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Oxidative Decarboxylation of Substituted 4-Oxoacid by Acid Bromate – A Kinetic and Mechanistic Study

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The kinetic study of the oxidation of 4-oxo-4-phenylbutanoic acid and its 12 different phenyl-substituted compounds by acid bromate in aqueous acetic acid medium were studied. The reaction is found first order in each of the reactant, the oxoacid, hydrogen ion and bromate ion. A mechanism involving the formation of enolate anion of the substrate, subsequent rate of electron transfer and the activation parameters have been computed.

Key Words: Kinetics, Decarboxylation, Substituted 4-oxoacid.

INTRODUCTION

Generally in the 4-oxoacids, the oxo carbonyl and carboxyl groups are found to be active independently without the influence upon each other. The kinetics of halogenation[1,2] of 4-oxo-4-phenybutanoic acid, hydrolysis of its ethyl ester[3,4] and the oxidative kinetics by permanganate[5] of substituted 4-oxo acids in aqueous acetic acid medium have been studied.

Bromate is known to be a powerful oxidizing agent in acidic medium. It has the redox potentials of 1.44 v. In presence of acid and bromide ions, bromate can exclusively act as bromine producing agent. In this study, Br^- ions are fixed[6-10] with Hg(II) ions on the addition of $Hg(OAc)_2$. Hence in presence of Hg(II), the oxidation by BrO_3^- due to Br(V) is established. An attempt is made to study the kinetics of oxidation of substituted and unsubstituted 4-oxoacids by acid bromate.

EXPERIMENTAL

Substituted 4-oxo-4-phenylbutanoic acids were prepared by Friedel-Craft's reaction of benzene and its analogs with succinic anhydride in presence of anhydrous $AlCl_3$. All the oxo acids were recrystallized from water and the purity was checked by physical and spectral studies.

The kinetic measurements were carried out using doubly distilled water. Solutions of oxoacid and bromate were prepared in $HOAc-H_2O$ mixtures. A stock solution of 0.02 M substrate, 0.002 M potassium bromate solution, 0.01 M mercuric acetate, 2 M sulphuric acid used.

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The kinetic study was followed by iodometric titrations. The pseudo first order rate constants were calculated by graphical method and the values were reproducible to within ± 3 %. The ionic strength of the medium (6.032) was maintained using sodium acetate. The kinetics of reaction were studied in 30, 40, 50 and 60 % (v/v) HOAc:H_2O in blackened flasks. Under the conditions of experiments the solvents are not oxidized. Rate constants were computed from the linear plot of log [$KBrO_3$] against time.

Stoichiometry and product analysis: A 0.1 M 4-oxo-4 phenylbutanoic acid, 2.0 M sulphuric acid and 0.5 M potassium bromate were used together in 50 % HOAc. The reaction was allowed for completion at 40 °C for about 6 h. The solution was then cooled and acidified for precipitation. The precipitate was extracted into diethyl ether which on evaporation gave benzoic acid only. This was confirmed by TLC and chemical analysis.

The stoichiometry of the reaction was observed 1:2.6 indicating that one mole of oxoacid require 2.6 moles of bromate ion for oxidation. The ultimate products of oxoacid are benzoic acid and CO_2.

RESULTS AND DISCUSSION

The oxidation of 4-oxo acids by acid bromate in aqueous acetic acid medium showed the following features:

(i) The rate of oxidation of 4-oxo acids by acid bromate is first order each with respect to 4-oxo acid and bromate (Table-1). The plots of log [$KBrO_3$] *versus* time for various concentration of oxo acid are linear (Figs. 1 and 1a).

TABLE-1
VARIATION OF [OXOACID]

[Oxoacid] 10^2 M	10^4 k_1 s^{-1}	10^2 $k_2 M^{-1}$ s^{-1}
2.0	2.18	1.09
3.0	3.31	1.10
4.0	4.36	1.09
5.0	5.57	1.11

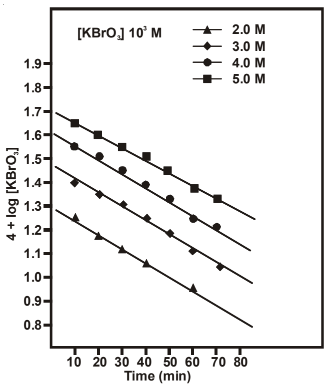

Fig. 1. Variation of [$KBrO_3$]

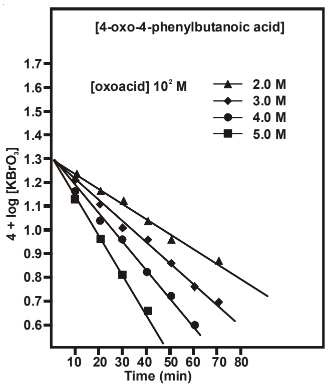

Fig. 1a. Variation of oxoacid

(ii) The oxidation of 4-oxo-4-chloro and 4-oxo-4-(2-naphthyl)phenyl butanoic acids also showed first order dependence each on substrate and oxidant (Tables 2 and 3).

