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A KINETIC AND MECHANISTIC STUDY OF TUNGSTEN (VI) CATALYSIS OF PERBORATE OXIDATION OF SUBSTITUTED 5-OXO ACIDS

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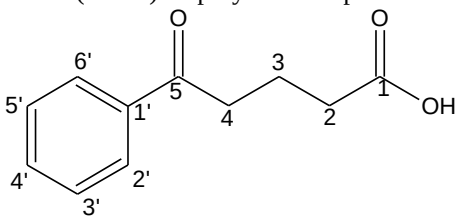
Abstract:

In aqueous acetic acid medium tungsten (VI) catalyzes perborate oxidation of 5-oxo acids. In aqueous acetic acid solution perborate generates hydrogen peroxide. The rates of tungsten (VI) catalyzed perborate and hydrogen peroxide oxidations are almost the same. The ionic strength of the medium has no influence on the oxidation rate but the rate falls moderately with decrease of dielectric constant of the medium. 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 >> *p*-methyl > *p*-phenyl > -H > *p*-chloro > *p*-bromo > *m*-nitro. A mechanism consistent with the observed kinetic data is proposed and discussed. A suitable rate law is derived based on the mechanism.

Introduction:

Sodium perborate ($NaBO_3.4H_2O$) 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 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. It is an effective reagent in organic synthesis and acetic acid is the solvent of choice [4]. 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 sulphides [7], anilines [8] and indole [9]. Perborate oxidizes 5-oxo acid and vanadium (V) catalyzes the oxidation [10]. This study reveals tungsten (VI) catalysis of the 5-oxo acid oxidation and the mechanism of catalysis is different from that of molybdenum (VI). 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 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)

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

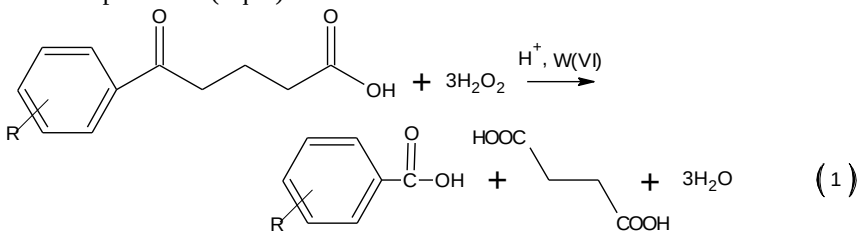
Experimental:

Materials: Sodium perborate, $NaBO_3.4H_2O$ (Riedel) and $Na_2WO_4.2H_2O$ (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 $\mu S.cm^{-1}$) 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 anhydride [15-19]. 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. Regression analysis of experimental data yielded the regression coefficient (*r*) and standard deviation (*s*).

Kinetic Measurements: The reaction mixture, containing 5-oxo acid, tungstate 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.

Reaction Stoichiometry and Product Analysis: The stoichiometry of the reaction was determined by equilibrating reaction mixture of various [perborate]/[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 ^oC).Then it was 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 [20]. 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: Tungsten (VI) catalyzes perborate oxidation of substituted 5-oxo acids in acid medium and the oxidation is first order with respect to perborate. Under the conditions $[5\text{-oxo acid}]_0 >> [oxidant]_0 >> [W^{VI}]$, plots of log $[perborate]_t$ *versus* time are linear for greater than 85% of the oxidation, with correlation coefficient of 0.995 and standard error of estimate not larger than 0.043. The specific rates in perborate at different $[perborate]_0$ are given in Table 1.

Table 1: Pseudo-first order rate constant for W^{VI} catalyzed perborate oxidation of substituted 5-oxo acids [a]

5-Oxoacid	$10^3 k^*$ (s^{-1})													
	10^4 [Perborate]$_0$ (mol dm^{-3})													
	288 K					298 K					308 K			
	4.0	5.0	6.0	8.0	10.0	4.0	5.0	6.0	8.0	10.0	5.0	6.0	8.0	10.0
***p*-OCH_3**	3.72	3.84	3.75	3.97	4.45	6.08	6.21	6.45	6.99	7.66	12.2	14.32	14.8	15.11
***p*-CH_3**	1.79	1.86	1.81	1.92	2.15	2.93	2.99	3.12	3.38	3.70	5.89	6.92	7.15	7.29
***p*-C_6H_5**	1.54	1.59	1.55	1.64	1.84	2.50	2.56	2.66	2.89	3.16	5.04	5.91	6.11	6.24
-H	1.23	1.27	1.24	1.31	1.47	2.01	2.05	2.13	2.31	2.53	4.03	4.73	4.89	4.99
***p*-Cl**	0.35	0.36	0.35	0.37	0.42	0.56	0.58	0.60	0.65	0.72	1.14	1.34	1.38	1.41
***p*-Br**	0.24	0.25	0.24	0.25	0.28	0.37	0.39	0.41	0.45	0.49	0.78	0.92	0.95	0.97
***m*-NO_2**	0.11	0.11	0.11	0.12	0.13	0.16	0.18	0.19	0.21	0.23	0.36	0.42	0.43	0.44

[a] $[5\text{–Oxo acid}]_0$ = 1.0 x 10^{-2} mol dm^{-3}; $[H^+]$ = 2.0 x 10^{-2} mol dm^{-3}; * $[W^{VI}]$ = 2.0 x 10^{-5} mol dm^{-3}; HOAc–H_2O = 1:1 *% (v/v)*. The rate of tungsten (VI) catalyzed oxidation is independent of $[H^+]$ of the medium. Table 2 presents constancy of specific reaction rate at different acidities. But, both the catalyzed and uncatalyzed oxidations occur only in acidic medium.

