



Homogeneous catalysis of oxovanadium(IV) in the oxidation of substituted 4-oxo acids by bromate in acid medium: A mechanistic study

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ABSTRACT

Oxovanadium(IV)-catalyzed oxidation of substituted 4-oxo-4-phenyl-butanoic acids (4-oxo acids) by bromate in acid medium leads to the formation of malonic acid and the corresponding benzoic acid. The reaction exhibits first order each in [bromate] and [acid], less than unity order each in [4-oxo acid] and [oxovanadium(IV)], and also shows solvent isotope effect ($k(\text{D}_2\text{O})/k(\text{H}_2\text{O}) \sim 1.8$). The reaction is failed to induce the polymerization of acrylonitrile. The decrease in the rate of reaction with increase in dielectric constant of the medium is observed with all the studied 4-oxo acids. Electron-releasing substituents in the phenyl ring accelerate the rate of oxidation to a large extent, the rate retardation by electron-withdrawing substituents, though perceptible, is not very much. The linear free-energy relationship is characterized by a smooth curve, concaves downward, in the Hammett's plot of $\log k$ versus σ , however, Hammett' plots are linear with excellent correlation coefficient, at four temperatures, when Brown and Okamoto's σ^+ values are used. The ρ^+ values are negative and decrease with increase in temperature. From the intersection of the lines in the Hammett and Arrhenius plots, the isokinetic relationship is discussed. The mechanistic pathway involving the cyclic oxidant–substrate–catalyst ternary complex is proposed, wherein the oxidation state of V(IV) is unaltered. The reaction is an example of the neighboring group participation and intramolecular catalysis.

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1. Introduction

The chemistry of vanadium is of topical interest as it has a wide number of accessible oxidation states offering a wide variety of compounds with diverse coordination numbers and stereochemistries, and is biologically very significant. Vanadium complexes of hydrazine derivatives of nitrogen heterocyclic are used in the treatment of arteriosclerosis and to lower blood pressure [1]. Vanadium is involved in phospholipids oxidation, sulfur metabolism and cholesterol biosynthesis [2]. Peroxo-hetero ligand vanadates represent a model system for studying some biochemical interaction of vanadium in living matter [3], and there is a relationship between the chemical composition and the biological activity (antitumour activity–toxicity). Several investigations into biologically relevant vanadium have been made [4–6]. Recent studies show that peroxovanadium complexes have potent insulin-like activity, suggesting that they could be orally active alternatives to insulin [7]. Therefore, vanadium compounds are gaining special importance.

In 4-oxo-4-phenylbutanoic acid and its phenyl substituted compounds (commonly known as γ -oxo acids or 4-oxo acids), two

carbon atoms separate the carbonyl and the carboxyl groups and so they behave both as oxocompounds and as acids without the direct influence of the other group [8–10]. The kinetics of iodination of 4-oxo acid [11] and the hydrolysis of its ethyl ester [12,13] has yielded interesting results. Intramolecular catalysis in the iodination of 4-oxo acid [11] and neighboring group participation in the hydrolysis of ethyl ester of 4-oxo acid [12,13] have been reported. Hence, 4-oxo acids are attractive substrates in terms of their mechanistic aspects.

The chemistry of bromate is quite interesting because of its ability to act as an oxidizing and brominating reagent [14]. Bromate oxidations of organic and inorganic reactions usually involve complications such as an induction period [15], autocatalysis [16] and involvement of two reactions [17,18]. Even bromate oxidations sometimes involve oscillation reactions [19–22]. Hence, the chemistry of bromate ion in an aqueous acid medium is of considerable interest, given its importance in mechanistic chemistry.

Lack of studies on the oxidation of 4-oxo acids by bromate in the presence of V(IV) has encouraged us to investigate the kinetic behavior of the title reaction in order to continue our study on the role of metal ions in oxidation reactions by bromate. Preliminary experimental results indicate that the reaction of 4-oxo acid with bromate in acidic medium without a catalyst was sluggish, but the reaction became facile in the presence of a small amount of V(IV) catalyst. Therefore, in order to explore the mechanism of

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4-oxo acid-bromate reactions in an acid medium and also to study the catalytic action of V(IV), oxovanadium(IV) has been selected as a catalyst. In the presence of oxovanadium(IV), the reduction of bromate with excess [4-oxo acid] is autocatalytic (an initial slow reaction followed by a fast reaction). The oxo acid reacts with bromate forming Br_2 and HOBr , which are reduced further to Br^- ions. The kinetics of the reaction of oxo acid with Br_2 has been studied and it was found that $k_{\text{HOBr}} > k_{\text{bromine}}$. Tribromide ions are kinetically inactive, hence, bromate ions are consumed not only by the reaction with oxo acid but also by the reaction with Br^- ions. If bromide ions are masked in the solution by adding a suitable complexing agent such as mercury(II), Br^- ions cannot take part in follow up reactions and the overall reaction loses its autocatalytic character. This is exactly what is observed with the addition of mercury(II) acetate. The added Hg(II) ions form non-ionized mercury(II)-bromocomplexes of high stability constants [23] (HgBr^+ , $K_1 = 2.51 \times 10^8 \text{ M}^{-1}$; HgBr_2 , $K_2 = 3.80 \times 10^8 \text{ M}^{-1}$) and the kinetic results remained the same over a wide concentration range (0.001–0.01 M) of mercuric acetate. In order to mask all the Br^- ions formed, an optimum concentration (0.005 M) of mercuric acetate is employed to pertain Br(V) oxidation only.

The main objectives of the present study are to: (i) ascertain the reactive species of the substrate, catalyst and oxidant, (ii) elucidate a plausible mechanism, (iii) deduce an appropriate rate law, (iv) identify the oxidation products, (v) find the catalytic efficiency of V(IV) and (vi) evaluate the related kinetic and thermodynamic parameters along with their linear free-energy relationships. This is the first report of the neighboring group participation and intramolecular catalysis in the oxidation of 4-oxo acids.

2. Experimental

2.1. Materials

4-Oxo acid, 4-oxo-4-(4'-methoxyphenyl)butanoic acid, 4-oxo-4-(4'-methylphenyl)butanoic acid, 4-oxo-4-(4'-chlorophenyl)butanoic acid were obtained from Aldrich chemical company. 4-Oxo-4-(3'-nitrophenyl)butanoic acid was prepared from nitrobenzene and succinic anhydride in 1:1 molar ratio using anhydrous aluminium chloride as a catalyst [24]. All the 4-oxo

acids were crystallized twice from water and their purity was checked by their melting points and UV, IR and NMR spectra. KBrO_3 (Reidal), H_2SO_4 and $\text{Hg}(\text{OAc})_2$ (E. Merck) were of analytical reagent grade and were used as received. D_2O (purity 99.4%) was obtained from the Baba Atomic Research Centre, Mumbai, India. Acetic acid (BDH) was purified by refluxing with chromic acid and acetic anhydride for 6 h and then distilled. A stock solution of vanadium(IV) was prepared by dissolving a known amount of $\text{VOSO}_4 \cdot \text{H}_2\text{O}$ (Sisco) in diluted sulfuric acid and was standardized using KMnO_4 [25]. An allowance for the amount of sulfuric acid present in the catalyst solution was also made while the reaction mixture for the studies was prepared. The other solutions were prepared with either doubly distilled water or purified acetic acid and were standardized by known methods. Fresh solutions were used for each kinetic run. The reaction vessels were coated from outside with black paint to avoid any photochemical reaction. A Shimadzu multipurpose recording double beam UV-visible spectrophotometer equipped with a temperature controller was used for absorption studies. Separation and identification of

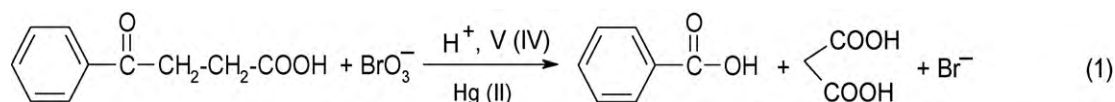
organic intermediates in the reaction were performed using high performance liquid chromatography (HPLC). The experiments were performed with Shimadzu equipment using an ion-exchange column at 45°C and a UV detector working at 220 nm. The intermediates and the products were identified from their retention time (t_r). Regression analyses of experimental data yielded the regression coefficient (r) and standard deviation (s).

2.2. Kinetic procedure

A thermostatic water bath was used to maintain the desired temperature within $\pm 0.1^\circ\text{C}$. The reaction mixture, containing 4-oxo acid, H_2SO_4 , mercuric acetate and V(IV) solutions, was thermally equilibrated for an hour at the desired temperature under subdued light. The reaction was initiated by the addition of temperature-equilibrated bromate solution of requisite concentration. The total volume of the reaction mixture was 100 ml in each case. 5 ml of aliquots of the reaction mixture was pipetted out at different time intervals and quenched with 4% potassium iodide solution. The progress of reaction was iodometrically monitored by estimating the unreacted bromate. However, before adopting iodometric method, it was ensured that the presence of 4-oxo acids in the quenching solution of potassium iodide did not change the bromate titer value. All the reactions were carried out under the conditions using ten (or more)-fold excess of 4-oxo acid over $[\text{KBrO}_3]$ at constant temperature. The pseudo-first order rate constants (k , s^{-1}) were computed from the linear plots of $\log[\text{bromate}]_t$ against time ($r \geq 0.99$; $s \leq 0.025$) up to 90% completion of the reaction, and the rate constants were reproducible within $\pm 5\%$. Rate constants did not alter in a nitrogen atmosphere and all the rate constants reported in this paper were obtained without nitrogen. Freshly prepared solutions of oxo acids in purified acetic acid were used to avoid any possible side reactions.

