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A KINETIC STUDY OF MOLYBDENUM (VI) CATALYSIS OF PERBORATE OXIDATION OF SUBSTITUTED 5-OXO ACIDS

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Abstract:

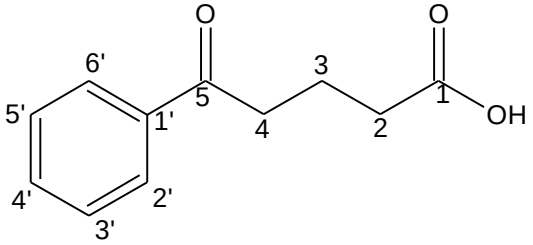
In aqueous acetic acid medium molybdenum (VI) catalyzes perborate oxidation of 5-oxo acid. The catalyzed oxidation is first order with respect to the oxidant and catalyst, and is zero order with respect to the reductant and acid. In aqueous acetic acid solution perborate generates hydrogen peroxide and the kinetic results reveal Oxodiperoxomolybdenum (VI) is likely to be the oxidizing species; its formation is rate limiting. The rates of molybdenum (VI) catalyzed perborate and hydrogen peroxide oxidations are almost the same. The ionic strength and the dielectric constant of the medium have no influence on the oxidation rate at low and also at high [H^+]. The kinetic constant and activation parameters have been calculated. A mechanism consistent with the observed kinetic data has been proposed and discussed. A suitable rate law has been derived based on the mechanism.

Key Words: Catalysis, Kinetics, Molybdenum (VI), Oxidation, 5-Oxo Acid & Perborate

1. Introduction:

Sodium perborate ($NaBO_3.4H_2O$) is a cheap, non-toxic, large scale industrial chemical used primarily in detergents and as a mild oxidant. It is a convenient source of hydrogen peroxide [1], commercially, industrially and also in the laboratory. PMR spectral analysis [2] and X-ray diffraction studies [3] conclude perborate as a true peroxysalt with water of crystallisation. Perborate is a heterocycle and is in a dimeric tetrahedral configuration with dihedral angle of 64^o and anionic formula: $B_2(O_2)_2(OH)_4^{2-}$ [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 perborate oxidation as hydrogen peroxide oxidation [8-10]. This stable and easily handled crystalline substance oxidizes organic sulphides [11-13], anilines [14] and indole [15]. Here we report the molybdenum (VI) catalysis of 5-oxo acid oxidation.

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 has been reported in the literature to be the enol form [16, 17]. 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 acid have been reported so far [18-21]. 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 acid by perborate and we report here for the first time the kinetics and mechanism of perborate oxidation of substituted and unsubstituted 5-oxo acid. The various unsubstituted and substituted 5-oxo acid (S1-S7) employed in the present study are listed below.



5-oxoacid (S1)

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

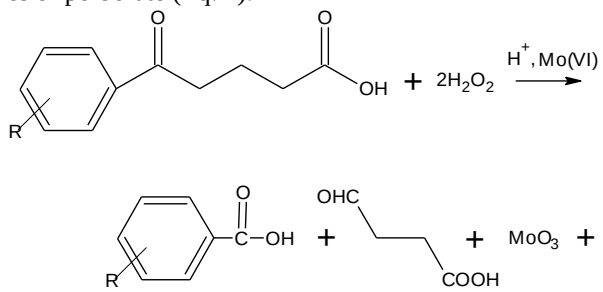
2. Experimental:

2.1 Materials: Sodium perborate, $NaBO_3.4H_2O$, (Riedel), KI and Na_2MoO_4 (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-oxoacid. Sodium metaborate and sulphuric acid were prepared in double distilled water. Double distilled water (conductivity < 10 $\mu S.cm^{-1}$) has been 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 acid (S2-S7) were prepared by Friedel-Crafts acylation of the substituted benzene with glutaric anhydride [22-26]. All the 5-oxo acid was 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. Regression analysis of experimental data yielded the regression coefficient (*r*) and standard deviation (*s*).