Table 2: Oxidation at different acidities [a]

5-Oxoacid	$10^3 k^*$ (s^{-1})						
	10^2 [H^+] (mol dm^{-3})						
	1.0	2.0	4.0	6.0	7.0	8.0	10.0
***p*-OCH_3**	11.02	12.20	12.47	12.38	12.32	12.02	12.23
***p*-CH_3**	5.32	5.89	6.03	5.98	5.95	5.81	5.91
***p*-C_6H_5**	4.55	5.04	5.15	5.11	5.09	4.96	5.05
-H	3.64	4.03	4.12	4.09	4.07	3.97	4.04
***p*-Cl**	1.03	1.14	1.16	1.16	1.15	1.12	1.14
***p*-Br**	0.70	0.78	0.79	0.79	0.79	0.77	0.78
***m*-NO_2**	0.32	0.36	0.37	0.36	0.36	0.35	0.36

[a][Perborate]$_0$ = 5.0 x 10^{-4} mol dm^{-3}; [5−Oxo acid]$_0$ = 1.0 x 10^{-2} mol dm^{-3}; *[W^{VI}] = 2.0 x 10^{-5} mol dm^{-3}; HOAc−H_2O = 1:1 % *(v/v)*; Temp.= 308 K. The rate of oxidation increases moderately with increasing [5-oxo acid]$_0$ (Table 3). At fixed [perborate]$_0$, [H^+] and the [catalyst], the oxidation rate doubles for a 20-fold increase in initial concentration of the reductant. Plot of k* versus [5-oxo acid]$_0$ is linear with a definite k*-intercept. (Fig. 1; correlation coefficient = 0.984, 0.985, 0.994, standard error of estimate = 1.15 × 10^{-4}, 1.66 × 10^{-4}, 1.38 × 10^{-4}, slope = 1.54 × 10^{-2}, 2.21 × 10^{-2}, 3.14 × 10^{-2} dm^3 mol^{-1} s^{-1}, intercept = 1.05 × 10^{-3} , 1.84 × 10^{-3} , 3.61 × 10^{-3} s^{-1}).

Table 3: Rate dependence on [5-oxo acid]$_0$ [a]

5-Oxoacid	$10^3 k^*$ (s^{-1})																	
	10^2 [5−Oxo acid]$_0$ (mol dm^{-3})																	
	288 K						298 K						308 K					
	0.5	1.0	3.0	5.0	8.0	10.0	0.5	1.0	3.0	5.0	8.0	10.0	0.5	1.0	3.0	5.0	8.0	10.0
p-OCH_3	3.57	3.85	3.91	5.54	6.78	8.02	6.54	6.21	6.99	8.63	11.5	12.02	11.14	12.2	13.35	16.26	18.24	20.22
p-CH_3	1.73	1.86	1.89	2.68	3.28	3.88	3.16	2.99	3.38	4.17	5.56	5.81	5.38	5.89	6.45	7.85	9.11	9.77
p-C_6H_5	1.48	1.59	1.61	2.29	2.80	3.31	2.70	2.56	2.89	3.56	4.75	4.96	4.60	5.04	5.51	6.71	7.61	8.35
-H	1.18	1.27	1.29	1.83	2.24	2.65	2.16	2.05	2.31	2.85	3.80	3.97	3.68	4.03	4.41	5.37	6.19	6.68
p-Cl	0.33	0.36	0.36	0.52	0.63	0.75	0.61	0.58	0.65	0.81	1.07	1.12	1.04	1.14	1.25	1.52	1.63	1.89
p-Br	0.23	0.25	0.25	0.35	0.43	0.51	0.42	0.39	0.45	0.55	0.74	0.77	0.71	0.78	0.85	1.04	1.08	1.29
m-NO_2	0.11	0.11	0.12	0.16	0.19	0.24	0.19	0.18	0.21	0.25	0.34	0.35	0.33	0.36	0.39	0.48	0.53	0.59

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

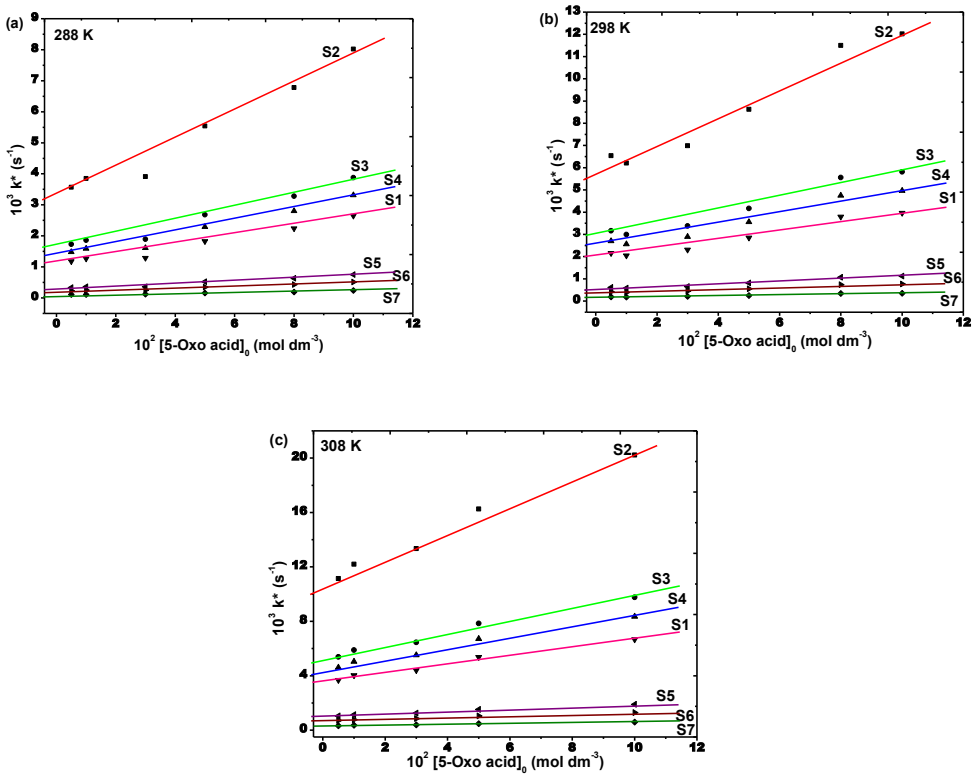


Figure 1: Dependence of k* on [5-oxo acid]$_0$ under the conditions of Table 2 at (a) 288 K, (b) 298 K, (c) 308 K. (S1) -H, (S2) 4'-Methoxy, (S3) 4'-Methyl, (S4) 4'-Phenyl, (S5) 4'-Chloro, (S6) 4'-Bromo, (S7) 3'-Nitro.