2.3. Stoichiometry and product analysis

The stoichiometry of the reaction was determined by equilibrating reaction mixture of various $[\text{bromate}]/[\text{4-oxo acid}]$ ratios at 40°C for 24 h, keeping all other reagents constant. Estimation of unconsumed bromate concentration revealed the consumption ratio of substrate to oxidant as:



The same stoichiometry was observed with all the substituted 4-oxo acids. The ultimate products of oxidation of 4-oxo acid are benzoic and malonic acids, identified by comparing the retention time (t_r) of the authentic samples. Bromide ion was identified by adding AgNO_3 solution, resulting in the formation of pale yellow AgBr precipitate. Benzoic acid, after separation by HPLC, was estimated quantitatively (92–96%, yield) with a standard curve at $\lambda_{\text{max}} = 235 \text{ nm}$. Malonic acid was further confirmed with its characteristic spot test through conversion into barbituric acid [26].

3. Results

3.1. Effect of concentrations

Molecular bromine production anticipated from the bromate–bromide reaction and its subsequent reaction with the 4-oxo acid was eliminated by the addition of bromocomplexing agent Hg(II). The added mercuric acetate over a wide concentration range (0.001–0.01 M) had no effect on the rate of reaction. In order to keep back all the Br^- ions formed, an optimum

Table 1
Effect of variation of $[\text{KBrO}_3]$ on the rate of V(IV)-catalyzed oxidation of 4-oxo acids by bromate in acid medium at 313 K.

4-Oxo acid	$k \times 10^4$ (s^{-1}) at $[\text{KBrO}_3] \times 10^4$ (M)				
	5.00	7.50	10.00	15.00	10.00
–H	2.57 (0.31) ^a	2.54 (0.30)	2.55 (0.31)	2.55 (0.31)	2.56 (0.30)
<i>p</i> -OCH ₃	46.03 (4.78)	46.06 (4.80)	46.06 (4.79)	46.08 (4.81)	46.06 (4.79)
<i>p</i> -CH ₃	5.75 (0.66)	5.75 (0.67)	5.75 (0.68)	5.73 (0.66)	5.75 (0.68)
<i>p</i> -Cl	0.81 (0.12)	0.83 (0.10)	0.82 (0.11)	0.84 (0.12)	0.82 (0.11)
<i>m</i> -NO ₂	0.31 (0.03)	0.31 (0.03)	0.32 (0.03)	0.31 (0.03)	0.31 (0.03)

Conditions: $[\text{substrate}] = 0.01$ M, $[\text{H}_2\text{SO}_4] = 1.0$ M, $[\text{V(IV)}] = 1.0 \times 10^{-4}$ M, $[\text{Hg(OAc)}_2] = 0.005$ M, $\text{HOAc-H}_2\text{O} = 1:1\%$ (v/v). Reported rate constants are the mean of duplicate experiments.

^a Values in parentheses are the uncatalyzed rate constants.

Table 2
Effect of variation of $[\text{substrate}]$ on the rate of V(IV)-catalyzed oxidation of 4-oxo acids by bromate in acid medium at 313 K.

[4-oxo acid] (M)	$k \times 10^4$ (s^{-1})				
	–H	<i>p</i> -OCH ₃	<i>p</i> -CH ₃	<i>p</i> -Cl	<i>m</i> -NO ₂
0.0075	2.19 (0.27) ^a	37.35 (3.83)	4.79 (0.45)	0.67 (0.07)	0.25 (–)
0.01	2.55 (0.31)	46.06 (4.79)	5.75 (0.67)	0.82 (0.11)	0.31 (0.03)
0.015	3.21 (0.47)	63.95 (7.19)	7.67 (1.00)	0.97 (0.15)	0.42 (0.05)
0.02	3.83 (0.63)	76.76 (9.59)	8.84 (1.34)	1.27 (0.21)	0.50 (0.06)
0.03	4.60 (0.95)	95.95 (14.39)	11.51 (2.01)	1.59 (0.31)	0.63 (0.10)
0.04	5.08 (1.27)	115.15 (19.19)	13.42 (2.68)	1.91 (0.42)	0.76 (0.13)
0.06	6.39 (1.91)	151.35 (28.78)	16.17 (4.03)	2.55 (0.63)	0.95 (0.21)

Conditions: $[\text{KBrO}_3] = 0.001$ M, $[\text{H}_2\text{SO}_4] = 1.0$ M, $[\text{V(IV)}] = 1.0 \times 10^{-4}$ M, $[\text{Hg(OAc)}_2] = 0.005$ M, $\text{HOAc-H}_2\text{O} = 1:1\%$ (v/v). Reported rate constants are the mean of duplicate experiments.

^a Values in parentheses are the uncatalyzed rate constants.

Table 3
Effect of variation of $[\text{H}_2\text{SO}_4]$ on the rate of V(IV)-catalyzed oxidation of 4-oxo acids by bromate in acid medium at 313 K.

[H ₂ SO ₄] (M)	$k \times 10^4$ (s^{-1})				
	–H	<i>p</i> -OCH ₃	<i>p</i> -CH ₃	<i>p</i> -Cl	<i>m</i> -NO ₂
0.25	0.68	12.57	1.73	0.21	–
0.50	1.27	25.58	3.46	0.40	0.16
0.75	1.91	38.38	5.08	0.62	0.24
1.00	2.55	46.06	5.75	0.82	0.31
1.25	3.03	63.95	7.67	0.95	0.40
1.50	3.83	76.76	9.59	1.27	0.48
2.00	4.81	95.95	12.51	1.58	0.63
3.00	7.03	152.82	18.19	2.30	0.92
^a S	1.01	1.00	1.02	1.00	1.00

Conditions: $[\text{substrate}] = 0.01$ M, $[\text{KBrO}_3] = 0.001$ M, $[\text{V(IV)}] = 1.0 \times 10^{-4}$ M, $[\text{Hg(OAc)}_2] = 0.005$ M, $\text{HOAc-H}_2\text{O} = 1:1\%$ (v/v). Reported rate constants are the mean of duplicate experiments.

^a S = slopes of $\log k$ versus $\log[\text{H}_2\text{SO}_4]$ plots.

concentration (0.005 M) of mercuric acetate was employed. In the presence of mercuric acetate, the oxidation of 4-oxo acid and phenyl substituted 4-oxo acids by bromate in acidic medium proceeds smoothly and is found to be clearly of first order on bromate as both determinations with respect to time (as evidenced by good fits of $\log[\text{bromate}]_t$ versus time plots) and concentration (as shown by the time order rate coefficient (k , s^{-1}), which is independent of initial bromate concentration), Table 1. The observed pseudo-first order rate constant (k , s^{-1}) increased non-linearly

(Table 2) with an increase in $[\text{substrate}]_0$. The log–log plots of k versus $[\text{substrate}]_0$ were linear ($r \geq 0.995$, $s \leq 0.03$) with slope values of 0.52–0.63. Further, dependence of k values on the initial substrate concentration were consistent with the Lineweaver–Burk kinetics in each case (Fig. 1a). The rate of the reaction increased linearly with an increase in $[\text{acid}]$ (Table 3) and the order with respect to $[\text{acid}]$ was found to be unity from the linear plots of $\log k$ versus $\log[\text{acid}]$. Zucker–Hammett plots of $\log k$ versus H_0 indicate non-involvement of water molecule in the rate determining step.

Table 4
Effect of variation of $[\text{V(IV)}]$ on the rate of V(IV)-catalyzed oxidation of 4-oxo acids by bromate in acid medium at 313 K.

[V(IV)] $\times 10^4$ (M)	$k \times 10^4$ (s^{-1})				
	–H	<i>p</i> -OCH ₃	<i>p</i> -CH ₃	<i>p</i> -Cl	<i>m</i> -NO ₂
0.50	1.53	28.78	3.83	0.57	0.19
1.00	2.55	46.06	5.75	0.82	0.31
2.00	4.03	69.18	9.18	1.43	0.47
4.00	6.15	95.95	14.22	2.08	0.69
8.00	8.04	129.87	21.99	3.22	1.05

Conditions: $[\text{substrate}] = 0.01$ M, $[\text{bromate}] = 0.001$ M, $[\text{H}_2\text{SO}_4] = 1.0$ M, $[\text{Hg(OAc)}_2] = 0.005$ M, $\text{HOAc-H}_2\text{O} = 1:1\%$ (v/v). Reported rate constants are the mean of duplicate experiments.

