

## Kinetics and mechanism of oxidation of $\gamma$ -oxoacids by acid permanganate

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Kinetics of oxidation of unsubstituted and substituted  $\gamma$ -oxoacids by acid permanganate in aqueous acetic acid medium have been studied at high and low  $[\text{H}_3\text{O}^+]$ . At high  $[\text{H}_3\text{O}^+]$ , the reaction is first order each in [oxoacid],  $[\text{MnO}_4^-]$  and  $[\text{H}_3\text{O}^+]$ . At low  $[\text{H}_3\text{O}^+]$ , the reaction is zero order in  $[\text{MnO}_4^-]$  and first order each in  $[\text{H}_3\text{O}^+]$  and the [oxoacid]. Variation in ionic strength of the reaction medium has no significant effect on the rate of oxidation. But the rate of the reaction is enhanced by lowering the dielectric constant of the reaction medium. Electron-releasing substituents in the aromatic ring accelerate the reaction rates and electron-withdrawing substituents retard them. The value of the reaction constant ( $\rho$ ) at 303 K (at  $[\text{H}_3\text{O}^+] = 1 \text{ M}$ ) obtained from the Hammett's plot is  $-1.49$  (corr. coeff. = 0.998). A mechanism consistent with the observed results has been suggested and the related rate laws deduced. Activation parameters have been computed.

Kinetics of oxidation of a variety of organic compounds by permanganate have been studied extensively<sup>1-3</sup>. But there is meagre information about the oxidation of  $\gamma$ -oxoacids and the present report incorporate the results of the title investigation.

### Materials and Methods

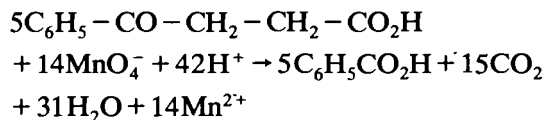
The parent  $\gamma$ -oxoacid, namely, 4-oxo-4-phenylbutanoic acid and the phenyl substituted  $\gamma$ -oxoacids were prepared by the Friedel-Crafts acylation of the substituted benzenes with succinic anhydride<sup>4</sup>. All the chemicals used were Analar grade. Potassium permanganate was used as such and acetic acid was distilled over chromic oxide before use. Perchloric acid was used as a source of hydrogen ions and sodium perchlorate was added to maintain the ionic strength constant. Sodium fluoride was added as a complexing agent to suppress the autocatalysis common in permanganate oxidations<sup>5</sup>.

The kinetics of the reaction was followed titrimetrically by standard iodometric procedure. A large excess of oxoacid was taken as compared to permanganate concentration.

### Product analysis and stoichiometry

The reaction mixture of  $\gamma$ -oxoacid and permanganate was allowed to remain together till the completion of the reaction and the product was found to be the corresponding benzoic acid which was char-

acterised by m.p. and co-IR spectra. The stoichiometric results obtained indicate that one mole of the oxoacid required 2.8 mole of permanganate for oxidation.



### Results and Discussion

A scrutiny of the kinetic data reveals the following

(i) At  $[\text{H}_3\text{O}^+] = 1 \text{ mol dm}^{-3}$ , the reaction shows first order dependence on  $[\text{MnO}_4^-]$  as shown in Table 1 over the initial  $[\text{MnO}_4^-]$  concentration range of  $1.0 \times 10^{-3}$  to  $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ .

(ii) At  $[\text{H}_3\text{O}^+] = 0.04 \text{ mol dm}^{-3}$ , the reaction shows zero order dependence on  $[\text{MnO}_4^-]$  as shown in Table 2.

(iii) The variation of the rate constant at  $1 \text{ mol dm}^{-3} [\text{H}_3\text{O}^+]$  for various [oxoacid] is given in Table 1. The second order rate constant obtained by dividing the observed rate constant by [oxoacid] is found to be constant which indicates that the reaction is first order in [oxoacid].

