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

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Kinetics of oxidation of acetophenone oxime and its para substituted derivatives with Bi(V) fluoride complex is studied in $HClO_4$ (1.0 M) and HF (1.5 M) mixture at 30°C. The product analysis indicates that the rate increases with the increase in concentration of hydrogen ions. The rate follows first order kinetics each in Bi(V) and oxime. The mode of electron transfer from the substrate to the Bi(V) has been indicated *via* bridged outer sphere mechanism. The mechanism involving the formation of an iminoxy radical in the rate determining step is proposed.

Key Words: Acetophenone oxime, Perchloric acid, Bi(V).

INTRODUCTION

Bi(V) has useful synthetic applications[1-3] but its solution chemistry has not been well explored due to inability to get it in solution. However, in mixture of HF (1.50 M) and $HClO_4$ (1.0 M), digestion of sodium bismuthate gave a transparent solution which is stable at ambient temperature[4].

Oxidative hydrolysis[5] of oximes is generally utilized for the preparation of ketones since acid hydrolysis of oximes to ketones does not proceed in high yield. There is no work done on the kinetics of oxidative hydrolysis of the substituted acetophenone oximes with Bi(V). It has been observed that Bi(V) in $HClO_4$-HF mixture converts acetophenone oximes (APO) or its para-substituted compounds into respective ketones at a measurable rate. The kinetic study is carried out in $HClO_4$-HF mixture and mode of electron transference substrate to the oxidation.

EXPERIMENTAL

Preparation and standardization of Bi(V) solution

Sodium bismuthate [BDH 85%] was used as a source of Bi(V). A known quantity of sodium bismuthate was digested in a known volume of mixture of HF (1.50 mol dm^{-3}) and $HClO_4$ (1.0 mol dm^{-3} and filtered for undissolved salt. The filtrate gave a transparent solution of Bi(V). The solution was standardized by modified iodometric method adopted by Wright *et al.*[6] and Gupta *et al.*[6].

The remaining chemicals are used of AnalaR or GR grade acetophenone oxime or its *p*-substituted derivative were prepared from the corresponding ketones by the standard procedure. The oximes were dissolved in N,N′-dimethylformamide

(DMF) (E. Merck) and the resulting solution was used in studies. The reaction was verified spectrophotometrically and was found to be pseudo first order. The decrease in the absorbance due to disappearance of Bi(V) was followed at different time intervals at 550 nm. Bi(V) obeyed Beer's law at 550 nm in the concentration range studied.

The reaction was conducted in a teflon bottle immersed in water bath thermostated at desired temperature. The progress of the reaction was followed by oxidant [Bi(V)] unconsumed iodometrically[7, 8]. The reaction rate was not affected by stray light.

RESULTS AND DISCUSSION

The stoichiometry of the reaction was determined by taking an excess of oxidant of Bi(V) concentration over that of APO at concentration of $[HClO_4] = 1.0$ mol dm^{-3} and $[HF] = 1.5$ mol dm^{-3}. The reaction mixture was kept under thermostated water bath at 30°C and excess of Bi(V) was determined idiommetrically after completion of 6 h. The stoichiometry of the reaction was found to be 2 : 1, *i.e.*, 2 mole of Bi(V) reacted with 1 mole of oxime[9].

The oxidation product was ketone and hydroxylamine was obtained.

Effect of Bi(V): Bi(V) as oxidant which was disappearance acid followed first order rate law. The rate constant decreased with the increase in initial concentration of Bi(V) (Table-1). The initial rates (IR) were computed by plane mirror method. The plot of IR against [Bi(V)][10] was a linear straight line passing though the origin indicating first order reaction. Each experiment was performed at constant ionic strength ($\mu = 1.2$ M) maintained by the addition of $NaClO_4$. The concentration of [Bi(V)] greater than 1.0×10^{-3} M was not taken.

TABLE-1
EFFECT OF OXIDANT ON REACTION RATE

$[APO] = 1 \times 10^{-3}$ M, $[H^+] = 0.05$ M, $\mu = 2.6$ M, Temp. = 30°C

$[Bi(V)] \times 10^3$ M	$K \times 10^4$ s^{-1}
4.00	2.4
3.50	2.6
3.00	3.3
2.50	3.6
2.00	4.0

Effect of Substrate: The acetophenone oxime (APO) acted as substrate. The concentration of [APO] was varied at a fixed concentration of [Bi(V)]. The data in Table-2 show that the rate of oxidation increased with increase in concentration of oxime and showed first order dependence on the oxime concentration. Plot of 1/K *vs.* 1/[oxime] gave a straight line passing through the origin suggesting that there is no prior complex formation between the oxidant and the substrate. However, this does not always rule out the possibility of formation of transitory oxidant-substrate complex. It indicates that the formation constant of such an intermediate complex is very low.

TABLE-2

VARIATION OF RATE CONSTANT WITH SUBSTRATE CONCENTRATION

$[Bi(V)] = 0.90 \times 10^{-3}$ M, $[H^+] = 0.05$, H = 2.64 M, Temp. = 30°C

Oxime × 10^3 M	K × 10^4 s^{-1}	K/[oxime] × 10^4
1.0	2.21	2.21
1.5	3.53	2.35
2.0	4.50	2.25
2.5	5.80	2.12
3.0	7.67	2.56

Effect of acid concentration: The concentration of $HClO_4$ was varied from 0.025–0.6 M and 1.5 μHF at fixed ionic strength (μ = 2–6) mol dm^{-3} adjusted with $LiClO_4$ and at a fixed concentration of [Bi(V)] 0.90×10^{-3} M and [APO] 1×10^{-3} M. From the data in Table-3, it is seen that the rate is higher in $HClO_4$ than in HF. It is further observed that the reaction showed a fractional order dependence on hydrogen ion concentration.