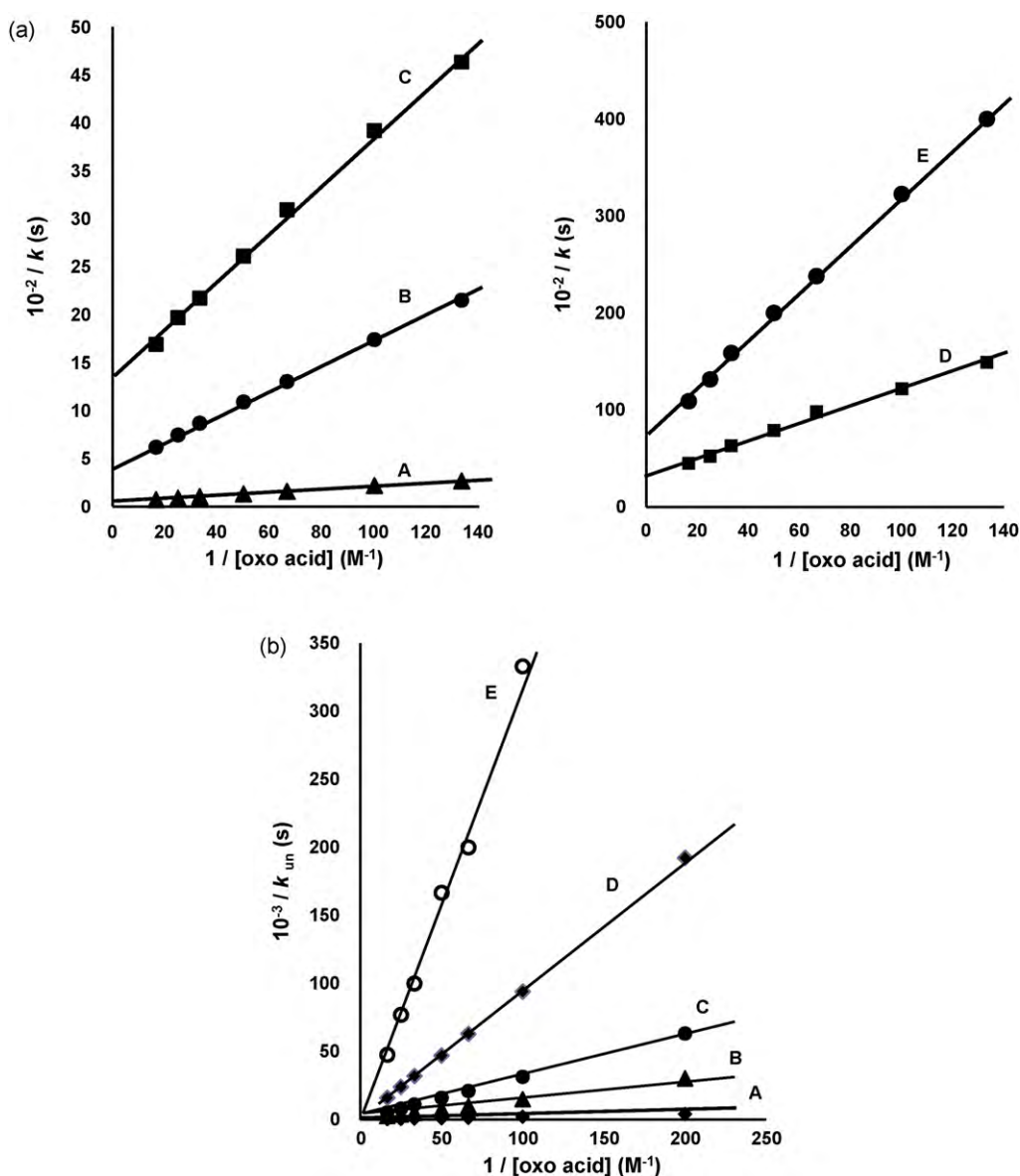


Fig. 1. (a) Plots between $1/k$ and $1/[\text{substrate}]$ for V(IV)-catalyzed reactions under the conditions of Table 2. (A) *p*-OCH₃, (B) *p*-CH₃, (C) -H, (D) *p*-Cl, and (E) *m*-NO₂. (b) Plots between $1/k_{un}$ and $1/[\text{substrate}]$ for uncatalyzed reactions under the conditions of Table 2. (A) *p*-OCH₃, (B) *p*-CH₃, (C) -H, (D) *p*-Cl, and (E) *m*-NO₂.

The H_0 values were taken from Paul and Long [27] assuming that H_0 values do not change much in a media containing acetic acid up to 50%. A change in the concentration of added salt like NaClO₄ had a marginal effect on the reaction rate. The observed rate constants (k , s^{-1}) increased with an increase in [oxovanadium (IV)] (Table 4) and slopes of less than unity (0.45–0.66) were obtained when $\log k$ was plotted against $\log[V(\text{IV})]$ for all the substrates under study. Further, $1/k$ versus $1/[\text{catalyst}]$ plots (Fig. 2, $r \geq 0.985$; $s \leq 0.03$) resulted variable intercepts on the $1/k$ axis for the studied substituted 4-oxo acids. The rates of uncatalyzed reactions are negligible.

3.2. Effect of solvent polarity

Varying the acetic acid and water composition in the reaction mixture varied dielectric constant (D) of the medium. The decrease in dielectric constant of the reaction medium increased the reaction rate for all the substrates under study (Table 5) and the plots of $\log k$ versus $1/D$ were linear (Fig. 3). The inertness of the solvent towards the oxidant has also been tested.

3.3. Test for free radicals

The addition of monomers such as acryl amide or acrylonitrile to the reaction system, in an atmosphere of nitrogen, did not alter the reaction rate or indicate polymer formation, ruling out the participation of free radical intermediates in the oxidation reaction. To further confirm the absence of free radicals in the reaction pathway, the reaction was carried out in the presence of 0.05 M of 2,6-di-*t*-butyl-4-methylphenol (butylated hydroxyl toluene or BHT). It was observed that the BHT was recovered unchanged, almost quantitatively.

3.4. Kinetic isotope effect

Rate of oxidation increased in the D₂O medium and $k(\text{D}_2\text{O})/k(\text{H}_2\text{O}) \sim 1.80$, at all the studied temperatures for all the studied 4-oxo acids (Table 6). The solvent isotope effect suggests a proton-catalyzed reaction.

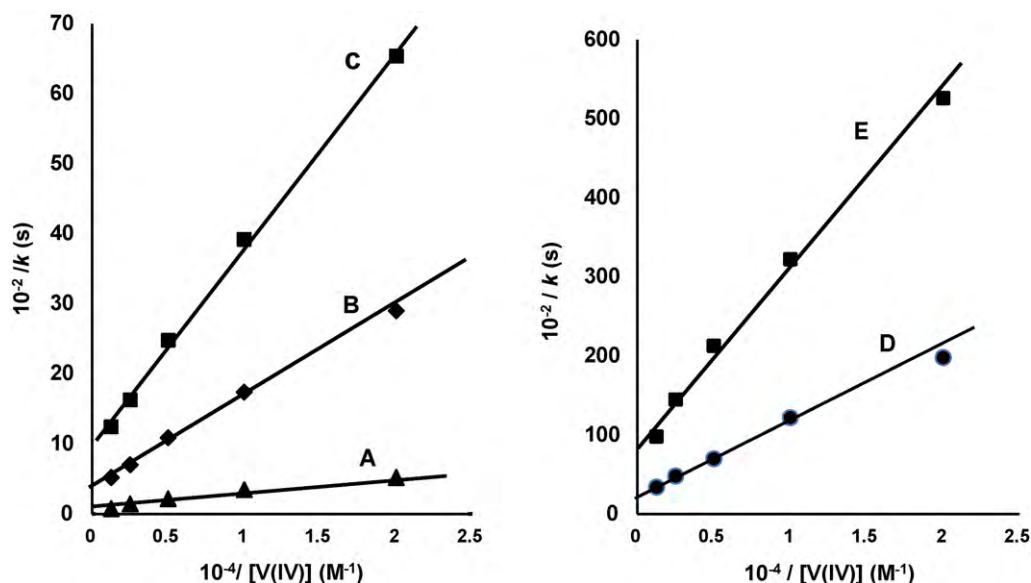


Fig. 2. Plots between $1/k$ and $1/[\text{catalyst}]$ under the conditions of Table 4. (A) $p\text{-OCH}_3$, (B) $p\text{-CH}_3$, (C) -H , (D) $p\text{-Cl}$, and (E) $m\text{-NO}_2$.

Table 5

Effect of varying solvent composition on the rate of V(IV)-catalyzed oxidation of 4-oxo acids by bromate in acid medium at 313 K.

