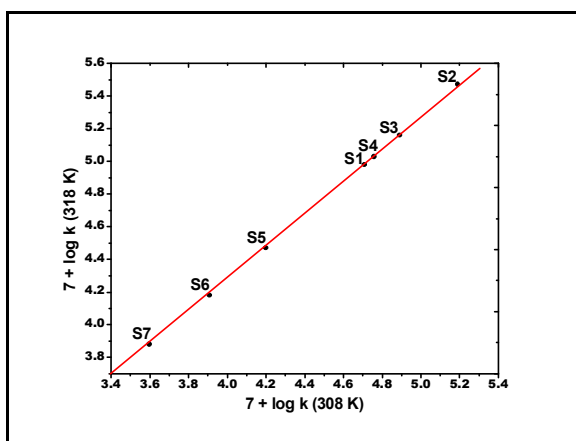
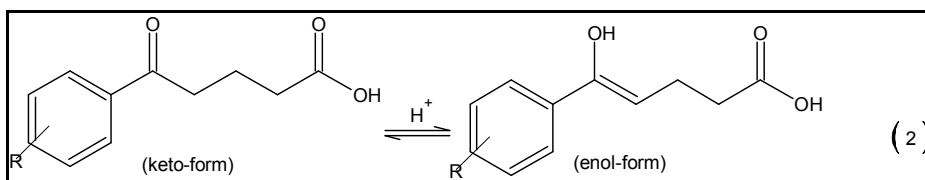


Fig. 5 Exner's plot of $\log k_{318K}$ against $\log k_{308K}$ under the conditions of Table 5.(S1) -H, (S2) 4'-Methoxy, (S3) 4'-Methyl, (S4) 4'-Phenyl, (S5) 4'-Chloro, (S6) 4'-Bromo, (S7) 3'-Nitro.

Discussion

Active species of reactants

The oxo acid is a weak acid ($pK_a = 5.77$ at 40°C in aqueous solution)²², and the undissociated form of the substrate can be taken as the only form in acidic media. In acid solutions, 5-oxo acid undergoes keto enol tautomerism (Eq. 2).

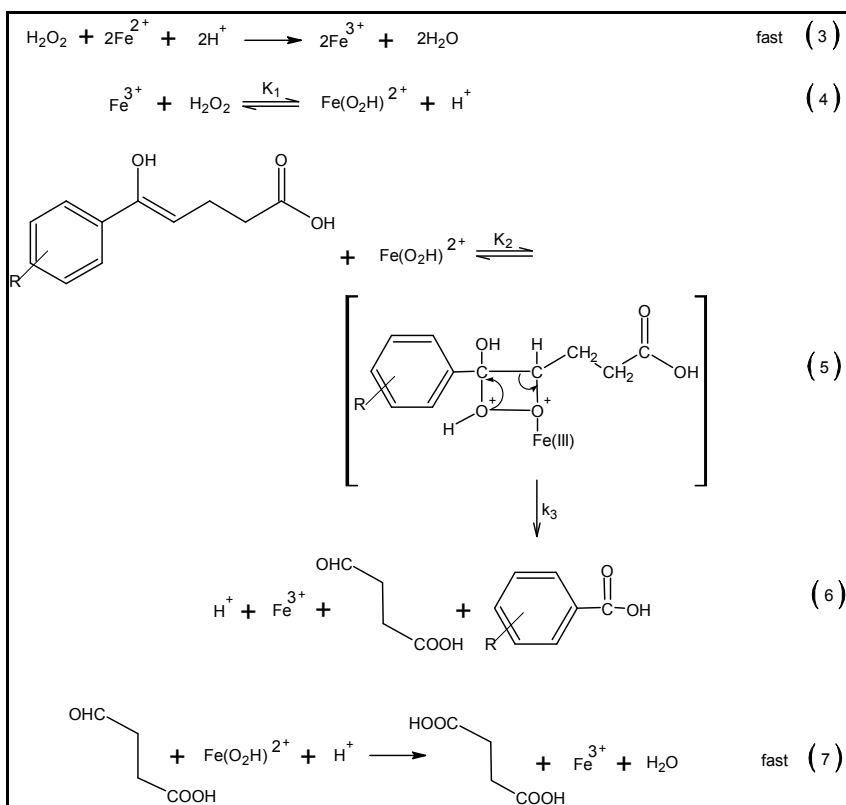


In crystalline state sodium perborate exist as a dimer with anionic formula: $B_2(O_2)_2(OH)_4^{2-}$. But in aqueous solution it affords hydrogen peroxide^{1,23}. Although perboric acid is reported to exist in equilibrium with hydrogen peroxide, the equilibrium constant reveals that even in the presence of large excess of boric acid the concentration of perboric acid is insignificant²⁴. For example, at $[H_3BO_3]_0 = 0.01 \text{ mol dm}^{-3}$, $[(HO)_2BOOH]/[H_2O_2] = 1 \times 10^{-4}$. The similar rates of iron(II) catalyzed oxidation of 5-oxo acids by perborate and hydrogen peroxide under identical conditions, indicates that hydrogen peroxide is oxidizing species of perborate.

