

Kinetics and Mechanism of Oxidation of Malonic Acid with Bi(V) in HClO₄-HF Mixture

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The kinetics of oxidation of malonic acid with Bi(V) has been investigated in HClO₄ (1.0 M) and HF (1.50 M) mixture. The rate followed first order kinetics each in Bi(V) and malonic acid. The reaction rate is independent of [H⁺]. Addition of HF and (F⁻) ion has not effect on the reaction rate. The reaction rates decreased with the increase in ionic strength. The mode of electron transfer from the substrate to Bi(V) has been indicated *via* bridged outer sphere mechanism.

Key Words: Kinetics, Oxidation, Malonic acid, Bi(V), HClO₄, HF.

INTRODUCTION

Though Bi(V) has useful synthetic and analytical applications¹⁻³ but its solution chemistry has not been well explored due to the inability to get Bi(V) in the solution in common solvent. However, Bi(V) is obtained in solution⁴ in a mixture of HClO₄ (1.50 M) and HF (1.0 M) and is stable for long when refrigerated. The oxidation of malonic acid with Bi(V) in HClO₄-HF mixture was undertaken for investigation to elucidate the mode of electron transfer from the substrate to the oxidant. Keeping in view of the fact that the redox reaction involving malonic acid are of interests both from chemical as well as industrial points of view.

EXPERIMENTAL

Preparation and standardization of Bi(V) solution: A known quantity of sodium bismuthate (BDH AnalaR) was digested in known volume of the mixture of HF (1.50 M) and HClO₄ (1.0 M) and filtered for undissolved salt. The filtrate gave a clear and colourless solution of Bi(V). The solution of Bi(V) was standardized by known methods⁹. A known volume of Bi(V) solution was added to KI (0.1 M) solution and pH of the solution was adjusted to 2-3 with NaOH solution. The titration was carried out only in presence of EDTA with the standardized Na₂S₂O₃ solution. Stock solution of an appropriate concentration of malonic acid was prepared. All

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others chemicals were either of AnalR or G.R. grade. Doubly distilled and CO₂ free water used throughout the investigation work.

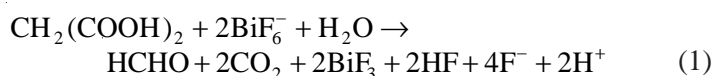
Reactions were conducted in a Teflon bottle immersed in water bath thermostated at a desired temperature. The kinetic of the reaction was motivated by withdrawing aliquots of 5.0 mL at different intervals of time and estimating the remaining Bi(V) iodometrically as reported earlier⁹.

RESULTS AND DISCUSSION

The stoichiometry of the reaction was determined by taking an excess of Bi(V) concentration over that of malonic acid at fixed concentration of [HClO₄] = 1.0 mol dm⁻³ and [HF] = 1.5 mol dm⁻³. These reaction mixture were kept in a thermostated water bath at 20°C and the excess of Bi(V) was determined iodometrically^{5,6} after ensuring the completion of the reaction after 12 h. The stoichiometry of the reaction was found to be 2:1 *i.e.* two mol of Bi(V) reacted with one mol of malonic acid.

The higher ratios of $\frac{\Delta[\text{Bi(V)}]}{\Delta[\text{Acid}]}$ are ascribed

the decomposition of Bi(V). The stoichiometry can be represented by the equation.



The oxidation product of malonic acid was detected by conventional method. The oxidation product of malonic acid had also been found as CO₂ by other workers^{9,10}.

Bismuth(V) dependence: The concentration of Bi(V) was varied from 0.4×10^{-3} - 3×10^{-3} mol dm⁻³ at fixed concentration of malonic acid (1.0×10^{-2} mol dm⁻³). The initial rate were computed by plan mirror method⁷. The plot of initial rate (i.r.) *vs.* Bi(V) yielded straight line passing through passing through the origin indicating first order in Bi(V). The values of second order rate constant (k) calculated from initial rates at different temperatures are given in Tables 2-4.

Malonic acid dependence: The concentration of malonic acid (H₄C₃O₄) was varied in the range 0.4×10^{-2} - 0.95×10^{-2} mol dm⁻³ at a fixed concentration of Bi(V) *i.e.* 2.0×10^{-3} mol dm⁻³ and also at a fixed concentration of [HClO₄] = 1.0 mol dm⁻³ and [HF] = 1.5 mol dm⁻³ (Tables 2-4). Initial rates were calculated by plan mirror method⁷. The plot of initial rate (i.r.) *vs.* the concentration of malonic acid has zero intercept on the ordinate yielding a straight line. Thus the order with respect to malonic acid (H₄C₃O₄) was found to be one.

Hydrogen ion dependence: [H⁺] was varied by changing the concentration of HClO₄ (1.0 mol dm⁻³ - 2.25 mol dm⁻³) at a fixed concentration of Bi(V) (2.0×10^{-3} mol dm⁻³), malonic acid (1.1×10^{-2} mol dm⁻³) and also at

fixed ionic strength ($I = 2.50 \text{ M}$) adjusted with requisite quantity of LiClO_4 solution. It was assumed that at the high concentration of HClO_4 there was no contribution of HF towards $[\text{H}^+]$ *i.e.* H^+ ion concentration was due to the contribution by HClO_4 only. The reaction rates remained unaffected by changing $[\text{H}^+]$.