HOAc–H ₂ O % (v/v)	<i>D</i>	$k \times 10^4$ (s ⁻¹)				
		–H	<i>p</i> -OCH ₃	<i>p</i> -CH ₃	<i>p</i> -Cl	<i>m</i> -NO ₂
30–70	53.18	1.43	25.58	2.42	0.47	0.15
40–60	46.48	1.91	35.43	3.36	0.58	0.19
50–50	39.78	2.55	46.06	5.75	0.82	0.30
60–40	33.08	3.83	86.36	8.39	1.17	0.47
70–30	26.08	6.41	160.76	25.47	2.70	0.95

Conditions: $[\text{V(IV)}] = 1.0 \times 10^{-4}$ M and other conditions as in Table 4. *D* = dielectric constant of the medium. Reported rate constants are the mean of duplicate experiments.

3.5. Effect of temperature

The oxidation reactions were studied in the temperature range of 298–323 K. Activation energy (E_a) of the reactions was calculated from the least-square slopes of linear Arrhenius plots (Fig. 4, $r \geq 0.99$; $s \leq 0.02$) 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 7. The average error limits in the values of ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger (at 313 K) are ± 3 kJ mole⁻¹, 8 J K⁻¹ mole⁻¹ and ± 4 kJ mole⁻¹, respectively. The plot of ΔH^\ddagger versus ΔS^\ddagger was linear (Fig. 5, $r \geq 0.997$, $s \leq 0.03$) and the isokinetic temperature (β) obtained is 377.3 K. The β calculated from the Exner's plot (Fig. 6, $r \geq 0.987$; $s \leq 0.04$) of $\log k_{323\text{K}}$ against $\log k_{313\text{K}}$ is 375.2 K, which is in good agreement with the value obtained from the ΔH^\ddagger against ΔS^\ddagger plot.

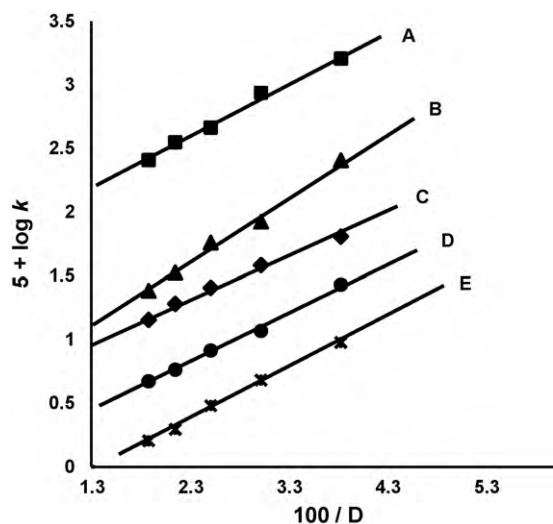


Fig. 3. Plots between $\log k$ and $1/D$ under the conditions of Table 5. (A) $p\text{-OCH}_3$, (B) $p\text{-CH}_3$, (C) -H , (D) $p\text{-Cl}$, and (E) $m\text{-NO}_2$.

3.6. Structural effect

Structural modifications in the phenyl moiety of 4-oxo acid result in varied reactivity; while electron-releasing substituents (donors) accelerate the rate of oxidation to a large extent, and the rate retardation by electron-withdrawing substituents (attractors), though perceptible, was not very much (Table 8). The free-energy relationship is characterized by a smooth curve; concaves downward, in the Hammett's plot of $\log k$ versus σ

Table 6

Solvent isotope effect on the rate of V(IV)-catalyzed oxidation of 4-oxo acids by bromate in acid medium at 313 K.

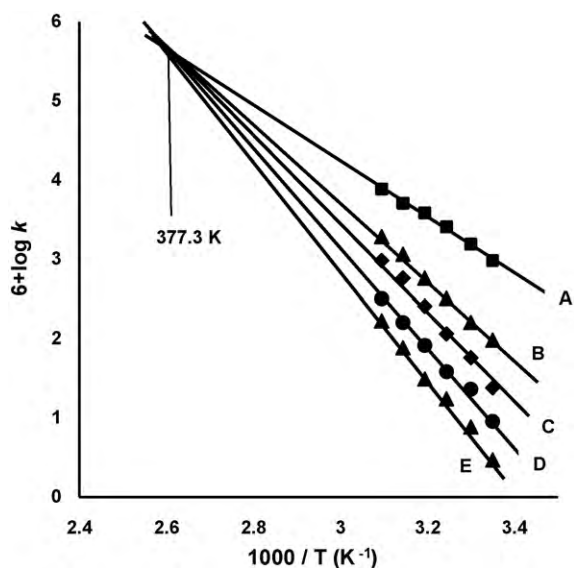
4-Oxo acid	$k(\text{H}_2\text{O}) \times 10^4$ (s ⁻¹)	$k(\text{D}_2\text{O}) \times 10^4$ (s ⁻¹)	$k(\text{D}_2\text{O})/k(\text{H}_2\text{O})$
–H	2.55	4.59	1.80
<i>p</i> -Methyl	5.75	10.23	1.78
<i>p</i> -Chloro	0.82	1.49	1.82
<i>m</i> -Nitro	0.31	0.56	1.80

Conditions: $[\text{substrate}] = 0.01$ M, $[\text{KBrO}_3] = 0.001$ M, $[\text{H}_2\text{SO}_4] = 1.0$ M, $[\text{V(IV)}] = 1.0 \times 10^{-4}$ M, $[\text{Hg(OAc)}_2] = 0.005$ M, HOAc–H₂O/D₂O = 1:1% (v/v). Reported rate constants are the mean of duplicate experiments.

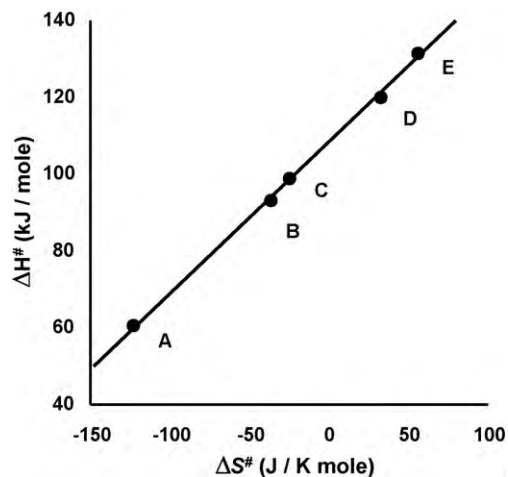
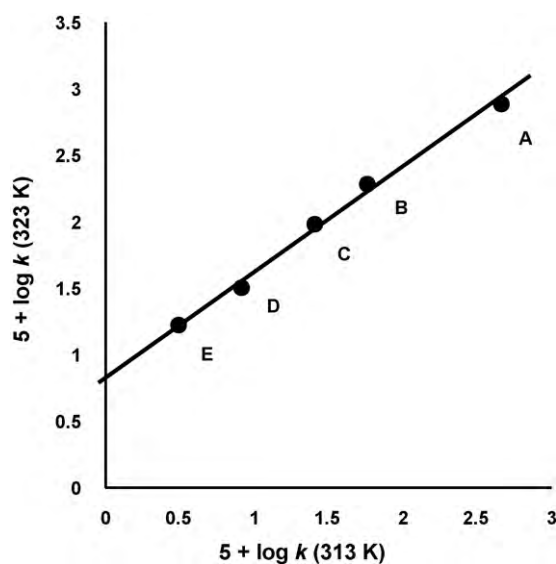
Table 7

Values of rate constant at different temperatures and activation parameters at 313 K of V(IV)-catalyzed oxidation of 4-oxo acids by bromate in acid medium.

Temp. (K)	$k \times 10^5 \text{ (s}^{-1}\text{)}$				
	-H	<i>p</i> -OCH ₃	<i>p</i> -CH ₃	<i>p</i> -Cl	<i>m</i> -NO ₂
298	–	95.95	9.59	1.24	0.29
303	5.32	154.3	15.99	2.30	0.76
308	11.51	255.5	32.20	3.83	1.73
313	25.58	383.8	57.57	8.22	3.09
318	57.57	508.0	115.1	15.9	7.67
323	95.95	767.6	191.9	31.98	16.76
<i>E_a</i> (kJ/mole)	101.47	63.18	95.73	122.54	134.02
ΔH^\ddagger (kJ/mole)	98.87	60.58	93.13	119.94	131.42
ΔS^\ddagger (J/mole K)	-24.0	-123.1	-36.5	32.5	55.9
ΔG^\ddagger (kJ/mole)	106.67	100.10	104.57	109.75	113.92

Conditions: [substrate] = 0.01 M, [KBrO₃] = 0.001 M, [H₂SO₄] = 1.0 M, [V(IV)] = 1.0 × 10⁻⁴ M, [Hg(OAc)₂] = 0.005 M, HOAc-H₂O = 1:1% (v/v).**Fig. 4.** Arrhenius plots between $\log k$ and $1/T$ showing the isokinetic temperature under the conditions of Table 7. (A) *p*-OCH₃, (B) *p*-CH₃, (C) -H, (D) *p*-Cl, and (E) *m*-NO₂.