Effect of Catalyst: At fixed [perborate]$_0$, [5-oxo acid]$_0$ and [H^+], the variation of oxidation rate with the [W^{VI}] is non-linear (Table 4, Fig. 2). At low [W^{VI}] the rate increases with increasing [W^{VI}], while at high [W^{VI}] the rate is independent of the [W^{VI}] ─ a unique behavior generally observed when [catalyst] >> [reactant] [21].

Table 4: Rate dependence on [W^{VI}] at 288 K, 298 K & 308 K [a]

5-Oxoacid	$10^3 k^*$ (s^{-1})								
	10^5 [W^{VI}] (mol dm^{-3})								
	288 K								
	0	1.0	2.0	3.0	4.0	5.0	6.0	8.0	10.0
p-OCH_3	0.30	2.82	3.85	3.99	3.91	4.20	4.42	4.29	4.33
p-CH_3	0.15	1.36	1.86	1.95	1.89	2.12	2.14	2.08	2.09
p-C_6H_5	0.13	1.16	1.59	1.64	1.61	1.73	1.83	1.78	1.79
-H	0.1	0.93	1.27	1.27	1.29	1.39	1.46	1.42	1.43
p-Cl	0.03	0.26	0.36	0.41	0.36	0.41	0.41	0.40	0.40

***p*-Br**	0.02	0.18	0.25	0.25	0.25	0.27	0.28	0.28	0.28
***m*-NO_2**	0.01	0.08	0.11	0.14	0.12	0.14	0.13	0.13	0.13

5-Oxoacid	$10^3 k^*$ (s^{-1})								
	10^5 [W^{VI}] (mol dm^{-3})								
	298 K								
	0	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**8.0**	**10.0**
***p*-OCH_3**	0.61	4.39	6.21	7.66	8.01	8.17	8.11	7.98	7.99
***p*-CH_3**	0.29	2.12	2.99	3.70	3.88	3.95	3.95	3.79	3.86
***p*-C_6H_5**	0.25	1.81	2.56	3.16	3.29	3.38	3.38	3.29	3.30
-H	0.20	1.45	2.05	2.53	2.56	2.70	2.66	2.59	2.64
***p*-Cl**	0.06	0.41	0.58	0.71	0.69	0.76	0.69	0.66	0.75
***p*-Br**	0.04	0.28	0.39	0.49	0.43	0.52	0.46	0.46	0.51
***m*-NO_2**	0.02	0.13	0.18	0.24	0.23	0.24	0.23	0.23	0.23

5-Oxoacid	$10^3 k^*$ (s^{-1})								
	10^5 [W^{VI}] (mol dm^{-3})								
	308 K								
	0	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**8.0**	**10.0**
***p*-OCH_3**	1.09	7.51	12.20	13.38	13.77	14.65	14.95	15.89	16.17
***p*-CH_3**	0.53	3.63	5.89	6.46	6.65	7.08	7.30	7.68	7.81
***p*-C_6H_5**	0.45	3.10	5.04	5.53	5.69	6.05	6.11	6.56	6.68
-H	0.36	2.48	4.03	4.42	4.55	4.84	5.04	5.25	5.34
***p*-Cl**	0.10	0.70	1.14	1.25	1.29	1.37	1.39	1.48	1.51
***p*-Br**	0.07	0.48	0.78	0.86	0.88	0.94	0.97	1.02	1.03
***m*-NO_2**	0.03	0.22	0.36	0.39	0.40	0.43	0.44	0.47	0.47

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

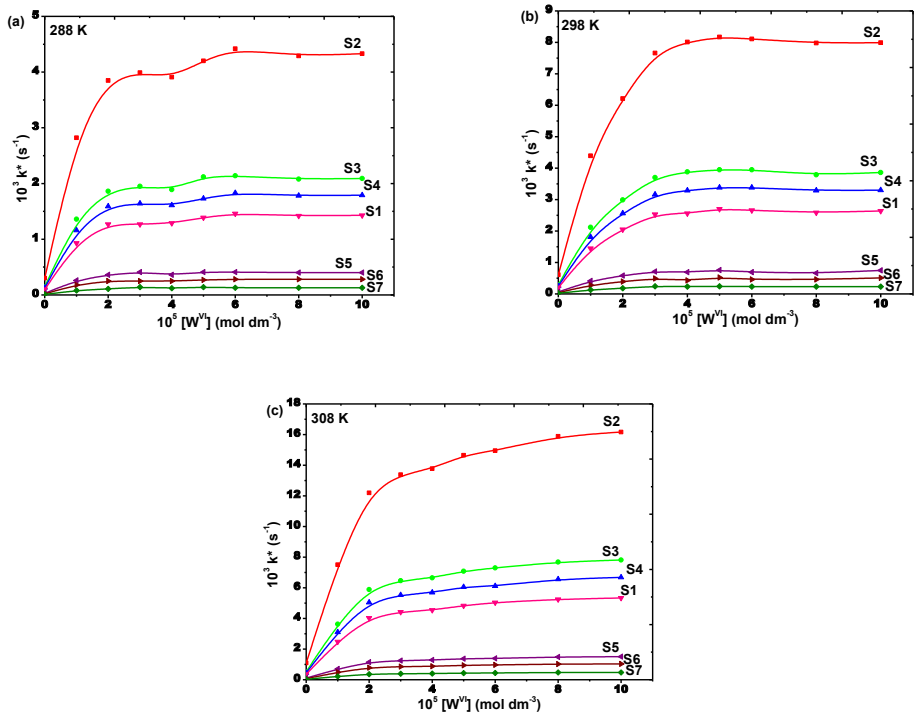


Figure 2: Dependence of k* on [W^{VI}] under the conditions of Table 4 at (a) 288 K, (b) 298 K, (c) 308 K. (S1) -H, (S2) 4'-Methoxy, (S3) 4'-Methyl, (S4) 4'-Phenyl, (S5) 4'-Chloro, (S6) 4'-Bromo, (S7) 3'-Nitro.