Table-2

(4-oxo-4-(chlorophenyl butanoic acid) 10^2 M	10^4 k_1 s^{-1}	10^2 $k_2 M^{-1}$ s^{-1}
5.0	1.47	2.94
6.0	1.78	2.96
7.0	2.07	2.95
8.0	2.37	2.96

Table-3

(4-oxo-4-(2-naphthyl)phenyl butanoic acid 10^2 M	10^5 k_1 s^{-1}	10^5 $k_2 M^{-1}$ s^{-1}
0.5	3.50	1.75
1.0	6.81	3.40
1.5	10.32	5.16
3.0	20.52	10.26

A plot of log [$KBrO_3$] against time is found to be linear over 60 % of the reaction showed first order dependence on bromate (Fig. 2). The correlation coefficient is found to be 0.999. The same result have been obtained in the oxidation of other substituted 4-oxo acids (Tables 4 and 5).

TABLE-4
VARIATION OF BROMATE WITH 4-OXO-4-PHENYL BUTANOIC ACID

[$KBrO_3$] 10^3M	1.0	2.0	3.0	4.0	5.0
10^4 k_1 s^{-1}	2.19	2.18	2.19	2.22	2.20

TABLE-5
VARIATION OF BROMATE WITH SUBSTITUTED 4-OXOACID

Substituted 4-oxoacid	10^4 k_1 s^{-1}			
	10^3 [$KBrO_3$] M			
	2.0	3.0	4.0	5.0
4-OCH_3	4.96	4.91	4.98	4.90
4-OC_2H_5	4.68	4.63	4.60	4.39
4-CH_3	3.82	3.36	3.33	3.31
4-C_6H_5	1.92	1.90	1.93	1.86
2-C_2H_5	1.36	1.34	1.31	1.39
4-Cl	1.13	1.10	1.15	1.16
4-Br	1.06	1.03	1.01	1.09

(iii) The rate of the reaction increases linearly with increase in [H^+] acid (Table-6). The plot of log k, against log [H^+] is linear with a slope of unity (Fig. 3). This establishes that the reaction is first order with respect to hydrogen ion.

(iv) The lowering of the dielectric constant of the medium enhances the reaction rate significantly (Table-7).

The increase in concentration of acetic acid decreases the polarity of the solvent or in other words lower the dielectric constant of the medium (Fig. 4). This favours the reaction in which neutral molecules are formed from ions[11]. This fact is consistent with the formation of $HBrO_3$.

TABLE-6

$[H_2SO_4]$ 10^2 M	10^4 k_1 s^{-1}	10^2 $k_2 M^{-1}$ s^{-1}
0.5	5.11	10.22
1.0	9.16	9.16
1.5	15.35	10.23
2.0	21.86	10.90
2.5	27.41	10.97
3.0	32.99	10.98