(substituent constant) at all the studied temperatures (Fig. 7). However, the Hammett' plots are linear, with excellent correlation coefficient at four temperatures (Fig. 8, $r \geq 0.995$, $s \leq 0.03$), when exalted substituent constant (Brown and Okamoto's σ^+) values [28] are used. The reaction constants (ρ^+) are nega-

**Fig. 5.** Plot between ΔH^\ddagger and ΔS^\ddagger : isokinetic relationship under the conditions of Table 7. (A) *p*-OCH₃, (B) *p*-CH₃, (C) -H, (D) *p*-Cl, and (E) *m*-NO₂.**Fig. 6.** Exner's plot of $\log k_{323\text{K}}$ against $\log k_{313\text{K}}$ under the conditions of Table 7. (A) *p*-OCH₃, (B) *p*-CH₃, (C) -H, (D) *p*-Cl, and (E) *m*-NO₂.**Table 8**

Effect of substituent on the rate of V(IV)-catalyzed oxidation of 4-oxo acids by bromate in acid medium at 313 K.

Substituent	σ	σ^+	$k \times 10^4 \text{ (s}^{-1}\text{)}$	$5 + \log k$
-H	0.00	0.00	2.55	1.4065
<i>p</i> -OCH ₃	-0.27	-0.78	46.06	2.6633
<i>p</i> -CH ₃	-0.17	-0.31	5.75	1.7597
<i>p</i> -Cl	0.23	0.11	0.82	0.9138
<i>m</i> -NO ₂	0.71	0.67	0.31	0.4913

Conditions as in Table 7.

tive and decrease (in magnitude) with increase in temperature (Table 9).

4. Discussion

4.1. Role of mercury(II) acetate

The presence of mercuric acetate (in excess of bromate concentration) simply means that Br₂ oxidation has been completely

Table 9Effect of temperature on the reaction constant (ρ^+).

Temperature (K)	308	313	318	323
Reaction constant (ρ^+)	-1.50	-1.33	-1.20	-1.09

Conditions as in Table 7.

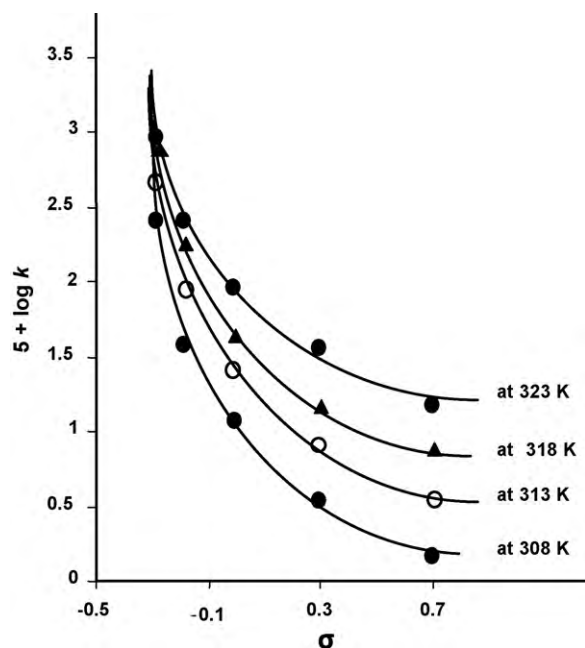
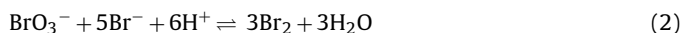


Fig. 7. Hammett' plots between $\log k$ and σ at different temperatures under the conditions of Table 7.

suppressed; Br_2 otherwise would have been formed by interaction of bromate and bromide (the reduction product of bromate) as:



It is pertinent to point out here that, Cortes and Faria [29] observed acetate ion catalysis in bromate–bromide reaction and the experimental results were interpreted in a six term rate law, with and without involvement of acetate ion. The mechanism proposed considers that when acetate binds to bromate it facilitates its second protonation. However, in the present study of oxovanadium(IV)-catalyzed oxidation of substituted 4-oxo acids by bromate (in 1:1 HOAc– H_2O medium containing sulfuric acid) no catalytic effect of acetate ion is observed when mercuric acetate is added to the reaction mixture over a wide concentration range (0.001–0.01 M).

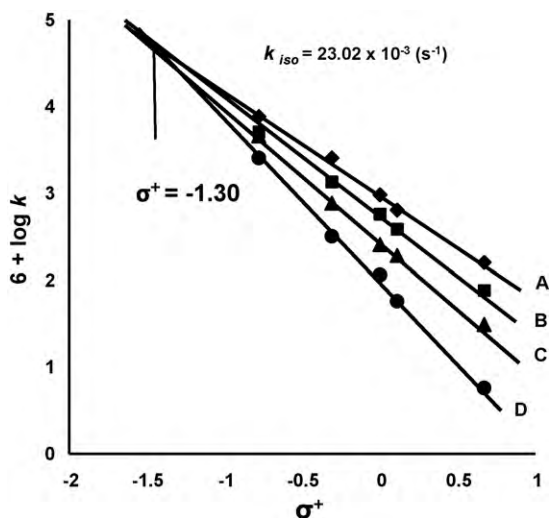
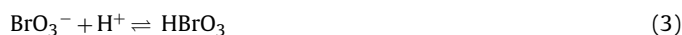


Fig. 8. Hammett' plots between $\log k$ and σ^+ at different temperatures showing the k_{iso} (s^{-1}) and σ^+_{iso} under the conditions of Table 7. (A) 323 K, (B) 318 K, (C) 313 K, and (D) 308 K.

Before further discussion, it is necessary to make clear that, in the present study, no free radicals are present and that the reaction rates are independent of [mercuric acetate]. These considerations confirm only the complex-forming ability of mercury(II) with bromide ions in these reactions. $\text{Hg}(\text{II})$ ion acts as a scavenger [16–18] for any Br^- ion formed, as unionized HgBr^+ and HgBr_2 [23], thus ensuring that the oxidation takes place purely through bromate. The reported rate constants therefore, stand for pure bromate (uncontaminated with Br_2) oxidation.

4.2. Active species of reactants

In acid solutions, the reactive species of bromate are likely to be BrO_3^- and protonated bromate. Hence, the oxidation may be a reaction involving one of the oxidant species. Based on the earlier propositions made in bromate oxidations (in acid medium) by Indelli et al. [30], Anbar and Guttman [31], Wright and Barton [32], and Rabai et al. [33], the following equilibrium steps (Eqs. (3)–(6)) may be considered.



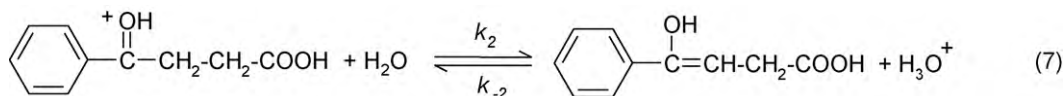
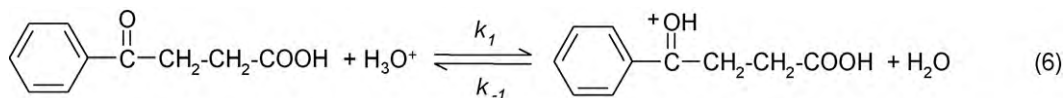
These authors [30–33] consider the H^+ attack to bromate forming intermediates HBrO_3 and H_2BrO_3^+ . However, BrO_3^- is a very weak base and does not attract the H^+ efficiently [29]. As HBrO_3 is a very strong acid [34], the H_2BrO_3^+ species will not be formed at the acid concentrations used to study the bromate–oxo acid reaction. Another point to be considered is the possibility of bromate, after two protonations, losing water and forming the BrO_2^+ species as considered by other authors [31,35,36]. However, this possibility has been ruled out by the results [37,38] on the rate of exchange of isotopic oxygen between the oxyanion XO_3^- ($\text{X}=\text{Cl}, \text{Br}$) and water as these rates are significantly low. These results indicate BrO_3^- ion is the active species of oxidant, and excludes the involvement of HBrO_3 , H_2BrO_3^+ and BrO_2^+ in the reaction.

The fractional order (<1) dependence on [substrate] and a definite intercept in the $1/k$ versus $1/[\text{oxo acid}]$ plot (Fig. 1a) indicates that the substrate is involved in the complex formation. Uncatalyzed bromate oxidation of 4-oxo acids exhibited first order each in [4-oxo acid] and [bromate], and $1/k_{\text{un}}$ versus $1/[\text{substrate}]$ plots were linear passing through the origin (Fig. 1b). The apparent order of less than unity (0.45–0.66) with respect to $[\text{V}(\text{IV})]$ and a definite intercept in the $1/k$ versus $1/[\text{V}(\text{IV})]$ plot (Fig. 2) may be attributed to a complex formation between 4-oxo acid and $\text{V}(\text{IV})$, which subsequently involves in the reaction with BrO_3^- .