(iv) Rate measurements in solutions of different  $[\text{HClO}_4]$  in the range 0.5 to 2.0  $\text{mol dm}^{-3}$  (as shown in Table 1) indicate that the reaction is first order in  $[\text{H}_3\text{O}^+]$ . The plot of  $\log k_{\text{obs}}$  against  $\log [\text{H}_3\text{O}^+]$  is

Table 1—Oxidation of  $\gamma$ -oxoacid, 4-oxo-4-phenylbutanoic acid by acid permanganate

$[\text{NaClO}_4] = 5 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $[\text{NaF}] = 5 \times 10^{-2} \text{ mol dm}^{-3}$ ;  
Solvent = HOAc (30% v/v); temp. = 303 K

$10^3[\text{KMnO}_4]$ (mol dm <sup>-3</sup> )	$10^2[\text{oxoacid}]$ (mol dm <sup>-3</sup> )	$[\text{H}^+]$ (mol dm <sup>-3</sup> )	$10^5 k_1$ (s <sup>-1</sup> )
1.0	2.0	1.0	6.90
2.0	2.0	1.0	6.85
3.0	2.0	1.0	6.82
4.0	2.0	1.0	6.84
5.0	2.0	1.0	6.83
2.0	1.0	1.0	3.41
2.0	3.0	1.0	10.23
2.0	4.0	1.0	13.71
2.0	5.0	1.0	17.13
2.0	3.0	0.5	5.32
2.0	3.0	1.25	12.80
2.0	3.0	1.5	16.12
2.0	3.0	2.0	20.16

Table 2—Oxidation of 4-oxo-4-phenylbutanoic acid by acid permanganate at  $[\text{H}_3\text{O}^+] = 0.004 \text{ mol dm}^{-3}$

$[\text{NaF}] = 0.05 \text{ mol dm}^{-3}$ ;  $[\text{H}_3\text{O}^+] = 0.04 \text{ mol dm}^{-3}$ ;  
Solvent = 50% HOAc; temp. = 303 K

$[\text{NaClO}_4] = 0.05 \text{ mol dm}^{-3}$ ;  $[\text{oxoacid}] = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$

$10^3[\text{KMnO}_4]$ (mol dm <sup>-3</sup> )	$10^5$ (first order rate constant) (s <sup>-1</sup> )	$10^3 \times$ (Zero order rate constant) (mol dm <sup>-3</sup> s <sup>-1</sup> )
2.0	1.65	3.365
3.0	1.017	3.358
4.0	0.640	3.349

linear with unit slope revealing that the reaction is first order in  $[\text{H}_3\text{O}^+]$  in the above  $[\text{H}_3\text{O}^+]$  range.

(v) The change in the polarity of the medium has a marked effect on the reaction rate. As acetic acid percentage is increased three times, the reaction rate also increases by about three times. For instance under the conditions:

$$[\text{Oxoacid}] = 0.025 \text{ mol dm}^{-3},$$

$$[\text{MnO}_4^-] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[\text{H}^+] = 1.0 \text{ mol dm}^{-3}; [\text{NaClO}_4] = 0.05 \text{ mol dm}^{-3}$$

$[\text{NaF}] = 0.05 \text{ mol dm}^{-3}$  and  $T = 303 \text{ K}$ , the rate constant increases from  $6.90 \times 10^{-5} \text{ s}^{-1}$  to  $18.61 \times 10^{-5} \text{ s}^{-1}$  for the parent oxoacid when acetic acid percentage increases from 20% to 60%. The trend in the rate observed may be due to more than one factor. It may be attributed to the lowering of dielectric constant of the medium which favours reactions involving protonation. Further, the enoli-

sation of the oxoacid may be catalysed by acetic acid and this may also contribute to rate enhancement.

A mechanism has been proposed involving the attack of permanganic acid on the enol form of the substrate in the rate determining step. The protonation of permanganate ion leads to the formation of permanganic acid<sup>6,7</sup>. The enolisation is proposed to be the necessary step prior to the oxidation of the substrate; the above two are assumed following the mechanism suggested for acid catalysed permanganate oxidation of ketones<sup>8,9</sup>. The mechanism is given in Scheme 1.