2.2 Kinetic Measurements: The reaction mixture, containing 5-oxo acid, molybdate 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 log $[perborate]_t$ 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.

2.3 Reaction Stoichiometry and Product Analysis: The stoichiometry of the reaction was determined by equilibrating reaction mixture of various [perborate]/[5-oxoacid] ratios at 313 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 ^oC).Then it has been estimated quantitatively using UV-Vis spectrophotometry with a standard curve at λ_{max} = 235 nm. Succinic acid was identified by its melting point (185 ^oC) and also tested with its characteristic spot test [27]. Identification of the products, namely, benzoic and succinic acids, were also made by comparing the R_f values of the authentic samples.

3. Results:

3.1 Effect of Concentrations: Molybdenum (VI) catalyzes oxidation of 5-oxo acid. Under the conditions: [Mo(VI)] <<< $[perborate]_0$ << $[5\text{-oxo acid}]_0$ plots of log $[perborate]_t$ *versus* time are linear at least up to about 80% of the oxidation with correlation coefficient not <0.997 and standard error of estimate not >0.033. The pseudo-first order rate constant (k') remains constant with varying $[perborate]_0$. The catalyzed oxidation is zero order with respect to 5-oxo acid. The rate remains constant when $[5\text{-oxo acid}]_0$ is increased by 20-fold. Constancy of the rate in the acidity range 0.01-0.2 mol dm^{-3} reveals that the oxidation is independent of $[H^+]$ in the medium. However, both the catalyzed and unanalyzed oxidations occur only in acidic solution (Table 1).

Table 1: Pseudo-first order rate constant for Mo(VI) catalyzed Perborate Oxidation of Substituted 5-Oxo acid[a]

$10^4[Perborate]_0$ (mol dm^{-3})	$10^2[5\text{-Oxo acid}]_0$ (mol dm^{-3})	$10^2[H^+]$ (mol dm^{-3})	$10^3k'$ (s^{-1})						
			p-OCH_3	*p*-CH_3	*p*-C_6H_5	-H	*p*-Cl	*p*-Br	*m*-NO_2
2.0	1.0	2.0	10.84	5.19	4.08	2.98	0.80	0.51	0.21
4.0	1.0	2.0	11.19	5.34	4.21	3.07	0.83	0.53	0.22
5.0	1.0	2.0	10.66	5.09	4.01	2.93	0.79	0.50	0.21
8.0	1.0	2.0	9.75	4.66	3.67	2.68	0.72	0.46	0.19
10.0	1.0	2.0	10.33	4.94	3.89	2.84	0.76	0.49	0.20
5.0	0.5	2.0	9.86	4.72	3.72	2.72	0.73	0.46	0.19
5.0	3.5	2.0	10.74	5.14	4.05	2.96	0.79	0.50	0.21
5.0	5.0	2.0	10.4	5.01	3.95	2.89	0.77	0.49	0.20
5.0	8.0	2.0	9.94	4.76	3.75	2.74	0.73	0.46	0.19
5.0	10.0	2.0	10.03	4.80	3.78	2.76	0.74	0.47	0.20
5.0	1.0	1.0	9.63	4.61	3.63	2.65	0.71	0.45	0.19
5.0	1.0	4.0	9.85	4.71	3.71	2.71	0.72	0.46	0.19
5.0	1.0	7.0	9.30	4.45	3.50	2.56	0.68	0.43	0.18
5.0	1.0	15.0	8.50	4.07	3.20	2.34	0.62	0.40	0.16
5.0	1.0	20.0	7.81	3.74	2.94	2.15	0.57	0.36	0.15

[a]10^6[Mo(VI)] = 2.0 mol dm^{-3}; HOAc-H_2O = 1:1 *% (v/v)*; Temp.= 308 K.