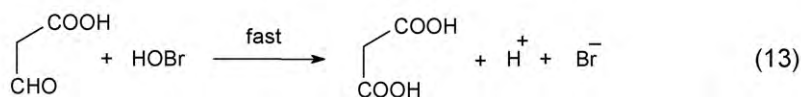
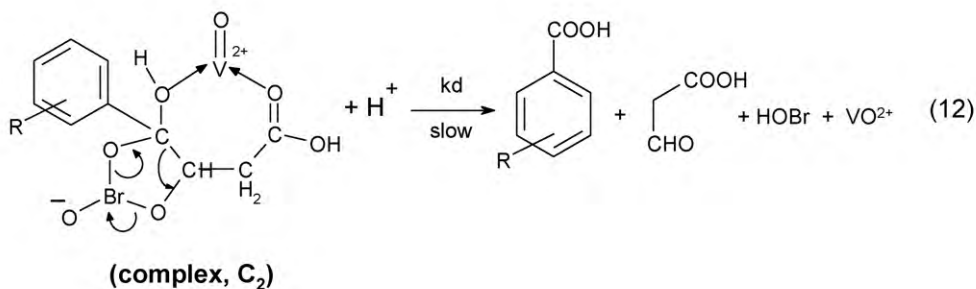
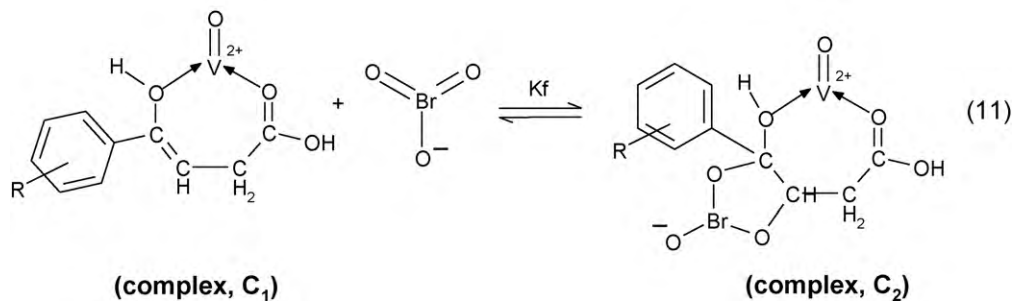
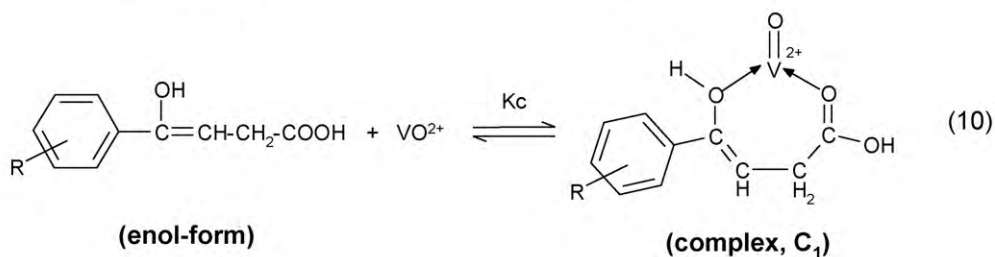
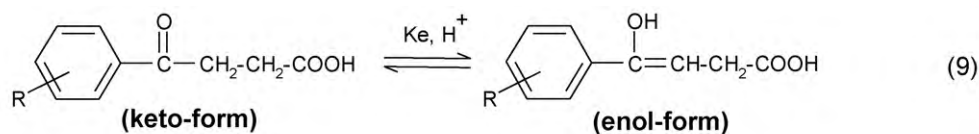
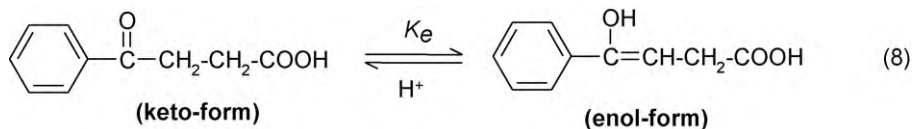
$\text{V}(\text{IV})$ is one of the stable oxidation states of vanadium and, moreover, it is one equivalent oxidant/reductant in many oxidations to be converted either to $\text{V}(\text{V})$ or $\text{V}(\text{III})$. The absence of any effect of added acrylonitrile on the reaction discounts the possibility of one-electron oxidation/reduction leading to the formation of free radicals. Therefore, it is assumed that in the oxidation of 4-oxo acids by bromate, the oxidation state of $\text{V}(\text{IV})$ is not altered during the oxidation reaction. Further, the absorption maximum (λ_{max}) of oxovanadium(IV) at 745 nm with $\epsilon = 20$ ($\text{dm}^3 \text{mole}^{-1} \text{cm}^{-1}$) remained the same during the course of the reaction, the substrate forms preferably an outer sphere complex with the catalyst $\text{V}(\text{IV})$.

The 4-oxo acid is a weak acid ($\text{pK}_a = 5.77$ at 40°C in aqueous solution [39]) and the undissociated form of the substrate can be taken as the only form in acidic media. 4-Oxo acid enolizes in acid medium to form the enol and proceeds by a concerted or push-

pull mechanism, and the rate of enolization was determined by bromination method [40].



Thus, the enolization reaction is represented as:



Scheme 1.

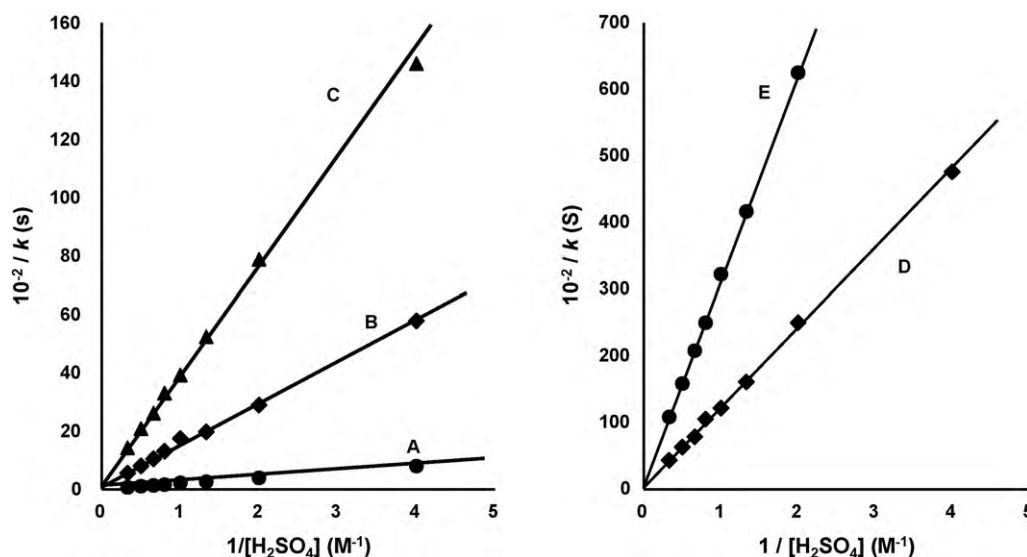


Fig. 9. Plots between $1/k$ and $1/[\text{acid}]$ under the conditions of Table 3. (A) *p*-OCH₃, (B) *p*-CH₃, (C) -H, (D) *p*-Cl, and (E) *m*-NO₂.

In oxidation reactions, the keto group of the substrate can react either directly or through the enol form. Oxidation rates faster than the rates of enolization have been observed with ceric ion [41], manganic ion [42], cobaltic and vanadate ions [43], mercuric perchlorate [44] and alkaline diperiodatoargentate(III) [45] as oxidants, indicating that the keto group of the substrate reacts directly. All of these oxidants undergo one-electron reduction, and the reactions proceeded via a free radical mechanism [41–45].

The rates of oxidation and enolization were found to be equal in the oxidation reactions by manganic pyrophosphate [46], thallium triacetate [47] and diperiodatonickelate(IV) [48]. These reactions were zero order in [oxidant], indicating the enol formation as the rate determining step.

In the present investigation, the rate of enolization (measured by the bromination method [40]) is greater than the rate of oxidation by a factor of ~12–15 and the enolization step can be visualized as proceeding via the enol form of the keto group of 4-oxo acid. Hence, the step involving enol formation can be assumed to be a fast step and thus is not the rate determining step of the reaction.

4.3. Mechanism

Based on aforesaid reasons and in accordance with the experimental results, the mechanism as shown in Scheme 1 is proposed for the V(IV)-catalyzed bromate oxidation of 4-oxo acids.

The mechanistic pathway is demonstrated as the enol form of the 4-oxo acid forms an outer sphere complex with V(IV). Bromate reacts with the complex C₁, giving the cyclic bromate ester (complex C₂) through the carbon–oxygen–bromine bond. V(IV)-enol complex formation enhances the reactivity of the *-ene* bond of the complex C₁ to form the cyclic bromate ester. The decomposition of the complex C₂ involving C–C and O–Br bonds, in a slow step, results open structures, benzoic acid and formyl acetic acid. The oxidation state of V(IV) is unaltered during the course of the reaction. The formyl acetic acid on oxidation with the formed HOBr converts into malonic acid along with the formation of Br⁻ ion. Formation of formyl acetic acid as the intermediate was confirmed by comparing with the retention time (*t_r*) of the authentic sample. Benzoic and malonic acids were the final products of oxidation. It is pertinent to point out here that malonic 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.