The reaction involves two protons, one for the formation of  $\text{HMnO}_4$  and another for the enolisation of the oxoacid. Hence, the reaction could be expected to exhibit second order dependence on  $[\text{H}_3\text{O}^+]$ . But the experimental results indicate (a) first order dependence only on  $[\text{H}_3\text{O}^+]$  whether the mineral acid concentration is high or low, (b) first order dependence only on  $[\text{oxoacid}]$  again at high and low mineral acid concentration and (c) first order dependence on  $[\text{MnO}_4^-]$  at high mineral acid concentration and zero order dependence on  $[\text{MnO}_4^-]$  at low mineral acid concentration.

These results can be explained using the limiting conditions of high and low  $[\text{H}_3\text{O}^+]$  as follows

$$-\frac{d}{dt}[\text{MnO}_4^-] = \frac{k_2 k_3 k_4 [\text{H}_3\text{O}^+] [\text{X}] [\text{HMnO}_4]}{(k_{-2} k_{-3} [\text{H}_3\text{O}^+] + k_4 (k_{-2} + k_3) [\text{HMnO}_4])} \quad \dots (7)$$

At high mineral acid concentration  $k_{-2} k_{-3} [\text{H}_3\text{O}^+] > k_4 (k_{-2} + k_3) [\text{HMnO}_4]$ .

Hence Eq. 7 simplifies to the form,

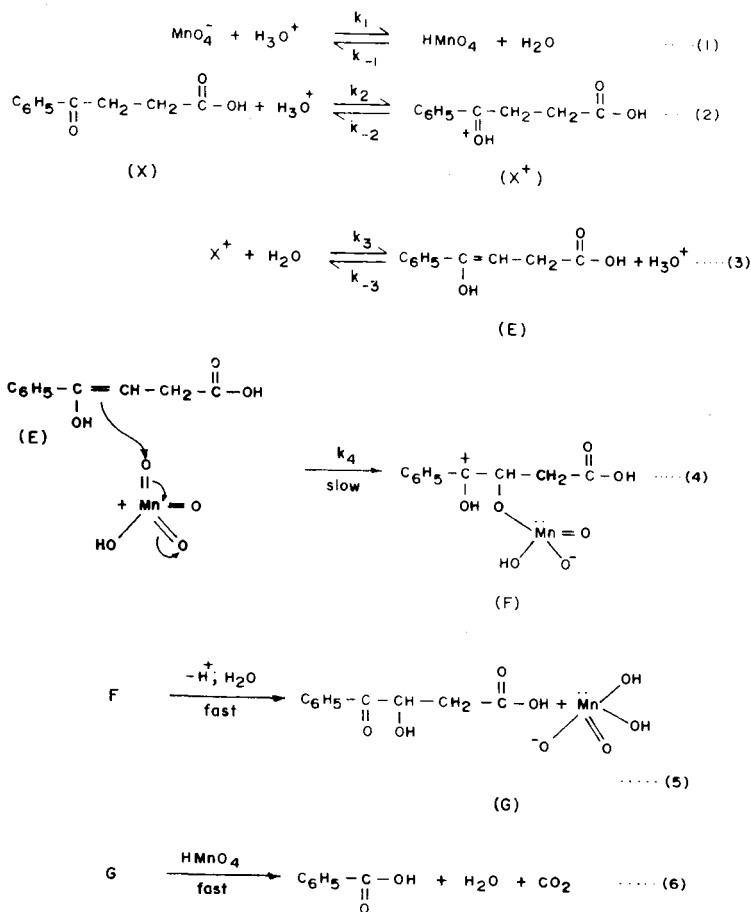
$$-\frac{d}{dt}[\text{MnO}_4^-] = \frac{k_2 k_3 k_4 [\text{H}_3\text{O}^+] [\text{X}] [\text{HMnO}_4]}{k_{-2} k_{-3} [\text{H}_3\text{O}^+]}$$

$$= \frac{k_2 k_3 k_4 [\text{X}]}{k_{-2} k_{-3}} [\text{HMnO}_4]$$

$$\text{i.e. } -\frac{d}{dt}[\text{MnO}_4^-] = \frac{k_2 k_3 k_4 [\text{X}] [\text{MnO}_4^-] [\text{H}_3\text{O}^+]}{k_{-2} k_{-3} K_a} \quad \dots (8)$$

where the dissociation constant of  $\text{HMnO}_4$ ,

$$K_a = \frac{[\text{MnO}_4^-] [\text{H}_3\text{O}^+]}{[\text{HMnO}_4]}$$



Scheme 1

Hence observed rate constant at high

$$[\text{H}_3\text{O}^+] = \frac{k_2 k_3 k_4}{k_{-2} k_{-3} K_a} \quad \dots (9)$$