But, in the present study, it is interesting to note that [5-oxo acid]$_0$ >> [oxidant]$_0$ >> [W^{VI}]. Double reciprocal plot of (k* − k') versus [W^{VI}], and statistically more balanced Hanes plot {[W^{VI}]/(k* − k') *versus* [W^{VI}]} are linear with positive y-intercepts (Fig. 3; Hanes plot: correlation coefficient= 0.998, 0.996, 0.998,

standard error of estimate = 1.55×10^{-3}, 1.46×10^{-3} , 3.57×10^{-4}, slope = 711, 372, 176 s and intercept = 3.79×10^{-3}, 2.91×10^{-3}, 2.42×10^{-3} mol dm^{-3} s 288 K, 298 K and 308 K, respectively).

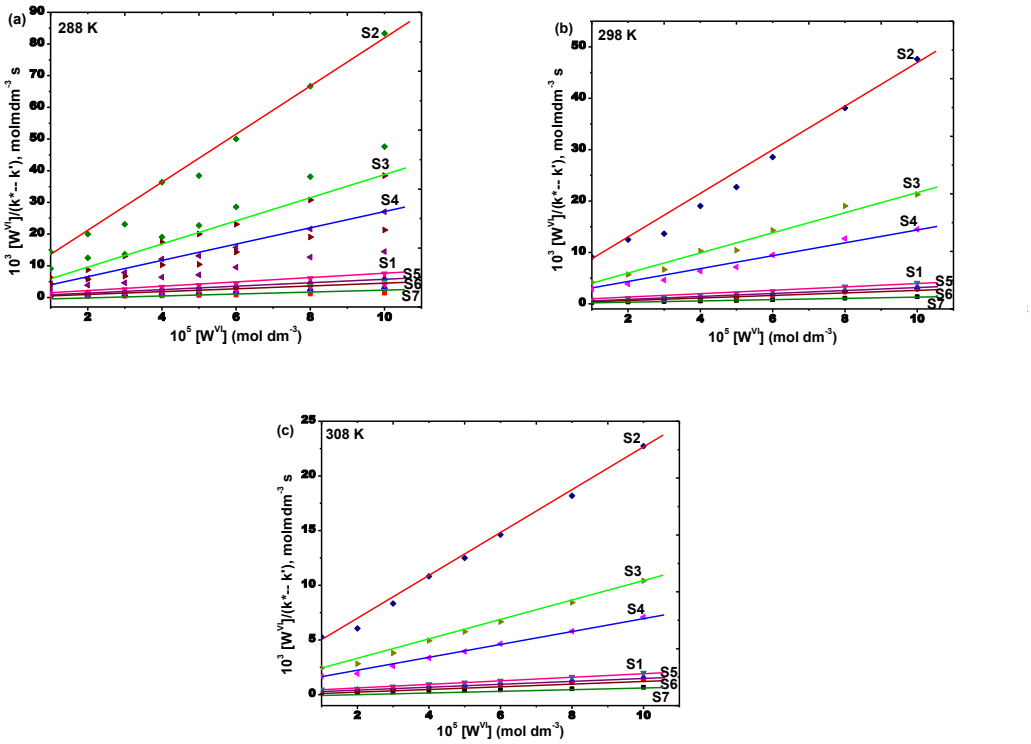


Figure 3: Hanes plot under the conditions of Table 4 at (a) 288 K, (b) 298 K, (c) 308 K.
(S1) -H, (S2) 4'-Methoxy, (S3) 4'-Methyl, (S4) 4'-Phenyl, (S5) 4'-Chloro, (S6) 4'-Bromo, (S7) 3'-Nitro.

Although the uncatalyzed oxidation, under the conditions reported in Table 4, is slow, correction is given for the oxidation through uncatalyzed path. The true rate of catalyzed oxidation is k*– k'; k* is the rate in presence W^{VI} and k' is that in absence. The rate dependence on [W^{VI}], studied at high [5-oxo acid]$_0$, shows that with increasing [W^{VI}] the rate increases at low [W^{VI}] but decreases marginally at high [W^{VI}] (Table 5, Fig. 4).

Table 5: Rate dependence on [W^{VI}] at high [5–oxo acid]$_0$ [a]

5-Oxoacid	$10^3 k^*$ (s^{-1})					
	10^5 [W^{VI}] (mol dm^{-3})					
	1.0	**2.0**	**4.0**	**6.0**	**8.0**	**10.0**
***p*-OCH_3**	3.72	8.02	9.02	12.47	10.66	9.78
***p*-CH_3**	1.79	3.88	4.36	6.03	5.15	4.72
***p*-C_6H_5**	1.54	3.31	3.73	5.15	4.40	4.04
-H	1.23	2.65	2.98	4.12	3.52	3.23
***p*-Cl**	0.35	0.75	0.84	1.16	0.99	0.91
***p*-Br**	0.24	0.51	0.58	0.79	0.68	0.63
***m*-NO_2**	0.11	0.24	0.27	0.37	0.31	0.29

[a][Perborate]$_0$ = 5.0 x 10^{-4} mol dm^{-3}; [5–Oxo acid]$_0$ = 1.0 mol dm^{-3}; [H^+] = 2.0 x 10^{-2} mol dm^{-3}; HOAc–H_2O = 1:1 *% (v/v)*; Temp. 288 K.