4.4. Rate law and its verification

Taking all the steps of Scheme 1 for the oxidation of 4-oxo acid and stoichiometry of the reaction, the following rate law Eq. (14) may be written in terms of loss of concentration of bromate ion.

$$\text{Rate} = \frac{-d[\text{Br(V)}]_T}{dt} = \frac{kdKeKcK_f[\text{H}^+][\text{V(IV)}][\text{oxo acid}][\text{Br(V)}]_T}{1 + KeKcK_f[\text{V(IV)}][\text{oxo acid}]} \quad (14)$$

The obtained rate law could explain the fractional order each in [substrate] and [catalyst], and first order each in [H⁺] and [bromate].

$$\frac{\text{Rate}}{[\text{Br(V)}]_T} = k = \frac{kdKeKcK_f[\text{H}^+][\text{V(IV)}][\text{oxo acid}]}{1 + KeKcK_f[\text{V(IV)}][\text{oxo acid}]} \quad (15)$$

$$\frac{1}{k} = \left[\frac{1}{kdKeKcK_f[\text{V(IV)}][\text{oxo acid}]} + \frac{1}{kd} \right] \frac{1}{[\text{H}^+]} \quad (16)$$

At constant (1.0 M) acid concentration, Eq. (16) reduces to Eq. (17)

$$\frac{1}{k} = \frac{1}{kdKeKcK_f[\text{V(IV)}][\text{oxo acid}]} + \frac{1}{kd} \quad (17)$$

According to Eq. (16), other conditions being constant, $1/k$ versus $1/[\text{H}^+]$ should be linear passing through origin and the same is observed (Fig. 9). Similarly, according to Eq. (17), the plots of $1/k$ versus $1/[\text{oxo acid}]$ (at constant catalyst concentration), and $1/k$ against $1/[\text{catalyst}]$ (at constant substrate concentration) should be linear with a definite (the same) intercept on the $1/k$ axis. Such a realization (Figs. 1a and 2) supports the validity of the rate law (Eq. (14)) and hence the validity of the proposed reaction mechanism (Scheme 1). The proposed mechanism is further corroborated by the solvent influence on the reaction rate. The intermediate complex C₂ is less polar than the reactants due to dispersal of charge; hence, decreasing polarity of the solvent media is expected to stabilize the complex C₂ in preference to the reactants there by enhancing the reaction rate. Such a solvent influence has actually been observed (Table 5).

From the intercept and slope data of Fig. 1a and also Fig. 2, the decomposition constant (*kd*) and, enolization and complexation constants (*Ke* and *KcK_f*), can be evaluated and the obtained values are presented in Table 10. Using the values of *Ke*, *Kc*, *K_f* and *kd*, the rate constants (*k*, s⁻¹) under different experimental conditions were calculated according to Eq. (15) and compared with the experimental data. There is a good agreement (within ± 5% error)

Table 10

Evaluated decomposition constant (kd), enolization and formation constants (Ke , Kc , K_f) of V(IV)-catalyzed oxidation of 4-oxo acids by bromate in acid medium at 313 K using Eq. (17).

Substituent	$kd \times 10^4$ (s^{-1}) (decomposition constant)	$Ke, Kc, K_f \times 10^{-5}$ (formation constants)
<i>p</i> -OCH ₃	143.55 ± 1.0	5.33 ± 0.5
<i>p</i> -CH ₃	23.71 ± 0.5	4.84 ± 0.41
-H	9.45 ± 0.3	4.43 ± 0.30
<i>p</i> -Cl	3.12 ± 0.08	4.06 ± 0.23
<i>m</i> -NO ₂	1.33 ± 0.02	3.20 ± 0.11

Conditions as in Tables 2 and 4.

between them. This further supports the envisaged reaction mechanism (Scheme 1).

4.5. Structural influences and linear free-energy relationships

The order of reactivity among the phenyl substituted 4-oxo acids is: *p*-methoxy \gg *p*-methyl $>$ -H $>$ *p*-chloro $>$ *m*-nitro. The plot of $\log k$ versus Hammett's sigma values is a smooth curve; concaves downward, at all the studied temperatures (Fig. 7). The curvature may be attributed to (i) a gradual change in the reaction mechanism when one passes from electron-donating to electron-withdrawing substituents, (ii) a change in the rate determining step and (iii) a change in the nature of transition state.

Variation in the rate within a reaction series may be caused by a change in the enthalpy of activation (ΔH^\ddagger) or entropy of activation (ΔS^\ddagger) or both, however, these quantities vary extensively in a parallel fashion. A plot of ΔH^\ddagger versus ΔS^\ddagger is linear according to the following equation.

$$\Delta H^\ddagger = \Delta H_0^\ddagger + \beta \Delta S^\ddagger$$

β is called the isokinetic temperature. It has been asserted that apparently linear correlations of ΔH^\ddagger with ΔS^\ddagger are sometimes misleading and the evaluation of β by means of the above equation lacks statistical validity [49]. Exner advocates an alternative method for the treatment of experimental data [50]. If the rates of several reactions in a series have been measured at two temperatures and $\log k_2$ (at T_2) is linearly related to $\log k_1$ (at T_1), i.e., $\log k_2 = a + b \log k_1$, he proposed that β can be evaluated from the equation:

$$\beta = \frac{T_1 T_2 (b - 1)}{T_2 b - T_1}$$

We have calculated the isokinetic temperature (β) to be 375.2 K by plotting $\log k$ at 323 K versus $\log k$ at 313 K (Fig. 6). The value of β (375.2 K) is higher than the experimental temperature range of 298–323 K, indicating that the rate is governed by the enthalpy of activation [51]. The linearity in the Exner's plot suggests that these reactions follow a similar mechanism [52]. This is also corroborated by near constancy in ΔG^\ddagger values.

From the preceding discussion, it may be construed that the curve in plot of $\log k$ versus σ (Fig. 7), is a result of the change in the nature of the transition state when one goes from electron-releasing to electron-withdrawing substituents, i.e., electronic perturbation effect. The transition state (Scheme 1) involves both the C–C bond-breaking and the C–O bond-making. If both the steps are influenced in the same way by the substituents, a linear Hammett's plot is expected. However, if the two processes influence in different ways, a curvature in the Hammett's plot will be obtained. Electron-releasing substituents may lead to a transition state, where the C–C bond-breaking has progressed to a greater extent than the C–O bond formation, while with electron-attracting substituents C–O bond formation may be more extensive than C–C bond-breaking. The activation parameters do also speak in favor

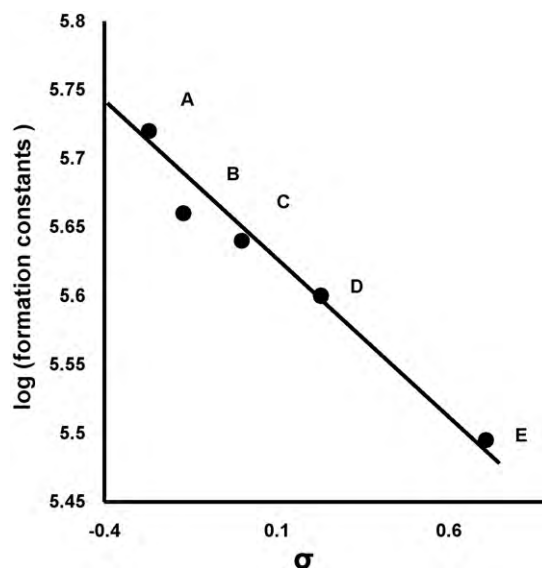


Fig. 10. Plot between $\log(\text{formation constants})$ and σ under the conditions of Table 10. (A) *p*-OCH₃, (B) *p*-CH₃, (C) -H, (D) *p*-Cl, and (E) *m*-NO₂.

of this view. The ΔH^\ddagger value is seen to decrease with increasing electron-donating ability of the substituents (Table 7). At the same time ΔS^\ddagger becomes more negative, reflecting a more solvated transition state. For electron attractors like nitro group, bond formation is apparently more important, since substitution of nitro group increases ΔH^\ddagger resulting in decreased solvolysis rate, ΔS^\ddagger becomes positive. From these observations it is clear that there is a direct conjugation between the substituent and the reaction centre. When there is a direct conjugation between the substituent and the reaction centre, the plot of $\log k$ value corresponding to Hammett's sigma value does not fall on line. Higher values of sigma viz., exalted (Brown and Okamoto's σ^+) values [28] are to be used for fitting all the points on the line. This situation is observed in the present study and the plot of $\log k$ versus σ^+ is found to be linear with a slope value of -1.33 at 313 K (Fig. 8). The reaction constant (ρ^+) decreases (in magnitude) with an increase in temperature (Table 9). The negative value of reaction constant (ρ^+) suggests the sensitivity of the reaction to the effects of electronic perturbation. It also provides information about the nature of the transition state involved during the reaction. A reaction involving positive charge development in the transition state is aided by electron-releasing substituents and ρ^+ value will be negative [53]. In the present kinetic study, the acceleration of reaction rate with the electron-releasing substituents and the negative value of the reaction constant (ρ^+) indicate explicitly that the mechanism of oxidation of 4-oxo acids by bromate, in the presence of V(IV) catalyst, involves the development of positive charge in the transition state. The reaction constant (ρ^+) depends on the concentration of the enol form of the substrate and the electron-releasing substituents tend to delocalize the positive charge on enol form of the substrate and hence facilitate the formation of carbocation in the transition state. Oxidation reactions involving the formation of carbocation normally have a large negative ρ^+ values. The ρ^+ value (-1.09 to -1.50) in the present study may be attributed to the nature of observed rate constant (k), which is composite of several terms like enolization, complexation and oxidation.

