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Kinetics and Mechanism of Oxidation of Formaldehyde with Bi(V) in $HClO_4$-HF Mixture

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Kinetics of oxidation of formaldehyde with Bi(V) fluoride complex have been investigated in $HClO_4$-HF mixture. The reaction is first order in each reactant. Hydrogen ion and ionic strength (HF) and added fluoride (F^-) have no effect on the reaction rates. The mode of electron transference for the substrate (HCOOH) to the oxidant [Bi(V)] has been indicated *via.* a bridged outer sphere mechanism.

INTRODUCTION

Though Bi(V) has useful synthetic and analytical applications[1-3] but its solution chemistry has not been well explored due to the inability to get Bi(V) in solution in common solvent. However, Bi(V) is obtained in solution[4] in a mixture of $HClO_4$ (1.0 M) and HF (1.50 M) and is stable for long when refrigerated. The title reaction was undertaken for investigation to elucidate the mode of electron transference from the substrate the oxidant and also keeping in view the fact that the redox reaction involving aldehydes are of interests both from pure chemical and industrial points of view.

EXPERIMENTAL

Preparation and standardisation of Bi(V) solution: A known quantity of sodium bismuthate (BDH AnalaR) was digested in a known volume of the mixture of HF (1.50 M) and $HClO_4$ (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 standardised by modified iodometric method[5]. 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. Then the titration was carried out only in presence of EDTA with standardised $Na_2S_2O_3$ solution. Stock solution of an appropriate concentration of formaldehyde was prepared. All other chemicals were either of AnalaR or G.R. grade. Doubly distilled and CO_2 free water was used throughout the investigation work.

Reactions were conducted in a teflon bottle immersed in a water bath thermostated at desired temperature. The kinetics 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 stated above.

Kinetic investigations were carried out under pseudo-first order conditions

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taking [formadehyde] in excess over [Bi(v)]. It was noticed that HCOOH did not oxidise into CO_2 when the concentration of HCOOH was below 2×10^{-3} M. Under the experimental condition the concentration of HCOOH produced would be always around 1×10^{-3} M. So any possibility of further oxidation of HCOOH into CO_2 was ruled out.

RESULTS AND DISCUSSION

Stoichiometry: The stoichiometry of the oxidation reaction with an excess of concentration of Bi(V) over that of formaldehyde corresponded to the reaction represented by equation

$$\underset{\text{Hydrated form of formaldehyde}}{H_2C(HO)_2} + BiF_6^- = HCOOH + 2HF + BiF_3 + F^-$$

Kinetics: The concentrations of Bi(V) and HCHO were varied in the range (0.3×10^{-3} M–2.0×10^{-3} M) and (1×10^{-3} M–5×10^{-3} M) respectively and a fixed concentration of $HClO_4$ (1.0 M) and HF (1.50 M). Initial rates were computed by plane mirror method. The plots of initial rates *vs.* [Bi(V)] and initial rates *vs.* [HCHO] yielded straight lines passing through the origin indicating 1st order with respect to each reactant (Fig. 1(A) and (B) and Table-1)

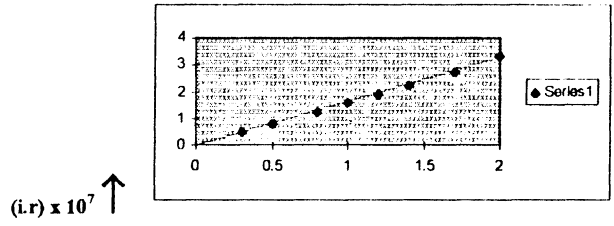


Fig. 1 (A). Plot of initial rates (i.r.) *vs.* [Bi(V)], [HCHO] = 4.0 times 10^3 mol dm^{-3} [$HClO_4$] = 1.0 mol dm^{-3}, [HF] = 1.50 mol dm^{-3}