3.2 Effect of Catalyst: The oxidation is first order with respect to molybdenum (VI). The rate of oxidation increases linearly with [Mo(VI)] (Fig. 1, k' *versus* [Mo(VI)] plot: correlation coefficient = 0.996,0.997; standard error of estimate = 3.87 × 10^{-4}, 7.06 × 10^{-4}; slope = 1.19 × 10^{3}, 2.23 × 10^{3} dm^3 mol^{-1} s^{-1}; and intercept = 4.38 × 10^{-4}, 1.63 × 10^{-3} s^{-1} at 288 K and 308 K, respectively). At 288 K, the uncatalysed oxidation, under the conditions reported in Table 2, is very slow.

Table 2: Rate Dependence on Mo(VI) at 288 K & 308 K[a]

5-Oxoacid	$10^3k'$ (s^{-1})															
	10^6 [Mo(VI)] (mol dm^{-3})															
	288 K								308 K							
	0	0.5	1.0	2.0	3.0	5.0	8.0	10.0	0	0.5	1.0	2.0	3.0	5.0	8.0	10.0
p-OCH_3	0.33	2.75	6.54	10.63	15.75	21.50	34.73	46.52	1.37	4.27	14.27	24.80	32.56	46.21	72.35	84.35
p-CH_3	0.16	1.32	3.13	5.09	7.54	10.29	16.62	22.26	0.66	2.34	6.83	11.87	15.58	22.72	34.62	40.36
p-C_6H_5	0.13	1.04	2.47	4.01	5.94	8.11	13.09	17.53	0.52	1.27	5.38	9.35	12.27	17.34	27.26	31.78
-H	0.1	0.76	1.81	2.93	4.34	5.92	9.56	12.8	0.38	0.94	3.93	6.83	8.96	11.57	19.9	23.2
p-Cl	0.02	0.20	0.48	0.78	1.16	1.59	2.56	3.44	0.10	0.42	1.05	1.83	2.40	4.27	5.34	6.23
p-Br	-	0.12	0.30	0.49	0.73	1.01	1.63	2.19	0.06	0.23	0.66	1.16	1.52	2.41	3.40	3.96
m-NO_2	-	0.05	0.12	0.20	0.30	0.42	0.68	0.92	0.02	0.12	0.27	0.48	0.63	1.29	1.42	1.66

[a] 10^4 [Perborate]$_0$ = 5.0 mol dm^{-3}; 10^2 [5-Oxo acid]$_0$ = 1.0 mol dm^{-3}; 10^2 [H^+] = 2.0 mol dm^{-3}; HOAc-H_2O = 1:1 *% (v/v)*.