Mechanism

Iron(III) oxidizes 5-oxo acids to benzoic acid. Perborate in acidic medium, oxidizes iron(II) to iron(III). Hence one of the possible mechanism is oxidation of iron(II) to iron(III) followed by the reduction of iron(III) to iron(II) by 5-oxo acids. However, the Fe(II)–Fe(III) cycle is unlikely in this catalysis. Chemical tests confirm the presence of iron(III) and the absence of iron(II) in the reaction solution when the oxidation is in progress. Formation of the Michaelis-Menten type complex between iron(III) and 5-oxo acid is also unlikely.

Another possible mechanism is of the Fenton-type. But this mechanism is also ruled out as the oxidation is not through radical pathway. ESR spectral study of the reaction solution, while the oxidation is in progress, does not show the presence of any radical. The iron(II) catalyzed oxidation is insensitive to the addition of vinyl monomer and the reaction solution fails to initiate polymerization of acrylonitrile. Although Fe_2O_5 and Fe_2O_2 are suggested as intermediate in iron(II) or iron(III) catalyzed decomposition of hydrogen peroxide they are not considered as the active oxidizing species in the present work²⁵. If they were to be the oxidizing species, contrary to the experimental findings, the oxidation should be second order with respect to the catalyst. In acidic solution hydrogen peroxide affords iron(III) peroxo species^{26,27}. This species contains iron and peroxide in the ratio 1:1 and is formulated as $\text{Fe}(\text{O}_2\text{H})^{2+}$. The following mechanism accounts for the observed kinetic results (Scheme 1).



Scheme 1

Rate law

The rate law for the catalyzed oxidation is

$$\frac{-d[\text{perborate}]}{dt} = \frac{K_1 K_2 k_3 [\text{Fe(II)}][5\text{-oxoacid}][\text{perborate}]}{(1 + K_2 [5\text{-oxoacid}])}$$

The specific rate in perborate of the catalyzed oxidation is

$$k^* \cdot k' = \frac{K_1 K_2 k_3 [\text{Fe(II)}][5\text{-oxoacid}]}{(1 + K_2 [5\text{-oxoacid}])}$$

The kinetic constants, calculated from the slope and intercept of the Hanes plot are

$$K_1 k_3 = 98.2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

$$K_2 = 26.6 \text{ dm}^3 \text{ mol}^{-1} \text{ (at 308 K)}.$$

The rate law is compatible with the experimental results, viz., first order with respect to [perborate], zero order in $[\text{H}^+]$, the Michaelis-Menten type dependence on [5-oxo acid], almost the same rates of oxidation by perborate and hydrogen peroxide under identical conditions, the absence of enhancement or inhibition of perborate and hydrogen peroxide oxidations by borate or boric acid, etc.

Conclusions

Iron(II) catalyzed perborate oxidation of substituted 5-oxo acids in acidic solution is associated with isokinetic relationship. In aqueous solution perborate generates hydrogen peroxide. Under the conditions $[\text{Fe(II)}] \ll \ll [\text{perborate}]_0 \ll [5\text{-oxo acid}]_0$, the oxidation is first order with respect to the oxidant and catalyst. The rate of catalyzed oxidation displays the Michaelis-Menten kinetics on the reductant and is independent of $[\text{H}^+]$ of the medium. Hydrogen peroxide is the reactive species of perborate and the kinetic results reveal formation of iron(III) peroxo species-5-oxo acid complex. The variation of oxidation rate with ionic strength of the medium is quite small at low $[\text{H}^+]$ but appreciable at high $[\text{H}^+]$. The oxidation rate increases with decreasing dielectric constant of the medium at low and high acidities. The rates of iron(II) catalyzed perborate and hydrogen peroxide oxidations are almost the same. Borate and boric acid do not influence the oxidations. Electron releasing substituents accelerate the reaction rate and electron withdrawing substituents retard the reaction. The order of reactivity among the studied 5-oxo acids is *p*-methoxy \gg *p*-methyl $>$ *p*-phenyl $>$ -H $>$ *p*-chloro $>$ *p*-bromo $>$ *m*-nitro. Activation parameters have been evaluated using Arrhenius and Eyring's plots. A mechanism consistent with the observed kinetic data is proposed and discussed. A suitable rate law is derived based on the mechanism. The experimental protocol suggests that this reaction could find utility as a regioselective route for the synthesis of carboxylic acids, specially substituted benzoic acids.

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