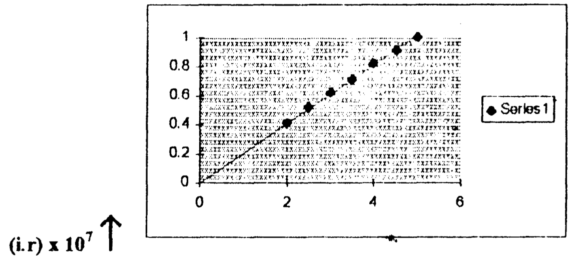


Fig. 1 (B). Plot of initial rates (i.r.) *vs.* [HCHO], [Bi(V)] = 0.5×10^3 mol dm^{-3} [$HClO_4$] = 1.0 mol dm^{-3} [HF^-] = 1.50 mol dm^{-3}

The value of (k_{obs}) increased linearly with the increase in [HCHO] exhibiting first order with respect to HCHO.

The second order rate constants (k) were calculated from (k_{obs}) against [HCHO] plots and are collected in Table-1.

TABLE-1
SECOND ORDER RATE CONSTANT (k) FOR THE REACTION BETWEEN Bi(V) and HCHO in $HClO_4$-HF MIXTURE

$[HClO_4] = 1.0$ mol dm^{-3}, [HF] = 1.50 dm^{-3}, Temp. – 20°C

$[Bi(V)] \times 10^3$ (mol dm^{-3})	$[HCHO] \times 10^4$ (mol dm^{-3})	$(I.R.) \times 10^7$ (mol dm^{-3} s^{-1})	$k_{obs} \times 10^4$ (s^{-1})	$k \times 10^{-2}$ (dm^{-3} mol^{-1} s^{-1})
0.3	4.0	0.48	1.60	4.0
0.5	4.0	0.80	1.60	4.0
0.8	4.0	1.25	1.56	3.9
1.0	4.0	1.60	1.60	4.0
1.2	4.0	1.90	1.58	3.9
1.4	4.0	2.20	1.57	3.9
1.7	4.0	2.70	1.59	4.0
2.0	4.0	3.32	1.60	4.0
0.5	2.0	0.41	0.80	4.0
0.5	2.5	0.52	1.00	4.0
0.5	3.0	0.62	1.20	4.0
0.5	3.5	0.71	1.40	4.0
0.5	4.0	0.82	1.60	4.0
0.5	4.5	0.91	1.80	4.0
0.5	5.0	1.00	2.00	4.0

I.R.—Initial rates

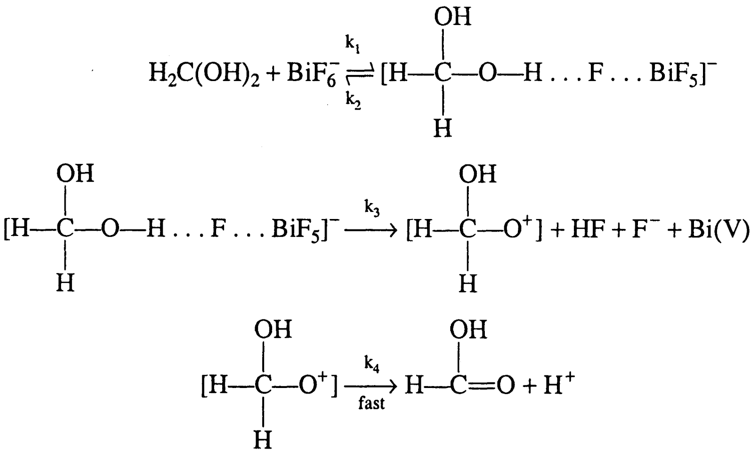
Hydrogen ion dependence: $[H^+]$ was varied by changing the concentration of $HClO_4$ at fixed concentration of Bi(V). (1.0×10^{-3} M) $[HCHO] = 4 \times 10^{-3}$ and also at a fixed ionic strength (I = 2.50) adjusted with requisite quantity of $LiClO_4$ solution. The reaction rates remained unaffected. It may be assumed that HF did not contribute towards $[H^+]$ under the high concentration of $HClO_4$ (1.0 M). So $[H^+]$ was due to $HClO_4$ only.