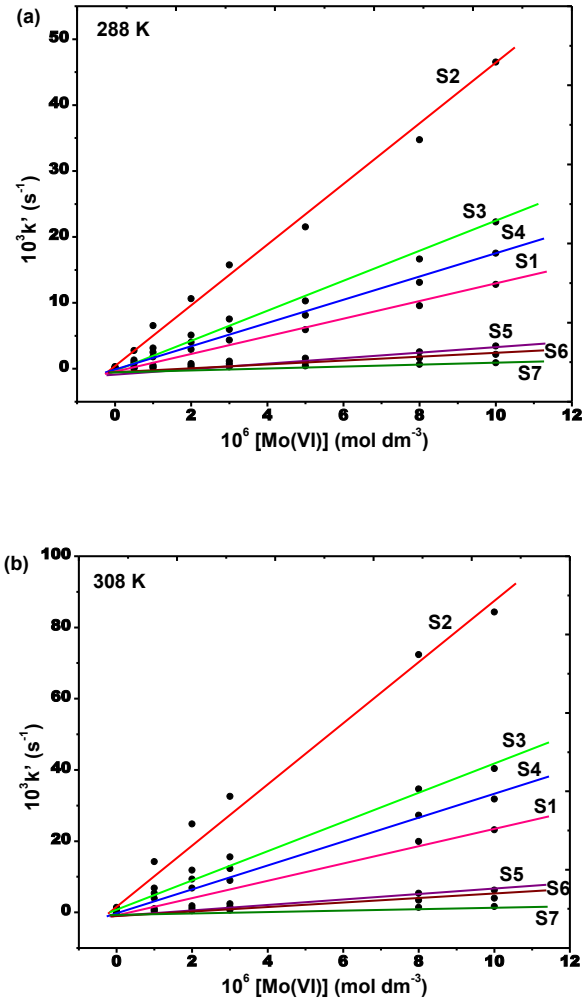


Figure 1: (a) Linear Dependence of k' on [Mo(VI)] under the conditions of Table 2 at 288 K. (S1) -H, (S2) 4'-Methoxy, (S3) 4'-Methyl, (S4) 4'-Phenyl, (S5) 4'-Chloro, (S6) 4'-Bromo, (S7) 3'-Nitro. (b) Linear Dependence of k' on [Mo(VI)] under the conditions of Table 2 at 308 K. (S1) -H, (S2) 4'-Methoxy, (S3) 4'-Methyl, (S4) 4'-Phenyl, (S5) 4'-Chloro, (S6) 4'-Bromo, (S7) 3'-Nitro.

3.3 Influence of Salt Effect and Solvent Polarity: Influence of ionic strength of the reaction medium, varied with potassium nitrate, has no influence on the oxidation rate at low or high [H^+] (Table 3). Varying the acetic acid and water composition in the reaction mixture varied dielectric constant (D) of the medium. At low as well as high [H^+] the decrease of dielectric constant of the reaction medium, has no influence on the oxidation rate. Table 4 presents the pseudo-first order rate constant in perborate at different dielectric constants.

Table 3: Influence of Ionic Strength[a]

$10[KNO_3]$ (mol dm^{-3})	10^2 $[H^+]$ (mol dm^{-3})	$10^3 k'$ (s^{-1})						
		p-OCH_3	*p*-CH_3	*p*-C_6H_5	-H	*p*-Cl	*p*-Br	*m*-NO_2
0	1.0	24.45	11.70	9.22	6.73	1.80	1.14	0.47
1.0	1.0	22.36	10.70	8.43	6.16	1.65	1.05	0.44
2.0	1.0	22.07	10.56	8.32	6.08	1.63	1.03	0.43
0	15.0	21.06	10.08	7.94	5.80	1.55	0.98	0.41
1.0	15.0	18.01	8.62	6.79	4.96	1.33	0.84	0.35
2.0	15.0	19.37	9.27	7.30	5.33	1.43	0.91	0.38

[a]10^4 $[Perborate]_0$ = 5.0 mol dm^{-3}; 10^2 $[5\text{-Oxo acid}]_0$ = 1.0 mol dm^{-3}; $10^6[Mo(VI)]$ = 2.0 mol dm^{-3}; HOAc-H_2O = 1:1 *% (v/v)*; Temp.= 308 K.

Table 4: Influence of Dielectric Constant of the Medium[a]

D	AcOH-H_2O % (v/v)	10^2 $[H^+]$ (mol dm^{-3})	$10^3 k'$ (s^{-1})						
			p-OCH_3	*p*-CH_3	*p*-C_6H_5	-H	*p*-Cl	*p*-Br	*m*-NO_2
53.18	30-70	1.0	22.23	10.64	8.38	6.12	1.64	1.04	0.43
46.48	40-60	1.0	22.82	10.92	8.60	6.28	1.68	1.07	0.44
39.78	50-50	1.0	24.45	11.70	9.22	6.73	1.80	1.14	0.47
33.08	60-40	1.0	24.80	11.87	9.35	6.83	1.83	1.16	0.48
26.08	70-30	1.0	24.20	11.58	9.12	6.66	1.79	1.14	0.47
53.18	30-70	15.0	17.93	8.58	6.76	4.94	1.32	0.84	0.35
46.48	40-60	15.0	19.70	9.43	7.43	5.43	1.45	0.92	0.38
39.78	50-50	15.0	21.06	10.08	7.94	5.80	1.55	0.98	0.41
33.08	60-40	15.0	18.91	9.05	7.13	5.21	1.40	0.89	0.37
26.08	70-30	15.0	20.77	9.94	7.83	5.72	1.53	0.97	0.40