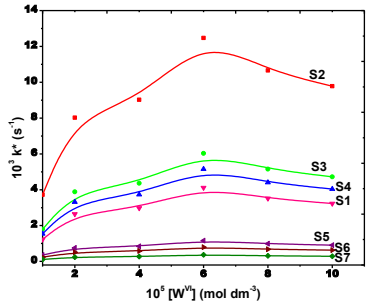


Figure 4: Dependence of k* on [W^{VI}] at high [5-oxo acid]$_0$ under the conditions of Table 5 at 288 K.

(S1) -H, (S2) 4'-Methoxy, (S3) 4'-Methyl, (S4) 4'-Phenyl, (S5) 4'-Chloro, (S6) 4'-Bromo, (S7) 3'-Nitro.

Influence of Salt Effect and Solvent Polarity: The rate of [W^{VI}] catalyzed oxidation is independent of ionic strength of the medium but the rate falls moderately with decrease of dielectric constant of the medium. The ionic strength was varied with KNO_3 and the dielectric constant was decreased by varying the composition of acetic acid and water (Tables 6 & 7).

Table 6: Influence of ionic strength [a]

10 [KNO_3] (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	11.02	5.32	4.55	3.64	1.03	0.70	0.32
1.0	9.81	4.74	4.05	3.24	0.92	0.63	0.29
2.0	10.38	5.02	4.29	3.43	0.97	0.66	0.30

[a][Perborate]$_0$ = 5.0 x 10^{-4} mol dm^{-3}; [5−Oxo acid]$_0$ = 1.0 x 10^{-2} mol dm^{-3}; [H^+] = 1.0 x 10^{-2} mol dm^{-3}; *[W^{VI}] = 2.0 x 10^{-5} mol dm^{-3};

HOAc−H_2O = 1:1 *% (v/v)*; Temp.= 308 K.

Table 7: Influence of dielectric constant of the medium [a]

D	AcOH—H_2O % (v/v)	$10^3 k^*$ (s^{-1})						
		p-OCH_3	*p*-CH_3	*p*-C_6H_5	-H	*p*-Cl	*p*-Br	*m*-NO_2
53.18	30-70	15.11	7.29	6.24	4.99	1.41	0.97	0.44
46.48	40-60	12.93	6.25	5.34	4.27	1.21	0.83	0.38
39.78	50-50	11.02	5.32	4.55	3.64	1.03	0.70	0.32
33.08	60-40	8.99	4.34	3.71	2.97	0.84	0.58	0.26
26.08	70-30	8.36	4.04	3.45	2.76	0.78	0.53	0.25

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

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 solution has insignificant effect on the oxidation rate (Table 8). The reaction solution, when the oxidation is in progress, does not induce polymerization of vinyl monomer acrylonitrile. Also, initial addition of acrylonitrile to the reaction mixture fails to suppress the oxidation rate (Table 8). During the course of oxidation, the reaction solution does not show an e.s.r. signal (Bruker X-band) for any radical.

Table 8: Influence of borate and boric acid on the rate [a]

10^2 $[NaBO_2]_0$ (mol dm^{-3})	10^2 $[H_3BO_3]_0$ (mol dm^{-3})	$10^3 k^{*b}$ (s^{-1})							$10^3 k^{*c}$ (s^{-1})						
		p-OCH_3	*p*-CH_3	*p*-C_6H_5	-H	*p*-Cl	*p*-Br	*m*-NO_2	*p*-OCH_3	*p*-CH_3	*p*-C_6H_5	-H	*p*-Cl	*p*-Br	*m*-NO_2
–	–	12.20	5.89	5.04	4.03	1.14	0.78	0.36	15.11	7.29	6.24	4.99	1.41	0.97	0.44
1.0	–	10.69	5.16	4.41	3.53	0.99	0.68	0.31	14.50	7.01	5.99	4.79	1.35	0.93	0.43
–	1.0	12.08	5.84	4.99	3.99	1.13	0.77	0.35	15.08	7.28	6.23	4.98	1.41	0.96	0.44
–	–	12.08[d]	5.84[d]	4.99[d]	3.99[d]	1.13[d]	0.77[d]	0.35[d]	–	–	–	–	–	–	–

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

[b][Perborate]$_0$ = 5.0 x 10^{-4} mol dm^{-3}.

[c][Perborate]$_0$ = 1.0 x 10^{-3} mol dm^{-3}.

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

Effect of Hydrogen Peroxide: Under identical conditions, the rates of tungsten (VI) catalyzed oxidation of 5-oxo acids by perborate and hydrogen peroxide are almost the same (Table 9). Boric acid and borate fail to influence the rate of [W^{VI}] catalyzed peroxide oxidation.

Table 9: Oxidation by hydrogen peroxide [a]

10^2 $[NaBO_2]_0$ (mol dm^{-3})	10^2 $[H_3BO_3]_0$ (mol dm^{-3})	$10^3 k^*$ (s^{-1})													
		Hydrogen peroxide							Perborate						
		p-OCH_3	*p*-CH_3	*p*-C_6H_5	-H	*p*-Cl	*p*-Br	*m*-NO_2	*p*-OCH_3	*p*-CH_3	*p*-C_6H_5	-H	*p*-Cl	*p*-Br	*m*-NO_2
–	–	15.38	7.43	6.35	5.08	1.44	0.98	0.45	15.11	7.29	6.24	4.99	1.41	0.97	0.44
1.0	–	15.05	7.27	6.21	4.97	1.40	0.96	0.44	14.50	7.01	5.99	4.79	1.35	0.93	0.43
–	1.0	15.62	7.55	6.45	5.16	1.46	0.99	0.46	15.08	7.28	6.23	4.98	1.41	0.96	0.44

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

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. 5; $r \geq 0.96$; $s \leq 0.02$) 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 10.