The linear plot of $\log(\text{formation constants})$ versus σ (Fig. 10) and the linearity in the plot of $\log kd$ versus σ^+ (Fig. 11), rather than $\log kd$ versus σ (Fig. 12) are further evidences for the electronic perturbation effects in the transition state.

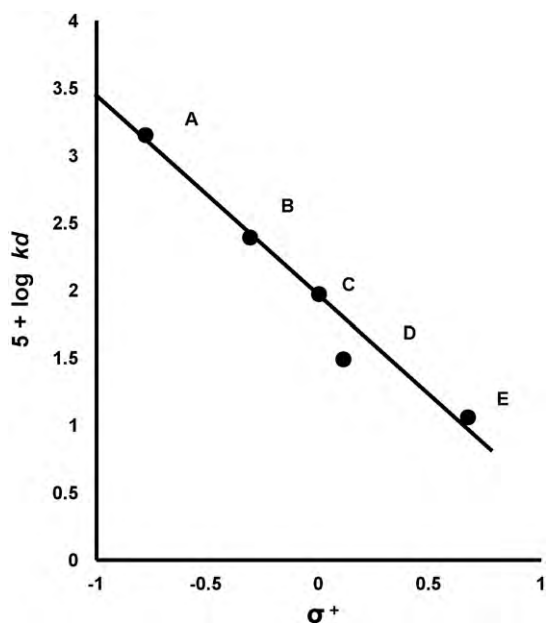


Fig. 11. Plot between $\log kd$ and σ^+ under the conditions of Table 10. (A) *p*-OCH₃, (B) *p*-CH₃, (C) -H, (D) *p*-Cl, and (E) *m*-NO₂.

4.6. Isokinetic relationships

The Hammett' reaction constant (ρ^+) decreases (in magnitude) with increase in temperature, from -1.50 at 308 K to -1.09 at 323 K (Table 9). The Hammett' lines intersect at a point corresponding to an σ^+_{iso} value of -1.30 and a k_{iso} value of $23.02 \times 10^{-3} \text{ s}^{-1}$ (Fig. 8). An oxo acid with a substituent having this σ^+ value (-1.30) will be oxidized by bromate with the same rate at all temperatures. Such an insensitivity of the reaction rate to temperature is a pointer to the existence of an isokinetic phenomenon. Introduction of a nitro group in the phenyl ring, which has a higher σ^+ value results in an increase in the rate constant with temperature.

A reaction series which exhibit a common point of intersection in the Hammett' plot (Fig. 7) is expected to have a common point of intersection in the Arrhenius plot also [52]. The Arrhenius plots are

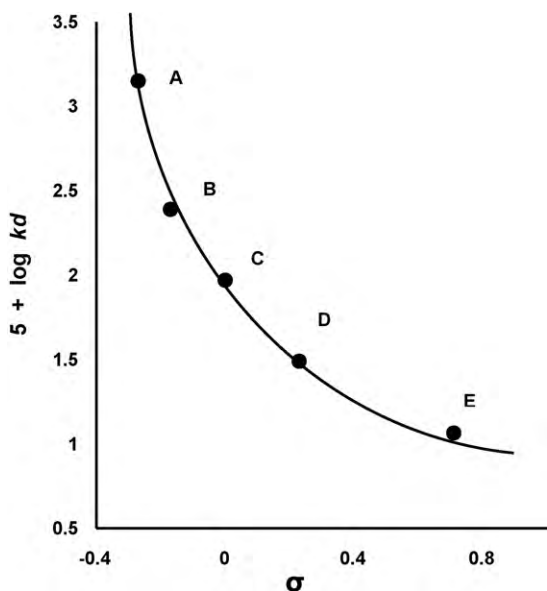


Fig. 12. Plot between $\log kd$ and σ under the conditions of Table 10. (A) *p*-OCH₃, (B) *p*-CH₃, (C) -H, (D) *p*-Cl, and (E) *m*-NO₂.

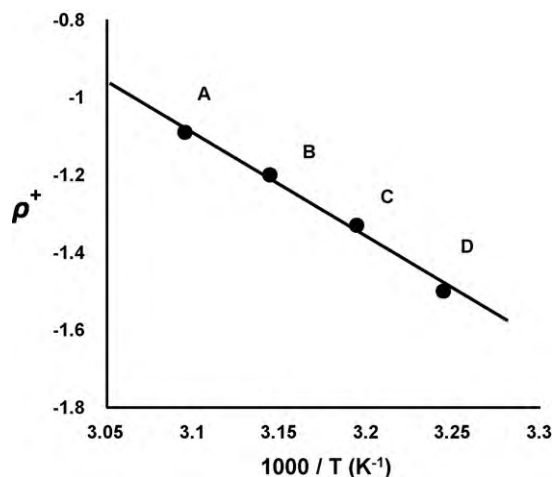


Fig. 13. Plot between ρ^+ against $1/T$ under the conditions of Table 9. (A) 323 K, (B) 318 K, (C) 313 K, and (D) 308 K.

shown in Fig. 4. From the plots of ΔH^\ddagger against ΔS^\ddagger , and ρ^+ against $1/T$ (Fig. 13), the T_{iso} value is found to be 377.3 K, which is in good agreement with the value obtained (375.2 K) from the slope of the Exner's plot (Fig. 6). It is interesting that although the rate constant is composite involving multi-reaction steps—an anti-compensation effect is not observed.

5. Conclusions

From the Hammett and Arrhenius plots associated with isokinetic relationship, it is noted that the ρ^+ values are negative and decrease with increase in temperature. Electron-releasing substituents accelerate the reaction rate and electron-withdrawing substituents retard it. The structure-reactivity correlations are made on the basis of the results obtained and suggest a carbocationic reaction center in the transition state. It can be concluded that V(IV) acts as an efficient catalyst in the oxidation of 4-oxo acids by bromate in acid medium. This reaction is an example of the neighboring group participation and intramolecular catalysis.

The experimental protocol suggests that this reaction could find utility as a regioselective route for the synthesis of carboxylic acids, specially malonic and substituted benzoic acids.

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Appendix A. Supplementary data

$$\begin{aligned} \text{Rate} &= -\frac{d[\text{Br(V)}_T]}{dt} = kd[\text{Complex } C_2][\text{H}^+] \\ &= kdK_f[\text{Complex } C_1][\text{BrO}_3^-][\text{H}^+] \\ &= kdK_fKcKc[\text{V(IV)}][\text{oxo acid}][\text{H}^+][\text{BrO}_3^-] \end{aligned}$$

But, bromate is present in complexed and uncomplexed forms. Hence, the total bromate concentration is given as:

$$\begin{aligned} [\text{Br(V)}]_T &= [\text{BrO}_3^-] + [\text{Complex } C_2] \\ &= [\text{BrO}_3^-] + K_fKcKc[\text{V(IV)}][\text{BrO}_3^-][\text{oxo acid}] \\ [\text{Br(V)}]_T &= [\text{BrO}_3^-] \{1 + K_fKcKc[\text{V(IV)}][\text{oxo acid}]\} \end{aligned}$$

$$\text{BrO}_3^- = \frac{[\text{Br(V)}]_T}{1 + K_f K_c K_e [\text{V(IV)}][\text{oxo acid}]}$$

In terms of total bromate concentration

$$\text{Rate} = \frac{-d[\text{Br(V)}]}{dt} = \frac{k d K_f K_c K_e [\text{H}^+][\text{V(IV)}][\text{oxo acid}][\text{Br(V)}]_T}{1 + K_f K_c K_e [\text{V(IV)}][\text{oxo acid}]}$$

$$\frac{\text{Rate}}{[\text{Br(V)}]_T} = k = \frac{k d K_f K_c K_e [\text{H}^+][\text{V(IV)}][\text{oxo acid}]}{1 + K_f K_c K_e [\text{V(IV)}][\text{oxo acid}]}$$

$$\frac{1}{\bar{k}} = \left[\frac{1}{k d K_f K_c K_e [\text{V(IV)}][\text{oxo acid}]} + \frac{1}{k d} \right] \frac{1}{[\text{H}^+]}$$

At constant (1.0 M) acid concentration

$$\frac{1}{\bar{k}} = \frac{1}{k d K_f K_c K_e [\text{V(IV)}][\text{oxo acid}]} + \frac{1}{k d}$$

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