[a]10^4 $[Perborate]_0$ = 5.0 mol dm^{-3}; 10^2 $[5\text{-Oxo acid}]_0$ = 1.0 mol dm^{-3}; $10^6[Mo(VI)]$ = 2.0 mol dm^{-3}; Temp.= 308 K.

3.4 Effect of Hydrogen Peroxide: Under identical conditions, the rate of molybdenum (VI) catalyzed oxidation of 5-oxo acid by perborate is almost the same as that by hydrogen peroxide (Table 5).

Table 5: Oxidation by Hydrogen Peroxide[a]

10^4 $[Oxidant]_0$ (mol dm^{-3})	10^2 $[H^+]$ (mol dm^{-3})	$10^3 k'$ (s^{-1})					
		p-OCH_3		-H		*m*-NO_2	
		Hydrogen peroxide	Perborate	Hydrogen peroxide	Perborate	Hydrogen peroxide	Perborate
5.0	2.0	25.01	24.80	6.89	6.83	0.49	0.48
10.0	2.0	25.49	25.01	7.02	6.89	0.50	0.49
5.0	15.0	20.98	21.06	5.78	5.80	0.41	0.41
10.0	15.0	24.62	24.89	6.78	6.85	0.48	0.49

[a]10^2 $[5\text{-Oxo acid}]_0$ = 1.0 mol dm^{-3}; $10^6[Mo(VI)]$ = 2.0 mol dm^{-3}; HOAc-H_2O = 1:1 *% (v/v)*; Temp.= 308 K.

3.5 Influence of Borate and Boric Acid: Boric acid or borate neither retards nor enhances the oxidation. Initial addition of orthoboric acid or metaborate to the reaction medium has an insignificant effect on the oxidation rate (Table 6). Boric acid and borate also fail to influence the rate of molybdenum (VI) catalyzed hydrogen peroxide oxidation. Addition of vinyl monomer acrylonitrile to the reaction solution has little effect on the oxidation rate. Further, when the reaction is in progress, the solution fails to polymerize the vinyl monomer. During the course of oxidation, the reaction solution does not give an e.s.r. signal (Bruker X-band) for any radical.

Table 6: Influence of Borate and Boric Acid on the Oxidation Rate[a]

10^2 $[NaBO_2]_0$ (mol dm^{-3})	10^2 $[H_3BO_3]_0$ (mol dm^{-3})	$10^3 k'$ (s^{-1})					
		p-OCH_3		-H		*m*-NO_2	
		Hydrogen peroxide	Perborate	Hydrogen peroxide	Perborate	Hydrogen peroxide	Perborate
-	-	25.01	24.80	6.89	6.83	0.49	0.48
-	1.0	24.97	24.68	6.87	6.79	0.49	0.48
1.0	-	24.68	24.39	6.79	6.71	0.48	0.47
-	-	-	24.59	-	6.77[b]	-	0.48

[a]10^4 $[Oxidant]_0$ = 5.0 mol dm^{-3}; 10^2 $[5\text{-Oxo acid}]_0$ = 1.0 mol dm^{-3}; 10^2 $[H^+]$ = 2.0 mol dm^{-3}; $10^6[Mo(VI)]$ = 2.0 mol dm^{-3}; HOAc-H_2O = 1:1 *% (v/v)*; Temp.= 308 K.

[b]10^2 [Acrylonitrile] = 1.0 mol dm^{-3}.