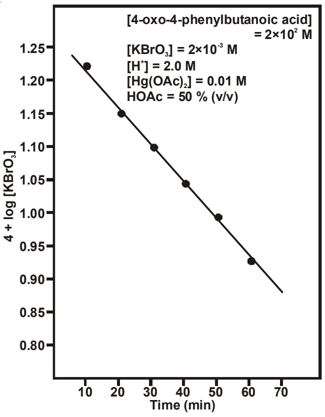

Fig. 2. First order plot

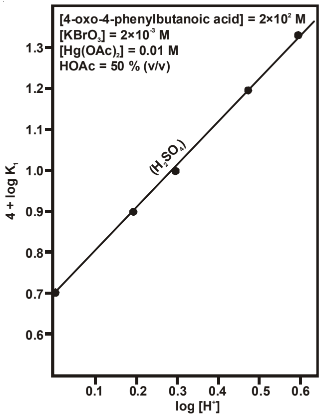

Fig. 3. Plot of log k *vs.* log $[H^+]$

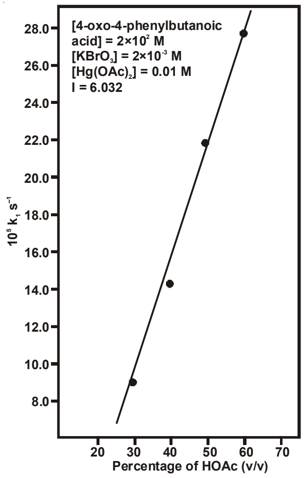

Fig. 4. Effect of varying HOAc

TABLE-7
EFFECT OF SOLVENT POLARITY

Substituted 4-oxo acid substituent	10^4 k_1 s^{-1}			
	AcOH (%)			
	30	40	50	60
4-OCH_3	3.88	4.16	4.98	5.62
4-OC_2H_5	3.71	4.01	4.68	5.91
4-CH_3	1.99	2.15	3.34	3.99
4-H	0.89	1.40	2.18	2.72
4-C_6H_5	0.75	1.10	1.92	2.46
4-Cl	0.41	0.99	1.08	1.44
4-Br	0.51	0.83	1.06	1.21
3-NO_2	0.08	0.11	0.28	0.49

$$BrO_3^- + H_3O^+ \rightleftharpoons HBrO_3 + H_2O$$

(v) The variation of the ionic strength of the reaction medium has little influence on the rate of the reaction (Table-8). This is an indication of reaction between neutral molecules or a neutral molecule and an ion[12].

TABLE-8
EFFECT OF IONIC STRENGTH

Ionic strength	10_4 k_1 s^{-1}		
	4-H	4-OCH_3	3-NO_2
6.20	2.16	4.98	0.31
6.40	2.10	4.91	0.33
6.60	2.19	4.88	0.30
6.80	2.20	4.92	0.28

(vi) No polymerzation was observed when acrylonitrile is added to the reaction system indicating that the reaction did not proceed by free radical mechanism.

(vii) The electron-releasing groups in the phenyl ring accelerate the reaction rate while electron-withdrawing groups retard the rate. The rate data on temperature effects in 50 % aqueous acetic acid in the range of 313-333 K (Table-9) and the Activation parameters are calculated (Table-11) from the Arrhenius plots (Figs. 5-7).

TABLE-9

Substituted 4-oxoacids	10^4 k_1 s^{-1}			
	303 K	313 K	323 K	333K
4-Methyl	2.48	5.00	8.45	17.36
4-Ethoxy	2.34	4.71	7.71	18.06
3,4-Dimethyl	1.81	3.60	7.57	14.00
4-Methyl	1.67	3.32	6.57	13.37
4-H	1.09	2.20	4.23	8.06
2-Naphthyl	0.68	1.40	2.68	5.20
4-Bromo	0.53	1.05	2.29	4.73
1-Naphthyl	0.31	0.60	1.51	3.11
4-Biphenyl	0.96	2.01	3.71	8.40
3,4-Dichloro	0.19	0.39	0.93	1.97
3-Nitro	0.14	0.31	0.67	1.60

The order of reactivity of substituents is found to be 4-methoxy > 4-ethoxy > 3,4-dimethyl > 4-H > 4-biphenyl > 2-naphthyl > 4-chloro > 4-bromo > 1-naphthyl > 3,4-dichloro > 3-nitro groups.

To correlate the effect of substituents on the reaction rate and to find out the validity of LFER in the present series. Hammett's equation $\log k = \log k^0 + \rho\sigma$ is applied. The values of reaction constant 'ρ' with correlation coefficient 'r' obtained from Hammett plot (Figs. 8-10) are shown in Table-10.

TABLE-10

Temperature (K)	Reaction constant ‘ρ’	Correlation coefficient ‘r’
303	-1.23	0.997
313	-1.09	0.996
323	-1.10	0.999
333	-1.06	0.997