Effect of ionic strength: The ionic strength was varied in the range (1.0–2.5 M) with requisite quantity of $HClO_4$ at a fixed concentration of

$$Bi(V) = 1.0 \times 10^{-3}\ M, \quad [HCHO] = 4 \times 10^{-3}\ M$$
$$HF = 1.5\ M, \quad HClO_4 = 1.0\ M$$

The reaction rates decreased with the increase in ionic strength showing the interaction between a neutral molecule (HCHO) and a charged species (BiF_6^-) or charged species of opposite nature.

Effect of HF and (F^-): The reaction kinetics were followed by changing [HF] in the range (0.75–2.0 M), [NaF] in the range (0.1 M–0.5 M). In each case the reaction rates remained unaffected. As the reaction rates were independent of [HF] and [F^-] it is assumed that reactive species are [BiF_6^-] in the mixture of $HClO_4$-HF. This fact has been established by other workers[7–9] also. Keeping the point in view that formaldehyde exits in hydrated form in aqueous solution. a plausible mechanism in conformity with the experimental observation may be suggested as



$$H_2C(OH)_2 + BiF_6^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [H-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-O-H\ldots F\ldots BiF_5]^-$$

$$[H-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-O-H\ldots F\ldots BiF_5]^- \xrightarrow{k_3} [H-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-O^+] + HF + F^- + Bi(V)$$

$$[H-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-O^+] \xrightarrow[\text{fast}]{k_4} H-\overset{\overset{OH}{|}}{C}=O + H^+$$

Applying steady state treament the rate law was derived as:

$$-\frac{dBi(V)}{dt} = \frac{k_1k_3k_4[HCHO][Bi(V)]}{k_2 + k_3k_4}$$

$$= k[HCHO][Bi(V)]$$

where $k = \dfrac{k_1k_3k_4}{k_2 + k_3k_4}$ second order rate constant

$k_{obs} = k[HCHO]$

Plot of k_{obs} *vs.* [HCHO] yielded a straight line passing through the origin in conformity with the rate law. The value of k was calculated from the slope ($k = 4 \times 10^{-2}$ mol dm^{-3} s^{-1} at 20°C) (Fig. 1(C)).

Kinetic investigations were carried out at 20, 25 and 30°C and calculated second order rate constants (k) are found to be 4×10^{-2} dm^3 mol^{-1} s^{-1}, 5.4×10^{-2} dm^3 mol^{-1} s^{-1} and 7×10^{-2} dm^3 mol^{-1} 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 42.31 kJ mol^{-1} and –127.33 J K^{-1} mol^{-1} respectively at 20°C. The low value of energy of activation but higher value of entropy of activation may be ascribed to the outer sphere bridged intermediate. The hydrogen bonding permits a facile electron transference from oxygen atom to Bi(V) leading to internal oxidation reduction.

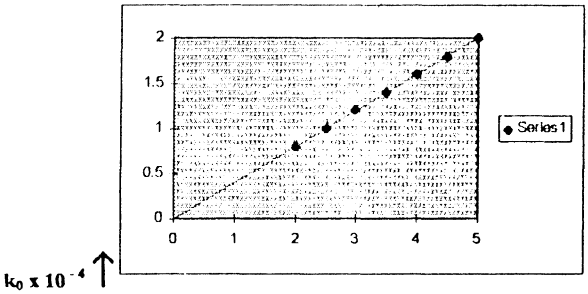


Fig. 1 (C). Plot of k_0 *vs.* [HCHO], [Bi(v)] = 0.5×10^3 mol dm^{-3}, [$HClO_4$] = 1.0 mol dm^{-3}, [HF] = 1.5 mol dm^{-3}, [I] = 2.50 mol dm^{-3}, Temp. = 20°C

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