3.6 Effect of Temperature: The oxidation reactions were studied in the temperature range of 288 - 308 K. Activation energy (Ea) of the reactions was calculated from the least-square slopes of linear Arrhenius plots (Fig. 2, $r \geq 0.97$; $s \leq 0.02$) of log *k versus* 1/T. The related thermodynamic parameters viz. enthalpy of activation

($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$) and Gibbs free-energy of activation ($\Delta G^{\#}$) calculated using appropriate equations are presented in Table 7.

Table 7: Values of rate constant at different temperatures and activation parameters[a]

5-Oxoacid	10^3 *k'* (s^{-1})		$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (J K^{-1} mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
	288 K	308 K			
***p*-OCH_3**	10.63	24.80	49.78	-147.80	426.16
***p*-CH_3**	5.09	11.87	43.46	-154.11	444.27
***p*-C_6H_5**	4.01	9.35	41.36	-156.22	450.32
-H	2.93	6.83	38.89	-158.71	457.47
***p*-Cl**	0.78	1.83	27.95	-169.62	488.79
***p*-Br**	0.49	1.16	23.74	-173.84	500.90
***m*-NO_2**	0.20	0.48	16.66	-180.92	521.22

[a]10^4 [Perborate]$_0$ = 5.0 mol dm^{-3}; 10^2 [5-Oxo acid]$_0$ = 1.0 mol dm^{-3}; 10^2 [H^+] = 2.0 mol dm^{-3}; 10^6[Mo(VI)] = 2.0 mol dm^{-3}; HOAc-H_2O = 1:1 *% (v/v)*.

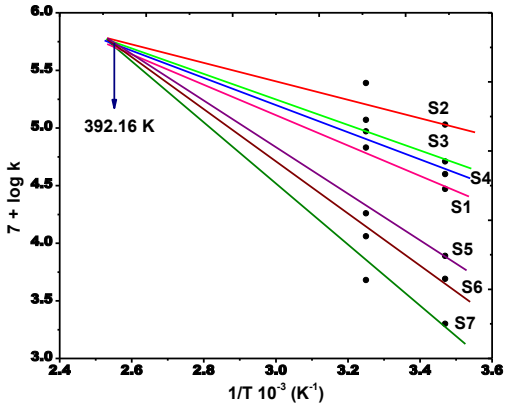


Figure 2: Arrhenius plots between log *k* and *1/T* showing the isokinetic temperature under the conditions of Table 7.
(S1) -H, (S2) 4'-Methoxy, (S3) 4'-Methyl, (S4) 4'-Phenyl, (S5) 4'-Chloro, (S6) 4'-Bromo, (S7) 3'-Nitro.

3.7 The Isokinetic Relationship: The plot between $\Delta H^{\#}$ and $\Delta S^{\#}$ is linear (Fig. 3, $r \geq 0.96$, $s \leq 0.029$) and the isokinetic temperature (β) obtained is 392.2 K. The β calculated from the Exner's plot (Fig. 4, $r \geq 0.989$; $s \leq 0.04$) of log k_{308K} against log k_{288K} is 390.4 K, which is in good agreement with the value obtained from the $\Delta H^{\#}$, against $\Delta S^{\#}$ plot. The isokinetic relationship in the present study implies that all the 5-oxo acids undergo oxidation by the same mechanism [28].

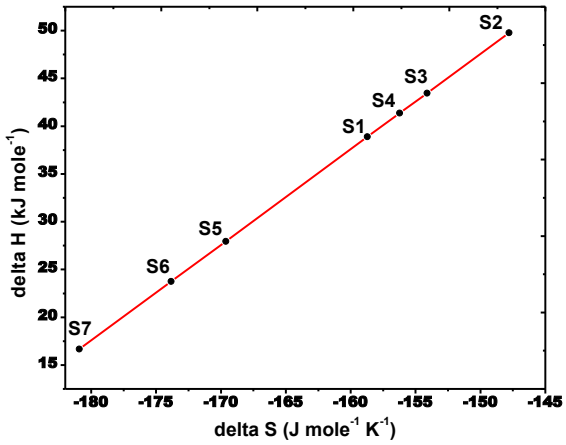


Figure 3: Plot between $\Delta H^{\#}$ and $\Delta S^{\#}$: isokinetic relationship under the conditions of Table 7.
(S1) -H, (S2) 4'-Methoxy, (S3) 4'-Methyl, (S4) 4'-Phenyl, (S5) 4'-Chloro, (S6) 4'-Bromo, (S7) 3'-Nitro.