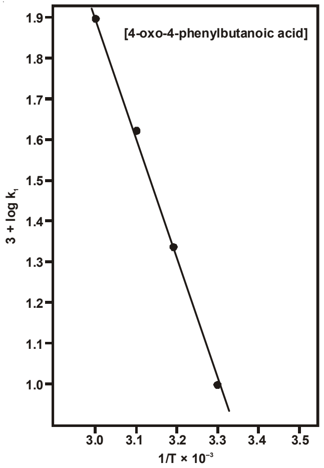

Fig. 5. Arrhenius plot

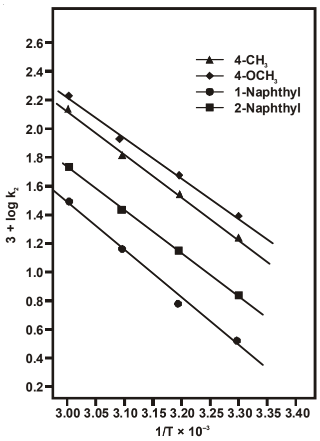

Fig. 6. Arrhenius plot

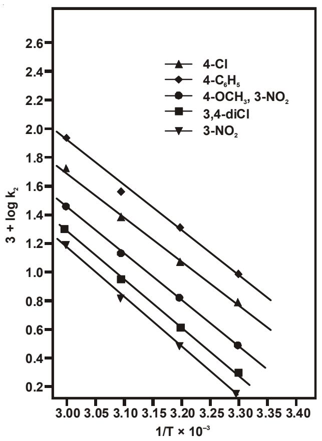

Fig. 7. Arrhenius plot

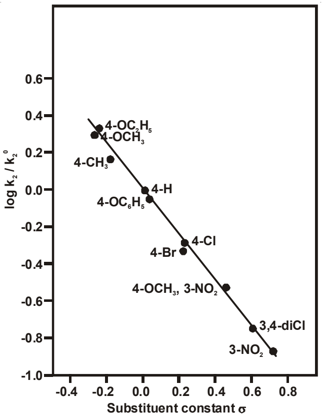

Fig. 8. Hammett plot at 313 K

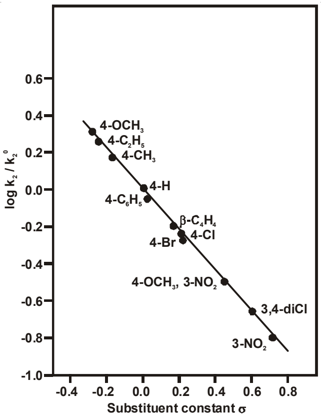

Fig. 9. Hammett plot at 323 K

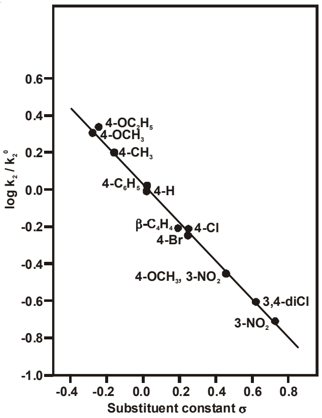

Fig. 10. Hammett plot at 333 K

The Hammett's plots for the oxidation of 4-oxo acids by acid bromate at various temperature 303, 313, 323 and 333 are found to be linear. The values of substituent constant, 'σ' are taken from Jaffe[13]. The reaction constant 'r' values obtained from the Hammett plots are negative.

The reaction constant 'ρ' at every temperature indicates the sensitivity of the reaction to the effect of electronic perturbation and about the nature of transition state. The reaction involving a development of positive charge in the transition state is aided by electron-releasing substituents and the value of 'ρ' is negative[14].

Considering the above kinetic evidences, the rate law mechanism may be proposed.

$$E + HBrO_3 \underset{\text{Slow}}{\overset{k_3}{\rightleftharpoons}} \text{Complex} \longrightarrow \text{products}$$

Applying the steady state approximation we get the rate equation

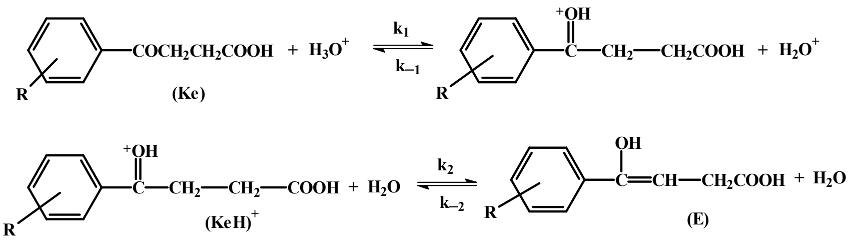

TABLE-11
ACTIVATION PARAMETERS

Substituent	E_a KJ mol^{-1}	$\Delta H^{\neq}_{at303k}$ KJ mol^{-1}	$\Delta S^{\neq}_{at303k}$ JK^{-1} mol^{-1}	$\Delta G^{\neq}_{at303k}$ KJ mol^{-1}
4-Methoxy-3-nitro	71.17	68.65	-99.27	98.73
3-Nitro	71.48	68.96	-105.03	100.79
3,4-Dichloro	63.97	61.45	-126.80	99.87
1-Naphthyl	63.82	61.35	-123.20	98.63
3,4-Dimethyl	56.73	54.21	-131.97	94.20
4-Bromo	55.84	53.32	-145.06	97.28
2-Naphthyl	51.05	48.53	-158.87	96.67
4-Chloro	52.65	50.13	-154.81	97.04
4-H	55.70	53.18	-139.68	95.50
4-Methyl	65.21	62.69	-96.41	94.42
4-Biphenyl	66.14	63.62	-106.24	95.80
4-Ethoxy	57.03	54.57	-128.93	93.58
4-Methyl	53.14	50.22	-145.62	93.43

$$\text{Rate} = \frac{k_1, k_2, k_3[\text{Ke}][\text{H}_3\text{O}][\text{BrO}_3]}{k_{-2}, k_{-1}[\text{Ke}][\text{H}_2\text{O}]}$$

From the activation parameters table, the E_a for oxoacids with electron releasing substituents are relatively lower than that with electron withdrawing substituents. The entropy of activation is negative for all 4-oxo acids ranging from -96.41 to -158.87 JK mol^{-1}, which supports the above mechanism.