Table 10: Values of rate constant at different temperatures and activation parameters [a]

5-Oxoacid	$10^3 k^*$ (s^{-1})			$\Delta H^{\#}$	$\Delta S^{\#}$	$\Delta G^{\#}$
	288 K	298 K	308 K	(kJ mol^{-1})	(J K^{-1} mol^{-1})	(kJ mol^{-1})
***p*-OCH_3**	3.85	6.21	12.20	48.63	-102.61	296.01
***p*-CH_3**	1.86	2.99	5.89	42.31	-108.74	313.59
***p*-C_6H_5**	1.59	2.56	5.04	40.02	-109.88	316.85
-H	1.27	2.05	4.03	37.53	-112.18	323.45
***p*-Cl**	0.36	0.58	1.14	26.61	-122.33	352.58
***p*-Br**	0.25	0.39	0.78	22.40	-125.97	363.02
***m*-NO_2**	0.11	0.18	0.36	14.93	-132.09	380.57

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

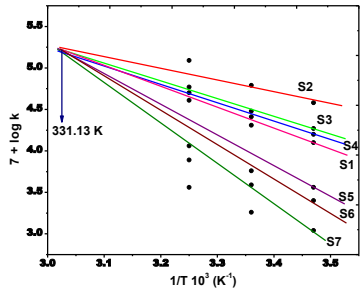


Figure 5: Arrhenius plots between log *k* and *1/T* showing the isokinetic temperature under the conditions of Table 10.
(S1) -H, (S2) 4'-Methoxy, (S3) 4'-Methyl, (S4) 4'-Phenyl, (S5) 4'-Chloro, (S6) 4'-Bromo, (S7) 3'-Nitro.

Isokinetic Relationships: The plot between $\Delta H^{\#}$ and $\Delta S^{\#}$ is linear (Fig. 6; $r \geq 0.97$, $s \leq 0.029$) and the isokinetic temperature (β) obtained is 331.1 K. The β calculated from the Exner's plot (Fig. 7; r ≥ 0.987; s ≤ 0.04) of log k_{298K} against log k_{288K} is 330.4 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 [22].

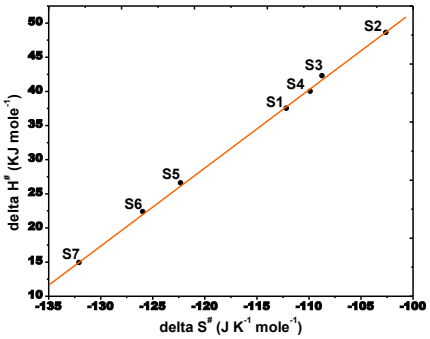


Figure 6: Plot between $\Delta H^{\#}$ and $\Delta S^{\#}$: isokinetic relationship under the conditions of Table 10.
(S1) -H, (S2) 4'-Methoxy, (S3) 4'-Methyl, (S4) 4'-Phenyl, (S5) 4'-Chloro, (S6) 4'-Bromo, (S7) 3'-Nitro.

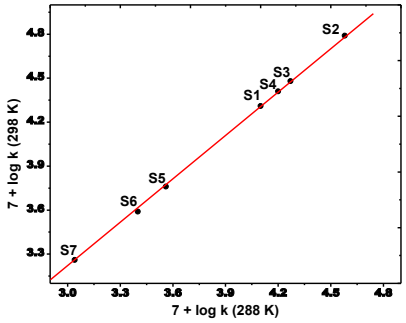
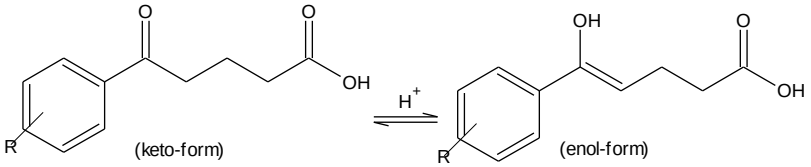


Figure 7: Exner's plot of log k_{298K} against log k_{288K} under the conditions of Table 10.

(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 ^oC in aqueous solution)[23], and the undissociated form of the substrate can be taken as the only form in acidic media. In acid solutions, 5-oxo acids undergoes keto enol tautomerism (Eq. 2).

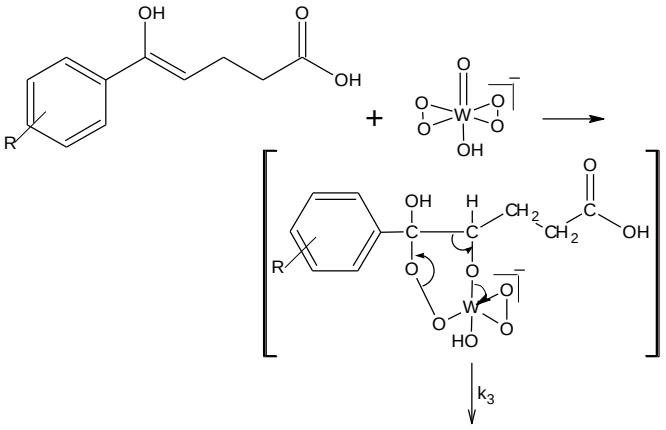


(2)