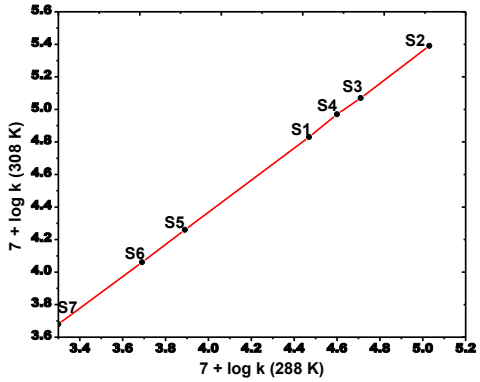
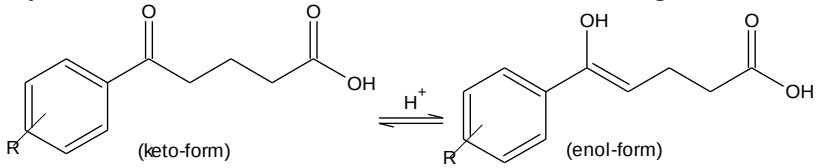


Figure 4: Exner's plot of log k_{308K} against log k_{288K} under the conditions of Table 7. (S1) -H, (S2) 4'-Methoxy, (S3) 4'-Methyl, (S4) 4'-Phenyl, (S5) 4'-Chloro, (S6) 4'-Bromo, (S7) 3'-Nitro.

4. Discussion:

4.1 Active Species of Reactants: Perborate is peroxoborate and in aqueous solution generates H_2O_2 [4]. Although perboric acid exists in solution [29], even at $[H_3BO_3]_0$ = 0.01 mol dm^{-3} the ratio of $[(HO)_2BO_2H]$: $[H_2O_2]$, calculated from the reported value of the equilibrium constant [30], is insignificant. Hence, it is concluded that, at the experimental acidities, perborate exists effectively as hydrogen peroxide. The almost identical rates of molybdenum (VI) catalyzed oxidation of 5-oxo acid by perborate and hydrogen peroxide, under identical conditions, suggests that the reactive species of perborate is hydrogen peroxide. The oxo acid is a weak acid (pK_a = 5.77 at 40 ^oC in aqueous solution) [31], 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).



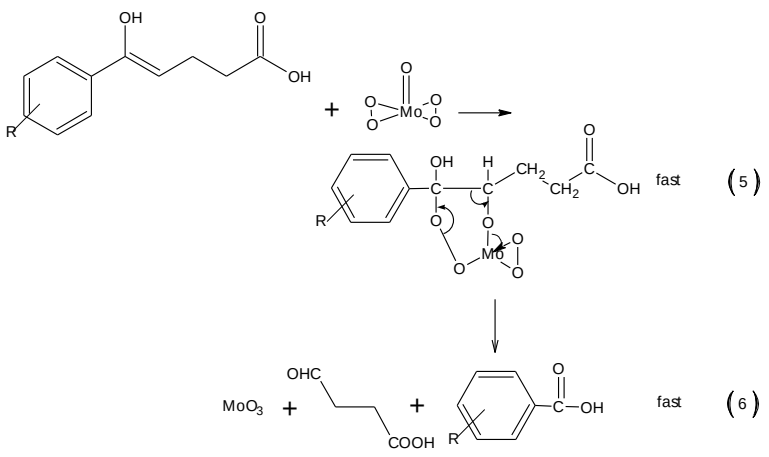
(2)