A careful analysis of the activation parameters table revealed that the present series is neither isoentropic nor isoenthalpic[15].

The slope of the isokinetic relationship plot ($\Delta H^{\neq}$ *vs.* $\Delta S^{\neq}$) gives a value of 337 K as isokinetic temperature (Fig. 11). The validity of this value can be tested by Exner's plot (Figs. 12-14). From the slope of the Exner plot, the isokinetic temperature (β) is calculated and found to be 345 K. This value agrees with the value obtained from isokinetic plots.

The validity of isokinetic relationship in the present study implies that all the 4-oxoacids undergo oxidation by the same mechanism[16].

This is again confirmed from the values of reaction constant 'ρ' at different temperatures. A plot of 'ρ' *vs.* 1/T gives a straight line with an intercept of 341 K (Fig. 15).

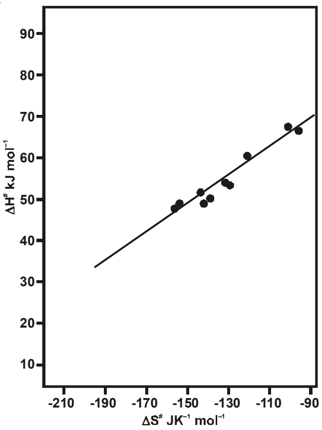

Fig. 11. Plot of $\Delta S^{\#}$ *vs.* $\Delta H^{\#}$

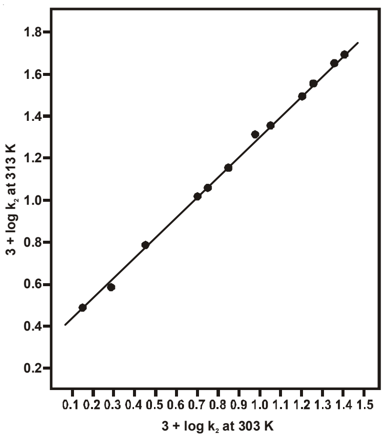

Fig. 12. Exner plot

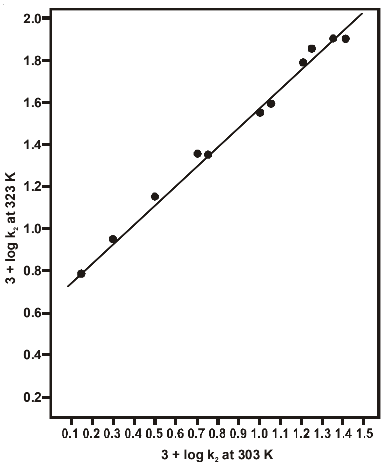

Fig. 13. Exner plot

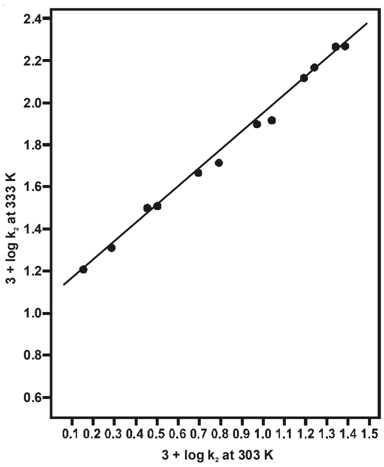

Fig. 14. Exner plot

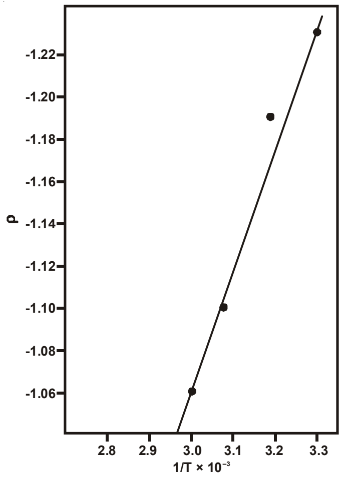

Fig. 15. Plot of ρ *vs.* 1/T

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