At lower mineral acid concentration,

$$k_4(k_{-2} + k_3)[\text{HMnO}_4] > k_{-2} k_{-3} [\text{H}_3\text{O}^+]$$

Hence Eq. 7 becomes,

$$\begin{aligned} -\frac{d}{dt} [\text{MnO}_4^-] &= \frac{k_2 k_3 k_4 [\text{H}_3\text{O}^+] [\text{X}] [\text{HMnO}_4]}{k_4(k_{-2} + k_3) [\text{HMnO}_4]} \\ &= \frac{k_2 k_3}{(k_{-2} + k_3)} [\text{H}_3\text{O}^+] [\text{X}] \quad \dots (10) \end{aligned}$$

Possibly under conditions of lower acidity enol removal (step 4) is faster than enol formation (step 3) and at higher acidity conditions, the enol removal is less rapid than its formation. Such a difference in order with respect to oxidant concentrations under the conditions of high and low  $[\text{H}_3\text{O}^+]$  has been reported

ed<sup>10,11</sup> in the oxidation of cyclohexanone by  $\text{IrCl}_6^{2-}$  and tris-2,2'-bipyridylruthenium(III) ion.

Again in step 4,  $\text{Mn}^{\text{VII}}$  is reduced to  $\text{Mn}^{\text{V}}$  as hypomanganate ester (F) and this is followed by its hydrolysis to form the  $\alpha$ -hydroxy ketone (G) which undergoes further oxidation. The formation of hypomanganate is believed to be a reaction intermediate in the acid medium permanganate oxidation of many organic and inorganic compounds<sup>12</sup>.

The observed rate constant under high  $[\text{H}_3\text{O}^+]$  is of composite nature as shown in Eq. 9. Consequently the observed  $\rho$  value is also dependent on  $k_2$ ,  $k_3$ ,  $k_4$ ,  $k_{-2}$  and  $k_{-3}$ . No attempt has been made to resolve the  $\rho$  value into its components. Special mention needs to be made about the enolisation (step 3) of the substrate. In the bromination of the title compounds for which enolisation is the rate determining step it has been reported that  $\rho$  value is  $-0.75$  (ref. 13).

The order of reactivity is: *p*-methoxy > *p*-ethoxy > *p*-methyl > *p*-ethyl > H > *p*-phenyl > *p*-chloro > *p*-bromo > *m*-nitro. The Hammett plot is linear with a slope giving  $\rho = -1.49$  at 303 K.

Table 3—Rate constants and activation parameters

Substituent	$10^5 k_1 (s^{-1})$				$\Delta H^\ddagger$ (KJ mol <sup>-1</sup> )	$-\Delta S^\ddagger$ (JK <sup>-1</sup> mol <sup>-1</sup> )
	303	313	323	333 K		
H	6.85	12.94	25.24	45.82	51.17	123.49
-p-C <sub>6</sub> H <sub>5</sub>	6.64	12.88	24.04	44.77	51.37	123.04
-p-Cl	3.32	7.43	13.52	24.04	52.43	119.86
-p-Br	3.03	6.78	11.51	20.94	53.67	116.40
-m-NO <sub>2</sub>	0.66	1.48	3.90	6.04	61.41	96.42
-p-C <sub>2</sub> H <sub>5</sub>	12.05	20.94	39.91	66.23	45.77	136.53
-p-CH <sub>3</sub>	12.91	24.05	44.77	70.96	45.64	136.38
-p-OC <sub>2</sub> H <sub>5</sub>	17.02	28.25	52.61	93.55	45.51	134.51
-p-OCH <sub>3</sub>	19.10	30.27	56.37	102.57	44.90	135.58

The activation parameters evaluated (Table 3) indicate negative entropy of activation. The value of isokinetic temperature is found to be 425 K. This is in close agreement with the value obtained from the plot of  $\Delta H^\ddagger$  against  $\Delta S^\ddagger$ .

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