Molybdenum (VI) dimerizes in acidic solution. But, the total equilibrium concentration of the dimer, calculated from the equilibrium constants [32], is negligible and always <0.027% of the total [Mo(VI)] under the experimental conditions. The speciation of monomeric molybdenum (VI) are $HMoO_3^+$, MoO_3, (H_2MoO_4), $HMoO_4^-$ and MoO_4^{2-} [32, 33]. Calculations of concentrations of the different monomeric species at the experimental acidities, using the equilibrium constants reported already [32, 34], reveals that molybdenum (VI) exists as MoO_3 and $HMoO_3^+$, and concentrations of MoO_4^{2-} and $HMoO_4^-$ are <0.01 and 0.7% 0f the total [Mo(VI)], respectively. The concentration of the protonated species $HMoO_3^+$ increases from 6.6 to 58.6% of the total [Mo(VI)] when $[H^+]$ of the medium is increased from 0.01 to 0.2 mol dm^{-3}.

4.2 Mechanism:

rapid (3)

slow (4)



fast (5)

fast (6)

With Molybdenum (VI), in acidic solution, hydrogen peroxide yields dioxoperoxomolybdenum (VI) [$MoO_2(O_2)$] and oxodiperoxomolybdenum (VI) [$MoO(O_2)_2$]. The protonated species also yields oxodiperoxomolybdenum (VI) [32] and the tetraperoxo species, $Mo(O_2)_4^{2-}$, is formed in basic solution [33, 35]. The first order dependence of rate on [oxidant] and [Mo(VI)], along with the non-dependence on [5-oxo acid] implies slow and rate-determining formation of oxodiperoxomolybdenum(VI), followed by rapid oxidation of 5-oxo acid (Scheme 1) [36, 37]. Further, the rate of formation of oxodiperoxomolybdenum(VI) reported by Ghiron and Thomson [37] supports Scheme 1. The formation is first order with respect to hydrogen peroxide and molybdenum (VI), and at pH 4.0 and 298 K, the specific rate is 1.89×10^3 mol dm^{-3}. Also, oxodiperoxomolybdenum(VI) is a remarkable oxygen transfer reagent and diperoxo complex is more reactive than monoperoxo species [37].

Scheme 1: Benzoic and succinic acids were the final products of oxidation. It is pertinent to point out here that succinic acid is stable and does not undergo further oxidation. The proposed mechanism is also in accordance with the observed stoichiometry. This reaction is an example of the neighboring group participation and intramolecular catalysis.

4.3 Rate Law: The rate law for the proposed mechanism is:

$$-d\,[\text{oxidant}]/dt = k_2\,[\text{Mo(VI)}]\,[\text{oxidant}]$$

and the pseudo-first order rate constant is:

$$k' = k_2\,[\text{Mo(VI)}]$$

The rate law conforms the experimental findings, namely first order each with respect to the oxidant and catalyst, zeroth order with respect to the reductant and H^+ of the medium, and the same rates of oxidation by perborate and hydrogen peroxide under identical conditions. The kinetic constant (k_2) has been determined as 1.19×10^3 and 2.23×10^3 dm^3 mol^{-1} s^{-1} at 288 K and 308 K, respectively.

5. Conclusions:

Molybdenum (VI) catalyzed perborate oxidation of substituted 5-oxo acid in acidic solution is associated with isokinetic relationship. In aqueous acetic acid solution perborate generates hydrogen peroxide and the kinetic results reveal formation of oxodiperoxomolybdenum (VI) is first order with respect to the oxidant and catalyst, and is rate limiting. Oxidation of 5-oxo acid by oxodiperoxomolybdenum (VI) is fast. The reaction rate is accelerated by the electron donating groups compare with the electron withdrawing groups. The order of reactivity among the studied 5-oxo acid is *p*-methoxy >> *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 has been proposed and discussed. A suitable rate law has been 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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