Perborate is peroxoborate but in aqueous solution yields H_2O_2 [1]. In acidic medium, even in presence of excess of boric acid ($[H_3BO_3]_0$ or $[NaBO_2]_0$ = 1.0 x 10^{-2} mol dm^{-3}), calculation of the relative concentrations of perboric acid and peroxoborate ($[(HO)_2$ BOOH] / $[H_2O_2]$ and $[(HO)_3BO_2H]$ / $[H_2O_2]$) using the equilibrium constants reported already [24], shows that they are non-existent. The almost same rate of oxidation by perborate and hydrogen peroxide, under identical conditions, supports the proposition that the reactive species of perborate is H_2O_2. The dependence of the oxidation rate on the total $[W^{VI}]$ is not simple. Since tungsten(VI) polymerizes in acidic solution one of the possible explanations for the complex dependence is polymerization of tungsten(IV) in the reaction solution [25-27]. However, under the experimental conditions, existence of polymeric tungsten (VI) species is unlikely. This suggestion stems from the fact that the specific oxidation rate in perborate remains constant with increasing acidity of the medium, and the degree of polymerization increases with increasing acidity. If tungsten (VI) were to dimerize with large dimerization constant, contrary to the experimental findings, plot of k* *versus* $\sqrt{[W^{VI}]}$ should be linear. Also, at 10 micro molar concentrations tungsten (VI) is reported to exist predominantly in monomeric form [25, 26].

$$WO_3 + H_2O_2 \underset{}{\overset{K_1}{\rightleftharpoons}} WO_2(O_2) + H_2O \qquad (3)$$

$$WO_2(O_2) + H_2O_2 \xrightarrow{k_2} WO(OH)(O_2)_2^- + H^+ \qquad (4)$$



$$WO(OH)(O_2)^- + OHC\text{-}(CH_2)_2COOH + \text{(R-C6H4-C(=O)-OH)} \qquad (5)$$

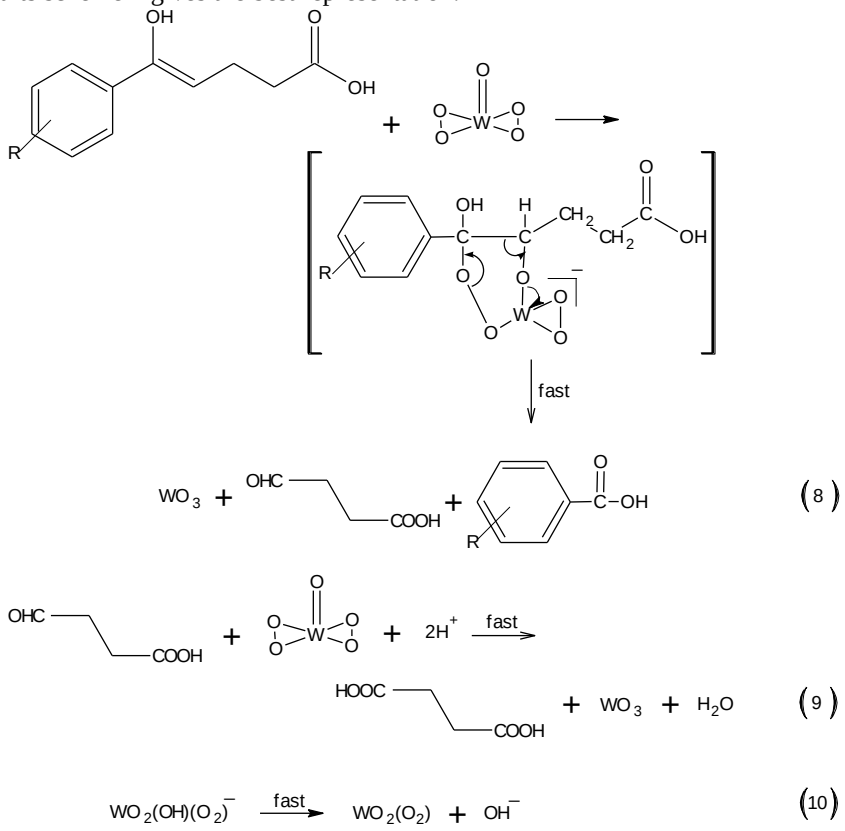
$$WO(OH)(O_2)_2^- + WO_3 \xrightarrow{k_4} WO_2(OH)(O_2)^- + WO_2(O_2) \qquad (6)$$

$$WO(OH)(O_2)_2^- \xrightarrow{k_5} WO(O_2)_2 + OH^- \qquad (7)$$

In the present study tungsten (VI) is used in the form of tungstate and the speciation of monomeric tungsten (VI) are HWO_3^+, $WO_3(H_2WO_4)$, HWO_4^- and WO_4^{2-}. Using the values of equilibrium constants reported already [25], the relative abundance of the monomeric tungsten(VI) species in the acidity range 0.01 - 0.1 mol dm^{-3} are calculated as $[WO_4^{2-}]/[WO_3]$ = 1.4 x 10^{-2} − 1.4 x 10^{-4}, $[HWO_4^-]/[WO_3]$ = 0.64 − 6.4 x 10^{-2} and $[HWO_3^+]/[WO_3]$ = 1.0 x 10^{-2} − 0.1. Hence, it may be concluded that the predominant from of monomeric tungsten(VI) is WO_3 and at high $[H^+]$ HWO_3^+ is also present while at low $[H^+]$ HWO_4^- is abundant. In acidic medium H_2O_2 complexes with tungsten(VI) affording dioxoperoxotungsten(VI) ($WO_2(O_2)$) and oxodiperoxotungsten(VI) ($WO(O_2)_2$). Coordinated water molecules are omitted in the formulations. The tetraperoxy species, ($W(O_2)_4^{2-}$) is formed in basic medium [28]. With excess of H_2O_2 ($[H_2O_2]$ >> $[W^{VI}]$)

diperoxo species is formed and the diperoxo species is more reactive than monoperoxo species [29, 30]. Hydrolysis of oxodiperoxo species results in oxohydroxodiperoxotungsten (VI) and the hydrolysis constant is 0.74 mol dm^{-3} [31]. Oxodiperoxotungsten (VI) is more acidic than oxodiperoxomolybdenum (VI) [32]. The hydrolysis constant of the latter is 1.4 x 10^{-2} mol dm^{-3} [29]. Oxohydroxodiperoxotungsten (VI) also formed at low acidity, from tungsten (VI) and H_2O_2, and the formation is a second-order reaction –first order each with respect to H_2O_2 and tungsten (VI) [32].