TABLE-1
STOICHIOMETRIC RESULTS OF OXIDATION OF MALONIC ACID
WITH Bi(V) IN HClO_4 (1.0 M) – HF (1.5 M) MIXTURE AT 20°C

$[\text{Bi(V)}] \times 10^3 \text{ M}$	$[\text{H}_4\text{C}_3\text{O}_4] \times 10^3 \text{ M}$	$[\Delta\text{Bi(V)}]/[\text{H}_4\text{C}_3\text{O}_4]$
4.1	1.0	2.10
4.7	1.5	2.12
6.4	1.5	2.10
8.2	2.0	2.11
10.0	2.0	2.12

TABLE-2
PSEUDO-FIRST ORDER (k^o) AND SECOND ORDER RATE
CONSTANT (k) FOR REACTION BETWEEN Bi(V) AND MALONIC
ACID IN HClO_4 (1.0 M) – HF (1.5 M) MIXTURE AT 20°C

$[\text{Bi(V)}] \times 10^3 \text{ M}$	$[\text{H}_4\text{C}_3\text{O}_4] \times 10^3 \text{ M}$	(i.r.) $\times 10^6 \text{ M s}^{-1}$	$k \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$
0.4	10.0	0.29	
0.6	10.0	0.43	
0.8	10.0	0.57	
1.0	10.0	0.70	
1.2	10.0	0.84	
1.5	10.0	1.05	
1.8	10.0	1.26	
2.0	10.0	1.40	
2.5	10.0	1.75	
3.0	10.0	2.10	7.1
2.0	4.0	4.00	
2.0	5.0	5.04	
2.0	6.0	6.04	
2.0	7.0	7.04	
2.0	7.5	7.60	
2.0	8.0	8.08	
2.0	9.0	9.08	
2.0	9.5	9.60	

Ionic strength dependence: Ionic strength changed in the range (1.0 mol dm^{-3} - 2.5 mol dm^{-3}) adjusted by adding LiClO_4 solution. The reaction rates decreased with the increase in ionic strength indicating that reacting species are ion (BiF_6^-) and neutral molecules malonic acid⁸.

TABLE-3
SECOND ORDER RATE CONSTANT (k_0) FOR REACTION BETWEEN
Bi(V) AND MALONIC ACID IN HClO₄ (1.0 M) – HF (1.5 M)
MIXTURE AT 25°C

[Bi(V)] × 10 ³ M	[H ₄ C ₃ O ₄] × 10 ³ M	(i.r.) × 10 ⁶ M s ⁻¹	k × 10 ² M ⁻¹ s ⁻¹
0.4	10.0	0.38	
0.6	10.0	0.56	
0.8	10.0	0.76	
1.2	10.0	1.15	
1.5	10.0	1.43	
1.8	10.0	1.72	
2.0	10.0	1.91	
2.5	10.0	1.39	
3.0	10.0	2.87	
2.0	4.0	3.98	9.3
2.0	5.0	4.96	
2.0	6.0	5.94	
2.0	7.0	6.94	
2.0	7.5	7.44	
2.0	8.0	7.94	
2.0	8.5	8.44	
2.0	9.0	8.96	
2.0	9.5	9.42	

TABLE-4
SECOND ORDER RATE CONSTANT (k) FOR REACTION BETWEEN
Bi(V) AND MALONIC ACID IN HClO₄ (1.0 M) – HF (1.5 M)
MIXTURE AT 30°C

[Bi(V)] × 10 ³ M	[H ₄ C ₃ O ₄] × 10 ³ M	(i.r.) × 10 ⁶ M s ⁻¹	k × 10 ² M ⁻¹ s ⁻¹
0.4	10.0	0.42	
0.6	10.0	0.64	
0.8	10.0	0.85	
1.2	10.0	1.28	
1.5	10.0	1.59	
1.8	10.0	1.91	
2.0	10.0	2.13	
2.5	10.0	2.65	
3.0	10.0	3.19	
2.0	4.0	4.30	10.6
2.0	5.0	5.36	
2.0	5.5	5.92	
2.0	6.0	6.44	
2.0	6.5	6.98	
2.0	7.0	7.56	
2.0	7.5	8.08	
2.0	8.0	8.60	
2.0	8.5	9.18	
2.0	9.0	9.74	

Effect of HF and F⁻: The reaction kinetics were followed by changing [HF] in the range (0.75 - 2.0 mol dm⁻³), [NaF], in the range (0.1-0.5 mol dm⁻³). In each case the reaction rates remained unchanged. As the reaction rates were independent of [HF] and [NaF], it is suggested that reactive species are (BiF₆⁻) in the mixture of HClO₄ and HF as has also been assumed in the reaction of Bi(V) with hypophosphorus acid⁹, phosphorus acid¹⁰ and aspartic acid¹¹. Such an assumption is also strengthened by like complexes of Sb(V) in HCl medium^{12,13}.