TABLE 3

DEPENDENCE OF RATE CONSTANT ON ACID CONCENTRATION

$Bi(V) = 0.9 \times 10^{-3}$ M, $[APO] = 1 \times 10^{-3}$ M, μ = 2.6 M, Temp. = 30°C

Acid concentration (M)	In presence of HF (K × 10^4 s^{-1})	In presence of $HClO_4$ (K × 10^4 s^{-1})
0.025	—	1.3
0.050	1.8	2.3
0.100	2.3	3.7
0.200	2.5	4.9
1.000	3.6	—
1.200	4.0	—

Effect of Salt Concentration: Addition of NaF in presence of HF (1.5 M) decreased the rate whereas the addition of $NaClO_4$ in presence of 1.0 M $HClO_4$ increased the rate slightly. This shows that the chloride ion exhibits a retarding influence on the reaction. The retarding influence of chloride ion may be attributed to the formation of a less active oxidant species O═Bi—A. It is known[11] that anions form complex species with acid bismuthate ion.

However, ionic strength showed a little positive effect on the rate with $NaClO_4$. This indicates that the reaction is possible of an ion-dipole type.

Effect of Temperature: Rate increased with increased temperature and plot of log K *vs.* 1/T is linear (Table-4). Activation energy (ΔE*) and activation entropy (ΔS*) evaluated from the linear plot are 14.4 and 30.5 kcal mol^{-1}, respectively. The activation entropy by value shows that the reaction is bimolecular.

TABLE-4
TEMPERATURE EFFECT ON RATE CONSTANT (K)

Bi(V) = 0.9×10^{-3} M, [APO] = 1×10^{-3} M, [H^+] = 1.5 M, $\mu = 2.64$

Temp. (°C)	$K \times 10^4\ s^{-1}$
30	2.3
35	3.4
40	5.1

TABLE-5
EFFECT OF ANIONS ON RATE CONSTANT

Bi(V) = 0.9×10^{-3} M, [APO] = 1×10^{-3} M, [HF] = 1.5 M, [$HClO_4$] = 1×10^{-4} M

NaF	$K \times 10^4\ s^{-1}$	$NaClO_4$	$K \times 10^4\ s^{-1}$
0.0	4.5	0.0	4.5
0.2	4.2	0.2	4.5
0.4	3.7	0.4	4.8
0.6	3.0	0.6	4.9
0.8	2.8	0.8	4.9
1.0	2.5	1.0	4.9

Effect of Solvent: The studies were carried out on aquo-DMF solutions containing high percentage of water. It is obvious that the rate increases with the increase in dielectric constant. The reaction is, therefore, between (1) two molecules forming a polar product and (2) two ions of same sign/opposite sign and neutral molecule[12].

TABLE-6
EFFECT OF DMF-H_2O ON RATE CONSTANT

[APO] = 1×10^{-2} M, [Bi(V)] = 0.9×10^{-3} M [H^+] = 1.5 M, $\mu = 2.6$, Temp. = 30°C.

DMF % (v/v)	$K \times 10^4\ s^{-1}$
10	8.8
20	6.1
30	39
60	0.7

Effect of Substituent: It is observed that the rate increased as the electron-donating nature of the substituent increased (Table-7). A linear plot with a negative slope (f = 0.7) is obtained when log K is plotted against f. This suggests that a hydrogen atom[13] is lost in the initial reaction, since it is established that the first step is a one-electron step involving the formation of an iminoxy radical in the oxidation of oximes.

TABLE-7
EFFECT OF SUBSTITUENT ON RATE OF HYDROLYSIS AT 30°C

$[X—C_5H_4—C{=}NOH] = 1 \times 10^{-2}$ M, $[Bi(V)] = 0.9 \times 10^{-3}$ M, $[H^+] = 1.5$ M, $\mu = 2.6$ M

Substituent	S	$K \times 10^4\ s^{-1}$
p-NO_2	0.78	0.59
p-Cl	0.23	1.80
H	0.00	2.30
p-Me	–0.17	2.82
p-Ome	–0.27	3.21

Effect of Mn^{2+} ions: Watanabe and Westheimer[13] successfully used the induced oxidation of Mn(II) as a diagnositc tool to determine the oxidation state of the intermediates Bi(V). However, in the present investigation, rate did not change even in the presence of 1×10^{-2} M of Mn(II).

Further, the hydrolysis of BiF_6 should be slowed down. A plausible mechanism according to the observed excremental results is as follows:

$$\text{Oxime} + Bi^{5+} + H_2O \xrightarrow[BiF_6]{Slow/K_1} \text{Iminoxy radical} + Bi^{3+}$$

$$Bi^{3+} + \text{Iminoxy radical} + H_2O \xrightarrow[K_2]{Fast} \text{Nitroso compound}$$

$$\text{Dimer} \xrightarrow[K_4]{Fast} 2\ \text{Ketones} + H_2N_2O_2\ (\text{Oxidation product of } NH_2OH)$$

The intermediate product nitro compound is very small in comparison to K_2 and K_3. A simple rate law is derived as

$$\text{Rate} = [APO][Bi(V)]$$

The second order rate calculated at 30°C is 2.3×10^2 mol s^{-1}. The iminoxy radical is the rate determining step.

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