Mechanism: The rate dependence on $[5\text{-oxo acid}]_0$ reveals that the oxidation is through two paths ─the first and major one is independent of $[5\text{-oxo acid}]_0$, and the second and minor path is first order with respect to 5-oxo acids. Since the tungsten (VI) catalyzed oxidation is first order with respect to the oxidant, formation of the reactive oxidizing species is slow and rate controlling in the major path. The minor path is slow and rate-limiting oxidation of 5-oxo acids by another reactive oxidizing species. Interaction of diperoxy species with the uncomplexed catalyst results in monoperoxy species [33]. Reactivity of oxodiperoxotungsten(VI) is greater than that of oxohyroxodiperoxotungsten(VI) [31] and of the several reaction mechanisms designed to explain the experimental results scheme 1 gives the best representation.



Scheme 1: Reaction mechanism for the tungsten(VI) catalyzed perborate oxidation of substituted 5-oxo acids

Rate Law: With the assumptions $K_1[H_2O_2] >> 1$, $k_4[WO_3] = k_4'[W^{VI}]$ and $k_4'[W^{VI}] + k_5 >> k_3[5\text{-oxo acid}]$, the rate law for the proposed mechanism of catalysis is

$$-d[\text{oxidant}]/dt = \frac{(k_3[5\text{-oxo acid}] + k_5)\, k_2\, [W^{VI}]\, [\text{oxidant}]}{(k_4'[W^{VI}] + k_5)}$$

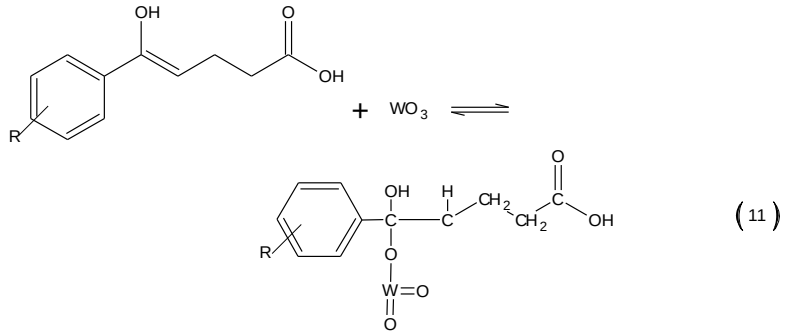
and the pseudo-first order rate constant in oxidant,

$$k^*\text{-}k = \frac{(k_3[5\text{-oxo acid}] + k_5)k_2[W^{VI}]}{(k'_4\,[\,W^{VI}] + k_5)}$$

The rate law is in conformity with the experimental findings, namely first order with respect to the oxidant, linear dependence of rate on $[5\text{-oxo acid}]_0$, increase of rate with increasing $[W^{VI}]$ leading to a limiting rate at high $[W^{VI}]$, non-dependence of the oxidation rate on $[H^+]$, absence of inhibition by borate and boric acid, and the almost same rate of oxidation by perborate and H_2O_2. The specific oxidation rate in perborate decreases with increasing $[W^{VI}]$ at high [5-oxo acid] and $[W^{VI}]$. One of the possible explanations is complexation of the uncomplexed catalyst (WO_3) with 5-oxo acids [34].

At 2.0 x 10^{-5} mol dm^{-3} W^{VI}, the percentage of oxidation through [5-oxo acid]-independent path decreases from 89 to 40 and 97 to 54 when [5-oxo acid] is increased from 5.0 x 10^{-3} – 10.0 x 10^{-2} mol dm^{-3} at 288 K and 308 K respectively. Rate-determining formation of dioxoperoxotungesten(VI) followed by rapid oxidation of 5-oxo acids as the mechanism of catalysis also satisfies the kinetic requirements. If dioxoperoxotungsten(VI) were to be the oxidizing species, the $WO_2(O_2)$ – WO_3 cycle should demand the same

specific oxidation rate even at low $[oxidant]_0$. Kinetic studies at low $[oxidant]_0$, under the conditions reported in Table 1, yield lower specific oxidation rates in perborate. For example, at $[oxidant]_0 = 1.0 \times 10^{-4}$ mol dm^{-3}, $[5\text{-oxo acid}]_o = 1.0 \times 10^{-2}$ mol dm^{-3} , $[H^+] = 2.0 \times 10^{-2}$ mol dm^{-3} and $[W^{VI}] = 2.0 \times 10^{-5}$ mol dm^{-3}, the specific rate in perborate is 0.47×10^{-3} s^{-1} at 288 K. The proposition that diperoxy species is the oxidizing species explains the lower specific oxidation rate at low $[oxidant]_0$. At low $[oxidant]_0$ complxation of tungsten(VI) is likely is to be incomplete. The concentration of monoperoxy species may not be equal to but less the concentration of the catalyst, and hence the rate.



(11)

Conclusions:

Tungsten (VI) catalyzed perborate oxidation of substituted 5-oxo acids in acidic solution is associated with isokinetic relationship. In aqueous acetic acid solution perborate generates hydrogen peroxide. Under the conditions $[W^{VI}] <<< [perborate]_0 << [5\text{-oxo acid}]_0$, the oxidation is first order with respect to perborate and is independent of $[H^+]$ of the medium. The dependence of the oxidations rate on the [catalyst] is of Michaelis – Menten type. The oxidation is through two paths; the major one is independent of [5-oxo acid] and the minor path is first order with respect to the reductant. The rates of tungsten (VI) catalyzed perborate and hydrogen peroxide oxidations are almost the same. Borate and boric acid do not influence the oxidations. 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 acids 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 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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