The proper speciation of Bi(V) is hindered due to non-absorbing nature of Bi(V) fluoro complexes in UV and visible region⁴ and corrosive effect of HF on glass and metals.

Effect of Bi(III): The concentration of Bi(III) was varied from 2.5×10^{-3} to 1.0×10^{-3} mol dm⁻³ at fixed concentration of Bi(V) = 1.0×10^{-2} mol dm⁻³, malonic acid = 1.1×10^{-2} mol dm⁻³. The rate of reaction remains unchanged with the changing concentration of Bi(III) indicating that the Bi(III) is not involving in any equilibrium proceeded by the rate determining step in the reactions mechanism.

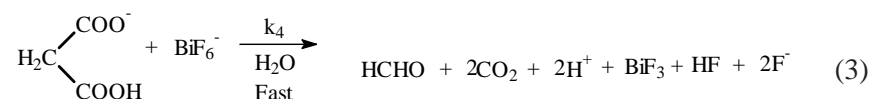
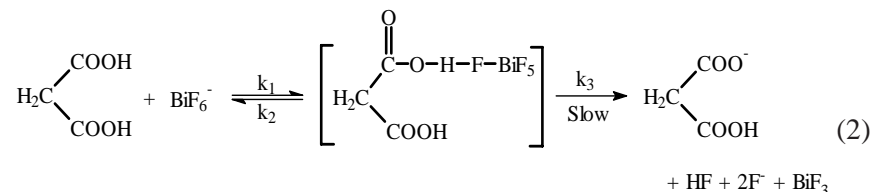
Temperature dependence: The rate of the reaction was computed at three different temperatures 20, 25 and 30°C. The energy of activation and other parameters were calculated. Energy of activation (E_a) was calculated from the plot of log k vs. 1/T. The results are given in the Table-5.

TABLE-5
TEMPERATURE DEPENDENCE OF OXIDATION REACTION OF
MALONIC ACID WITH Bi(V) IN HClO₄ – HF MIXTURE

Temp. (°C)	3 + log k	10 ³ 1/T
20	1.85	3.41
25	1.97	3.36
30	2.03	3.30

As the reaction rates are independent of [NaF] and [HF] it is obvious that the ultimate fluorospecies of Bi(V) are involved and as such there appears to be non-involvement of NaF and HF in any equilibrium step proceeded by the rate determining step. A detailed information about the fluorospecies of Bi(V) in HClO₄-HF mixture is lacking and thus it is assumed that Bi(V) exist as BiF₆⁻ and protonated from HBiF₆.

Considering BiF₆⁻ and CH₂(COOH)₂ as reactive species in the reaction. A plausible mechanism in conformity with the above experimental facts may be suggested as.



Applying steady state approximation, the rate law has been derived as

$$\begin{aligned}
 -\frac{d[\text{Bi(V)}]}{dt} &= \frac{k_1 k_3 k_4}{k_2 + k_3 k_4} [\text{CH}_2(\text{COOH})_2][\text{Bi(V)}] \\
 &= k[\text{CH}_2(\text{COOH})_2][\text{Bi(V)}] \quad \text{or, } k^o = k[\text{CH}_2(\text{COOH})_2]
 \end{aligned}$$

where k^o = Pseudo first order rate constant (observed) and k = Observed second order rate constant.

Plot of k^o vs. $[\text{CH}_2(\text{COOH})_2]$ was linear passing through the origin in conformity with the rate law. The constant (k) was calculated from the slope ($k = 8 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). Intermediate complex with hydrogen bonding assists in bringing Bi(V). The kinetic investigation were carried out at 20, 25 and 30°C and calculated second order rate constant (k) are found to be $(7.1 \pm 0.2) \times 10^{-2}$, $(9.3 \pm 0.31) \times 10^{-2}$ and $(10.6 \pm 0.12) \times 10^{-2} \text{ mol}^{-2} \text{ dm}^3 \text{ s}^{-1}$, respectively. The thermodynamic parameters were calculated in a conventional method. The energy of activation (E_a) and entropy of activation (ΔS^*) are found to be $25.08 \pm 0.34 \text{ KJ mol}^{-1}$ and $-118.32 \pm 2 \text{ J K}^{-1}$, respectively at 20°C (Table-6). The low value of energy of activation but high negative value of entropy of activation may be ascribed to the hydrogen bond intermediate, which causes a facile electron transfer from oxygen atom to Bi(V).

TABLE-6
THERMODYNAMIC PARAMETERS OF OXIDATION REACTION
OF MALONIC ACID WITH Bi(V) IN HClO₄ – HF

log A (s ⁻¹)	3.32
E _a (KJ mol ⁻¹)	25.08
ΔG (KJ)	-4.77
ΔH (KJ)	22.64
ΔS (J K ⁻¹)	-181.32

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